

# 1 Chlorine: History, Manufacture, Properties, Hazards, and Uses

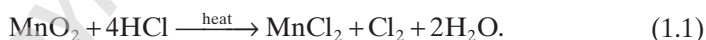
## HISTORICAL BACKGROUND

### Elemental 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% of the earth's crust in the form of soluble chlorides, such as common salt (NaCl), carnallite ( $\text{KMgCl}_3 \cdot 6\text{H}_2\text{O}$ ), and sylvite (KCl). In nature, it exists only as the negative chloride ion with a valence of  $-1$ . Because its properties in the gaseous, liquid, and aqueous states differ widely, each phase will be discussed separately.

### Chlorine Gas

Medieval Arab chemist Geber must have known this element (ca. 720–810). Chlorine was discovered, in its gaseous state, in 1774 by Karl W. Scheele, a Swedish chemist, when he heated manganese dioxide with hydrochloric acid.<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 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,

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gives off oxygen and leaves behind muriatic acid. Considering this residue proof of Lavoisier's theory, Berthollet called it oxygenated muriatic acid.<sup>2</sup> However, Humphry Davy 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, in which muriatic acid is combined with hydrogen. Therefore, Lavoisier's theory that all acids contain oxygen had to be discarded. Davy proposed to name the gas "chlorine" from the Greek *chloros*, variously translated "green," "greenish yellow," or "yellowish green," in allusion to its color.

Pelletier in 1785 and Karsten in 1786 succeeded in producing 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 the crystals could not be formed by cooling the gas even to  $-40^{\circ}\text{F}$  in the absence of moisture. It is now known that these crystals are in fact chlorine hydrate ( $\text{Cl}_2 \cdot 8\text{H}_2\text{O}$ ) and will form under standard conditions with chlorine gas in the presence of moisture and at a temperature of at least  $49.3^{\circ}\text{F}$ .

### Chlorine Liquid

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

Michael Faraday (1791–1867) also observed liquid chlorine. On March 5, 1823, he was visited in his laboratory 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 concluded the oil in the sealed tube was liquid chlorine.<sup>1</sup>

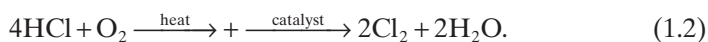
## MANUFACTURE OF CHLORINE

### History

From 1805 to 1888, Scheele's gas remained a laboratory curiosity—and a dangerous one—until it began to be produced on a commercial scale. This occurred when Kneitsch discovered in 1888 that dry chlorine did not attack iron or steel, which made it possible to package chlorine as a liquid under pressure.

Until then, chlorine had been 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 was known as Javelle water. James Watt, the inventor, obtained a license for the manufacture of Javelle water and brought it to Scotland for Charles Tennant. In 1789, Tennant produced another liquid bleaching compound, a chlorinated milk of lime. A year later, he improved it by making it into a dry compound, known as bleaching powder. The chlorine for producing it was obtained by Berthollet's method of heating sodium chloride, manganese, and sulfuric acid in lead stills. At the same time, chlorine was also being made on a limited scale by the Weldon process, which employed the reaction discovered by Scheele, who reacted hydrochloric acid with manganese dioxide. This method was given considerable impetus when Gossage invented coke towers in 1836 for the absorption of waste hydrochloric acid.<sup>1</sup> The cheap hydrochloric acid produced from these towers was used in the Weldon process. However, the Weldon process became nearly obsolete in 1868 after 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> In this process, a mixture of hydrochloric acid and air is heated. About 70% of the hydrogen chloride is converted to chlorine as it mixes with the air and steam. The gas is then condensed, and the steam absorbs the hydrogen chloride, forming a very strong muriatic acid mixed with hydrogen chloride gas. This mixture is passed first through a superheater at a temperature about 430°C, then through a decomposer consisting of a brick- or pumice-lined chamber impregnated with cupric chloride catalyst, and is finally washed first with water and then with sulfuric acid. The remaining mixture of nitrogen and oxygen contains 10% of chlorine gas, which can be used in manufacturing liquid or powdered bleach. The remaining HCl is recycled back through the process. Considering the amount of chlorine produced, the plant is extremely bulky. The reaction is



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

The hydrogen chloride used in the Deacon process was 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 emerging electrolytic methods.

### Electrolytic Processes

**History.** In 1883, Faraday postulated the laws that govern the action produced by passing 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 manufacturing chlorine by the electrolyte process in 1851. However, at that time electric current generators of sufficient size were not available. When they became available, interest in electrochemistry was greatly stimulated. In 1890, the first commercial production of chlorine by the electrolytic method, the chlor-alkali process, was introduced by the Elektron Company in Griesheim, Germany.<sup>1</sup> The first manufacturer to use an electrolytic plant in America was the Oxford Paper Company at Rumford Falls, Maine, in 1892. In 1894, Mathieson Chemical Company acquired the rights to the Castner mercury cell and began to produce bleaching powder at a demonstration plant in Saltville, Virginia. In 1897, this operation was moved to Niagara Falls, New York. The original Castner rocking cells were operated successfully until they were shut down in 1960.<sup>3,4</sup>

At first, the electrolytic process was used primarily for making caustic. Chlorine was an unwanted by-product. At the Niagara Falls plant, a small amount of chlorine was used for making bleach and hydrochloric acid; the remainder was discharged into the Niagara River. Not until 1909 was liquid chlorine manufactured commercially. It was first packaged in 100-lb steel cylinders. The demand for it grew slowly but steadily, mostly 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 use in chemical warfare.<sup>1</sup>

**Current Practice.** Today, chlorine is manufactured primarily by using three types of electrolytic cells: membrane, diaphragm, and mercury. Other methods, which are designed to fit the raw material containing the chlorine ion, include electrolysis of hydrochloric acid, salt process, and hydrochloric acid oxidation processes. Chlorine is also a by-product of heavy metal recovery, such as the tungsten sponge process, or extraction of magnesium from magnesium chloride ore.

## ELECTROLYTIC CELL DEVELOPMENT

### The Ideal Electrochemical Cell

An electrochemical cell is composed of an anode, a cathode, and a separator forming an anode chamber and a cathode chamber. The function of the separator is to isolate the two chambers while allowing selected ions in the liquid to migrate from the anode chamber into the cathode chamber. A brine of

sodium chloride and water is introduced into the anode chamber, where oxidation of the chloride ion takes place. Chlorine gas is released at the anode. The sodium ions are attracted to the negatively charged cathode and are transported through the separator. If the separator is doing a perfect job, all of the chloride will be contained on the anode side of the cell.

Water is reduced at the cathode and hydrogen gas is evolved. The remaining hydroxide ion combines with the sodium ion to form sodium hydroxide solution (caustic), which exits the cathode chamber. The ideal separator will keep all the hydroxide ions on the cathode side of the cell.

### Process Developments

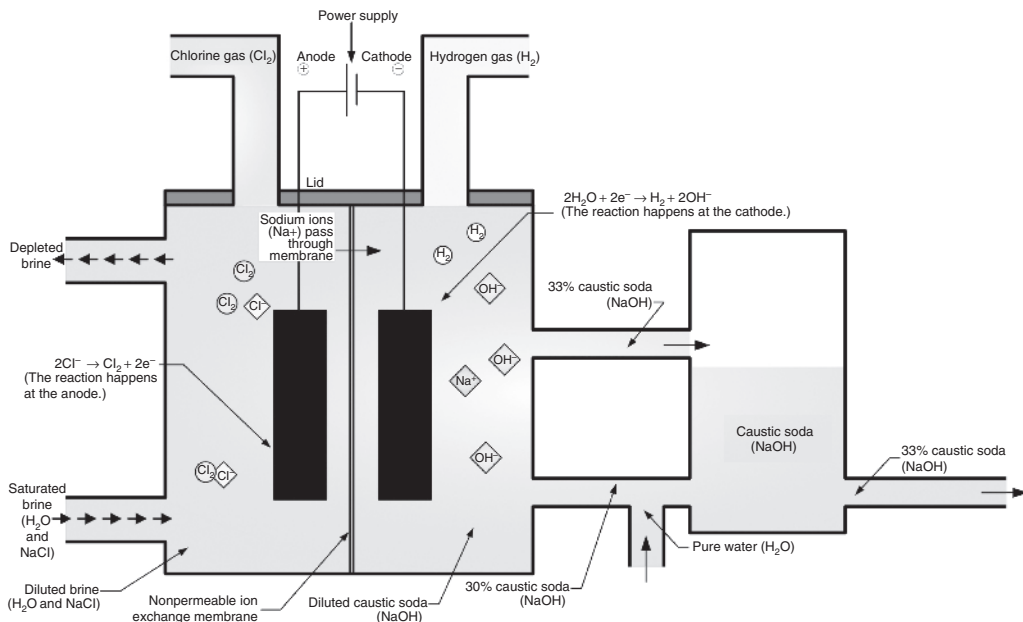
In practice, electrolytic cells are plagued with a variety of problems such as corrosion, erosion of electrodes, and plugging of the separator. All of these problems contribute to maintenance costs. There is also great concern over the cost of electrical energy required to drive the oxidation reaction. In recent years, industry has made important advances on all of these fronts. Energy consumption has been significantly reduced by improvements to cell design and improvements to the electrical equipment used to convert alternating current (AC) to direct current (DC).

Major advances that have revolutionized electrolytic cell design include the use of new materials of cell construction and diaphragms, as well as the use of cladding processes that eliminate or retard the corrosion of cell components. The chlor-alkali industry has long sought a stable metal anode for chlorine production. In 1968, Diamond Shamrock Corporation announced the development and commercialization of new types of metallic anodes, which it named dimensionally stable anodes (DSA).<sup>5</sup> These anodes have been instrumental in reducing both capital and operating costs. As their name implies, they retain their size and shape during use and have a life longer than 10 years in diaphragm cells, compared with about 180 days for the older graphite anode. Moreover, they eliminate hydrocarbon contamination of chlorine caused by the graphite, which poses a health problem in potable water chlorination (see the section "Impurities in the Manufacture of Chlorine" in this chapter).

The anodes can be reactivated by redeposition of the metal coating. In addition to reducing the downtime and labor for anode replacement, the savings in the cost of graphite consumed per ton of chlorine produced is substantial.

### Membrane Cell

**Description.** A schematic of a membrane cell is shown in Figure 1.1<sup>6</sup>. An ion exchange membrane separates the cell into two compartments. This membrane allows sodium ions, and a very small quantity of water, to move into the cathode compartment but prevents the migration of chloride ions and chlorine gas across this barrier. The membrane also prevents the movement



**Figure 1.1.** Schematic of a membrane cell.

of hydroxyl ions from the cathode compartment to the anode compartment. Chlorine gas is formed at the anode and hydrogen gas is formed at the cathode.

A saturated brine solution enters the anode compartment, provides the chloride and sodium ions used in the process, and then flows out of the compartment to be dechlorinated, resaturated with sodium chloride, and recycled. The caustic formed by the sodium ions passing through the membrane is recycled through the cathode compartment. Pure water is added to this recycle stream. The excess caustic solution is stored prior to evaporation to increase the concentration of this product. The chlorine produced in the cell is hot and wet, and it contains trace concentrations of air, oxygen, and carbon dioxide. These contaminants are removed by cooling, drying, and liquefying the chlorine.

**History.** Hooker Chemicals and Plastics (now Occidental Chemical Corporation) and Diamond Shamrock Corporation began membrane cell development programs in the 1950s.<sup>7</sup> The largest producer of chlorine in the United Kingdom, the ICI Corporation, began to develop membrane cells 20 years later.<sup>8</sup> The concept was made feasible by the development of selective ion exchange membranes that could withstand the very harsh environment inside an electrolytic cell.

Approximately 23% of the chlorine manufactured in the United States and 20% of the chlorine manufactured in Canada during 2006 were produced using membrane cells. These percentages will increase in the future as mercury and diaphragm cells are phased out of service. None of the chlorine producers in Mexico used membrane cells in 2006.<sup>9</sup>

**Theory of Operation.** The membrane cell is a very good simulation of the ideal cell. The operation of any electrolytic cell is limited by the ability of its individual components to perform as required. To overcome these limitations, it is necessary to find the proper materials for the electrodes and the separator (membrane) that result in the greatest yield and purity of product with the least expenditure for energy and maintenance.

Salt, water, and electric current are the raw materials. Solid salt is dissolved in a saturator with fresh water and depleted brine. The saturated brine is chemically treated to precipitate impurities, which are removed by clarification and filtration. The filtered brine is then passed through an ion exchange process to lower the final concentration of calcium ion to less than 0.05 mg/l. The cell membranes are highly sensitive to calcium deposits, and if this limit is not achieved, process performance will suffer and maintenance costs will escalate.

Hydrochloric acid is added to the brine to neutralize part of the back migration of hydroxide ions. These ions reduce the formation of objectionable by-products before the purified brine is fed to the anode compartments of the cells. The salt is electrically decomposed to produce the chlorine gas generated at the anode. The sodium ions remain in solution and are transported through the membrane to the cathode, where they combine with hydroxide ions formed in the cathode chamber. The depleted brine leaving the anode chamber is treated to separate any remaining chlorine, and recycled to the brine saturator. The caustic solution formed in the cathode compartment flows to a caustic surge tank, where most of it is cooled and recycled to control the concentration and temperature of the caustic in the membrane cells. Softened water is added to the caustic solution to maintain the desired product concentration. The hydrogen produced in the cathode chambers may be vented or recovered. The feed brine contains about 320 g/l of sodium chloride and not more than 30 g/l of chlorate ion. Depleted brine has a pH range of 2–5 and contains about 170 g/l sodium chloride. The chlorine produced is 97%–99.5% pure, and contains 3.0%–0.5% oxygen. This oxygen is removed by liquefaction and evaporation downstream from the cell. The caustic product, which is approximately 30% by weight sodium hydroxide, contains 40–50 ppm sodium chloride and 5–15 ppm chlorate ion. The hydrogen is 99.9% pure.

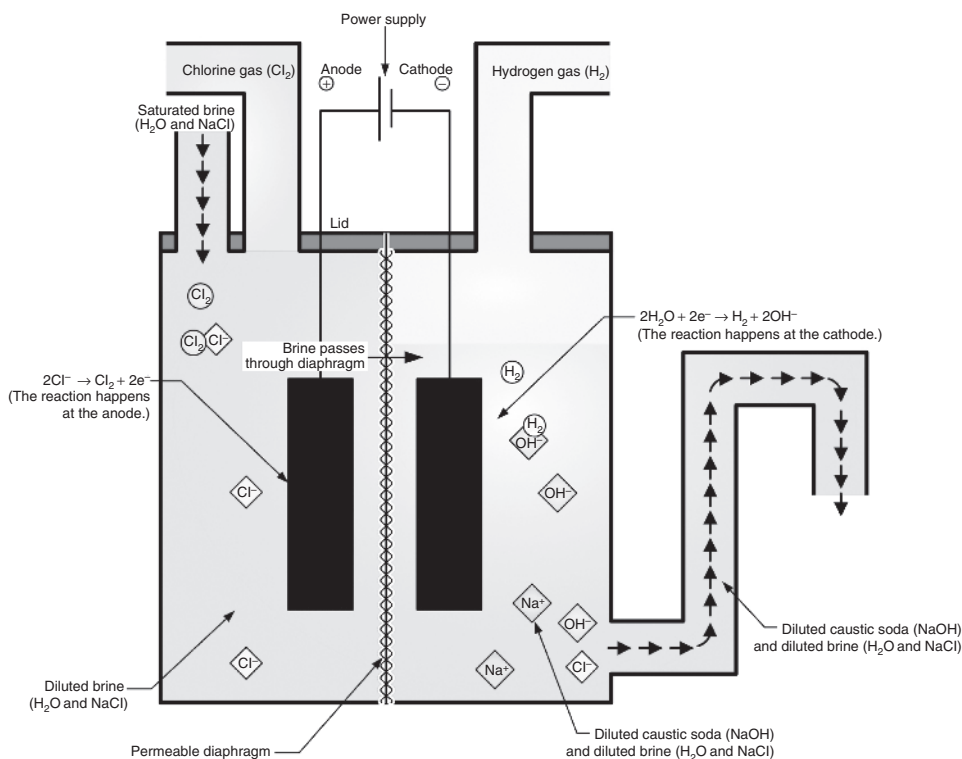
**Advantages and Disadvantages of Membrane Cells.** One of the most important advantages of the membrane cell is that the overall plant process requires less energy than either the mercury cell or the diaphragm cell. However, the membranes are relatively expensive and have a short service life.

Membrane cells require the use of very pure solid salt to make the influent brine. The brine prepared from this salt must also be purified to a greater degree than the brine used with other types of electrolysis cells.

Membrane cells produce a very pure grade of caustic directly from the cell. However, the highest concentration of caustic that can be produced by these cells is about 33%–35%. Higher concentrations of caustic are desirable for many uses of this product. Additional caustic concentration steps are, therefore, provided at most of the chlor-alkali plants that use membrane cells. The chlorine gas produced by membrane cells contains some oxygen that must be removed by liquefaction and evaporation. The hydrogen gas is very pure. Membrane cells do not utilize either mercury or asbestos, which minimizes adverse impacts on workers at the plants and on the environment.

### Diaphragm Cells

**Description.** A schematic of a diaphragm cell is shown in Figure 1.2.<sup>6</sup> A permeable diaphragm separates the cell into two compartments. Brine enters



**Figure 1.2.** Schematic of a diaphragm cell.

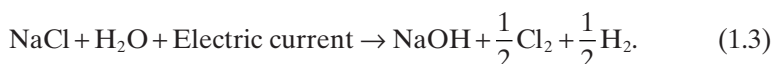


the cell in the anode compartment, flows through the diaphragm, and exits the cell from the cathode compartment. Chlorine gas is formed at the anode, and hydrogen gas is formed at the anode. Both of these gases are vented from the cell and processed elsewhere in the plant. The liquid discharged from the cathode compartment is a mixture of diluted brine and dilute sodium hydroxide. This mixture is concentrated, and the brine is removed from the caustic, by additional treatment steps downstream from the cell. The salt removed from the caustic solution is recycled to prepare additional brine. The chlorine leaving the cell contains the contaminants previously identified in the description of the gas discharged from membrane cells.

**History.** Diaphragm cells were initially designed in the 1880s. Several hundred configurations of these cells have been developed since that time. These modifications have focused on improvements to the anodes and the diaphragms. Details about designs currently in use can be obtained from equipment manufacturers and from the technical literature.

Diaphragm cells were used to make approximately 66% of the chlorine produced in the United States and 76% of the chlorine produced in Canada during 2006.<sup>9</sup> Use of these cells will gradually decline as new facilities are constructed using membrane cells. Two of the chlorine plants in Mexico used diaphragm cells in 2006.<sup>9</sup>

**Theory of Operation.** The overall chemical reaction in a diaphragm cell is



The principal anode reaction is



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



The principal cathode reaction is



$$\frac{107.880}{0.00111801} = 96,493\text{C}. \quad (1.8)$$

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

$$\frac{A \times 86,400 \text{ s/day}}{96,493 \text{ C}} \times \frac{35.457 \text{ gCl}_2}{454 \text{ g/lb}} = 0.07 \quad (1.9)$$

$$A \times 0.07 = \text{lb/day Cl}_2$$

A diaphragm cell using 135,000 A of electricity, with a current efficiency of 95.8% will produce 9053 lb of chlorine per day.

Since chlorine gas evolves at the anode and hydrogen gas evolves at the cathode, the sodium ion in the influent brine is free to associate with the excess hydroxyl ion formed in the cathode compartment when the depleted brine flows into the second chamber.

The flow through the porous diaphragm produces a differential hydraulic head between the two chambers. This difference in water level prevents migration of hydrogen gas into the influent chamber.

Flow through the porous diaphragm also inhibits migration of hydroxyl ions from the cathode to the anode compartment. This is desirable because the presence of hydroxyl ion in this compartment will result in the formation of hypochlorite ion instead of elemental chlorine.

Purified brine is added at the cell inlet at a temperature of 60–70°C. By maintaining the pH of this solution between 3 and 4 and by maintaining a differential head between the solution levels in the two chambers, the diaphragm cell can be kept in chemical equilibrium to produce hydrogen gas at the cathode and 11%–14% sodium hydroxide in the effluent from the cathode compartment. The spent brine discharged from this compartment contains approximately 322 g/l of sodium chloride. Facilities are needed downstream from the cell to remove this salt and to increase the concentration of the sodium hydroxide.<sup>10</sup>

The most common material used to make diaphragms has been asbestos. Fluorinated polymer resins have been used since the early 1980s to strengthen the asbestos membranes. However, special steps are required in the manufacturing and disposal of all products containing asbestos because of the environmental hazards associated with this material. New fluoropolymer-based diaphragms entered the marketplace in 1997. These diaphragms are more expensive than asbestos but they have a longer life and provide more stable operation in the cells.

***Advantages and Disadvantages of Diaphragm Cells.*** Diaphragm cells require lower purity brines than membrane cells. They also use lower voltage and less electric power than mercury cells. However, the sodium hydroxide produced in diaphragm cells is both dilute and contaminated with chloride ion. Evaporative concentration of this solution is required to increase the concentration of the sodium hydroxide and remove the chloride contamination. The chlorine gas produced by diaphragm cells contains some oxygen that must be removed by liquefaction and evaporation. The hydrogen gas is very pure. There are high costs associated with handling and disposal of asbestos membranes.

These costs can be avoided by using the newer membranes that are now available.

### Mercury Cells

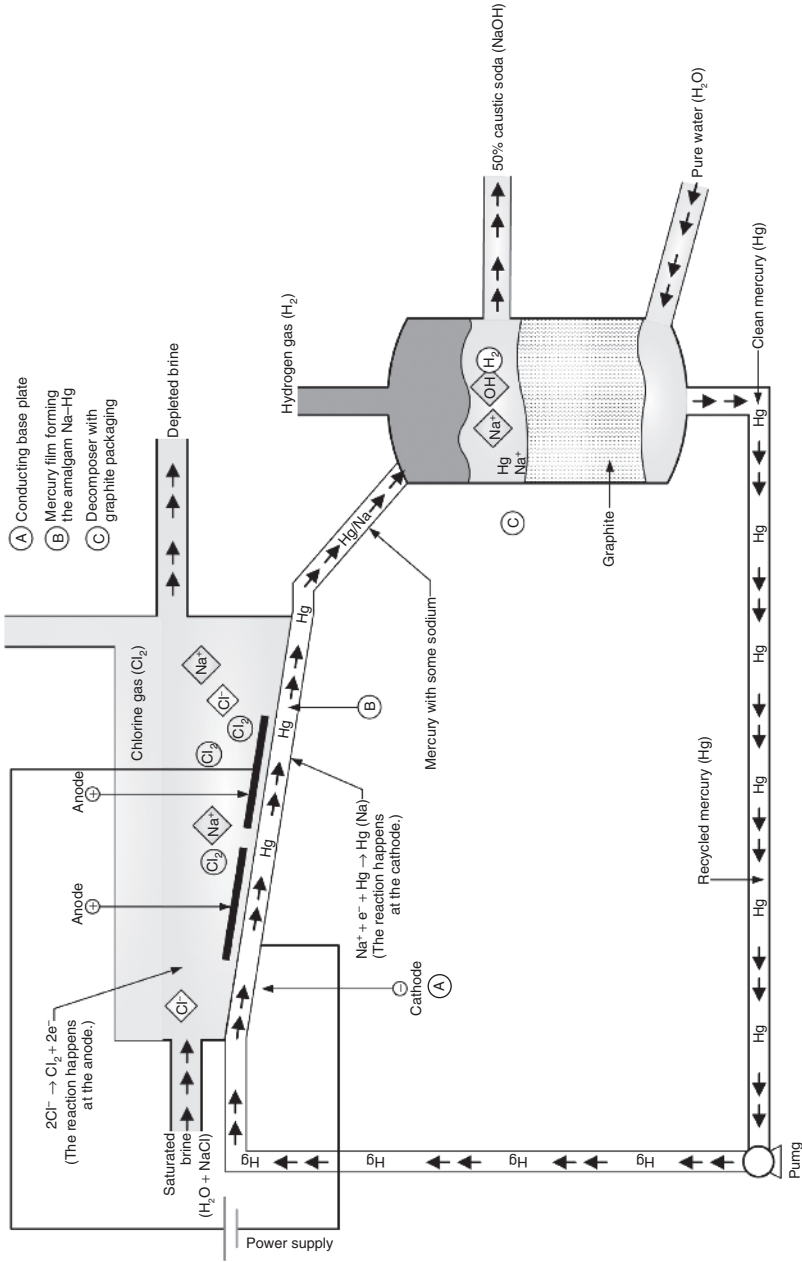
**Description.** A schematic of a mercury cell is shown in Figure 1.3.<sup>6</sup> The cell has two parts: (a) the electrolyzer and (b) the amalgam decomposer. The electrolyzer is a covered tray with a sloped metal bottom that functions as a conducting base plate in the electrolysis process. Titanium metal anodes are located a short distance above the bottom of the tray. Concentrated salt brine and a supply of mercury enter the shallow end of the tray and flow toward the deep end. The mercury spreads out on the bottom of the tray and is the cathode for electrolysis of the brine. Chlorine gas is liberated at the anodes and bubbles out of the brine to exit at the top of the tray. Sodium is deposited at the surface of the flowing mercury cathode where it dissolves to form a very dilute sodium/mercury amalgam. The hydrogen formed at the cathode is entrapped in this amalgam and leaves the electrolyzer in this mixture. The depleted brine flows out of the electrolyzer, is resaturated with sodium chloride, and is then recycled back to the inlet of this process.

The sodium/mercury amalgam and the entrapped hydrogen flow to the amalgam decomposer. This consists of a closed vessel that contains a graphite catalyst. Pure water flows into the bottom of the catalyst bed and reacts with the amalgam to free the sodium ions and hydrogen. The clean mercury flows out the bottom of the decomposer and is pumped back to the inlet of the electrolyzer. The caustic solution and the hydrogen gas are processed elsewhere in the plant.

**History.** Two men on different continents simultaneously discovered the mercury cell process for producing chlorine and caustic. Each discoverer was unaware of the other's efforts. One was an American, Hamilton Y. Castner; the other an Austrian, Karl Kellner. Both applied for patents in 1892.<sup>3,4</sup>

The first Castner cell installation was a 550-A demonstration plant designed in 1897 for the Mathieson Chemical Company at Saltville, Virginia. The plant was later moved to Niagara Falls, New York, where it was operated successfully until 1960, when it was replaced with a 100,000-A installation using an upgraded version of the original mercury cells. These mercury cells are no longer in use.<sup>3,4</sup>

In the 1970s, mercury cell facilities in North America were found to be discharging excessive amounts of mercury in their effluent. Additional monitoring also showed significant quantities of mercury being volatilized and discharged into the air. Despite steps taken by chlorine manufacturers to reduce these emissions, public and regulatory pressure to discontinue the use of mercury cells has continued. By 2005, more than 100 mercury cell facilities had been converted to using membrane or diaphragm cells, and by 2007 only five mercury cell installations remained in operation in the United States.



**Figure 1.3.** Schematic of a mercury cell.

Plans have been announced to convert several of these plants to membrane or diaphragm cell facilities by mid- to late 2009.

In Europe, there were 48 mercury-based chlorine plants in 2005, which accounted for almost 50% of European chlorine production capacity. The industry has agreed to voluntarily phase out these plants or to convert them to nonmercury technology by 2020. Public pressure is being applied to accelerate this schedule. The World Bank does not finance construction of chlorine production facilities that use mercury cell technology.

Mercury cells were used to produce about 9% of the chlorine manufactured in the United States and 4% of the chlorine manufactured in Canada during 2006. There were four mercury cell plants operating in Mexico in 2006, and new construction was underway at all of these plants. It is not known whether any mercury cells will be retired when this work is completed.<sup>9</sup>

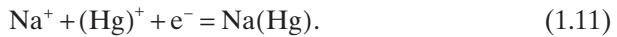
**Theory of Operation.** The principal chemical reactions in a mercury cell are as follows:

### 1. Electrolyzer

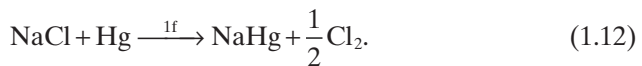
At the anode:



At the cathode:

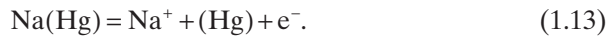


Overall reaction:

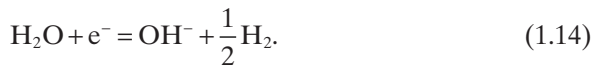


### 2. Decomposer

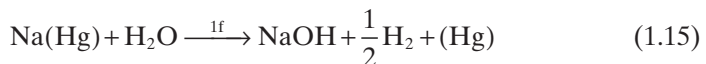
At the anode:



At the cathode



Overall reaction:



The main differences between the mercury cell and the diaphragm cell are as follows: The spent brine is withdrawn separately from the mercury amalgam. The caustic is produced in the decomposer as a by-product from preparation of the amalgam to be returned as the mercury cathode. Both processes use about 1.7 tons of salt per ton of chlorine produced. The net result is essentially the same as produced by diaphragm cells. The ingredients are the same, except for the inventory of mercury.

**Electrolyzer.** The purified, saturated (305 g/l) alkaline brine solution is fed to the electrolyzer portion of the cells where the pH is adjusted with HCl to a range of 2.5–5. The pH is somewhat dependent on the amount of calcium sulfate that can be tolerated in the brine. The pressure on the anode side is atmospheric ( $\pm 15$  mmHg). DC in the amount specified for the cell rating is applied at 4–4.5V between the metal anode and the mercury cathode, with the chlorine being liberated at the anode. The spent brine is monitored as it leaves the cell to keep its sodium chloride concentration at 260–280 g/l and its temperature no higher than 85 °C. This is done by regulating the quantity of brine fed to the cells. The spent brine is dechlorinated by air stripping, regenerated by contacting it with solid salt, the pH is adjusted to 10 with sodium hydroxide, and the solution is settled and filtered. The regenerated brine is recycled to the cells. The chlorine gas produced in the electrolyzer is treated in the same way as the chlorine produced in diaphragm cells.

**Decomposer.** The decomposer is a tower packed with lumps of graphite. A distributor plate spreads the amalgam over the top of this packing. Purified and softened water enters the bottom of the packing and flows out the top of the packing as 50% sodium hydroxide. Sodium amalgam in contact with the graphite packing and water is decomposed into sodium hydroxide and hydrogen. The hydrogen, which is collected from the top of the decomposer, is wet and contains some mercury vapor and entrained caustic spray. These contaminants are removed by cooling the hydrogen in a scrubber or a condenser. The mercury flows out of the bottom of the decomposer and is pumped back to the electrolyzer.

This method produces a 50% caustic solution (diaphragm cells produce 11%–12% caustic, and membrane cells 30%–35% caustic). The caustic solution is filtered to remove the graphite particles picked up in the decomposer, which contains some of the mercury recovered from the sludge during filtering. The mercury recovered from the chlorine, hydrogen, caustic, and sludge is recycled back to the electrolyzer.

**Occupational Health.** All industries that produce or use hazardous chemicals must comply with rules promulgated by the federal Occupational Safety and Health Administration (OSHA) under 29CFR 1910 or with rules established and enforced by state OSHA agencies. These rules are addressed later in this chapter.

The Chlorine Institute (CI) recommends medical surveillance of all personnel working in chlorine production, use, or handling facilities who are potentially exposed to chlorine gas above the American Conference of Governmental Industrial Hygienists (ACGIH) guideline of 0.5 ppm time-weighted average (TWA) or the 1 ppm short-term exposure limit (STEL).<sup>11</sup> It is especially important for workers in the cell area of mercury cell plants to undergo regular health checks because they are potentially exposed to two hazardous chemicals.<sup>12</sup>

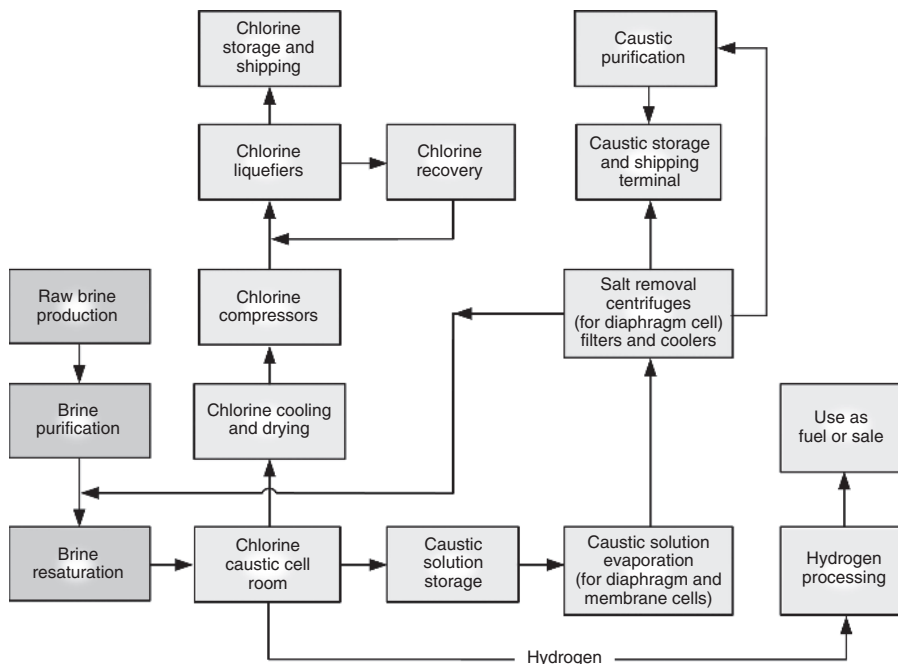
The U.S. Environmental Protection Agency (USEPA) promulgated the Final Rule for mercury emissions from mercury cell chlor-alkali plants on December 19, 2003.<sup>13</sup> This rule limits the allowable quantities of mercury in emissions from by-product hydrogen streams, end box ventilation system vents, mercury thermal recovery unit vents, and the storage areas for mercury-containing wastes. In addition, the rule establishes comprehensive standards for work practice that must be met in mercury cell rooms. These standards include specific design, operation, and maintenance requirements; inspection, monitoring, and reporting requirements; and specify the actions for responding to liquid mercury spills and the collection of liquid mercury.

The USEPA rule does not regulate atmospheric emissions of chlorine and hydrochloric acid from mercury cell, diaphragm cell, or membrane cell plants.

***Advantages and Disadvantages of Mercury Cells.*** Mercury cells produce a pure 50% concentration solution of sodium hydroxide. There is no need for evaporative concentration of the caustic produced in a mercury cell plant. However, trace concentrations of mercury will occasionally contaminate the caustic. Some purchasers will not buy caustic from these plants because of this potential hazard. Mercury cells produce a pure chlorine gas with virtually no oxygen contamination. But a higher voltage is required in this cell than in the other two types of cells. The electrical power requirements of mercury cells are 10%–15% higher than the power requirements of the other two cell types. The costs of brine purification in mercury cell plants are higher than those in the other two types of cells. The major disadvantage of mercury cells is the mercury itself. The chlor-alkali industry has made large financial investments to minimize exposure of workers to mercury in these plants and to ensure that mercury does not contaminate the environment. However, strong pressure to eliminate the continued use of this technology will continue to be exerted.

### **Process Diagram for a Typical Chlor-Alkali Plant**

Figure 1.4 is a process diagram of a typical chlor-alkali plant producing chlorine and sodium hydroxide by electrolysis.<sup>14</sup> Most of the unit processes shown in this figure are required in the plant regardless of the type of cell used, that is, membrane, diaphragm, or mercury; however, the scope of the individual processes will vary depending on the needs of the cell and the characteristics



**Figure 1.4.** Process diagram of a chlor-alkali plant.

of the chlorine and sodium hydroxide produced. These differences will be discussed below.

The ingredients required for all of the cells are brine, water, and electric power. Brine is obtained in one of two ways: (a) from rock salt delivered to the plant and dissolved in water or (b) locating the plant adjacent to underground deposits of salt, from which brine is produced by injecting water into a well. Impurities such as calcium, magnesium, and iron must be removed from the brine by adding sodium carbonate and sodium hydroxide, followed by sedimentation and filtration. The brine used in membrane cells must be further treated by ion exchange to remove trace impurities that could plug the membrane. The water used to prepare the brine must also be free of ammonia and all chemical compounds containing nitrogen. This is necessary to prevent the formation of nitrogen trichloride during electrolysis.

The salt content of the purified brine is increased to approximately 27% by heating to evaporate some of the water. Salt removed from the sodium hydroxide produced in diaphragm cells is also recycled to the inlet of the electrolysis cell. This recycle stream is not present when membrane or mercury cells are used.

The electrical power required for electrolysis is usually obtained from a high-voltage AC source that has been stepped down and rectified to 3–5V of DC. Depending on the type, size, and design of the cell, power consumption



is usually about 2200–2900 kWh per ton of chlorine produced in a diaphragm cell plant. Electrical power consumption in the membrane cell process is about 2000–2400 kWh per ton of chlorine. Approximately 3600–3900 kWh are required to produce a ton of chlorine in a mercury cell.

The gas leaving the cathode of the electrolysis cell is about 99.8% pure hydrogen. It is scrubbed with water to cool it and to remove traces of caustic or other impurities (salt in diaphragm cells and mercury vapor in mercury cells). The purified hydrogen is then compressed for use in various processes or as fuel.

The gas leaving the anode is about 97.5% pure chlorine. The contaminants usually consist of a mixture of water vapor, oxygen, nitrogen, and carbon dioxide. This gas is hot (approximately 210 °F or 100 °C), moist, and extremely corrosive. It is usually cooled with water in a packed tower, dried by scrubbing with sulfuric acid, and then compressed to about 60 psi, before being fed into a fractionating tower to remove impurities such as chloroform and chlorinated hydrocarbons. These impurities are removed at the bottom of the tower in a solution containing little or no chlorine.

After leaving the fractionating tower, the chlorine gas is liquefied by refrigeration and pumped to storage tanks, from which it is repumped into tank cars and ton containers. Manufacturers generally prefer to ship liquid chlorine in rail tank cars to packagers who transfer it into tanker trucks, ton containers, and 150-lb cylinders. Trucks are used to transport the ton containers and 150-lb cylinders to the consumer.

The packagers have liquid bleach manufacturing operations to utilize the “snift gas” that would otherwise be discharged to the atmosphere when the containers are being filled. Some packagers also prepare bulk shipments of commercial-strength bleach for delivery to customers.

Manufacturing plants usually recover the snift, or “blow gas,” as well as the chlorine lost in the water used for cooling the gas. One process used to recover this chlorine is the Hooker process, which uses water to absorb the chlorine in the gas. This water is then used in the cooler, and upon leaving the cooler, is heated with steam and then acidified to strip it of chlorine, which is returned to the packaging cycle. Another process, the Diamond–Alkali process uses carbon tetrachloride to absorb the chlorine. The carbon tetrachloride is then heated and stripped from the chlorine.<sup>10</sup>

The sodium hydroxide formed in the electrolysis cell is sent to storage tanks pending the additional treatment required to produce a marketable product. Very high-quality sodium hydroxide is produced in membrane cells, so the only additional treatment required is evaporation to increase the concentration of the solution to the level desired by customers. The concentration of the sodium hydroxide produced by mercury cells is high enough for direct commercial use, but this product should be monitored to make certain that trace amounts of mercury are not present. The spent liquor discharged from diaphragm cells usually contains about 11.5% sodium hydroxide and 16% sodium chloride. Before it can be marketed, the salt must be removed, and

the concentration of caustic must be raised to 35%–50%. This is done by first evaporating the liquid. The salt is then separated from the caustic solution by centrifugation and filtration. This salt is washed to remove residual caustic, dissolved, and recycled back into the brine system. The caustic is cooled and settled to remove additional salt prior to pumping the purified solution into storage tanks.

## OTHER CHLORINE MANUFACTURING PROCESSES

The following processes are available but are not in widespread use. They are useful in using excess hydrochloric acid.

### Salt Process

The salt process for producing chlorine is based on the reaction between sodium chloride and nitric acid. This process was initially developed to manufacture sodium nitrate for the fertilizer industry. Allied Chemical Company implemented this process, on a commercial basis, at Hopewell, Virginia, in 1936. The overall reaction is



In this process, dilute nitric acid (55% or less) is first concentrated by evaporation to 63%–66%, mixed with sodium chloride, and heated with steam to cause the reaction that produces nitrosyl chloride, chlorine, and sodium nitrate in equal molar quantities. The solution is stripped of nitrosyl chloride and chlorine, which are scrubbed, dried, and liquefied with refrigerated brine. The nitrosyl chloride–chlorine mixture is then passed through a separating column; the chlorine leaves as a gas from the top of the column and is reliquefied and sent to storage. The nitrosyl chloride leaves the column at the bottom as a liquid and is sent to a recovery operation. Additional oxidation of this nitrosyl chloride can be used to recover additional chlorine.

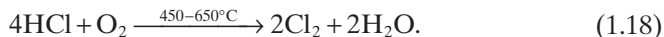


The nitrogen tetroxide gas produced in this reaction can be separated from solution and marketed separately, or the solution can be recycled to manufacture sodium nitrate.<sup>10</sup>

### HCl Oxidation Processes

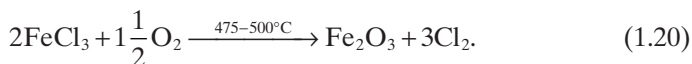
The market for chlorine has expanded rapidly, while the market for hydrochloric acid has declined. This situation has created a demand for the production of chlorine from the hydrochloric acid produced as a by-product from

other chemical processes. This demand has revived the Deacon process, which is attractive because of its simplicity. It involves a mildly exothermic reaction, with low electric power and thermal energy use. The reaction—HCl oxidation—takes place in the vapor phase over a copper base catalyst as follows:



There are no side reactions or competing reactions: The principal problem is the development of operating conditions that best balance the higher rate of reaction achieved at higher temperatures against higher yields obtained at lower temperatures. The Air Reduction Company improved the Deacon process to make it practical to produce chlorine at a ton-per-day rate from by-product HCl at about 27% chlorine by volume with air, and about 90% chlorine with 95% oxygen.<sup>3</sup>

The Grosvenor Miller process, with a fixed-bed system, utilizes the following reactions:<sup>10</sup>



A final-product gas containing a maximum of 70% chlorine can be obtained with this process by using a three- to five-bed continuous reactor system. The process is as follows: Reactor I is laden with dry ferric chloride at 250–300°C and is fed oxygen. The ferric chloride is converted to chlorine and ferric oxide. The gas formed in reactor I (which contains approximately 30% chlorine gas, 70% unreacted oxygen, hydrochloric acid vapor, and some air), passes into reactor II, which is a mixed bed of ferric oxide and ferric chloride maintained at 500°C to serve as both chlorinator and oxidizer. Some of the hydrochloric acid vapor in the gas entering reactor II reacts with ferric oxide to produce ferric chloride. This ferric chloride produced in this reaction, plus the ferric chloride in the bed of this chamber, react with the excess oxygen in the gas to produce additional chlorine. The chlorine gas does not react, so it and the remaining hydrochloric acid vapor and oxygen pass into reactor III, which is maintained at 250–400°C. This reactor was previously reactor I, and thus is oxygen laden. Reactor III strips the remaining hydrochloric acid vapor from the gas. The chlorine gas does not react, and it passes through reactor III, carrying with it steam and excess oxygen until this reactor becomes saturated with chlorides. At this point, the functions of reactor III are transposed to those of reactor I, and gas flow is III to II to I. There are other variations of this process, such as the Dow moving bed process and others using molten metallic chlorides as catalysts.

The Kel-Chlor process, developed by the M.W. Kellogg Company of Houston,<sup>15</sup> is a modification of the Deacon process. This modification was

developed to correct chemical equilibrium problems in the original process that produced low yields of chlorine. The Kel-Chlor process solved these problems by combining a very active catalyst (nitrogenous compound) with a powerful dehydrating agent (sulfuric acid). This reduces the activity of the steam to a negligible value and allows the reaction to proceed to completion.

### **Electrolysis of Hydrochloric Acid Solutions**

***Bayer MaterialScience Process.*** Bayer Corporation intends to finish construction of the world's largest hydrochloric acid recycling plant in 2008. This plant will be located in Shanghai, China, and will use a new oxygen-depolarized cathode technology in the production of chlorine. A smaller plant used to develop this technology was run in Brunsbüttel, Germany in 2003.<sup>16</sup>

***The Hoechst-Uhde Process.***<sup>17</sup> Considerable quantities of aqueous hydrochloric acid and hydrogen chloride gas are produced each year as by-products from a number of chemical manufacturing activities. These materials are difficult to dispose of; so a process that utilizes them is of special interest. The I.G. Farben Industrie began to develop a process in 1938 at its plant in Bitterfeld, Germany, using bipolar diaphragm cells, which had a limited production capacity, usually less than 50 tons of chlorine per day, and were subject to many fabrication and operating problems. A joint effort by Farbwerke Hoechst AG and Friedrich Uhde GmbH resulted in a successful design, which was placed into operation in 1963.

The first electrolysis unit in the United States was built in 1971–1972 at the Mobay Chemical Corporation in Baytown, Texas, by the Hoechst-Uhde Corporation. This plant had the capacity to produce 198 short tons of chlorine per day, and used waste hydrogen chloride gas from the manufacture of isocyanate. This plant is now owned by Bayer MaterialScience, and the plant capacity has been expanded.

## **IMPURITIES IN THE MANUFACTURE OF CHLORINE**

### **Historical Background**

Special attention has to be given to the production of chlorine when it is used for treatment of potable water, wastewater, and reclaimed water. The total amount of chlorine used for this purpose is only about 5% of all the chlorine produced in the United States. Industry thinks in terms of using thousands of pounds of chlorine per hour, whereas treatment plant users think in terms of hundreds of pounds per day.

In the early days of chlorination (1920s), metering equipment was continually plagued by fouling. The material causing this fouling was commonly called “gunk” or “taffy.” Its source was difficult to identify until Wallace and Tiernan

developed the bell-jar chlorinator (1922), which incorporated a self-cleaning pressure-reducing valve (visible through a glass dome) that operated under a vacuum. When this valve became plugged with enough “gunk” to stop the flow of chlorine, it would automatically shift from the throttled position to a wide-open position by raising the water level in the bell jar. In most cases, the wide-open valve would purge itself of the gunk and spew it all over the inside of the bell jar. This would allow the water level to decline, and the chlorinator would automatically resume operation. The material collected from the inside walls of the bell jars allowed customers to back up their complaints with samples of gunk. After receiving many such complaints, chlorine manufacturers added a fractionating tower<sup>18</sup> to their manufacturing process to eliminate the gunk (ca. 1935).

In July 1977, high concentrations of carbon tetrachloride were found in finished water from the Belmont and Queen Lane water treatment plants (WTPs) in Philadelphia.<sup>19</sup> The source of this material was traced to the chlorine used in the plants. When the chlorine supplier was changed, the problem disappeared. It was revealed that the manufacturer of the tainted chlorine was using a carbon tetrachloride scrubbing system to recover traces of chlorine from the off-gases produced during the manufacturing process. The problem was solved by separating the chlorine that was to be used for treatment of potable water from the chlorine that contained the gas recovered from the scrubbing system. This problem was investigated by the CI and several chlorine manufacturers. The outcome of this investigation led to the establishment of an interim maximum level for carbon tetrachloride in the chlorine used for potable water treatment. The USEPA set this level at 100mg/l, which was agreed to by the manufacturers’ association pending an assessment of what the chlorine industry was capable of producing.

The standard for the purity of chlorine used in potable water treatment is given in American National Standards Institute (ANSI)/American Water Works Association (AWWA) B301-04 which became effective September 1, 2004.<sup>20</sup> This standard limits the maximum concentration of carbon tetrachloride to not more than 100ppm (0.010%). However, testing for carbon tetrachloride is not required unless a carbon tetrachloride tail-gas scrubbing system is used to produce the chlorine. Chlorine supplied under this standard shall not contain more than 50ppm (0.005%) nonvolatile residue when loaded by the manufacturer into railroad tank cars or chlorine tank trucks. Up to 150ppm (0.015%) nonvolatile residue is allowed in the liquid chlorine later packaged in cylinders or ton containers. Other limitations are as follows: moisture not to exceed 150ppm (0.015%) by weight; heavy metals not to exceed 30ppm (0.003%) expressed as lead; mercury not to exceed 1ppm (0.0001%) reported as mercury; arsenic not to exceed 3ppm (0.0003%); and the sum of all heavy metals not to exceed 30ppm (0.003%) by weight expressed as lead.

AWWA has also issued standards for anhydrous ammonia (ANSI/AWWA B305-06) and aqua ammonia (ANSI/AWWA B306-07) used to form chloramines in potable water.<sup>21,22</sup>

All of the AWWA standards are revised periodically. The reader should contact this organization to determine which standards are in effect.

The following are the major sources of impurities found in chlorine:

1. moisture entrapment during packaging;
2. organic impurities in the salt;
3. hydrocarbons from valve lubricants, pump seals, and various packing materials used in the manufacturing process; and
4. recovery systems used to separate the chlorine product from entrained hydrogen and air.

The impurities produced from these sources are summarized in Table 1.1.

### Consequences of Impurities

Of the impurities listed in Table 1.1, moisture is the worst offender because it makes the chlorine highly corrosive, leading to the formation of ferric chloride, which causes fouling of the metering equipment (chlorinators). The next most offensive impurities are hexachloroethane and hexachlorobenzene, which form a taffylike substance commonly called “gunk” that can cause serious equipment fouling. These impurities can originate from valve-lubricating compounds, valve and pump packing, and gaskets used in the piping system. Most of these impurities are soluble in liquid chlorine. Ferric chloride plates out on metal piping, most notably in areas of chronic flashing, usually at restrictions or locations of turbulent flow. Ferric chloride appears to spread from the liquid to the vapor phase, so this contamination carries through the chlorination equipment. The largest deposits occur at points of pressure reduction and areas of reliquefaction. Both hexachloroethane and hexachlorobenzene tend to sublime at room temperature, and are usually deposited at points of pressure reduction in metering and control equipment.

**TABLE 1.1. Impurities in Commercially Available Chlorine**<sup>20,23</sup>

Gases	Volatile Liquids	Volatile Solids	Nonvolatile Solids
CO <sub>2</sub>	Bromine	Hexachlorbenzene	FeCl <sub>3</sub> ·6H <sub>2</sub> O
H <sub>2</sub>	Carbon tetrachloride	Hexachlorethane	—
O <sub>2</sub>	Carbonyl chloride (phosgene)	—	Fe <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> ·6H <sub>2</sub> O
N <sub>2</sub>	Chloroform	—	Nitrosyl chloride
NCl <sub>3</sub>	HCl, methylene chloride, moisture	—	Nitrogen tetroxide, H <sub>2</sub> SO <sub>4</sub>

### **Nitrogen Trichloride in Liquid Chlorine**

**Occurrence, Formation, and Significance.** Nitrogen trichloride ( $\text{NCl}_3$ ) was first observed in 1811 from the action of chlorine on a solution of ammonium chloride. When generated in the laboratory, this compound is a yellow oil with a pungent chlorinelike odor. It is practically insoluble in water but easily soluble in most organic solvents. It has been reported that a drop of the oil explodes violently when touched with a feather dipped in turpentine.<sup>24</sup>

Nitrogen trichloride is not listed as an impurity in chlorine produced in the United States or Canada, where its occurrence has been virtually nil since about 1930. It is occasionally found in chlorine produced elsewhere in the world.

Nitrogen trichloride is formed during the production of chlorine when ammonia nitrogen is present in the brine fed to the electrolytic cells. It is soluble to the extent of 7.3 mg/l in liquid chlorine, but it is not soluble in water or in the concentrated sulfuric acid that is used in the production of chlorine to remove moisture. Once  $\text{NCl}_3$  forms in the electrolytic cells, it will pass with the chlorine gas through the coolers, scrubbers, and acid-sealed pumps, and will be condensed with the liquid chlorine. The danger of explosion is greatest when the liquid chlorine in the container is depleted and only chlorine vapor remains. The  $\text{NCl}_3$  concentrates itself in the layer of liquid chlorine next to the vapor phase. As the liquid chlorine is used up, the concentration of  $\text{NCl}_3$  keeps increasing at the vapor-liquid interface.

**Explosions Caused by Nitrogen Trichloride.** The last reported chlorine explosions from  $\text{NCl}_3$  in liquid chlorine in the United States and Canada occurred 1929. However, many chlorine producers outside the United States, Canada, and the European Union are unaware of the dangers of  $\text{NCl}_3$ . An evaporator explosion was reported in India in 1965, and in 1981 White investigated several explosions in South America, all of which were the result of ammonia N in the water entering the chlorine cell at concentrations between 50 and 300 mg/l.

**Prevention of Nitrogen Trichloride Formation in Liquid Chlorine.** The most effective method of dealing with  $\text{NCl}_3$  is to remove all ammonia nitrogen from the water used to prepare the brine solution. This can be done by using breakpoint chlorination followed by aeration of the water.

A second method is to decompose the  $\text{NCl}_3$  formed during electrolysis by irradiating the chlorine gas exiting the cells with ultraviolet (UV) light in the spectrum of 3600–4400 before the chlorine enters the scrubbers. As it is difficult to monitor the effectiveness of removing the  $\text{NCl}_3$  by UV, it is more practical and reliable to use breakpoint chlorination, followed by aeration. However, the UV method has been used successfully to remove the small quantities of  $\text{NCl}_3$  formed when the raw water contains trace concentrations of ammonia.

### Silica Contamination

Contamination of chlorine by silica produces the formation of white silicon dioxide crystals ( $\text{SiO}_2$ ) when the chlorine gas enters the injector assembly of a chlorinator. The injector inlet port plugs up rapidly, which makes the chlorinator inoperable. The source of silica may be contaminated brine water or silicone grease used in valves by the chlorine packager. Silica contamination of brine water is most likely to occur when the chlorine is a by-product from a metal refining process such as the extraction of magnesium from magnesium chloride ore.

If the brine contains silica, electrolysis will convert the silica to silicon tetrachloride ( $\text{SiCl}_4$ ), which becomes a contaminant in the chlorine. When the liquid chlorine is vaporized, the chlorine vapor carries the  $\text{SiCl}_4$  through the chlorinator and into the injector. When chlorine comes into contact with the water in the injector, the  $\text{SiCl}_4$  is immediately transformed into  $\text{SiO}_2$  crystals, which eventually plug the injector inlet.

## PHYSICAL AND CHEMICAL PROPERTIES OF CHLORINE

### General

Chlorine has an atomic number of 17 and an atomic weight of 35.457. Molecular chlorine,  $\text{Cl}_2$ , has a weight of 70.914. Two isotopes of chlorine,  $\text{Cl}^{35}$  and  $\text{Cl}^{37}$ , occur naturally, and at least five other isotopes have been artificially produced.<sup>25</sup> Ordinary atomic chlorine consists of a mixture of about 75.4%  $\text{Cl}^{35}$  and 24.6%  $\text{Cl}^{37}$ . Chlorine usually forms univalent compounds, but it can also combine with a valence of 3, 4, 5, or 7 (Chapter 2).

In its elemental form, chlorine is a greenish yellow gas that can be readily compressed into a clear, amber-colored liquid that solidifies at atmospheric pressure at about minus 150°F. Chlorine gas forms into a soft ice upon contact with moisture at 49.3°F and at atmospheric pressure. (This is chlorine hydrate,  $\text{Cl}_2 \cdot 8\text{H}_2\text{O}$ .)

In commerce, chlorine is always packaged as a liquefied gas under pressure in steel containers. The liquid is about 1½ times as heavy as water, and the gas is about 2½ times as heavy as air. The liquid vaporizes readily at normal atmospheric temperature and pressure. It has an unmistakable irritating, penetrating, and pungent odor. The properties of chlorine gas and liquid are listed in Tables 1.2 and 1.3, and on Figures A1 through A8.

Some of the properties of chlorine merit comment.

### Critical Properties

The *critical temperature*, above which chlorine exists only as a gas, despite the pressure is 291.2°F (144°C). The *critical pressure* is the vapor pressure of liquid chlorine at this critical temperature. The *critical density* is the mass of a unit volume of chlorine at the critical pressure and temperature.



**TABLE 1.2. Properties of Chlorine Gas**


---

Symbol: Cl<sub>2</sub>  
 Atomic weight: 35.457  
 Atomic number: 17  
 Isotopes: 33, 34, 35, 36, 37, 38, 39  
 Density (see Appendix) at 34 °F (1.1 °C) and 1 atm: 0.2006 lb/ft<sup>3</sup>  
 Specific gravity at 32 °F (0 °C) and 1 atm: 2.482 (air = 1)  
 Liquefying point at 1 atm: -30.1 °F (-34.5 °C)  
 Viscosity (see Appendix) at 68 °F (20 °C): 0.01325 cP (approximately the same as saturated steam between 1 and 10 atm)  
 Specific heat at constant pressure of 1 atm and 59 °F (15 °C): 0.115 Btu/lb/°F  
 Specific heat at constant volume at 1 atm pressure and 59 °F (15 °C): 0.085 Btu/lb/°F  
 Thermal conductivity at 32 °F (0 °C): 0.0042 Btu/h/ft<sup>2</sup>/ft  
 Heat of reaction with NaOH: 626 Btu/lb Cl<sub>2</sub> gas  
 Solubility in water at 68 °F (20 °C) and 1 atm: 7.29 g/l.

---

## Combining quantities:

1-lb chlorine gas combines with

- 1.10-lb commercial hydrated lime (95% Ca(OH)<sub>2</sub>)
- 2Ca(OH)<sub>2</sub> + 2Cl<sub>2</sub> = Ca(OCl)<sub>2</sub> + CaCl<sub>2</sub> + 2H<sub>2</sub>O 0.83-lb commercial quicklime (95% CaO)
- 2CaO + 2H<sub>2</sub>O + 2Cl<sub>2</sub> Ca(OCl)<sub>2</sub> + CaCl<sub>2</sub> + 2H<sub>2</sub>O 1.13-lb caustic soda (100% NaOH)
- 2NaOH + Cl<sub>2</sub> = NaOCl + NaCl + 2H<sub>2</sub>O 2.99-lb soda ash
- 2Na<sub>2</sub>CO<sub>3</sub> + Cl<sub>2</sub> + 2H<sub>2</sub>O = NaOCl + NaCl + 2NaHCO<sub>3</sub>

**TABLE 1.3. Properties of Liquid Chlorine**


---

Critical temperature	144 °C; 291.2 °F
Critical pressure	1118.36 psia
Critical density	573 g/l; 35.77 lb/ft <sup>3</sup>
Compressibility	0.0118% per unit vol per atm increase at 68 °F (20 °C)
Density (see Appendix) at 32 °F	91.67 lb/ft <sup>3</sup>
Specific gravity at 68 °F	1.41 (water = 1)
Boiling point (liquefaction point) at 1 atm	-34.5 °C; -30.1 °F
Freezing point	-100.98 °C; -149.76 °F
Viscosity (see Appendix) at 68 °F	0.345 cP [approximately 0.35 times water at 68 °F (20 °C)]
1-vol liquid at 32 °F and 1 atm	457.6-vol gas
1-lb liquid at 32 °F and 1 atm	4.98-ft <sup>3</sup> gas
Specific heat	0.226 Btu/lb/°F
Latent heat of vaporization	123.8 Btu/lb at -29.3 °F
Heat of fusion	41.2 Btu/lb at -150.7 °F

---

**Compressibility Coefficient**

The compressibility coefficient of liquid chlorine is greater than that of any other liquid element. The compressibility coefficient represents the percentage decrease in volume corresponding to a unit increase in pressure when the liquid is held at constant temperature. This physical characteristic is the reason

why the volume–temperature relationship of chlorine is very important, as described below.

### Volume–Temperature Relationship

The volume of liquid chlorine increases rapidly as its temperature rises. Because of this characteristic, coupled with noncompressibility, extreme care must be taken to prevent hydrostatic rupture of containers or pipelines by the expansion of liquid chlorine produced by a rise in temperature. All containers are filled to their prescribed weight of chlorine at 60 °F (15.6 °C) so that 15% of the container volume is vapor space.

The vapor space provided in a container when it is initially filled with liquid chlorine is intended to accommodate a temperature rise sufficient to melt the fusible plugs installed in these containers. A 150-lb cylinder is equipped with one fusible plug. A 1-ton container is equipped with six fusible plugs (three on each end). The metal in these plugs is designed to yield or melt between 158 and 165 °F (70–74 °C), thus relieving pressure in the container and preventing rupture in case of fire or other exposure to high temperature.

Figure A7 illustrates the volume–temperature relationship in a container filled to the authorized limit. From this curve, the container will be “skin-full” when the liquid chlorine temperature reaches 153.64 °F (65.58 °C). At this temperature (see Fig. A6), the vapor pressure is 290 psi. At the lowest melting temperature of the fusible metal plug (158 °F, 70 °C), the vapor pressure would be about 310 psi. This indicates that the criteria for filling a chlorine container does not provide enough volume to match the fusible plug melting temperature of 158–165 °F (70–74 °C). However, an elastic volumetric expansion of the metal in chlorine cylinders and ton containers occurs when the pressure increases. When these containers are hydrostatically tested at 500 psig, it is not uncommon for a 3% volumetric expansion to be observed. This increase in volume would easily permit a temperature higher than 160 °F (71 °C) without fear of rupture. Ton containers have an added expansion factor in the dished heads at both ends of the container. These heads can reverse from the concave configuration installed when containers are manufactured to a convex position before the vessels rupture. This reversal in configuration has been observed several times when ton containers were overpressured by nitrogen trichloride explosions.

Railroad tank cars and stationary chlorine storage tanks used for WTP or wastewater treatment plant (WWTP) services are usually fitted with a spring-loaded CI safety valve combined with a breaking pin assembly that breaks at 225 psig. On cars used in pulp and paper chlorination, the safety valve relieves at 375 psig because the chlorine is air-padded at a higher pressure.

Automatic shutoff valves and protective hoods for manway covers are available to protect operators of tank cars and storage tanks from exposure to chlorine when a leak occurs.

### **Density of Chlorine Vapor**

The density of chlorine vapor varies widely with change in pressure and moderately with change in temperature. This is a most important variable in calculating the pressure drop for gas flow in both vacuum and pressure systems. The relationships of vapor density at various pressures and temperatures are shown on Figures A1 and A2.

### **Density of Liquid Chlorine**

The density of liquid chlorine varies only slightly with temperature. At 40°F (4.4°C) it is 90.85 lb/ft<sup>3</sup>, and at 140°F (60°C) it is 79.65 lb/ft<sup>3</sup> (see Fig. A4).

### **Viscosity of Chlorine**

Viscosity is the measure of internal molecular friction when a substance is in motion. It is necessary to know this property for both liquid and gaseous chlorine because it is a variable in the calculation of the Reynolds number used to measure friction losses in pipelines. The temperature-viscosity relationship for both chlorine liquid and the gas is shown on Figure A3.

### **Latent Heat of Vaporization**

Latent heat is the heat required to change one mass of liquid to vapor without a change in temperature. If the temperature of liquid chlorine is at 70°F (21.1°C), it requires about 100 Btu to vaporize 1 lb of liquid chlorine (see Fig. A5).

### **Vapor Pressure**

Vapor pressure is the pressure of chlorine gas above liquid chlorine when the vapor and the liquid are in equilibrium. This relationship varies widely with temperature (see Fig. A6). It is necessary to know the range of vapor pressure that can occur when liquid chlorine is being transferred from tank cars to vaporizing equipment. Lowering the pressure in the transfer lines below the vapor pressure will produce gas bubbles in the liquid chlorine.

### **Specific Heat**

Specific heat is the amount of heat required to raise the temperature of a unit weight of chlorine vapor by 1°F. At atmospheric pressure and a temperature of 59°F (15°C), the specific heat requirement is 0.085 Btu/lb of chlorine.

### **Solubility of Chlorine Gas in Water**

Chlorine gas has limited solubility in water. At atmospheric pressure and 68°F (20°C), its solubility in water is 7.29 g/l. However, the equipment to produce

the chlorine solutions used in water and wastewater treatment facilities is operated at partial pressure (vacuum). At the vacuum levels used in this equipment, the maximum solubility of chlorine is about 5000 mg/l. The upper limit of solubility recommended by chlorinator manufacturers is 3500 mg/l. This arbitrary value has been used successfully to protect chlorine solution discharge systems from developing gas pockets in the solution piping and off-gassing at the point of application.

### **Solubility of Liquid Chlorine in Water**

The solubility of liquid chlorine in water is a controversial subject. Many people say that as soon as liquid chlorine is discharged into water, it flashes off into vapor, and during this flash-off the water temperature in the immediate vicinity of the chlorine discharge drops to 49 °F (9.4 °C) or lower. At this temperature, the chlorine vapor and the water combine to form a solid hydrate,  $\text{Cl}_2 \cdot 8\text{H}_2\text{O}$ , known as “chlorine ice.” However, the interesting part of this phenomenon is that this chlorine ice is highly soluble in water.

The solubility of chlorine vapor at various water temperatures and pressures is illustrated on Figure A8, and is discussed further below.

In 1940, the Standard Oil Company in Richmond, California, was using liquid chlorine to treat a cooling water system for its wax plant. The cooling water was seawater obtained from San Francisco Bay at a temperature of 50 °F (10 °C). The chlorine was applied to the suction of a 50,000 gpm pump. The chlorination system consisted of six inverted 150-lb cylinders manifolded to a common control valve in the pipeline leading to the pump suction. The liquid chlorine feed point was about 15 ft below the water surface adjacent to the pump suction. According to Figure A8, the solubility of liquid chlorine under these conditions would be approximately 12 lb of chlorine per 100 gal of cooling water (approximately 14,400 mg/l). Chlorine was applied intermittently at a rate sufficient to produce a 4–5 mg/l residual at the condensers in the wax plant, which were about 5 min downstream from the point of chlorination.

The 5-min chlorine demand of seawater is usually about 1.5 mg/l. Therefore, the chlorine dosage at the pump intake was approximately 6.5 mg/l, which means that the liquid chlorine feed rate was slightly less than 3 lb/min. The chlorine was applied for a total of about 60 min/day.

The remarkable thing about this installation was the absence of any operating problems. There were no incidences of flash-off, off-gassing, or pump corrosion, which proves that under proper conditions liquid chlorine actually is soluble in water.

Many years later, White and Tracy discharged liquid chlorine into the San Francisco Water Department’s Crystal Springs Reservoir to determine the feasibility of using an open reservoir for disposal of a leaking container in case of an emergency. This test consisted of releasing liquid chlorine from a 150-lb cylinder approximately 10 ft below the water surface at a

deep portion of the reservoir, where the water temperature was about 55 °F (12.8 °C).

The results were quite interesting: The liquid that rose from the end of the discharge pipe without flash-off, or any indication of turbulence, had the shape of an inverted ice cream cone. This cone had the color of pale amber. Within not more than about 6 in. from the surface, the water in the reservoir turned a pale green, indicating the formation of chlorine vapor, but there was no indication of chlorine hydrate formation. Some ammonia solution was squirted onto the water surface where off-gassing was considered likely. Surprisingly, only a small white puff of ammonium chloride vapor appeared just above the area where the water turned pale green. A slight chlorine odor was detected within a radius of 10–12 ft from the chlorine cone, but it disappeared quickly after the cylinder was shut down.

It should be noted that regulatory authorities do not recommend disposing of a leaking chlorine cylinder in a body of water. The hole in the container will rapidly increase because of the concentrated hydrochloric acid formed at the water–chlorine interface. The container will also float to the surface of the water after enough chlorine has escaped for it to become buoyant. Chlorine gas will then continue to escape to the atmosphere until the container is completely empty.

A chlorination facility formerly used by the Sanitation Districts of Los Angeles County in Carson, California, was somewhat unique in the water and wastewater treatment industry. The facility was shut down after the events of September 11, 2001 to avoid presenting 90-ton railcars of chlorine as targets for terrorists (S. Krai, pers. comm.). The installation manufactured a 15,000 mg/l calcium hypochlorite solution from liquid chlorine, lime slurry, and plant effluent. Over a period of 16 years, the capacity of this system was increased from 30,000 lb/day to 100,000 lb/day without changing any of the structures housing the equipment. Approximately 90,000 lb/day of liquid chlorine was dissolved into a mixture of lime slurry and 350 gpm of plant effluent using a water pressure at the chlorine injection point of about 30 psi. According to Figure A8, the solubility of liquid chlorine is about 10.5 lb/100 gal of effluent plus the slurry. This is approximately 53,000 lb/day of chlorine. However, the system was capable of using 100,000 lb/day of chlorine without experiencing any problems due to “flashing” or off-gassing at the point of injection.

### **Chemical Reactions**

In the absence of moisture, liquid chlorine will not attack ferrous metals, which makes it possible to store it in steel containers. However, absolutely “dry” liquid chlorine cannot be produced by the commercial processes currently available. The steel containers are therefore provided with extra wall thickness to offset the small amount of corrosion that will occur inside these containers.

Liquid chlorine will attack and very quickly destroy polyvinyl chloride (PVC) and rubber, hard or soft. Dry chlorine gas will not attack copper, ferrous metals, or ferrous alloys. It will support combustion of carbon steel at 483°F (250°C). Above a temperature of 291.2°F (144°C), chlorine exists only as a gas regardless of pressure.

Moist chlorine gas will attack copper and all ferrous metals, including stainless steel and ferrous alloys. Gold, platinum, and tantalum are the only metals that are totally inert to attack by moist chlorine gas. Because of the very high cost of these metals, silver is widely used in instruments that could come into contact with moist chlorine gas. The silver chloride formed on the surface of the silver when it comes into contact with moist chlorine gas is inert to further attack.

Aqueous solutions of chlorine are extremely corrosive. For this reason, PVC, fiberglass, Kynar, polyethylene, certain types of rubber, Saran, Kel-F, Viton, and Teflon are commonly used where exposure to both moist chlorine gas and chlorine solutions are likely.

Chlorine reacts with ethyl alcohol and ether in trace amounts to form solid, waxy hexachloroethane. It also reacts with grease and oils to form a voluminous frothy substance. Solid complex hydrocarbons are formed by the reaction of chlorine and various petroleum distillates. At normal temperatures, there are no reactions between chlorine gas and chloroform, wood alcohol, or carbon tetrachloride.

The chemical reactions of chlorine gas and chlorine solutions in potable water and wastewater treatment are discussed in other chapters.

## HAZARDS FROM CHLORINE VAPOR AND LIQUID

### Toxic Effects

Liquid chlorine is a skin and eye irritant that can cause severe damage resembling a burn or frostbite. The gas in low concentrations is an irritant to the mucous membranes, the respiratory system, and the eyes. The amount of gas exposure determines the severity of impairment.

There are two types of gassing by chlorine. The type usually referred to in the literature is the damage caused by inhaling dry chlorine gas. The second type, which is the more dangerous of the two, occurs when chlorine fumes are released from an aqueous solution. This occurs when a pipe carrying a concentrated chlorine solution is ruptured in a confined area. If the concentration of the solution exceeds approximately 750 ppm of titrable chlorine, gas will be rapidly released. Because these chlorine fumes are laden with moisture, they seem more tolerable to the respiratory tract, and the victim will unwittingly inhale large amounts of molecular chlorine. This can produce pulmonary edema that could cause death by “drowning” during sleep. A victim of moist chlorine inhalation should be immediately placed under the care of a physician.

Gassing from dry chlorine gas is more common and much more disagreeable. The victim will immediately sense a sudden stricture to the upper respiratory tract. This is nature's way of preventing passage of the gas into the lungs. The victim must attempt to get out of the area of the leak by immediately moving upwind, and take only very short breaths through the mouth while they are in the chlorine cloud. Normal breathing will cause coughing, which must be prevented because it draws chlorine further into the lungs. Exposure to dry chlorine gas will also cause irritation of the eyes.

### **First Aid**<sup>26-28</sup>

Prompt action is essential in severe cases of inhalation. The local emergency medical response team or fire department should be contacted immediately. Individuals responding to the crisis should don appropriate self-contained breathing apparatus before entering the area affected by the chlorine leak. The patient should be moved outdoors because the victim's clothing will have absorbed a considerable amount of chlorine. This chlorine will be further inhaled if the victim is moved indoors. If blankets are available, the clothing should be removed and the patient kept warm and quiet. If an emergency shower is available, the patient should be rinsed before being wrapped in blankets. The eyes should be flushed immediately with tepid water for at least 15 min. Artificial respiration should be started immediately if the victim stops breathing or starts to turn blue (cyanosis).

The emergency response team will immediately further decontaminate the victim by flushing the skin and hair with plain water for 3-5 min followed by additional washing with warm water and mild soap and a thorough rinse. Additional flushing will also be provided to the eyes. Moist oxygen or moist air will be administered as required. Cardiac monitoring will be initiated and steps taken to stabilize erratic heart rhythm. Bronchodilators may be administered if the victim is wheezing.

A physician should perform the procedures needed to reduce the formation of pulmonary edema, arrest declining blood pressure, and administer longer-term oxygen therapy.

After recovering from anoxemia or pulmonary edema, a severely gassed victim must be closely nursed for an extended period of time to prevent the development of pneumonia.

In treatment of mild cases of gassing, the first step is to leave the area of the fumes, breathe lightly, move slowly without exertion, remain quiet, keep warm, and resist the impulse to cough.

The victim will be at first seized with fear and may become panicky because they feel symptoms of suffocation. Assuring the victim these symptoms will subside with the passage of time can allay the fears. Sedatives should be given only under the supervision of qualified medical personnel.

For most patients, there are no residual symptoms attributable to severe gassing by chlorine. However, some anxiety reactions may linger for months. Victims with a history of asthma have had lingering effects of distress. Exposure

to chlorine can also lead to reactive airways dysfunction syndrome (RADS), a chemical irritant-induced type of asthma.

### Physiological Response

The USEPA Technology Transfer Network Air Toxics Web Site describes the following physiological responses to various concentrations of chlorine gas (see Table 1.4).

Death occurs very rapidly for most animals when the chlorine concentration in the air approaches 1000 ppm.

The data summarized in Table 1.4 indicate that physiological responses start to occur at very low chlorine concentrations. These levels are much lower than the concentrations cited in material safety data sheets (MSDS) to produce the same physiological reactions. The reason for this apparent discrepancy is the target audience for this information. The information in Table 1.4 applies to the general population, which includes children and the elderly. The MSDS prepared by chlorine manufactures, packagers, and users are for the use of healthy adults who chose to work in industries that use this chemical. Individuals continuously exposed to low levels of airborne chlorine gradually lose their sensitivity to it and usually do not start to experience stress until the concentration approaches 1 ppm. Everyone exposed to more than 30 ppm of chlorine will be adversely affected.

### Intentional Release

Unfortunately, in recent years, the intentional release of chlorine gas to cause physical harm and damage has become a distinct possibility. Chlorine cylinders have been used in terror attacks in Iraq, and attempts, some successful,

**TABLE 1.4. Concentrations of Chlorine Gas Required to Produce Physiological Responses<sup>29</sup>**

Effect	Parts of Chlorine per Million Parts of Air by Volume
Tickling of the nose	0.014–0.054
Tickling of the throat	0.04–0.097
Itching of the nose and cough, stinging, or dryness of the nose and throat	0.06–0.3
Burning of the eyes and pain after 15 min	0.35–0.72
Discomfort ranging from eye and respiratory irritation, coughing, shortness of breath, and headaches	Above 1.0
Chest pain, vomiting, labored breathing, and coughing	30
Toxic pneumonitis and pulmonary edema	40–60



have been made to obtain chlorine cylinders from packagers and water treatment facilities in the United States. Utilities need to become proactive in monitoring their in-plant supplies of chemicals and securing them to the maximum extent possible.

Concern over theft of chlorine containers, coupled with the hazards of transporting chlorine through populated areas in railcars, has led the U.S. Congress along with the Department of Homeland Security to evaluate the feasibility of discontinuing the use of chlorine gas for disinfecting drinking water and wastewater. Congress enacted a temporary chemical security legislation in October 2006. This law required the Department of Homeland Security to promulgate chemical plant security regulations by April 4, 2007. However, it exempted WTPs and WWTPs from these rules and did not address security concerns associated with the transportation of hazardous gases. Additional congressional hearings were conducted on chemical security during 2007 and more legislation is pending. The preliminary drafts of the bills being considered do not exempt WTPs and WWTPs from the new regulations. Final action on this legislation will probably be delayed until after the 2008 presidential election.

A secondary disinfectant must be carried throughout potable water distribution systems, and chlorine will be required to provide this secondary residual either as free chlorine or chloramine. If the use of chlorine gas is discontinued in WTPs, either the purchase of bleach from chlorine vendors or the installation of on-site chlorine generation facilities will be required.

Discontinuing the use of chlorine gas at WWTPs will require conversion to liquid bleach or installation of the alternative wastewater disinfection technologies discussed elsewhere in this book.

## **CHLORINE LEAKS**

### **Definitions**

Chlorine leaks, usually referred to as emissions or releases, are simply discharges of chlorine liquid or vapor (gas) into the atmosphere. Leaks are characterized as minor, major, or catastrophic.

Minor leaks usually occur at the start-up of a new installation or immediately after completion of maintenance or inspection procedures in an operating facility. These leaks usually are the result of gasket failures, valve packing that needs to be adjusted, or equipment malfunction.

Major leaks include “guillotine breaks” in a pipeline under pressure, broken flexible connections, fusible plug failures, and/or leaks produced by accidents associated with repair work done while a system is under chlorine supply pressure. Major leaks can also occur when the temperature of chlorine reaches 483 °F (250 °C) and spontaneous combustion takes place between chlorine and steel.

A catastrophic leak at a WTP or WWTP is a “one-in-a-million event” produced by rupturing a chlorine container or “blowout” of a fusible plug.

In potable water and wastewater chlorination systems that meter chlorine under a vacuum of 18–20 in. of mercury, the leaks are usually minor.

### **Fire and Building Codes**

In the United States, there are three major organizations that produce model fire codes. The International Fire Code Institute (IFCI), with headquarters in Austin, Texas, publishes the Uniform Fire Code (UFC), which is used predominantly in the western United States. The Building Officials and Code Administrators, International (BOCA), headquartered in Country Club Hills, Illinois, publishes a code used in the Midwest and in the northeastern United States. The Southern Building Code Congress International in Birmingham, Alabama, publishes the Standard Fire Prevention Code (SFPC), or Standard Building Code. This code covers the south-central and southeastern states. An additional organization, the National Fire Protection Association (NFPA) in Quincy, Massachusetts, does not produce a model code, but it does develop and publish numerous standards and technical documents. NFPA materials cover a number of subjects related to fire and building code issues, including hazardous materials and emergency response. NFPA standards are frequently referenced as code documents by governmental groups. In addition, the Uniform Building Code (UBC), published by the International Conference of Building Officials in Whittier, California, contains provisions that impact facilities that use chlorine.

These codes contain requirements establishing minimum distances between classes of chemicals, secondary containment systems, design of piping systems, need for gas detectors, installation of fire sprinkling systems, and requirements for emergency response teams.

These model codes are modified annually. Completely new editions of the codes are published every three years. To properly address these codes in the design, construction, and operation of facilities using chlorine, the local government should be contacted to determine which specific codes have been adopted and the applicable year for each code.

The requirements of these codes are discussed in more detail in Chapter 8.

### **Characteristics of a Major Liquid Chlorine Release**

**Brian Shera's Bucket.** The following demonstration of a catastrophic chlorine leak was conducted by Brian Shera of Pennwalt Corporation.

All observers were wearing an air pack breathing apparatus and were positioned upwind from the test site. The ambient temperature was about 60°F (15°C). Shera dug a hole about 6 in. in diameter and 10–12 in. deep in an open area of sandy soil using a posthole digger. Next, he withdrew liquid chlorine from an adjacent storage system into a bucket, walked a few steps, and poured

it into the hole. There had been an immediate flash-off of chlorine vapor when the bucket was being filled, so Shera calculated that the amount poured into the hole was close to 28 lb. There was a thin film of ice at the surface of the bucket after the flash-off and immediately before chlorine was poured into the hole. When he poured the chlorine into the hole, there was another brief flash-off, followed by another coating of the ice film. If 25% of the chlorine flashed off when it was poured into the hole (7 lb), then approximately 20 lb still remained to be vaporized by the ambient air, whose temperature was about 65 °F (18 °C). The exposed area of the hole was about 0.2 ft<sup>2</sup>. The observers continued to watch the intermittent flash-off phenomenon for over an hour, and when they left, there was a substantial amount of liquid chlorine remaining in the hole.

The most significant characteristics of a major leak demonstrated by this performance were the long drawn-out vaporization cycle and the rapidity of the freezing cycle. It also verified that the flash-off phenomenon would occur only when chlorine liquid is spilled into the atmosphere. In other words, a chlorine container of any kind cannot undergo flash-off unless a rupture occurs that exposes the liquid surface to the atmosphere—such as a dished head being blown off. However, the liquid that spills will flash off, and the remainder will vaporize at a rate of approximately 7 lb/h/ft<sup>2</sup> of the liquid chlorine.

## CALCULATING CHLORINE LEAK RATES

### Liquid Release

$$Q = 77A\sqrt{(P_1 - P_2)(\rho)} = \text{lb/s}, \quad (1.21)$$

where

$A$  = area of opening to atmosphere (ft<sup>2</sup>);

$P_1$  = upstream pressure (psi);

$P_2$  = downstream pressure (psi); and

$\rho$  = density of liquid chlorine upstream from the opening to atmosphere (lb/ft<sup>3</sup>).

### Vapor Release

$$Q = 36.64A\sqrt{P/V} = \text{lb/s}, \quad (1.22)$$

where

$A$  = area of opening to the atmosphere (ft<sup>2</sup>);

$P$  = upstream pressure (psi);

$V$  = 1/density of chlorine vapor at opening (lb/ft<sup>3</sup>).

### Tanker Truck Leak during Unloading

The following is a method for estimating the leak rate from a road tanker while transferring its contents to the consumer's storage tank. The cause of the leak is assumed to be a separation of the loading lines.

The usual capacity of a tanker is 17 tons. It can empty its contents in 2.75 h with a 30 psi pressure differential. Therefore, this flow rate is  $34,000 \text{ lb}/165 \text{ min} = 206 \text{ lb}/\text{min} = 3.43 \text{ lb}/\text{s}$ . Then, using the equation  $Q = 77A\sqrt{[(P_1 - P_2) \times p]}$  and substituting 3.43 lb/s for  $Q$  and 30 psi for  $P_1 - P_2$  and  $88 \text{ lb}/\text{ft}^3$  for  $p$ ,  $A$  is calculated as follows:

$$3.43 = 77A\sqrt{(30 \times 88)}$$

$$A = 3.43/77(51.38) = 0.00087$$

Use  $77A = 0.0667$  for convenience.

The tanker truck leak rate can be calculated for any differential pressure. The value of  $P_1$  would be based upon the pressure in the road tanker at the time of the leak. Assuming that the tanker pressure is 90 psi, the leak rate would be

$$Q = 0.0667\sqrt{(90 \times 88)}$$

$$Q = 0.0667 \times 88.99 = 5.94 \text{ lb}/\text{s}$$

$$Q = 356.44 \text{ lb}/\text{min}.$$

This is the worst-case scenario because the excess flow check valves would not only limit this flow rate but would more than likely stop the spill entirely, as has been the case in many railcar accidents when the valves on the dome of a derailed car are completely destroyed. The road tankers are fitted with 14,000 lb/h (233 lb/min) excess flow valves (EFVs) in order to shorten the transfer time.

### Guillotine Break in a Pipeline: Ton Container Supply

If the installation involves liquid withdrawal from ton containers, then evaporators will be an integral part of the chlorine supply system. Therefore, the worst-case scenario would be a rupture in the liquid header between the containers and the evaporators. To simplify the concept, the calculations should be confined to one container, one evaporator, and 100 ft of 1-in. header pipe.

The liquid discharged from the container must pass through a  $\frac{3}{8}$ -in.-diameter tubing in the dished head, then through the container shutoff valve,

then through the auxiliary shutoff valve, and finally through the header valve. All these components are flow restrictors compared with a 1-in. pipe. It is important that these restrictions be accounted for in calculating the chlorine leakage rate.

Circa 1950, operating personnel needed to know the maximum possible liquid withdrawal rate from a single ton container at the East Bay Municipal Utility District WWTP in Oakland, California. The chlorinator capacity was 18,000 lb/day. The test, which was performed several times, indicated that the maximum liquid chlorine flow rate into this chlorinator was only about 10,200 lb/day. The pressure drop between the ton container and the pipe entering the chlorinator ranged from 85 to 40 psi and averaged about 45 psi because there was a pressure-reducing valve between the evaporator and the chlorinator. The flow at this pressure drop has to be recalculated to reflect zero pressure at the leak. To apply a worst-case situation, let us assume a container pressure of 120 psi.

Using the liquid release formula,

$$Q = 77A\sqrt{[(P_1 - P_2) \times p]} = \text{lb/s}, \quad (1.21)$$

where

$$Q = 10,200 \text{ lb/day} = 0.1181 \text{ lb/s}$$

$$p = 88 \text{ lb/ft}^3.$$

Substituting in the above formula, the value of the unknown,  $77A$ , can be found:

$$Q = 77A\sqrt{(45 \times 88)}$$

$$Q = 0.1181 \text{ lb/s}$$

$$0.1181 = 77A \times 62.93$$

$$77A = 0.1181/62.93 = 0.00188.$$

Assuming a container pressure of 120 psi, chlorine density at 88 lb/ft<sup>3</sup>, and substituting  $77A = 0.00188$  in Equation (1.21), the liquid leak rate  $Q$  will be

$$Q = 0.00188\sqrt{(120 \times 88)}$$

$$Q = 0.1899 \text{ lb/s} \times 60 = 11.4 \text{ lb/min}.$$

This then is the worst-case leak rate from a single ton container “on line” when there is a guillotine break in the liquid chlorine header piping. When ton containers are being used for liquid withdrawal, an evaporator is also part

of the system, so when there is a guillotine break in the liquid header, the contents of the evaporator become part of the leak.

All chlorine evaporators are designed to vaporize chlorine at a temperature between 160 and 180°F (71 and 82°C), regardless of the feed rate. This means that the level of liquid chlorine in the evaporator remains fairly constant. It is safe to assume that the evaporator content is never more than 100lb. At 20lb/min, the evaporator will empty in about 5 min because of the chlorine header rupture. Therefore, the probable maximum chlorine release rate in the chlorinator room for each container “on line” and each evaporator will be 11.4 + 20lb/min for the first 5 min and then 11.4lb/min after that interval. If the guillotine break occurs in the container storage room, the probable maximum release rate in this room will be 11.4lb/min. Leak rates of this magnitude will rapidly reduce the air temperature in the chlorine room, or the chlorine storage room, and reduce the rate of chlorine vaporization.

### **A Major Leak from PVC Header Failure**

When a small WWTP in Alaska was being upgraded, the chief operator requested the plumbing contractor to replace the rusty steel chlorine header piping between the cylinder room and the chlorinator room with PVC piping to eliminate the rusting “problem.” This was done without anyone questioning this change.

When PVC piping is used to convey pressurized chlorine gas, the pressure must not exceed 2–3psi. If the pressure is increased above these limits, the PVC reacts with the chlorine. This reaction produces heat, and at about 150°F (65°C) the PVC begins to melt. This happened at the plant in Alaska. The plant operator was on duty from 7:30 a.m. to 4:00 p.m. on the day before the leak. On the following day, the fire department received a 911 call about a strong chlorine odor, and a large cloud was reported above the WWTP. The fire department called the plant operator, who arrived with an assistant and turned off the gas flow from the chlorine cylinder. The room temperature at the time was estimated to be about 100°F (37.7°C). The leak lasted about 2½h. Because there were no gauges and no scales in the cylinder room, the total quantity of chlorine leaked from the cylinder could not be determined.

One of the most interesting aspects of this leak was the formation and travel of the plume of chlorine vapor. Immediately after the cylinder was shut down, the firefighters opened two large doors, allowing 2200 cu ft of 100°F (37.7°C) air containing the chlorine to form a plume in the atmosphere, which was at 5°F (–15°C) and 90% humidity. The total amount of chlorine in this plume was estimated to be about 500lb.

Because of the weather conditions and the extreme heat of the chlorine-laden air discharged from the cylinder room, the plume rose quickly, affecting only the residents within 600–700 ft from the plant. This illustrates the importance of heat at the site of a leak. In this case, the chlorine plume rose quickly

(chimney effect) and drifted away from the site without causing significant damage at ground level.

### **Ton Container Flexible Connection Failure**

Severing the flexible connection tubing at the auxiliary container valve is a worst-case chlorine leak from a ton container. Without the flow restrictions produced by the header valve and 4 ft of  $\frac{3}{8}$ -in.-diameter flexible connector, the rate of chlorine release will exceed the rate from the typical rupture of a header pipe. Based on the calculations discussed earlier in this chapter, at 120 psi pressure in the container, a reasonable estimate would be a 20% increase in flow:  $(11.4 \times 0.2 = 2.28) + 11.4 = 13.68$  lb/min.

### **Fusible Plug Failure from Corrosion**

Corrosion is the most common cause of fusible plug failure. A  $\frac{3}{4}$ -in. plug consists of a  $\frac{3}{16}$ -in.-diameter lead core in a brass body. The small quantity of moisture contained in “dry” chlorine begins an immediate attack on the vulnerable brass body, eventually producing a cone-shaped hole with its base on the inside of the cylinder. The end result of this corrosive attack is a pinpoint hole between the brass body and the threaded steel of the dished cylinder head. Routine replacement of all fusible plugs is the best way to prevent leaks from occurring through these holes. Packagers should install new plugs at 5-year intervals to minimize this hazard.

When leaks do occur, field observations by White indicate that the diameter of the hole in the fusible plug is never larger than 0.1 in. before the problem is discovered.

**Liquid Release.** To assume a worst-case situation, the hole diameter is assumed to be 0.15 in., with the fusible plug located below the liquid level in the ton container. The pressure inside the container is assumed to be 120 psi. Therefore,

$$Q = 77 A \sqrt{[(120 - 0) \times p]} = \text{lb/s}, p = 81 \text{ lb/ft}^3$$

$$A = \pi D^2 / 4 = \pi (0.15)^2 / 4 = 0.018 \text{ in}^2$$

$$A = 0.000125 \text{ ft}^2$$

$$Q = 77 \times 0.000125 \sqrt{(120 \times 81)} = \text{lb/s}$$

$$Q = 0.949 \text{ lb/s} = 56.94 \text{ lb/min.}$$

**Vapor Release.** This is an important comparison because there is a huge difference in the chlorine release rate. When a fusible plug fails as a result of corrosion, the safety crew should attempt to rotate the container to move the leaking plug into the area filled with chlorine vapor. If this is done, the escaping vapor will cool the liquid chlorine to 40°F (4.4°C) in 3–4 min. This drop

in temperature should be taken into account when using the vapor release formula:

$$Q = 36.64A\sqrt{(P/V)} = \text{lb/s.} \quad (1.22)$$

The pressure of the chlorine gas in the container is reduced enormously because the escaping gas is at zero gauge pressure. Under these conditions, pressure in the container will be as low as 40 psi. The density of chlorine vapor at 40°F (4.4°C) is 0.77 lb/ft<sup>3</sup>. Therefore,

$$\begin{aligned} V &= 1/0.77 = 1.3 \text{ ft}^3/\text{lb} \\ Q &= 36.64 \times 0.000125 \sqrt{(40/1.3)} = 0.0254 \text{ lb/s} \\ Q &= 1.52 \text{ lb/min.} \end{aligned}$$

**Fusible Plug Blowout.** Fusible plug blowouts rarely occur, but it is frequently used as an example of a catastrophic failure that would be almost equivalent to completely rupturing the walls of a container. If a blowout were to occur, the worst-case situation would be for the total discharge to consist of liquid chlorine. There would be no “flash-off” unless ambient air reached the inside surface of the liquid chlorine in the container. Assuming pressure in the container pressure drops to 30 psi, which would be equivalent to a liquid temperature of 20°F (-6.7°C), the density of the liquid chlorine would be 93 lb/ft<sup>3</sup>.

The leak rate is calculated as follows:

$$\begin{aligned} Q &= 77A\sqrt{(P_1 - P_2)}p = \text{lb/s} \\ p &= \text{Density at } 20^\circ\text{F} = 93 \text{ lb/ft}^3 \\ A &= [\pi \times (0.75 \text{ in.})^2] / 4 = 0.44 \text{ in.}^2 = 0.003 \text{ ft}^2 \\ Q &= 77 \times 0.003 \sqrt{[(30 - 0) \times 93]} = 12.2 \text{ lb/s} \\ Q &= 732.09 \text{ lb/min.} \end{aligned} \quad (1.21)$$

Obviously, this calculation is based on an incorrect assumption. The contents of the container could never be discharged at that rate; otherwise, the container would be empty in less than 30 min. The scenario that is closer to what would actually happen is as follows. The rapid drop in pressure inside the container would produce sudden cooling of the liquid chlorine. This cooling would lower the pressure inside the container to atmospheric pressure. Then the liquid chlorine would go into a freeze-and-thaw cycle that would cause the escape of chlorine to extend over several hours (as described in the section “Brian Shera’s Bucket”). A fusible plug blowout is considered a one-in-a-million occurrence.



## SUMMARY

1. Whenever there is a major leak, the flash-off phenomenon will always prevent positive pressure from developing in a containment structure. The sudden vaporization caused by the flash-off cools the atmosphere in the enclosed space so fast that a negative pressure develops.
2. There will always be a significant amount of liquid chlorine that must be dealt with as soon as possible. Because liquid chlorine is much more soluble in water than chlorine vapor, it can be removed using a water-operated eductor or by pumping.
3. The only way liquid chlorine can be cooled by a leak is to withdraw vapor from it. Liquid flowing out of a container as a result of a major leak will not cool the cylinder or reduce the vapor pressure unless the source of the leak is a large hole in the container such as caused by a fusible plug blowout. When this type of leak occurs, the flash-off phenomenon begins as soon as the liquid chlorine is exposed to the room atmosphere, which will cool the room so quickly that it will usually produce negative atmospheric pressure in the room.
4. High temperatures inside chlorine storage or feeding rooms occasionally cause major chlorine leaks. If the temperature of the chlorine-laden air trapped inside these rooms is much higher than the temperature of the outside air, the plumes of chlorine vapor produced in this type of accident will move upward in the atmosphere and cause little ground-level damage. However, only trained professionals should authorize the intentional release of chlorine vapor into the environment.

## USEPA RISK MANAGEMENT PROGRAMS (RMPs)

The USEPA regulates the release of hazardous chemicals into the atmosphere under the authority granted to it by the Clean Air Act. A large number of toxic chemicals are included in these regulations. However, this discussion will focus on the accidental release of chlorine, anhydrous ammonia, and aqueous ammonia.<sup>30,31</sup>

The quantities of chemicals stored on-site determine whether a facility is required to develop and implement an RMP. The thresholds for chlorine, anhydrous ammonia, and aqueous ammonia are listed in Table 1.5.

The aqueous ammonia threshold in Table 1.5 is based on the weight of ammonia in solution and is applicable only when the concentration of the ammonia solution is 20% or higher.

A few states have adopted RMPs with lower chemical thresholds and more stringent rules than the USEPA RMP requirements. Organizations that develop an RMP should consult their state's current regulations before following the USEPA rules.

**TABLE 1.5. USEPA RMP Chemical Thresholds  
Applicable to Water and Wastewater Treatment Plants**

Chemical	EPA RMP Threshold (lb)
Chlorine	2,500
Anhydrous ammonia	10,000
Aqueous ammonia	20,000

The USEPA thresholds are based on the quantities of chemicals stored at a specific location. For example, when a maximum of 16 150-lb chlorine cylinders are stored in one building and additional 150-lb chlorine cylinders are in use in other buildings, all of these buildings can be considered separate processes if they are located far enough apart, so an accident (e.g., a fire or an explosion) in the chlorine storage building would not affect the cylinders in the other buildings.

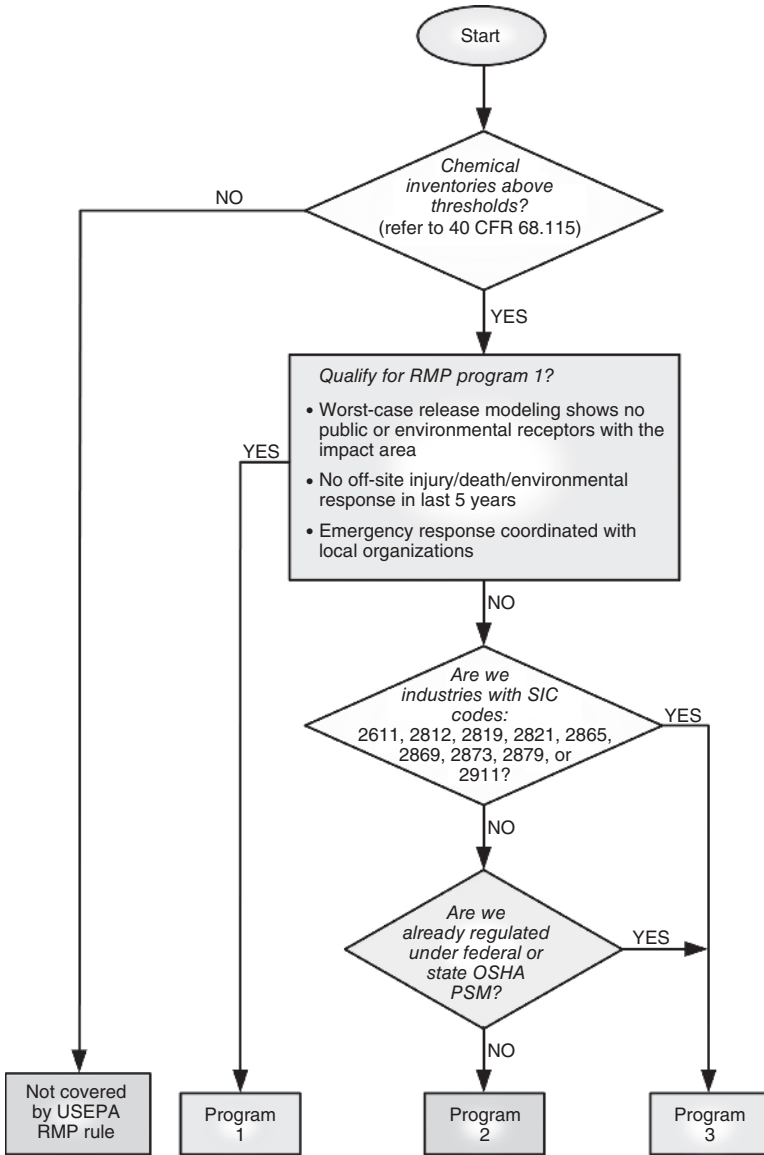
Treatment plants using 1-ton containers, bulk storage tanks, or railroad tank cars will exceed the USEPA threshold for chlorine and are required to implement an RMP. Chlorine manufacturers and packagers are also required to comply with this program.

The scope of the RMP required for a specific facility depends on the magnitude of risk associated with that facility. The USEPA has established three programs that must be met as the level of risk to the public or the environment increases. A decision tree for determining which program level is applicable to a specific facility is shown on Figure 1.5. Facilities are regulated under Standard Industrial Classification (SIC) codes. WTPs are classified under SIC 4941, and WWTPs are classified under SIC 4933. Neither of these types of plants is automatically required to meet the requirements of program 3. Chlor-alkali plants are subject to SIC 2812 and are required to comply with program 3.

The requirements of the three RMPs are summarized in Table 1.6. Prevention program 2 elements that were given different names by the USEPA from similar program 3 elements are listed in square brackets in this table.

The objectives of the management systems required in programs 2 and 3 are to identify the individual responsible for the development and implementation of the program and to establish formal procedures for the delegation of specific program responsibilities to other individuals in the organization. An organization chart defining the lines of authority between these individuals must be part of the management system.

A hazards assessment is required for all three programs; however, the assessment required under program 1 is not as extensive as those required under programs 2 and 3. All three programs require compilation of a 5-year accident history for the facility, which must include all incidents from RMP-related processes that resulted in on-site or off-site death or injury, evacuation from the site, sheltering in place, property damage, or environmental damage. In addition, the assessments for all three programs must include a worst-case



**Figure 1.5.** Decision tree for risk management programs (RMPs).

analysis to estimate the potential off-site area affected by the release of chlorine or ammonia. Programs 2 and 3 must also consider the impacts produced by an alternative release of these gases. A more detailed discussion of worst-case and alternative releases is included later in this chapter.

The topics that must be addressed in the accident prevention programs required by the USEPA RMP are identified in Table 1.6. Specific details

**TABLE 1.6. USEPA Risk Management Programs 1, 2, and 3 Requirements\***

RMP Element	Program 1	Program 2	Program 3
Management system	—	x	x
Hazard assessment			
Worst-case analysis	x	x	x
Alternative release analysis	—	x	x
5-year accident history	x	x	x
Prevention program			
Process safety information [Safety information]	—	x	x
Process hazard analysis [Hazard review]	—	x	x
Operating procedures	—	x	x
Training	—	x	x
Mechanical integrity [Maintenance]	—	x	x
Management of change	—	—	x
Pre-start-up review	—	—	x
Compliance audits	—	x	x
Incident investigation	—	x	x
Employee participation plan	—	—	x
Hot work permit	—	—	x
Contractors	—	—	x
Emergency response program	—	x	x

\*x indicates the element is included as one of the program requirements.

about each of these topics are provided in the Federal Register (40 CFR Part 68) dated June 20, 1996. Documents and manuals developed by the USEPA and others to assist in completing a comprehensive RMP can be obtained by contacting the National Service Center for Environmental Publications\* (phone: 1-800-490-9198), the AWWA,† the Water Environment Federation (WEF),‡ or the USEPA's Risk Management Hotline (phone: 1-800-824-9346).

The USEPA RMP requires the development and implementation of an emergency response program that shall include the following elements:

- procedures for informing the public and local emergency response agencies about accidental releases;
- documentation of proper first-aid and emergency medical procedures necessary to treat accidental human exposures;
- procedures for emergency response after an accidental release;

\*National Service Center for Environmental Publications, PO Box 42419, Cincinnati, OH 45242-0419.

†AWWA, 6666 W. Quincy Ave., Denver, CO 80235.

‡Water Environment Federation, 601 Wythe St., Alexandria, VA 22314-1994.

- procedures for inspection, testing, and maintenance of emergency response equipment;
- training for all employees in relevant procedures; and
- procedures to regularly review and update this program and to ensure that employees and local emergency response agencies are informed of any changes.

Prevention program 2 elements that were given names different from similar program 3 elements are listed in square brackets. Requirements for prevention program 2 elements may differ from prevention program 3 requirements, even when the name of the program element is the same. The reader should consult the American Water Works Association Research Foundation (AwwaRF) and WEF manuals for details about these elements.

The implementation date for the USEPA RMP was June 21, 1999. Plans for individual facilities are reviewed and updated at 5-year intervals.

### **OSHA Process Safety Management (PSM) Regulations**

The OSHA PSM rules are codified in the Federal Register (29 CFR 1910.119) and have been in effect since 1992. These rules require comprehensive management systems for handling highly hazardous chemicals by industry- and privately operated WTPs and WWTPs. Government-operated WTPs and WWTPs are also bound by PSM rules in OSHA plan states, which have their own state rules and enforcement programs approved by the federal OSHA. Organizations contemplating the development of a PSM plan should check with the state where their facility is located to determine which rules apply.

The threshold quantities of hazardous chemicals that trigger the development of an OSHA PSM plan are different from the thresholds established by the USEPA's RMP. The OSHA thresholds for chemicals used in WTPs and WWTPs are listed in Table 1.7.

The aqueous ammonia PSM threshold shown in Table 1.7 is based on the total weight of the solution and is only applicable when the ammonia concentration is higher than 44%.

The OSHA PSM program does not include the Management System and the Hazard Assessment elements required in the USEPA RMP. However, the Prevention Program and the Emergency Response Program elements are

**TABLE 1.7. OSHA PSM Chemical Thresholds  
Applicable to Water and Wastewater Treatment Plants**

Chemical	OSHA PSM Threshold (lb)
Chlorine	1,500
Ammonia (anhydrous)	10,000
Aqueous ammonia	15,000

essentially identical in both. This commonality is by design. The USEPA did not want to require facilities that were already included in the OSHA PSM to develop new safety programs. Eliminating the confusion associated with complying with two programs also makes it possible for OSHA inspectors to conduct site inspections, so that the USEPA does not have to employ personnel to perform this function.

The net effect of the USEPA and OSHA rules is that all public- and privately owned facilities producing, handling, or using significant quantities of hazardous chemicals are required to conduct proactive safety programs for the personnel employed in these facilities. The USEPA RMP expands the scope of this responsibility by requiring these facilities to also evaluate the potential impacts produced by the release of hazardous gases into the environment outside the boundaries of these facilities.

### **Worst-Case and Alternative Release Analyses**

The most controversial requirement of the USEPA RMP is preparation of a worst-case analysis for off-site release of hazardous gases and conveying this information to the general public. Most of this controversy stems from the USEPA definition of "worst case." For chlorine and ammonia, this is the release, as a gas, of all of the contents of the largest vessel on-site over a 10-min period. A very large area is impacted by a worst-case release. This could have a significant effect on public perception and emergency planning. The USEPA recognizes that a worst-case scenario may be highly improbable, that it may require active communication efforts to explain it to the public, and that it may not be the most appropriate basis for emergency planning. Careful selection of more credible alternative release scenarios that provide a better basis for emergency planning is very important.

The alternative release scenarios selected for analysis should be more likely to occur than the worst case, and must reach an end point off-site. They may be based on the accident history for the facility or on accidents known to have occurred at similar facilities. While not explicitly stated in the regulation, the intent is to select credible scenarios that would serve as realistic bases for developing on-site and off-site emergency response plans.

The procedure used to estimate the area affected by worst-case and alternative release scenarios is straightforward:

- determine the quantities of gas released and the time intervals over which these releases will occur;
- select a mathematical model to calculate the maximum distances at which toxic concentrations of gas are expected to occur;
- obtain a detailed map of the area surrounding the source(s) of the potential release(s);
- draw circles on this map showing the maximum distances at which potentially hazardous concentrations of gas are predicted to occur;

the location where the gas will be released is the centerpoint of these circles;

- determine the estimated population and the protected environmental receptors located inside these circles; and
- present this information to the USEPA by submitting one copy of the USEPA developed RMP Submittal Data Elements form for each release scenario.

The USEPA recommends that dispersion modeling to support RMP plans be done using the “RMP\*Comp” model available on the USEPA Emergency Management Web site.<sup>32</sup> This model is free, and the USEPA updates it. However, it is a planning model. Its only output is an estimate of the distance required to dilute the concentration of a hazardous gas to nontoxic levels.

More sophisticated models can be used to prepare RMP plans if an applicant desires to do so. However, much more documentation is required when this course is chosen. The USEPA recommends the use of more sophisticated models to track the plume produced when an accident actually occurs. A number of very good commercial models, and modeling firms, are available to perform this function.

The end point concentrations for hazardous gas plumes in 2007 were 3 ppm for chlorine and 150 ppm for ammonia. These are ERPG-2 values, set by the American Industrial Hygiene Association (AIHA) and revised when warranted by additional data. ERPG-2 is the maximum airborne concentration, below which it is believed that nearly all individuals could be exposed for up to 1 h without experiencing or developing irreversible or other serious health effects that could impair their ability to take protective action.

Maps suitable for RMP planning can be obtained from the U.S. Geological Survey (USGS). Population estimates can be obtained from the U.S. Census Bureau or from electronic databases such as LANDVIEW III. This is a public domain computer model that can be accessed from the Right-to-Know (RTK) Network at <http://www.rtk.net>.

## CHLORINE TRANSPORT ACCIDENTS

### Railroad Transportation

Railroads handle more than 1.7 million shipments of hazardous materials annually. These shipments consist of millions of tons of explosive, poisonous, corrosive, flammable, and radioactive materials. Rail transportation is a safe method for moving large quantities of hazardous materials. In 2004, there were only 29 accidents that involved the release of a hazardous material. In these accidents, a total of 47 hazardous materials cars released some amount of product (the capacity of a tank car is 34,500 gal). The Department of

Transportation (DOT) Hazardous Materials Information System's 10-year incident data for 1997 through 2007 identify a total of 17 fatalities resulting from hazardous material incidents occurring at railroad facilities.

On June 28, 2004, two trains collided in Macdona, Texas, breaching a loaded tank car containing chlorine. This car instantaneously released approximately 9400 gal of chlorine that formed a toxic vapor plume that engulfed the accident site to a radius of at least 700 ft before drifting away from the site. Four locomotives and 36 cars belonging to the two trains were derailed. This accident killed three people and seriously injured 30 others. The National Transportation Safety Board (NTSB) determined that the probable cause of the accident was train crew fatigue that resulted in the failure of the engineer and the conductor on one of the trains to appropriately respond to wayside signals governing the movement of their train. Damages to rolling stock, track, and signal equipment were estimated to be \$6.3 million. As of July 20, 2006, \$150,000 had been spent to clean up the environmental consequences. Other significant costs, including evacuation of the accident site, rerouting, and associated out-of-service expenses to the railroad, disruption to nonrailroad businesses, and settlement of damage claims arising from the accident had not yet been resolved by early 2008.<sup>33</sup>

On January 6, 2005, a freight train was improperly switched from a main line track onto an industry line track in Graniteville, South Carolina. This train struck an unoccupied parked train located on a rail spur leading to a textile manufacturing facility. The collision resulted in the derailment of three locomotives and 17 cars belonging to the two trains. One tank car was punctured in the shell by the coupler of another car and instantaneously released approximately 9220 gal of chlorine, creating a toxic vapor plume that engulfed the surrounding area. Approximately 5400 people located within a 1-mile radius of the derailment site were evacuated for several days. Nine persons were fatally injured and 554 sustained other injuries (75 requiring hospitalization). The NTSB concluded that the probable cause of the accident was the failure of a train crew to return a main line switch to its normal position after this crew had completed work on the industrial track owned by Avondale Mills. Property damage to the rolling stock and track owned by the railroad exceeded \$9.6 million. The railroad also reported spending \$41 million in 2005 for expenses related to the accident. The total direct costs of the accident were estimated to be approximately \$138 million, excluding chlorine cleanup costs. This estimate probably greatly underestimates the actual costs incurred by those affected by the accident. For example, according to the South Carolina Emergency Center and the USEPA Situation Reports, schools were closed for several days and mail service for the evacuated areas had to be forwarded to a neighboring post office. Preliminary estimates of costs to Aiken County, South Carolina, were in the millions of dollars as a result of potential damage to electrical systems and equipment in homes and businesses, cost of the first response and recovery operations, damage to fire and emergency response vehicles, and the treatment of the victims.



The fate of the textile manufacturing company, Avondale Mills, illustrates the significant long-term economic impacts of catastrophic hazardous materials transportation accidents. In May 2006, the company reached a \$215 million settlement with its primary property and casualty insurer for all claims related to the derailment. However, this was not enough to make the company whole. In July 2006, after spending \$140 million in unsuccessful efforts to clean and repair the facilities damaged by chlorine, the company declared it would be unable to recover financially from this accident and the subsequent disruption to its business plan. It was forced to close its 10 mills in South Carolina and Georgia and to lay off approximately 4000 employees.

A federal judge approved a class action settlement in excess of \$10.5 million between the railroad and almost 500 individuals who claimed to have suffered serious injuries after the derailment. In May 2005, a settlement was reached between the railroad and Graniteville residents and businesses who were evacuated but did not seek medical attention. Under the terms of this settlement, the railroad paid \$2000 to each person who was evacuated plus \$200 per person per day for the time they were away from their homes. These amounts were in addition to any property damage claims. The railroad settled separately with the families of the nine people killed in the action.<sup>33</sup>

The deaths, injuries, and economic costs caused by these accidents were large. However, in all three cases, NTSB investigators commented on the unique circumstances that made these losses much smaller than they could have been. All three accidents occurred during the early morning hours when few people were outside their homes. Each accident occurred in a rural area where the population density was relatively low. The meteorological conditions prevailing at the time of each accident limited the speed of expansion and the final size of the toxic plumes. All of these plumes also moved away from the accident sites in directions that minimized the number of people exposed to the toxic gases. Thus, impacts of these accidents could have been much worse than they actually were.

Numerous agencies of the federal government, academic researchers, private railroad companies, and committees from the Association of American Railroads had been working together to develop safer ways to ship hazardous chemicals before the three accidents discussed above. Their efforts were significantly accelerated by these events. Many approaches are being explored, among them design of a completely new type of railcar for transporting poison inhalation hazard (PIH) or toxic inhalation hazard (TIH) materials, development of recommended operating practices for trains hauling hazardous cargos, and establishment of performance standards for construction of chlorine and ammonia tank cars that would reduce the probability of a release in a given accident by 65%.

To provide additional focus in this area, The DOT proposed a rule on April 1, 2008 to "Improve the Safety of Railroad Tank Car Transportation of Hazardous Materials" (49 CFR Parts 171, 173, 174 and 179). This proposed rule would include the following requirements:<sup>33</sup>

- All tank cars built 2 years after the effective date of the final rule are to have tank head puncture-resistance systems conforming to the requirements of this rule.
- Each owner must bring 50% of its tank car fleet used to transport PIH materials into compliance with the tank head puncture-resistance requirements specified in the rules within 5 years of the effective date of the final rule.
- Five years after the effective date of the final rule, tank cars manufactured using nonnormalized steel for head or shell construction may not be used for transportation of PIH materials (these are primarily tank cars fabricated before 1989).
- Tank cars manufactured 8 years after the effective date of the final rule must meet both the tank head and the shell puncture-resistance system requirements specified in the rule.
- Tank cars that do not meet both the tank head and the shell puncture-resistance requirements specified in the rule cannot be used to transport PIH materials 8 years after the effective date of the rule.
- The insulation installed on tank cars used to ship chlorine must be improved to meet requirements specified in the rule.
- Tank cars used to transport bromine, ethylene oxide, and hydrogen chloride refrigerated liquid must meet both the tank head and the shell puncture-resistance requirements specified in the rule 8 years after the effective date of the rule.

The proposed rule also states that trains transporting tank cars containing PIH materials will have a maximum allowable speed of 50mph. However, if a tank car does not meet the tank head and shell puncture-resistance requirements specified in the rule, the maximum allowable speed will be reduced to 30mph when the train is moving over nonsignaled territory. (Nonsignaled territory means a rail line not equipped with a traffic control system or automatic block control system that conforms to the requirements of the proposed rule.)

The proposed rule is open for review and comment. Based upon the input received during the three public meetings held during the development of the proposed rule, many comments will be submitted to the DOT. After the issues raised in these comments have been resolved, a Final Rule will be promulgated.

None of the organizations that contributed to development of the proposed rule believe improved tank cars and slower train speeds will completely eliminate accidental releases of chlorine and ammonia into the atmosphere. Parallel efforts are also being pursued to reduce the numbers of tank cars containing PIH materials and to shorten the length of travel for tank cars conveying these materials.

One of the more effective nongovernmental programs developed to date to achieve these goals is the “Safety Initiative” started in October 2005 between Dow Chemical Company and Union Pacific Railroad (UP), Dow’s largest rail service provider.<sup>33</sup>

Specific goals in the Dow/UP agreement include the following:

- reducing idle times for hazmat shipments by 50% in high-threat urban areas;
- redesigning Dow’s customer supply chains to cut in half the amount of “highly hazardous chemicals” shipped by 2015;
- eliminating all nonaccidental leaks of certain hazardous chemicals by 2008;
- monitoring shipments of hazardous materials by satellite tracking tags and other sensors;
- improving the routing for hazardous material shipments;
- strengthen the Dow/UP commitment to Transportation Community Awareness and Emergency Response (TRANSSCAER); this is a voluntary national outreach effort that focuses on assisting communities to prepare for and respond to a possible hazardous materials transportation incident; its members are volunteer representatives from the chemical manufacturing, transportation, distribution, and emergency response industries, as well as the government; and
- redesigning Dow’s interdivision supply chains to reduce the number and distance of shipments involving high-hazard materials; this includes evaluating the potential for colocation of production and consuming facilities; the use of pipelines instead of rail in some instances; and conversion of highly hazardous products to less hazardous derivatives before shipping.

Dow reduced the amount of chlorine it ships by rail in the United States by 80% between 1999 and 2006.

The decrease in rail car shipments of chlorine to WTPs and WWTPs has not been so rapid. Only six WTPs and 19 WWTPs eliminated rail shipments of chlorine between 1999 and 2007. All six of the WTPs and 16 of the WWTPs changed to using rail delivery of liquid bleach. Three WWTPs converted to UV for disinfection.<sup>34</sup>

Twenty-four WTPs and 13 WWTPs still shipped chlorine by rail in 2007. Six of these utilities (four WTPs and two WWTPs) had firm plans to convert from chlorine gas to another disinfectant by 2009.<sup>34</sup>

### **Highway Transportation**

Statistics developed by the Railway Supply Institute (RSI) indicate that it is 16 times safer to move hazardous materials by rail than shipping the same

quantity of material over highways. However, it is very difficult to obtain specific information on the releases of chlorine or ammonia gas during highway accidents. One of the reasons for underreporting these accidents is that the amounts of gas released are usually small enough to not make them “news-worthy” unless there is a gas-related fatality involved. Another reason is the training received by the truck drivers employed by chlorine distributors in North America and Europe. These individuals and local hazmat teams know what to do when a leak occurs.

Occasionally, a “newsworthy” accident is reported. One example was reported in Austin, Texas, in May 2006.<sup>35</sup> A leak occurred in a 12,000-gal tractor-trailer filled with commercial-grade sodium hypochlorite solution. The driver parked the truck alongside a major highway while repairs were attempted. Attempts to stop the leak were not successful so the tractor-trailer was hauled to a nearby WWTP. A private hazmat contractor disposed of the hypochlorite solution over a period of several days. Residents of homes adjacent to the highway and the students in several nearby schools were evacuated until the chlorine fumes released by the spilled hypochlorite dissipated. The truck driver was treated in a hospital for breathing problems and later released. The only property damage was the grass killed in the drainage ditch adjacent to the highway.

**China.** A chlorine tanker burst a tire and ran head-on into another truck on a highway between Shanghai and Beijing in March 2005.<sup>36</sup> Both trucks turned over and the chlorine tank ruptured. At least 29 people were killed and 350 hospitalized. Approximately 10,000 people were temporarily evacuated from nearby villages.

**Egypt.** A major accident involving a chlorine tank truck occurred in Alexandria, Egypt, in December 1965. Five people died, including the truck driver and two would-be rescuers.

A chlorine tank truck, loaded with 7 tons of liquid chlorine, swerved to avoid hitting a passenger car, overturned, and sheared off a gas valve. The truck did not have a protective cover over the exterior valves or EFVs installed inside the tank. The most seriously exposed individuals were those who tried to rescue the injured and unconscious truck driver. Approximately 2 tons of chlorine leaked out before the opening for the gas valve was sealed. By this time, some 500 people were exposed to chlorine fumes.

## NOTABLE CONSUMER ACCIDENTS

### General

There have been a variety of accidents involving chlorine gas leaks at WTPs, WWTPs, and industrial plants. One of these accidents was discussed earlier

in this chapter (see the section “A Major Leak from PVC Header Failure”). Additional consumer accidents are discussed below.

### **A Fatal 1-Ton Container Leak**

One of the more serious chlorine accidents in North America at the consumer level occurred at a WTP. It caused the deaths of two people who lived close to the plant. A team of newspaper reporters who made a comprehensive investigation of this accident arrived at the following conclusions:

- The accident probably would not have occurred if there had not been a power failure during a brief rainstorm.
- If working gas masks had been conveniently available, the leak could have been halted immediately, and no injuries would have resulted.
- Residents adjacent to the plant would not have been affected if the chlorine container room had been farther than 65ft away from their homes.

An analysis of this accident leads to the following observations.

The power failure plunged the chlorine container room into practically total darkness (a rain squall shut out most of the exterior light). This caused a delay in the response of the operator who was on duty at the plant. He reported smelling a strong chlorine odor, indicating a severe leak, but he was unable to find a gas mask in the dark and immediately left the contaminated area.

Without power, the operator was unable to relieve the liquid pressure in the chlorine piping system. During a power failure, all of the liquid chlorine in the piping system between the containers and the metering equipment can discharge through any leaking joint unless the system is equipped with isolating valves. When power is available, the metering equipment can be used to withdraw liquid chlorine from the supply piping system, and thus avert a large leak.

Auxiliary lighting to illuminate the chlorine facilities and auxiliary power to operate the chlorine withdrawal system are essential safety features in chlorine handling facilities.

Readily accessible chlorine gas masks are of top priority. As soon as the fire department arrived with gas masks and emergency lights, the operator was able to locate the leaking connection. By this time power had been restored, and the operator was able to relieve the system of pressure and repair the leak.

Isolating valves are used to reduce the length of pressurized piping adjacent to a leak. This is why every container should be connected with an auxiliary valve attached to the container outlet valve. The outlet of the auxiliary valve is then connected to the inlet of the flexible connection and the outlet to the stationary header valve. Some operators prefer an auxiliary header valve at the outlet of the flexible connection, so that for liquid withdrawal the flexible

connection can be shut off at each end and removed during each container change without discharging liquid chlorine.

The deaths caused by this accident could have been avoided had the residents of the house been promptly evacuated when the operator became aware of the leak. The children of the victims did leave the house, which undoubtedly saved their lives.

### **A Leak from Four 1-Ton Containers**

This leak resulted in the discharge of the contents of four 1-ton chlorine containers that were “on line” at the time of the leak. Fortunately, there was no loss of life, but many nearby residents were treated for various degrees of chlorine inhalation.

This massive leak was the result of the following factors:

- The operator attempted to stop a leak at the stem of a chlorine header valve while the system was under full pressure from the four 1-ton containers.
- The leak was caused by structural failure of a bushing located in the 1-in. chlorine header into which the leaking header valve was threaded.
- The failure of the bushing was brought about by corrosion that occurred over a long period.

The lessons to be learned from this accident are as follows:

- Operators should never attempt to repair a chlorine leak while the system is under supply pressure.
- The first step in repairing a leak is to relieve the system of the pressure from the chlorine containers. Pressure gauges must be included in chlorine delivery piping systems to provide the operator with this vital information.
- Duplicate header systems can be constructed to allow replacement of the piping systems on an as-needed basis or on a regular schedule (i.e., every 5 years for systems passing 2 tons or more of chlorine per day, and every 10 years for those passing less than 2 tons per day).

### **A Leak from a Buried Chlorine Pipe**

This leak resulted from a freak accident and was compounded by mistakes made by persons untrained in accident response procedures.

A workman for a natural gas utility company was using a cutting torch in an industrial area. He was cutting into sections of empty, unused natural gas pipelines. By mistake he cut into a 6-in. underground buried pipeline about 7000-ft long that was used to convey chlorine gas from a chemical plant to a nearby plastics plant and was under tank pressure of about 85 psi.

About 1600lb of chlorine gas escaped into the atmosphere. Fortunately, the line was equipped with automatic shutoff valves at both ends. When the pressure dropped as a result of the hole made by the cutter's torch, these valves automatically closed.

A short distance from the site of the leak, 300–400 workers employed at a nearby refinery were waiting to be admitted to their work site. The morning air was cool, the humidity was about 70%, and the wind was blowing in their direction at 10–15 mph. Even though this was a massive leak, only 30 to 40 of these people were taken to the hospital for observation. It is probable that the high humidity, coupled with the strong wind, was responsible for the rapid dilution and dispersal of the chlorine into the atmosphere.

However, the high humidity and the body moisture on these workers caused the chlorine to be adsorbed into their clothing. The people who were taken to the hospital were herded into a small room where they were immediately exposed to the chlorine escaping from their clothing. A hospital attendant realized what was happening, and they were ushered outdoors and then brought in one at a time to have their clothing removed and to be given a wash-down shower. These workers remained in the hospital long enough for a thorough observation and time to get a change of clothes. None stayed in the hospital longer than one night.

The lessons to be learned from this accident are as follows:

- Pipelines carrying chlorine liquid or gas should never be buried. The preferred method is to place them in a grate-covered concrete channel at grade level or in overhead support systems.
- Persons exposed to chlorine should have their clothing removed as soon as possible and be given a warm shower to avoid further shock.
- Persons exposed to chlorine should not remain in a confined space, particularly in a room with rugs, carpets, drapes, or upholstered furniture, but should be moved into the open air as soon as possible.
- It is important to remember the difference between inhaling chlorine gas and the effects of inhaling “off-gassing” from a strong chlorine solution. The effects on the human pulmonary system are totally different: Chlorine gas produces a sharp throttling effect that simulates strangling. The off-gas from chlorine solution does not “throttle” the throat muscles but creates a mild-to-strong irritation in breathing that allows the chlorine to reach the lungs, where it generates watery mucus. Some cases of “off-gassing” are so severe that the victim dies while asleep after being exposed to moist chlorine.

### **A 14,000-lb Liquid Leak**

The largest known leak in a raw water pumping station occurred in an unattended facility that withdrew water from a lake and discharged it into an open channel to be conveyed to a WTP located at some distance from the lake. The

pumping station was controlled by operators at the WTP. There were no personnel on-site.

The chlorination facilities installed at the pumping station were used on an intermittent basis to keep the conveyance channel free from biological growths, which was part of the problem, because the chlorination equipment was not included in the routine maintenance program.

The chlorination system consisted of two chlorinators and two evaporators equipped with electrically heated water baths, installed with protective devices for both low and high temperatures, plus an automatic switch that was to shut down the evaporators if the water bath temperature exceeded 200°F (93°C). Because of the lack of routine maintenance, the electrical supply switch became fouled with debris from dead insects and became stuck with the heaters energized, so the water bath temperature rose high enough to produce a reaction between the chlorine and the steel tubing in the bath, which destroyed the tubing and allowed liquid chlorine to flow into the water. As the chlorine was stored in a 25-ton tank, there was an ample supply of chlorine available for volatilization. The leak continued until it was discovered by a WTP operator inspecting the raw water pumps.

Fortunately, the facility was located in a sparsely populated area, 3000–4000 ft from the nearest residences. A major WWTP was located about 6000 ft from the pumping station. The chlorine plume was hot enough to rise almost straight up, so no one at these locations was aware of the danger. This is another example of the chimney effect produced by hot chlorine vapor discharged into the cooler outdoor air (see the section “A Major Leak from a PVC Header Failure” earlier in this chapter).

The lessons to be learned from this accident are as follows:

- Chlorination facilities should be included in routine maintenance programs. This is especially important for unattended facilities at remote locations.
- Chlorine gas detectors should be installed at all chlorination facilities and should transmit an alarm to a location attended by a WTP operator. If an operator is not on duty 24/7, the alarm should roll over to a continuously attended police or fire station.

In addition to the problems discussed above, the design of the chlorination facilities at this pumping station had the following shortcomings:

- The chlorine diffusers were installed in the raw water pumps' discharge piping. This approach required the use of booster pumps to mix the chlorine solution into the raw water. Repairing a leak in a piping system containing a concentrated chlorine solution and being operated under substantial pressure is very difficult. Additional valves in the chlorine solution piping would remedy this problem.



- The piping and accessories between the storage tank and the evaporators were not correct. The only pipe from the tank to the evaporators was a liquid chlorine delivery line, with no pressure gauge on top of the tank. This prevented the operator from withdrawing chlorine gas from the tank or from evaluating conditions inside the tank. An operator should be able to feed either chlorine gas or liquid chlorine.

**Comment.** When shutting down an evaporator system, the first action should be to shut off the evaporator and then the discharge valve if it has not automatically shut off. If heat is a problem, liquid chlorine may boil back into the storage tank. If the pressure in the storage tank reaches its upper limit, the safety relief valve on the tank cover will release gas to the atmosphere. This would be a comparatively small leak that would tell the operator that the temperature in the evaporator water bath was too high.

### **A Tank Car Leak at a Chlorine Packager**

On August 14, 2002, approximately 48,000 lb of chlorine was released from a tank car parked in a rail siding owned by DPC Enterprises (DPC) near Festus, Missouri.<sup>37</sup> DPC receives liquefied chlorine in 90-ton tank cars and packages it into 150-lb cylinders and 1-ton containers for commercial, industrial, and municipal use in the St. Louis metropolitan area.

The accident occurred when a chlorine transfer hose ruptured. DPC had an emergency shutdown system to stop chlorine releases from tank cars, but it failed to operate and the cloud of chlorine gas made it impossible to reach the self-contained emergency breathing apparatus stored at the plant. An emergency response team manually closed the shutdown valves on top of the tank car approximately 3 h after the leak started.

The plume of chlorine from the leak tended to hug the ground and was only a few feet high. It slowly drifted away from the accident site. The wind was “calm” with short intervals of 3- to 5-mph speeds. Mathematical modeling after the accident calculated the ground-level, centerline concentration of chlorine in the plume to exceed 3 ppm at 3.7 miles from the release point.

The emergency evacuation plan for the area was inadequate. However, by using shelter-in-place at a high school and an assisted living facility, combined with door-to-door notification of residents of a trailer park and a housing development, it was possible to avoid serious injuries. The accident caused 63 people to seek medical evaluations for respiratory distress, three of whom were admitted into the hospital for overnight observation. No estimates of economic damage are available. However, the losses were probably small.

An investigation by the U.S. Chemical Safety and Hazard Investigation Board (CSB) determined that the hose ruptured because the metal braid in it was stainless steel rather than the Hastelloy C specified for this use. Neither

the manufacturer nor DPC confirmed that the hose was constructed of the proper material before it was put into service.<sup>38</sup>

The investigation also found that the EFVs installed in tank cars will not function when a hose rupture occurs. These valves are designed to close when chlorine flow rate exceeds 7000–32,000 pph, depending on the application. Chlorine flow rates never exceed 7000 pph when a hose fails because the friction losses in the valves, couplings, and the hose itself preclude flows of this magnitude. A survey of 30 municipal WTPs and WWTPs conducted by CSB after the DPC accident found that approximately 30% of these plants were relying on EFVs to stop chlorine flow if a transfer hose failed. Unfortunately, the USEPA and OSHA regulations discussed earlier in this chapter do not include specific requirements for chlorine tank car unloading systems. These systems also do not fall under DOT rules because the tank cars are the responsibility of the consignee once they are delivered. The NTSB has requested the DOT to issue new rules to remedy this regulatory gap. DOT regulations require tank trucks to be equipped with chlorine transfer systems because the truck's owner retains ownership of the chlorine until it has been transferred into the buyer's tank.

The CI has taken a very strong stand regarding the installation of chlorine transfer systems. All of its members must agree to install these systems at their facilities and to ensure that their customers are in compliance with the "Chlorine Customers Generic Safety and Security Checklist" published in CI Pamphlet 85.<sup>39</sup> Bulk chlorine customers (those who receive chlorine by railcars, barges, or tank trucks) were required to be in compliance with the checklist by December 31, 2007. Packaged chlorine customers (those who receive chlorine in ton containers or 150-lb cylinders) must be in compliance by December 31, 2008.

A chlorine transfer system consists of motor-operated valves on both ends of the chlorine transfer hose and a chlorine gas detector. The valves close automatically when the detector senses the presence of chlorine in the atmosphere. Operators can also press an emergency shutdown button if the detector fails to close the valves. This system failed to operate at the DPC facility because it had not been regularly maintained to prevent corrosion inside the electrical switches that operated the valves.

The rupture of a chlorine transfer hose at Honeywell International's Baton Rouge chemical plant on August 11, 2005 had a very different outcome. When chlorine began to escape from the tank car, the detector alerted control room operators, who stopped the release by remotely closing the emergency shutdown valves on the chlorine transfer hose. The chlorine release lasted less than 1 min. Several contractors working near the tank car inhaled some chlorine and were taken to a hospital where they were treated and released. All returned to work the next day. Tests conducted immediately after this accident showed that no chlorine gas had passed beyond the Honeywell property line.

### **Brush Fire**

A brush fire accompanied by “Santa Anna” winds produced failures in four 1-ton chlorine containers in use at a small WTP plant in Southern California. The fusible plugs on all four containers melted. One container was also breached. Apparently, the intense heat from the fire caused the pressure in this container to rise very rapidly while the atmosphere near the fusible plugs was not yet hot enough to melt the plugs. The intense fire raging outside the building dispersed the chlorine into the atmosphere without further adverse consequences.

The chlorine building was constructed of concrete block, with a brick facing and metal roof. The building was “scorched,” but structurally intact, after the fire but the chlorinators and chlorine piping were completely destroyed.

This incident illustrates the importance of locating structures that contain chlorine containers well away from flammable vegetation.

### **Frequency and Magnitude of Chlorine Leaks**

The causes of chlorine leaks at customer facilities are listed below. These causes are ranked in the order of severity of the leak and the hazard posed by its occurrence.

1. Fire
2. Flexible connection failure
3. Fusible plug corrosion
4. Accidents caused by carelessness and ignorance
5. Valve packing failure
6. Gasket failure
7. Piping failure
8. Equipment failure
9. Physical damage of containers in collision accidents
10. Container failure
11. Chlorine pressure gauge failure

These causes are discussed below.

1. Fire in WTPs or WWTPs chlorine storage or chlorinator rooms is not a serious hazard because there is very little flammable material in these rooms. The two case studies presented in this chapter illustrate that intense heat can be produced by reactions between chlorine and PVC and between chlorine and steel. However, neither of these accidents produced fires at the plants.

Fire is a very serious hazard at facilities where swimming pool chemicals are stored. The buildings housing these facilities often incur serious damage when stored granular hypochlorite spontaneously explodes. If 150-lb cylinders of chlorine are stored near the hypochlorite, they will either explode or their fusible plug will melt, releasing chlorine gas into the atmosphere. Fire officials should inspect the premises of swimming pool chemical companies often to ensure that such hazards are minimized.

In the early years, ton container explosions were caused by the spontaneous combustion of nitrogen trichloride. When chlorine is made from water containing ammonia nitrogen, the product will contain  $\text{NCl}_3$ , which is soluble in liquid chlorine. When the liquid is withdrawn, the  $\text{NCl}_3$  evolves as a vapor that will explode. This problem has been corrected in the United States. However, Americans have not done a very good job of exporting this information. In 1981, White investigated such explosions in Bogota, Colombia. During his investigation of the local chlor-alkali plant, he counted more than a dozen U.S.-made ton containers with their dished heads still intact although they had been blown from a concave to a convex position.

2. Probably the most frequent cause of chlorine emissions that expose operating personnel to risk is failure of the lines that connects the chlorine containers to metering and control equipment. These connecting lines are made of cadmium-plated annealed copper, 2000 psi in strength. Copper is used because it is flexible and has sufficient structural strength to withstand the pressure inside the chlorine container. However, each time an empty container is removed from a connector, the chlorine remaining in the tubing reacts with moisture in the room to form a tiny quantity of hydrochloric acid, which is corrosive to copper. Therefore, the flexible connectors have finite service lives. To check the condition of a flexible connector, it should be bent carefully; if it screeches slightly, it is due for replacement as the sound indicates that sufficient corrosion has occurred to cause failure of the connector.
3. Fusible plug failure without any evidence of elevated temperature caused by fire or direct sunlight is next in the order of hazard magnitude. A fusible plug may leak from corrosion between the lead alloy and the plug retainer. There is only one fusible plug on a 150-lb cylinder. It is located at the base of the outlet valve. There are three in each of the dished heads of a ton container.
4. Carelessness is another cause of chlorine accidents. One such accident involved a 6-in. buried chlorine gas line that was originally located entirely within the property of two chemical plants.<sup>40</sup> The property was subdivided 20 years after installation, and the ground above the piping was paved over. The chlorine gas line was mistakenly cut into by a

welder who was inactivating abandoned natural gas lines. The heat from the torch burned a small hole into the pipe, and the chlorine supported combustion of the carbon steel pipe. Within seconds, the hole was approximately 8 in. in diameter and allowed almost immediate discharge of the contents of 7000 feet of the 6-in. pipe. A few months later, the chlorine line was cut again on successive days by a backhoe excavating underground lines. After these experiences, the pipe was lowered from the original 2 ft to approximately 5 ft below the ground surface.

5. Valve packing failures are not known to have caused any serious problems. If the leak is minor, it can often be corrected by tightening the packing nut. The appropriate chlorine safety kit must be used to enclose serious leaks. The chlorine container can then be returned to the packager for final disposal.
6. Gasket failures are serious only when they occur on the seal between the dome and the tank of a chlorine tank car. Other gaskets are so located that the chlorine supply can be secured, the system emptied of gas, and the gasket replaced. Gasket failures on tank cars are rare. An appropriately trained hazmat team should be notified immediately when a gasket on a railcar is observed to be leaking.
7. Piping failures are rare, but are sometimes caused by unsuitable materials. Lines carrying liquid chlorine are a potential hazard. The correct materials for use in chlorine pipelines are discussed in Chapter 8.
8. Most equipment failures occur in the chlorine vaporizers between the storage containers and the metering and control equipment, primarily as a result of corrosion of the heat exchange pipes in the water bath. Failure is a function of the pipe wall thickness and the amount of chlorine passing through the vaporizer. This type of accident occurs rarely; however, regular inspection of the interior of the heat exchange pipes should be part of the preventive maintenance program.
9. Accidents producing chlorine or ammonia emissions from railroad tank cars are rare considering the quantities of these chemicals shipped. However, as indicated by the three examples earlier in this chapter, the impacts of such accidents are huge. It is to be hoped that the new tank cars and the changes in train speeds called for in the Federal Rule proposed in 2008 will further reduce such hazards. The voluntary actions by several chlorine manufacturers and users to reduce the number of chlorine shipments by railcars will also reduce the frequency of accidents.
10. Container failures, except those caused by fire, are extremely rare. The chlorine packagers throughout North America and Europe are keenly aware of the hazards associated with handling chlorine containers. This awareness has led to the development of strict programs for monitoring the physical condition of these containers and replacing them when

needed. Failures of chlorine tank cars are practically unheard of for a very good reason: Their owners inspect the interiors of these tanks frequently.

## PRODUCTION AND USES OF CHLORINE

### Annual Production

The CI publishes annual reports<sup>9</sup> summarizing the quantities of chlorine manufactured in North America. Chlorine production in the United States is subdivided into two categories: gas production (the total quantity of chlorine produced) and liquid production (the quantity of gas that is liquefied so it can be sent off-site). Between 1990 and 2006, 80%–87% of the gas produced in the United States was liquefied, and 17%–20% of the total was produced by industries that immediately used it to manufacture other products. Combining the chlorine production facilities and the manufacturing processes that use the chlorine at adjacent locations is one of the goals of the Dow/UP “Safety Initiative” discussed earlier in this chapter.

Total chlorine gas production in the United States during 2006 was approximately 11.3 million short tons. Total gas production in Canada during the same year was about 1.0 million metric tons. Mexico produced about 391,000 metric tons in 2006. The CI report does not include a breakdown between gaseous and liquid chlorine production for Canada and Mexico.

Annual chlorine gas production in the United States peaked in 2004 at 13.6 million short tons; Canada’s peak production was at 1.5 million metric tons in 1990. Mexico’s years of highest production were 1996 and 1997 at about 415,000 metric tons each. Chlorine is a basic building block in many products, so the demand for it fluctuates with the overall manufacturing economy.

The installed capacity of chlorine manufacturing facilities is also closely tied to the manufacturing base in specific geographic regions, as indicated in Table 1.8.

The information summarized in Table 1.8 was developed for the World Chlorine Council. It vividly illustrates the very rapid increase in total manufacturing capacity of the Pacific Rim countries during the past decade. Chlorine manufacturing capacity in China is growing very rapidly and is projected to overtake the manufacturing capacity of North America by 2010.

### End Uses of Chlorine

Chlorine is used in more than 50% of all industrial chemical processes. More than 90% of all pharmaceutical manufacturing processes use chlorine in one or more steps. Chlorine is used to make approximately 96% of all chemicals used in producing agricultural crops. The list goes on and on because chlorine

**TABLE 1.8. Distribution of Total Global Chlorine Manufacturing Capacity by Geographic Region<sup>41</sup> (Based on Total Capacity in 2005)**

Geographic Region	Percentage of Total World Capacity
North America	22
Western Europe	21
China	20
Other Asia	12
Japan	9
Central and Eastern Europe	5
Middle East and Africa	5
South America	3
Other	3
Total	100

**TABLE 1.9. World Chlorine Consumption by Different Sectors of the Economy<sup>41</sup>**

Economic Sector	Percentage of Total World Consumption
Vinyl	36
Phosgene	9
Hydrochloric acid	8
Propylene oxide	7
Chloromethane and chloroethane solvents	6
Water and wastewater treatment	5
Allylics	4
Pulp and paper	4
Other organics	7
Other inorganics	14
Total	100

is a truly versatile chemical. To illustrate this, the American Chemical Society published a visual aid many years ago for use in schools. This poster was titled "The Chlorine Tree." It now exists in many configurations that have been developed for specific purposes.

Uses of chlorine in different sectors of the world economy are summarized in Table 1.9. The information summarized in this table was developed for the World Chlorine Council and is based on 2002 consumption data.

Estimates of chlorine consumption by different sectors of the economy are also available for specific geographic areas (the United States, Western Europe, and so forth). However, the percentage distribution for chlorine consumption in these smaller geographic areas is remarkably similar to the data summarized in Table 1.9, which reflects globalization of the industrial economy. The great strides in worldwide transportation networks have made this possible. In 2002, the United States exported \$81.1 billion worth of

chemicals and allied products, and imported \$86 billion worth of chemicals. Liquid chlorine was not part of this international flow of materials because it is a basic building block for other chemicals. Most liquid chlorine shipments travel less than 300 miles from their point of manufacture. However, the higher-value chemicals that are derived from chlorine can travel many hundreds of miles to their final destination.

Only 5% of the total annual chlorine consumption is used in water and wastewater treatment. This percentage has not changed very much in the past several decades. Municipalities use about 2% of the chlorine, and the remaining 3% is used for industrial water treatment.

### **Help in Chlorine Emergencies**

Chemical Transportation Emergency Center (CHEMTREC)<sup>42</sup> was established in 1971 by the Manufacturing Chemists Association (MCA) as a public service hotline for firefighters, law enforcers, and other emergency responders. MCA has since changed its name to the American Chemical Council (ACC), but CHEMTREC has continued to grow and prosper because it is a very valuable source of assistance during emergency incidents involving chemicals and hazardous materials.

CHEMTREC's Emergency Communications Center is located in Arlington, Virginia. It is open 24h a day, 7 days a week.

When an emergency service specialist (EES) on duty at the center receives a telephone call about an emergency situation, he or she will immediately request the following information:

- caller's name and phone number;
- location of the emergency and description of the area;
- products and equipment involved;
- injuries;
- whether there was a fire; and
- the carrier's and the shipper's names and the name of the consignee.

The EES will provide immediate technical information to the accident scene from an extensive technical library. This can be done by telephone, fax, or electronically. The EES will also relay information to the shipper's or manufacturer's 24-h emergency contact expert and will link that expert to the emergency response team at the scene of the accident. If necessary, the EES will use CHEMTREC's telephone conferencing capabilities to link the local emergency response team to all of the individuals who have expertise in solving the problem. The EES can also link local medical personnel to experts who are experienced in treating injuries caused by the accident.

After the initial response to the emergency has been completed, CHEMTREC will prepare a written report of the incident based on the information collected. This report is immediately sent by fax or e-mail to the



shipper or shipper-designated compliance organization. In certain situations, CHEMTREC can relay written instructions provided by the registrant to the scene of the accident for disposing of small releases of the product. It also maintains a network of chemical industry and for-hire contract emergency response teams to assist in product containment, spill mitigation, and product removal.

PHONE—TOLL FREE—DAY OR NIGHT  
CHEMTREC  
1-800-262-8200

This number may be used for emergencies or to obtain information.

There are emergency response centers in Canada and Mexico that are similar to CHEMTREC. The center in Canada is named CANUTEC and is operated by the Canadian government. CANUTEC can be reached by telephone by calling collect to the following number:

CANUTEC  
613-996-6666 (Call Collect)  
Cellular: \*666 (Canada Only)

Non-emergency information may be obtained at 613-992-4624 (Call Collect).

The emergency response center in Mexico is named Sistema de Emergencias en Transporte para la Industria Quimica (SETIQ). SETIQ can be reached by telephone by calling collect to the following number:

SETIQ  
5255-5559-1588

Both of these emergency response centers have been extremely successful in assisting with incidents involving shipments either into or from these countries.

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