



THE CHLORINE INSTITUTE, INC.

# THE CHLORINE MANUAL

# CHLORINE

CHLORINE

DOT 105 500 W

SAFETY VALVE 275 LBS.  
TESTED 1-90 DEC 9-92

500 LBS.  
DEC 9-92

2 1/2" CH  
SHOES

*Sixth Edition*

AN AMERICAN NATIONAL STANDARD

# THE CHLORINE INSTITUTE, INC.

## MISSION STATEMENT

The Chlorine Institute, Inc. exists to support the chlor-alkali industry and serve the public by fostering continuous improvements to safety and the protection of human health and the environment connected with the production, distribution and use of chlorine, sodium and potassium hydroxides, and sodium hypochlorite; and the distribution and use of hydrogen chloride. This support extends to giving continued attention to the security of chlorine handling operations.

The Institute strives to meet these obligations by maintaining a scientific and technical organization that fully meets the needs and expectations of its members and the public.

The Institute works with government agencies, its members, and other stakeholders to encourage the use of credible science and proven technology in the development of voluntary actions and regulations to enhance safety and security in operations involving its Mission chemicals.

The Institute believes that its Mission chemicals are essential to society and can be produced and used safely.

### American National Standard - February 29, 2000

**This Publication has been approved as an American National Standard (ANS).** Approval of an ANS requires review by The American National Standards Institute (ANSI) that the requirement for due process, consensus, and other criteria for approval have been met by the standards developer. Consensus is established when, in the judgement of the ANSI Board of Standards Review, substantial agreement has been reached by directly and materially affected interests. Substantial agreement means much more than a simple majority, but not necessarily unanimity. Consensus requires that all views and objections be considered, and that a concerted effort be made toward their resolution.

The use of ANSs is completely voluntary; their existence does not in any respect preclude anyone, whether he or she has approved the standards or not, from manufacturing, marketing, purchasing, or using products, processes, or procedures not conforming to the standards. The ANSI does not develop standards and will in no circumstances give an interpretation of any ANS. Moreover, no person shall have the right or authority to issue an interpretation of an ANS in the name of the ANSI. Requests for interpretations should be addressed to the secretariat or sponsor whose name appears on the title page of this standard.

**Caution Notice:** This ANS may be revised or withdrawn at any time. The procedures of the ANSI require that action be taken periodically to reaffirm, revise, or withdraw this standard. Purchasers of ANSs may receive current information on all standards by calling or writing the American National Standards Institute.

# TABLE OF CONTENTS

<b>i. INTRODUCTION</b>		<b>5. EMPLOYEE TRAINING AND SAFETY</b>	<b>26</b>
• The Chlorine Manual		5.1 Employee Training	26
• Commitment to Responsible Care®		5.2 Personal Protective Equipment	26
• Checklists		5.3 Confined Space Entry	27
• References		5.4 Personal Exposure Monitoring	27
<b>1. GENERAL INFORMATION</b>	<b>1</b>	<b>6. MEDICAL ASPECTS AND FIRST AID</b>	<b>28</b>
1.1 Chlorine Manufacture	1	6.1 Hazards to Health	28
1.2 Chlorine in Transportation	1	6.2 Preventive Health Measures	28
1.3 Other Regulatory Aspects	2	6.3 First Aid	29
1.4 Chemical and Physical Properties	2	6.4 Medical Management of Chlorine Exposures	29
1.5 Terminology	3	<b>7. ENGINEERING DESIGN AND MAINTENANCE</b>	<b>31</b>
1.6 Health Hazards	4	7.1 Structures	31
1.7 Other Hazards	4	7.2 Ventilation	31
1.8 Containers	5	7.3 Material for Processing Equipment	32
<b>2. CYLINDERS AND TON CONTAINERS</b>	<b>6</b>	7.4 Electrolyzers (Cells)	32
2.1 Container Descriptions	6	7.5 Chlorinators	33
2.2 Container Valves	7	7.6 Vaporizers	33
2.3 Pressure Relief Devices	7	7.7 Support Equipment	33
2.4 Container Shipping	8	7.8 Piping Systems for Dry Chlorine	34
2.5 Container Labeling and Placarding	8	7.9 Piping Systems for Wet Chlorine	36
2.6 Container Handling	8	7.10 Stationary Storage	36
2.7 Container Storage	9	7.11 Equipment Maintenance	37
2.8 Container Use	9	7.12 Chlorine Neutralization	37
<b>3. BULK SHIPPING CONTAINERS</b>	<b>12</b>	<b>8. KEY REGULATIONS AND CODES</b>	<b>38</b>
3.1 General	12	8.1 Occupational Safety and Health Regulations 29 CFR	38
3.2 Tank Cars	12	8.2 Navigation and Navigable Water Regulations 33 CFR	39
3.3 Tank Motor Vehicles	16	8.3 Environmental Regulations 40 CFR	39
3.4 Portable Tanks	18	8.4 Shipping Regulations 46 CFR (Water Transportation)	40
3.5 Tank Barges	18	8.5 Transportation Regulations 49 CFR	41
<b>4. EMERGENCY MEASURES</b>	<b>20</b>	8.6 Fire Codes	42
4.1 General	20		
4.2 Response to a Chlorine Release	20		
4.3 Response to a Fire	20		
4.4 Releases	21		
4.5 Transportation Emergencies	22		
4.6 Disposal of Chlorine	24		
4.7 Absorption Systems	24		
4.8 Emergency Kits and Recovery Vessels	24		
4.9 Reporting	25		

<b>9. TECHNICAL DATA</b>	<b>43</b>
9.1 General	43
9.2 Atomic and Molecular Properties	43
9.3 Chemical Properties	43
9.4 Physical Properties	44
<b>10. SELECTED REFERENCES</b>	<b>52</b>
10.1 U.S. Government Regulations and Specifications	52
10.2 Canadian Regulations	52
10.3 Chlorine Institute References	52
10.4 American Conference of Governmental Industrial Hygienists	54
10.5 American Society of Mechanical Engineers	54
10.6 American Society for Testing Materials	54
10.7 American Water Works Association	55
10.8 Association of American Railroads	55
10.9 Compressed Gas Assn.	55
10.10 National Academy of Sciences	55
10.11 National Fire Protection Association	55
10.12 National Institute of Occupational Safety and Health	55
10.13 National Safety Council	55
10.14 NSF International	55
10.15 Water Environment Federation	55
10.16 World Health Organization	55
10.17 Chemical Industry Inst. Of Toxicology	56
10.18 Other References	56

---

## ILLUSTRATIONS

Fig. 2.1 Chlorine Cylinders	6
Fig. 2.2 Chlorine Ton Container	6
Fig. 2.3 Standard Cylinder Valve	7
Fig. 2.4 Standard Ton Container Valve	7
Fig. 2.5 Standard Fusible Plug for Ton Containers	7
Fig. 2.6 Lifting Beam for Handling Chlorine Ton Containers	8
Fig. 2.7 Yoke & Adapter Type Connection	11
Fig. 3.1 Chlorine Tank Car	12
Fig. 3.2 Valve Arrangement & Manway	13
Fig. 3.3 Standard Angle Valve	13
Fig. 3.4 Excess-Flow Valve	14
Fig. 3.5 Standard Pressure Relief Device	14
Fig. 3.6 Chlorine Tank Truck	17
Fig. 3.7 Chlorine Barge	19
Fig. 4.1 Chlorine Institute Emergency Kit A for Chlorine Cylinders	25

## CHARTS

Fig. 9.1 Vapor Pressure of Liquid Chlorine	46
Fig. 9.2 Temperature-Density Relation of Liquid Chlorine	47
Fig. 9.3 Equilibrium Solubility of Chlorine in Water	48
Fig. 9.4 Volume-Temperature Relation of Liquid Chlorine in a Container Loaded to its Authorized Limit	49
Fig. 9.5 Solubility of Water in Liquid Chlorine	50
Fig. 9.6 Solubility of Water in Liquid Chlorine	51

## TABLES

2.1 Container Dimensions and Weights	8
4.1 Recommended Alkalline Solutions for Absorption	24

---

## THE CHLORINE MANUAL

The widespread use of chlorine and the accompanying demand for reliable information on recognized procedures for the safe handling of chlorine resulted in the publication of the first Chlorine Manual by the Chlorine Institute in 1947. Subsequent editions have been published in 1954, 1959, 1969, and 1986.

The Chlorine Manual is a compendium of information available to the Institute based on experience with materials, equipment, regulations and practices contributing to the safe handling, storage, shipment and use of chlorine. Important properties of chlorine are included. There is a brief section on the production of chlorine, as well as methods of dealing with potential emergencies.

The reference section will provide to readers sources for more detailed information about matters on which the text material is based. Where questions remain -- on protective provisions or procedures, for example -- a chlorine user should consult the producer or supplier of the product or the chlorine handling equipment, or contact the Chlorine Institute.

Annually, the Institute updates its publications catalog. This free catalog can be obtained by contacting the Publications Department of the Institute. The information contained in the catalog also is available through the Institute's Internet website -- <http://www.cl2.com>.

## RESPONSIBLE CARE®

The Institute is a Chemical Manufacturers Association (CMA) Responsible Care® Partnership Association. In this capacity, the Institute is committed to: Fostering the adoption by its members of the Codes of Management Practices; facilitating their implementation; and encouraging members to join the Responsible Care® initiative directly.

Chlorine Institute members who are not CMA members are encouraged to follow the elements of similar responsible care programs through other associations such as the National Association of Chemical Distributors (NACD) Responsible Distribution Program or the Canadian Chemical Manufacturers Association's Responsible Care® program.

---

## CHECKLISTS

The Chlorine Institute is adding checklists to appropriate pamphlets to assist its members and non-members in self-audits or other reviews. These checklists are being added to new and existing pamphlets beginning in 1996.

Because the *Chlorine Manual* only summarizes some of the information contained in the other pamphlets, the reader should refer to the specific pamphlets and their checklists. These checklists are designed to emphasize major topics and highlight the key recommendations for someone who has already read and understood the pamphlets.

The Chlorine Institute encourages the use of the pamphlets and their checklists.

## REFERENCES

Chlorine Institute publications referenced in this publication are referred to by pamphlet number, drawing number, or by condensed name if no number exists.

At the beginning of Section 10 – “Selected References”, complete information about the Institute publications is provided. Other sources are referenced in this publication in the following manner: (Reference 10.4.1). Section 10 provides information on each of these references. In most cases, an address also is provided.

The Institute updates its publications catalog annually. This free catalog can be obtained by downloading from the CI website or contacting the Institute Publications Department, 1300 Wilson Boulevard, Arlington, VA 22209.

Ph: 703-741-5760  
Fax: 703-741-6068  
Web: <http://www.CL2.com>

---

# GENERAL INFORMATION

## 1.1 Chlorine Manufacture

Most chlorine is manufactured electrolytically by the diaphragm, the mercury or the membrane cell process. In each process a salt solution is electrolyzed by the action of direct electric current which converts chloride ions to elemental chlorine. Chlorine production for 1996 in short tons/year is estimated to be as follows: world -47 million, U.S. -13 million, Canada -1.2 million, and Mexico -0.4 million.

In the diaphragm cell process, sodium chloride brine is electrolyzed to produce chlorine at the positive electrode (anode) while sodium hydroxide (caustic soda) and hydrogen are produced at the negative electrode (cathode). In order to prevent the reaction of sodium hydroxide and hydrogen with the chlorine, the anode and cathode chambers are separated by a porous diaphragm.

In the mercury cell process recirculating mercury serves as the cathode. Chlorine is removed from the gas space above the anodes and elemental sodium is formed at the cathode. The sodium amalgamates with the mercury. The sodium-mercury amalgam then flows to a decomposer where it is reacted with purified water to produce sodium hydroxide and hydrogen with the mercury being recirculated.

The membrane cell process electrolyzes sodium chloride brine to produce chlorine at the positive electrode (anode) while sodium hydroxide and hydrogen are produced at the negative electrode (cathode). An ion selective membrane prevents the reaction of sodium hydroxide and hydrogen with chlorine.

Chlorine is also produced in a number of other ways, for example, by electrolysis of potassium chloride brine in membrane and mercury cells with co-production of potassium hydroxide; by electrolysis of molten sodium or magnesium chloride to make elemental sodium or magnesium metal; by electrolysis of hydrochloric acid; and by non-electrolytic processes. Further information on electrolyzers

and electrolytic methods can be found in Section 7.4 of this pamphlet. An additional reference is the Kirk-Othmer Encyclopedia of Chemical Technology which contains a section on chlorine and sodium hydroxide (Reference 10.18.7).

## 1.2 Chlorine in Transportation

### 1.2.1 General

Chlorine is normally shipped as a liquefied compressed gas. The transportation of chlorine in all modes of transportation is controlled by regulations. It is the responsibility of each person shipping or transporting chlorine to know and to comply with all applicable regulations.

### 1.2.2 United States

In the U. S., chlorine in commerce is regulated by the Department of Transportation (DOT). Chlorine is a Class 2, Division 2.3 poison gas and is assigned a poison Zone B inhalation hazard material. For land transportation and for carriage of containers by water, DOT regulations appear in Title 49 Code of Federal Regulations (CFR). DOT regulations covering tank barges appear in Title 33 and 46 CFR. See Section 8. Many states have adopted regulations substantially the same as DOT regulations.

In addition there may be local requirements.

### 1.2.3 Canada

In Canada, chlorine is classified as a Class 2, Division 2.3 poison gas with a secondary classification of Class 5, Division 5.1 oxidizer. Regulations are issued by Transport Canada (TC) for all modes of transportation under the "Transportation of Dangerous Goods Act and Regulations" TDG).

Many regulations are in accordance with those issued by the U.S. DOT, but some minor differences exist. The concerned reader may obtain additional information from Canada Communications Group, 45 Sacré-Coeur Boulevard, Hull, Quebec, Canada, K1A 0S9 or directly from the Canadian government.

#### 1.2.4 Mexico

In Mexico, chlorine is classified as a Class 2, Division 2.3 poison gas with a secondary classification of Class 5.1 Oxidizer.

Regulations for the transportation of hazardous materials are issued as part of Regulations for Surface Transportation of Hazardous Materials and Wastes, April 7, 1993 as published in the Diario Oficial de la Federacion. Most of the regulations are in accordance with those issued by the U.S. DOT.

#### 1.2.5 Other Countries

International shipments of chlorine must meet the requirements of the country of origin and the country of destination. Generally, hazardous material regulations throughout the world are similar as a result of standardized regulations provided through the United Nations and implemented by intermodal U.N. agencies. For instance, the International Maritime Organizations (IMO) publishes the International Maritime Dangerous Goods (IMDG) Code. Shipments of chlorine containers by vessels meeting the standards of the IMDG Code are accepted in most countries. There are similar U.N. agencies and recommendations for road, rail and air transportation systems. The United Nations designation for chlorine is U.N. 1017.

### 1.3 Other Regulatory Aspects

Chlorine manufacturers, packagers, and most consumers are subject to workplace regulations pertaining to chlorine throughout most of the world.

#### 1.3.1 United States

The Department of Labor's (DOL) Occupational Safety and Health Administration (OSHA)

issues regulations involved with worker protection. Environmental regulations are issued by the Environmental Protection Agency (EPA). When used as a disinfectant (water or waste treatment), chlorine is considered to be a fungicide and is subject to EPA regulations issued under the Federal Insecticide, Fungicide and Rodenticide Act (FIFRA). In addition, many state or local agencies now require that chlorine used in the drinking water treatment industry be certified to meet ANSI/NSF Standard 60 (Reference 10.14.1).

#### 1.3.2 Canada

Workplace regulations are issued through the Workplace Hazardous Materials Information System (WHMIS) and by individual provinces. Environmental regulations are primarily addressed through provincial governments in conjunction with Environment Canada.

#### 1.3.3 Other Countries

Similar regulations apply in many other countries. Various numbering systems of chemicals apply in certain regulatory programs.

For chlorine, the following are pertinent:

- The Chemical Abstracts Service (CAS) number is CAS 7782-50-5.
- The Registry of Toxic Effects of Chemical Substances (RTECS) number assigned in the U.S. by the National Institute for Occupational Safety and Health is F02100000.

### 1.4 Chemical and Physical Properties

Chlorine is an element and a member of the halogen family. Chlorine gas or liquid is not explosive or flammable, but it will support combustion. Both the liquid and gas react with many substances. Chlorine is only slightly soluble in water. The gas has a characteristic, penetrating odor, a greenish yellow color and is about two and one-half times as heavy as air. Thus, if chlorine escapes from a container or system, it will tend to seek the lowest level in the building or area in which the leak occurs.

Liquid chlorine is amber in color and is about one and one-half times as heavy as water. At atmospheric pressure, it boils at about -29°F (-34°C) and freezes at about -150°F (-101°C).

One volume of liquid chlorine, when vaporized, yields about 460 volumes of gas.

Although dry chlorine (gas or liquid) normally does not react with or corrode some metals such as copper or carbon steel, it is strongly reactive (strongly corrosive) when moisture is present. See Section 9.3.3.2.

## 1.5 Terminology

### 1.5.1 Chlorine

The chemical element in whatever state or condition it may exist under the conditions being considered. Chlorine's symbol is **Cl**, its atomic number is 17 and its atomic weight is 35.453. Chlorine almost always exists as a molecule with two chlorine atoms bound together as Cl<sub>2</sub>. Its molecular weight is 70.906.

### 1.5.2 Liquid Chlorine

The element, chlorine, in the liquid state. [The term "liquid chlorine" sometimes is used incorrectly to describe a hypochlorite solution. This is a misuse of the term and the Institute discourages its use.]

### 1.5.3 Chlorine Gas

The element, chlorine, in the gaseous state.

### 1.5.4 Dry Chlorine

Liquid or gaseous chlorine with its water content dissolved in solution. The solubility of water in chlorine varies with temperature and is shown in Figures 9.5 and 9.6. See Pamphlet 100. [The term "dry chlorine" sometimes is used incorrectly to describe a dry chlorinating compound (usually calcium hypochlorite or the chloroisocyanurates). This is a misuse of the term and the Institute discourages its use.]

The following are examples using Figures 9.5 and 9.6:

- Chlorine with a water content of 30 ppm at a temperature of 50° F (10° C) is dry. If this same chlorine (30 ppm) were at a temperature of -4° F (-20°C) the chlorine is wet.
- Chlorine at 41° F (5° C) is dry if the water content does not exceed 100 ppm.

### 1.5.5 Wet Chlorine

Liquid or gaseous chlorine with its water content exceeding the amount that is dissolved in solution. See Pamphlet 100. Chlorine is not wet just because it is in the liquid state.

### 1.5.6 Moist Chlorine

Synonymous with wet chlorine.

### 1.5.7 Saturated Chlorine Gas

Chlorine gas in such condition that the removal of any heat or an increase in pressure will cause some portion of it to condense to a liquid. [This term should not be confused with wet or moist chlorine.]

### 1.5.8 Saturated Chlorine Liquid

Chlorine liquid in such condition that the addition of any heat or a decrease in pressure will cause some portion of the chlorine to vaporize to a gas. [This term should not be confused with wet or moist chlorine.]

### 1.5.9 Chlorine Solution (Chlorine Water)

A solution of chlorine in water (for solubility of chlorine in water see Fig. 9.3). [The term "chlorine solution" sometimes is used incorrectly to describe hypochlorite solutions. This is a misuse of the term and the Institute discourages its use.]

### 1.5.10 Liquid Bleach

A solution of hypochlorite, usually sodium hypochlorite. This term rather than "liquid chlorine" should be used to describe a liquid hypochlorite product. See Section 1.5.2.

### 1.5.11 Container

In this publication, a container is a pressure vessel authorized by an applicable regulatory body for the transport of chlorine. It does not include pipelines or stationary storage tanks specifically designed and installed for transfer or storage.

### 1.5.12 Filling Density

By DOT regulation, the weight of chlorine that is loaded into a container may not exceed 125% of the weight of water at 60° F (15.6°C) that the container will hold.

### 1.5.13 Sodium Hydroxide

Normally the co-product produced as a solution when chlorine is generated through the electrolytic decomposition of sodium chloride solution. Sodium hydroxide is frequently referred to as caustic soda.

### 1.5.14 Potassium Hydroxide

A co-product produced as a solution when chlorine is generated through the electrolytic decomposition of potassium chloride salt solution. Potassium hydroxide is frequently referred to as caustic potash.

## 1.6 Health Hazards

Chlorine gas is primarily a respiratory irritant. In sufficient concentration, the gas irritates the mucous membranes, the respiratory tract and the eyes. In extreme cases difficulty in breathing may increase to the point where death can occur from respiratory collapse or lung failure. The characteristic, penetrating odor of chlorine gas usually gives warning of its presence in the air.

Also, at high concentrations, it is visible as a greenish yellow gas. Liquid chlorine in contact with skin or eyes will cause chemical burns and/or frostbite. See Section 6.

The American Conference of Governmental Industrial Hygienists (ACGIH) (Reference 10.4.1) has established a threshold limit value time-weighted average (TWA) of exposure to chlorine at 0.5 ppm. The TWA is based on a normal work schedule of 8 hours/day and 40 hours/week. ACGIH has established a threshold limit value short-term exposure limit (STEL) of 1 ppm for exposure to chlorine. The STEL is defined as a 15-minute TWA exposure.

In 1994, the National Institute for Occupational Safety and Health reduced its Immediately Dangerous to Life or Health (IDLH) concentration for chlorine to 10 ppm (Reference 10.12.1).

## 1.7 Other Hazards

### 1.7.1 Fire

Chlorine is neither explosive nor flammable; however, chlorine will support combustion.

### 1.7.2 Chemical Action

Chlorine has a very strong chemical affinity for many substances. It will react with many inorganic and organic compounds, usually with the evolution of heat. Chlorine reacts with some metals under a variety of conditions. See Section 9.3.3.2.

### 1.7.3 Corrosive Action on Steel

At ordinary temperatures, dry chlorine, either liquid or gas, does not corrode steel. Wet chlorine is highly corrosive because it forms hydrochloric and hypochlorous acids. Precautions should be taken to keep chlorine and chlorine equipment dry. Piping, valves and containers should be closed or capped when not in use to keep out atmospheric moisture. If water is used on a chlorine leak the resulting corrosive conditions will make the leak worse.

### 1.7.4 Volumetric Expansion

The volume of liquid chlorine increases with temperature. Precautions should be taken to avoid hydrostatic rupture of piping, vessels, containers or other equipment filled with liquid chlorine. See Figure 9.4.

### 1.7.5 Specific Manufacturing and Use Hazards

#### 1.7.5.1 Hydrogen

Hydrogen is a co-product of all chlorine manufactured by the electrolysis of aqueous brine solutions. Within a known concentration range, mixtures of chlorine and hydrogen are flammable and potentially explosive. The reaction of chlorine and hydrogen can be initiated by direct sunlight, other sources of ultraviolet light, static electricity, or sharp impact.

### 1.7.5.2 Nitrogen Trichloride

Small quantities of nitrogen trichloride, an unstable and highly explosive compound, can be produced in the manufacture of chlorine. When liquid chlorine containing nitrogen trichloride is evaporated, the nitrogen trichloride may reach hazardous concentrations in the residue. See Pamphlets 21 and 152.

### 1.7.5.3 Oils and Grease

Chlorine can react, at times explosively, with a number of organic materials such as oil and grease from sources such as air compressors, valves, pumps, oil-diaphragm instrumentation, as well as wood and rags from maintenance work.

## 1.8 Containers

### 1.8.1 Container Specifications

Chlorine shipping containers other than barges must comply with the authorized, numbered specification under which they have been fabricated. New containers must be fabricated according to the current specifications and the applicable regulations. Older containers may be continued in service in accordance with applicable regulations. Plans and specifications for construction of barges must be approved by the U.S. Coast Guard or the Canadian Coast Guard.

### 1.8.2 Container Types

- Cylinders (150-pound or less)

Fabricated to DOT (or TC) specification 3A480 or 3AA480. See Section 2. Cylinders conforming with some older specifications may still be used. Special cylinders conforming to DOT (or TC) specification 3BN480 or 3E1800 are applicable for specialized laboratory use.

- Ton Containers

Fabricated to DOT (or TC) specification 106A500X. See Section 2. Ton containers conforming with older specifications may still be used.

- Portable Tanks

Portable tanks fabricated to DOT Specification 51 with special requirements for chlorine.

- Tank Multi-Unit (TMU) Cars

Specially built railroad cars with cradles to carry 15 one-ton containers. The TMU car is nearly obsolete and will not be considered further in this manual.

- Tank Cars

Railroad tank cars fabricated to DOT (or TC) specifications 105J500W or 105S500W. See Section 3.2. Cars built to some older specifications may still be used.

- Tank Motor Vehicles

Tank trailers complying with DOT specification MC 331. See Section 3.3. Trailers conforming to ICC specification MC 330 may still be used.

- Tank Barges

Barges containing chlorine tanks, usually four. See Section 3.5.

### 1.8.3 Container Similarities

Containers are similar in the following aspects:

- They are constructed of steel.
- They are inspected and pressure tested at regular intervals as required by applicable regulations.
- They are equipped with one or more pressure relief devices.
- They are marked, labeled and placarded as required by applicable regulations.
- They are all built to meet federal government specifications.

# 2 CYLINDERS AND TON CONTAINERS

## 2.1 Container Descriptions

### 2.1.1 General

Cylinders and ton containers have many similarities in the way in which they are handled and many users of cylinders also use ton containers. Therefore, they are considered together in this section. The terms "cylinder," "ton cylinder," or "drum" should not be used to describe the ton container. Emergency equipment for handling ton containers is different from that used for cylinders and confusion can be avoided if the proper terms are used.

### 2.1.2 Cylinders

Chlorine cylinders are of seamless construction with a capacity of 1 to 150 lb (0.45 to 68kg); those of 100 lb and 150 lb (45.4 and 68 kg) capacity predominate. Approximate dimensions and weights of 100 lb and 150 lb cylinders are shown in Table 2.1 in this manual and in Pamphlet 151. These cylinders are the foot-ring type, bumped-bottom type or double-bottom type (Fig. 2.1) and are not permitted to be fabricated with more than one opening. The valve connection is at the top of the cylinder. The steel valve protective housing should be utilized to cover the valve during shipment and storage.

The DOT or TC specification number, serial number, identifying symbol, original tare weight,

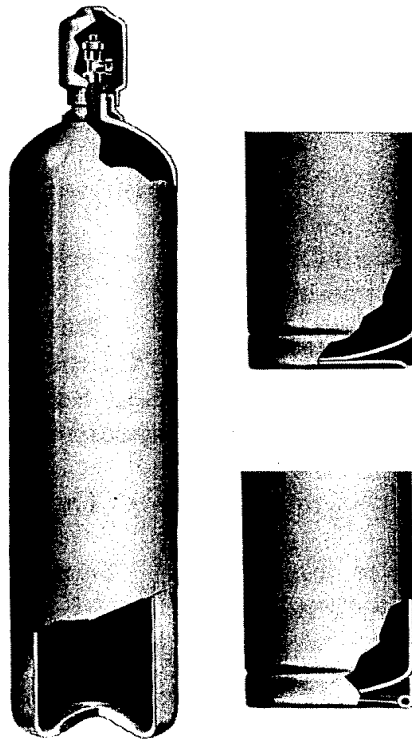


Figure 2.1 Chlorine Cylinder

inspector's official mark and date of hydrostatic test must be stamped on the metal near the cylinder neck. Usually the owner's name or symbol is stamped or embossed on the cylinder in this same area. It is illegal to mar or deface these markings. Tare weight means the weight of the empty cylinder and valve, but does not include the valve protective housing.

### 2.1.3 Ton Containers

Ton containers are welded tanks having a capacity of one short ton, 2000 lb (907 kg) and a loaded weight of as much as 3650 lb (1655 kg) (Fig. 2.2). Approximate dimensions and weight are shown in Table 2.1. The heads are concave and forge welded to the shell. The sides are crimped inward at each end to form chimes which provide a substantial grip for lifting beams. The container valves are protected by a removable steel valve protective housing.

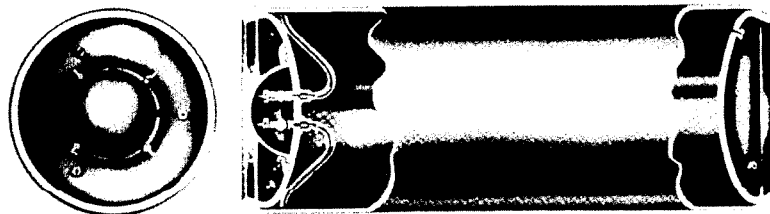


Figure 2.2 Chlorine Ton Container

(A few containers of different designs are in service.)

**Note: The Institute recommends that all pre-1936 ton containers manufactured by the American Welding Service Company not be used in chlorine service.**

The DOT or TC specification number, the material and cladding material (if any), the owner's or the builder's identifying symbol and serial number, the inspector's mark, the test date(s), and the water capacity must all be stamped into the chime at the valve end. This information also may be stamped on a brass plate secured to the tank head opposite the valve end. It is illegal to mar or deface these markings. In addition to the above required markings, the original tare weight is stamped either on the chime or on the brass plate. Tare weight means the weight of the empty container with valves and fusible plugs, but does not include the protective valve housing. Usually the owner's name or symbol is stamped on the container or embossed on the brass plate.

## 2.2 Container Valves

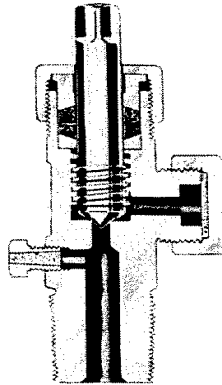
### 2.2.1 Cylinders

A standard cylinder valve is shown in Fig. 2.3. Other valves also may be recommended for chlorine service. See Pamphlet 17. The valve outlet threads are not standard pipe threads, but are special straight threads (designated as 1.030 inch – 14NGO-RH-EXT). See Section 2.8.5 for details on recommended connections.

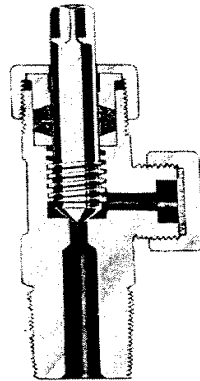
Cylinder valves are equipped with a fusible metal pressure relief device or, as more commonly named, a fusible plug. See Section 2.3.1.

### 2.2.2 Ton Containers

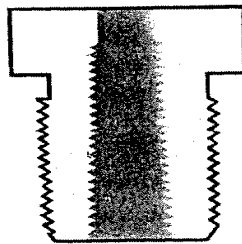
Each ton container is equipped with two identical valves near the center of one end. These valves are standard ton container valves (Fig. 2.4). See Drawing 110. They are different from the standard cylinder valve in that they have no fusible metal plug and usually have a larger internal passage. Other valves also may be recommended for chlorine service. See Pamphlet 17. Each valve connects to an internal education tube (Fig. 2.2).



**Figure 2.3 Standard Cylinder Valve**



**Figure 2.4 Standard Ton Container Valve**



**Figure 2.5 Standard Fusible Plug**

## 2.3 Pressure Relief Devices

### 2.3.1 Cylinders

Cylinder valves are equipped with a fusible metal relief device or fusible plug. Most valves have a threaded plug containing the fusible metal screwed into a tapped hole in the valve body, below the valve seat. (A few have fusible metal cast directly into a threaded hole in the valve body.) The fusible metal is designed to yield or melt between 158°F and 165°F (70°C and 74°C) to relieve pressure and prevent container rupture if exposed to fire or other high temperature. The relief device is activated only in the event of a temperature increase.

### 2.3.2 Ton Containers

All ton containers are equipped with fusible metal pressure relief devices (Fig. 2.5). Most have six fusible metal plugs, three in each end, spaced 120° apart. The fusible metal is designed to yield or melt between 158°F and 165°F (70°C and 74°C) to

**Table 2.1 Container Dimensions and Weights**

Capacity		Tare Weight		Outside Diameter		Overall Height (1) or	Length
lb.	(kg)	lb.	(kg)				
100	45	63-115	29-52	8.25-10.75	210-273	39.5-59	1003-1499
150	68	85-140	39-64	10.25-10.75	260-273	53.0-56	1346-1422
2000	907	1300-1650	590-748	30	762	79.75-82.5	2026-2096

Note: (1) Height to top of valve protective housing; height to center line of valve outlet is about 31/2" (89 mm) less.

relieve pressure and prevent rupture of the container in case of fire or other exposure to high temperature. The relief device is activated only in the event of a temperature increase.

## 2.4 Container Shipping

### 2.4.1 Cylinders

Cylinders may be shipped by highway, rail or water. Highway shipments may be truckload or less-than-truckload (LTL) lots. Suitable restraints are necessary to prevent cylinders from shifting during transportation. See Pamphlet 76.

### 2.4.2 Ton Containers

Most ton containers are shipped by highway. Such trucks must have suitable holddown devices to prevent the containers from shifting during transportation. Trucks are sometimes equipped with a crane and lifting beam (Figure 2.6) to facilitate loading and unloading. See Pamphlet 76.

## 2.5 Container Labeling and Placarding

Containers in transportation must be suitably labeled and the vehicle placarded as required by regulations.

## 2.6 Container Handling

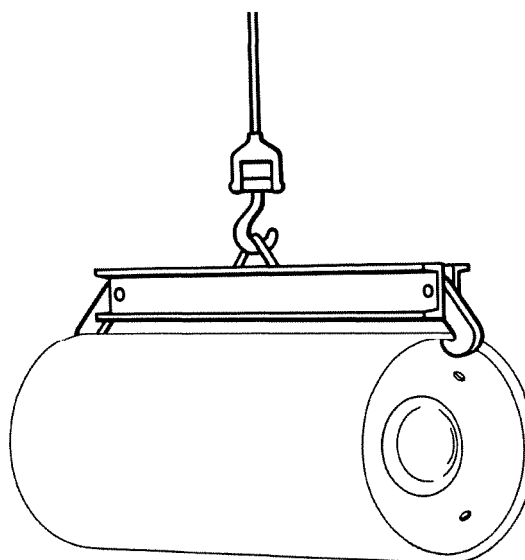
### 2.6.1 General

Chlorine containers must be handled with

care. During shipment and storage, container valve protective housings should be in place. Containers should not be dropped and no object should be allowed to strike them with force. It is convenient to load and unload containers from a truck to a dock at truck bed height. If such a dock is not provided, a hydraulic tail gate can be used. Containers should be secured to prevent them from rolling. See Pamphlet 76.

### 2.6.2 Cylinders

Cylinders can be moved about in a plant area using a properly balanced hand truck. The truck should have a clamp or chain two-thirds of the way up the cylinder wall to hold the cylinder in place. If cylinders must be elevated by hoist, a specially designed cradle or carrier should be used. Slings and magnetic devices are



**Figure 2.6 Lifting Beam for Handling Chlorine Ton Containers**

unacceptable. Cylinders must not be lifted by the valve protective housing because the neck ring to which the housing is attached is not designed to carry the weight of the cylinder.

### 2.6.3 Ton Containers

Ton containers are typically moved using a monorail or crane with a lifting beam (Fig. 2.6). See Drawing 122. They can be rolled on rails or roller conveyers designed for this purpose. If a fork lift truck is used, the ton container must be adequately restrained to prevent it from falling off, particularly when the truck changes direction. The fork lift truck must be rated to handle the gross weight of the container (3300-3650 lb or 1500-1655 kg).

## 2.7 Container Storage

Containers may be stored indoors or outdoors. If stored indoors, the storage area should comply with the provision of Sections 7.1 and 7.2. If stored outdoors, the storage area should be clean so that accumulated trash or other combustible material does not present a fire hazard. Containers should not be stored near elevators or ventilating systems because dangerous concentrations of gas may spread rapidly if a leak occurs. All containers should be stored to minimize external corrosion. If standing water can collect around the containers, suitable platforms or supports should be provided. Provisions should be made to permit routine inspection of all containers. Containers should not be stored where heavy objects could fall on them or where vehicles could strike them. Because chlorine is heavier than air, subsurface storage areas should be avoided. Access to storage by unauthorized persons should be controlled.

Exposure of containers to flame, intense radiant heat or to steam lines must be avoided. If the metal in the vicinity of the fusible plug reaches approximately 158<sup>o</sup>F (70<sup>o</sup>C), the fusible metal plug is designed to melt and chlorine will be released.

Full and empty containers should be stored separately. Even though a container is empty, the valve outlet cap(s) and the valve protective housing should be in place. Cylinders should be stored in an upright position. OSHA regulations require cylinders be properly secured to prevent toppling. Ton containers should be stored on their sides above the ground or floor on steel or concrete supports. In earthquake zones, special storage consideration should be made.

Chlorine containers should be segregated from flammable and oxidizing materials and from materials such as ammonia, hydrocarbons and other materials which are reactive with chlorine. Easy access to containers is important in the event of a leak.

## 2.8 Container Use

### 2.8.1 General

Before connecting or disconnecting a container, the operator should make sure that all safety and emergency equipment is available and operable. Containers and valves must not be modified, altered, or repaired by anyone other than the owner.

### 2.8.2 Gas Discharge

Cylinders are normally secured in the upright position and deliver chlorine as gas. Ton containers chocked in a horizontal position and with the valves in a vertical line (Fig. 2.2) deliver gas from the upper valve and liquid from the lower valve See Pamphlet 17.

The flow of chlorine gas from a container depends on the internal pressure which, in turn, depends on the temperature of the liquid chlorine. In order to withdraw gas, liquid chlorine must vaporize. Unless enough external heat is available, the temperature of the chlorine will be reduced as the liquid vaporizes and, consequently, the pressure in the container will fall. At low withdrawal rates, surrounding air may provide sufficient heat so that the pressure in the container remains adequate to maintain a uniform flow. At high withdrawal rates, the

temperature and pressure within the container may fall because of the cooling effect of vaporization. As this happens, the rate of flow will gradually diminish and may even appear to stop, giving a false indication of an empty cylinder.

In humid conditions, condensation will form on the outside of the container. At excessive withdrawal rates, the liquid will be cooled to such an extent that frost will form on the outside of the container. The insulating effect of the frost will cause a further decrease in the discharge rate. Discharge rates will diminish as the container empties because there is progressively less area of container wall in contact with the remaining liquid chlorine. Discharge rates may be increased by circulating room temperature air around the container with a fan.

**Note: Never heat a container in a bath of water, or apply direct steam, heat belts, etc.**

Chlorine gas discharge rate results vary significantly because of local ambient temperature, humidity and air circulation, as well as the variations in the piping system and feeding equipment connected to the container. The maximum dependable, continuous discharge rate of chlorine gas from a cylinder is about 1-1.5 lb/day/<sup>o</sup>F. This discharge rate assumes an ambient temperature of at least 60<sup>o</sup>F (about 15<sup>o</sup>C) and natural air circulation. The maximum dependable discharge rate for a ton container under similar conditions is about 6-8 lb/day/<sup>o</sup>F.

If the gas discharge rate from a single container will not meet the flow requirements, two or more may be manifolded together. Alternately, liquid from one or more containers may be sent to a vaporizer for increasing the chlorine gas delivery rate. See Section 2.8.3.

When discharging through a gas manifold, all containers should be at the same temperature to prevent transfer of gas from a warm container to a cool container.

### 2.8.3 Liquid Discharge

For special use, cylinders can be inverted to

deliver liquid chlorine. In such cases, appropriate racks should be used.

Liquid chlorine is delivered from the lower valve of a ton container. Very high liquid withdrawal rates can be obtained. The rate depends on the temperature of the chlorine in the container and on the back pressure. The dependable continuous discharge rate of liquid chlorine under normal temperature conditions and against a pressure of 35 psig (241 kPag) is at least 400 lb/hr (181 kg/hr) for ton containers. The manifolding of ton containers discharging liquid chlorine should not be attempted without taking precautions to equalize the pressure. Drawing 183 depicts a system for equalizing pressures by manifolding the gas valves. It is not sufficient to depend on ton containers reaching the same pressure merely by storing them in the same working area. Piping evacuation procedures should be established so liquid chlorine is not trapped in the system.

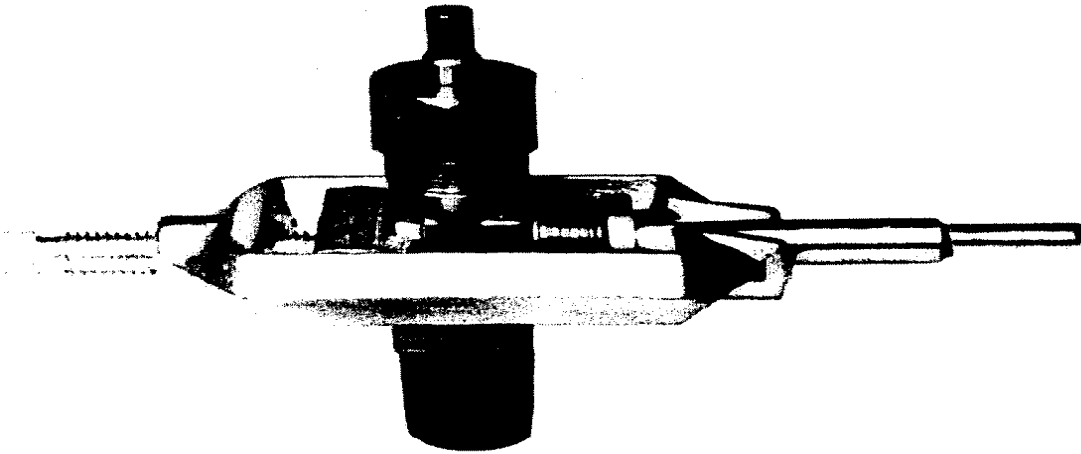
### 2.8.4 Weighing

Because chlorine is shipped as a compressed liquefied gas, the pressure in a container depends on the temperature of the chlorine (Fig. 9.1). The pressure is not related to the amount of chlorine in the container. Container contents can be determined accurately only by weighing.

### 2.8.5 Connections

A flexible connection must be used between the container and the piping system. Copper tubing with a diameter of 1/4-inch or 3/8-inch is recommended. Flexible metallic hoses or fluoroplastic hoses as described in Institute Pamphlet 6 are also acceptable materials.

If a system is to remain in operation while containers are being connected or disconnected, auxiliary (isolating) container valves must be used. These should be located at the container end of the flexible connector to minimize the escape of gas and the entrance of atmospheric moisture. Flexible connections should be inspected on a regular basis. They should be



**Figure 2.7 Yoke & Adapter-Type Connection**

replaced whenever there is any sign of deterioration.

The CGA Connection 820 yoke and adapter is the Institute recommended connection to the container valve outlet (Fig. 2.7). See Drawings 130 and 131. A flat gasket on the face of the valve is part of the connection. The CGA 660 connection is not recommended for connecting to a cylinder or ton container valve.

A new gasket should be used each time a connection is made.

### 2.8.6 Opening Valves

The container valve is opened by turning the valve stem in a counter-clockwise direction. One full turn of the stem permits maximum discharge. More stem turns should not be made. Special 3/8-inch square box wrenches are available for turning the valve stem. A wrench, no longer than 8 inches, should be used. Never use a wrench extension (cheater bar). The valve can be opened by striking the end of the wrench with the heel of the hand. No greater force should be used. If this action is not successful, the chlorine supplier should be contacted for assistance. Once the valve is opened, the wrench can be left in place so that the valve can be closed quickly.

***Note: Loosening the packing nut may increase the risk of a chlorine leak. Proper precautions must be taken.***

Once connections have been made, pressurize the system with a small amount of chlorine. Test for leaks by using vapor from a 26° Baumé aqua ammonia (ammonium hydroxide) solution. See Section 4.4.2. If a leak is found, it must be remedied before proceeding. After testing, if no leaks exist, start continuous flow. See Pamphlet 151.

### 2.8.7 Disconnecting Containers

As soon as a container is empty, the valve should be closed. Prior to disconnecting, a means of removing the chlorine trapped in the flexible connecting line should be provided. This can be accomplished by either purging the line with dry air or nitrogen with a dew point of -40°F (-40°C) or lower or by applying a vacuum. The container should be cautiously disconnected in case residual chlorine remains in the lines. The outlet cap should be applied promptly and the valve protective housing should be replaced. The open end of the disconnected flexible line should be capped promptly to keep atmospheric moisture from entering the system.

# 3 BULK SHIPPING CONTAINERS

## 3.1 General

Bulk chlorine is shipped in tank cars, tank motor vehicles, portable tanks and barge tanks. Most common chlorine shipments are made in single-unit tank cars of 55 or 90 ton capacity. Chlorine may also be transferred in bulk by pipeline which is discussed in Pamphlet 60.

## 3.2 Tank Cars

### 3.2.1 General

The following is generalized information on chlorine tank cars. For more detailed information, see Pamphlet 66.

### 3.2.2 Specifications

The most commonly used tank cars (Fig. 3.1) have a chlorine capacity of 55 or 90 tons. However, 16, 30, and 85 ton cars are authorized and are in use. By regulation, tank cars may not be loaded with chlorine in excess of these

nominal weights.

Chlorine tank cars must comply with 49 CFR 179.102-2. Similar text appears in TC Regulations at 79.102-2. An exception for older cars appears in 49 CFR 173.314(c) note 12 and TC regulation 73.314(c) note 12.

The regulations require tank cars to be equipped with a pressure relief device whose setting is stenciled on the side of the car. Tank cars equipped with manual angle valves must have interior reduction pipes used for liquid discharge equipped with excess flow valves of approved design. Tank cars equipped with pneumatically operated valves (POVs) should be equipped with a ball-check valve on all four valve openings.

Tank cars must be insulated with four inches of insulating material. The insulation reduces the increase in vapor pressure during hot weather and helps maintain pressure needed to unload the car during cold weather. The current standard is two inches of glass fiber placed over two inches of ceramic fiber. Older cars are equipped with four inches of cork or urethane foam.

Figure 3.1 Chlorine Tank Car



### 3.2.3 Manway Arrangement

#### 3.2.3.1 General

Five fittings are mounted on the manway cover within the protective housing (Fig. 3.2). Four of these are angle valves and the fifth, located in the center, is a pressure relief device designed to relieve if excessive pressure builds up in the tank car.

#### 3.2.3.2 Angle Valves

The manually operated angle valve constructed according to Drawing 104 (Institute Standard Angle Valve) (Fig. 3.3) has a forged steel body and a Monel<sup>®</sup> stem and seat. The outlet is a 1-inch female ANSI standard taper pipe thread and is fitted with a pipe plug.

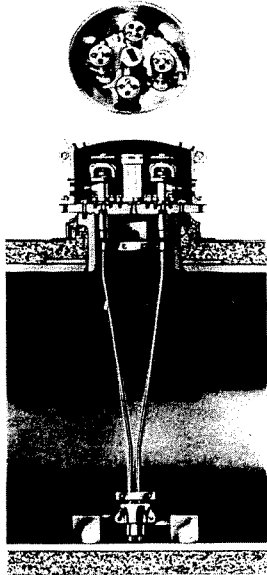


Figure 3.2 Valve Arrangement & Manway

The two angle valves on the longitudinal centerline of the tank car are for liquid discharge. The two angle valves on the transverse centerline are connected to the vapor space.

Equivalent manual angle valves from various valve producers and approved by the Association of American Railroads Tank Car Committee may also be used. The exterior appearance of these valves is similar to the

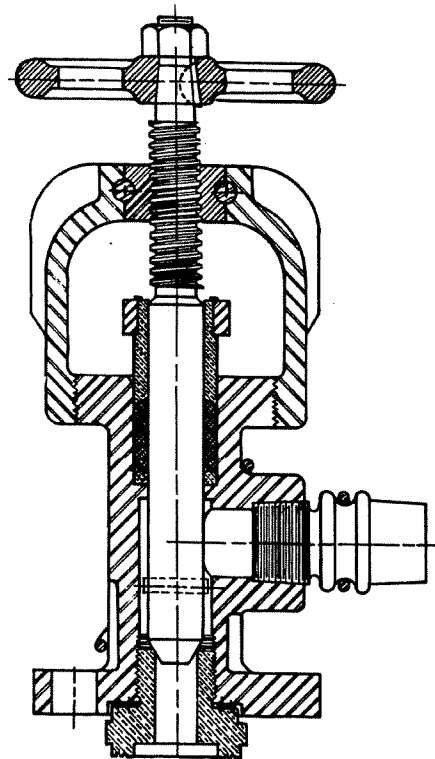
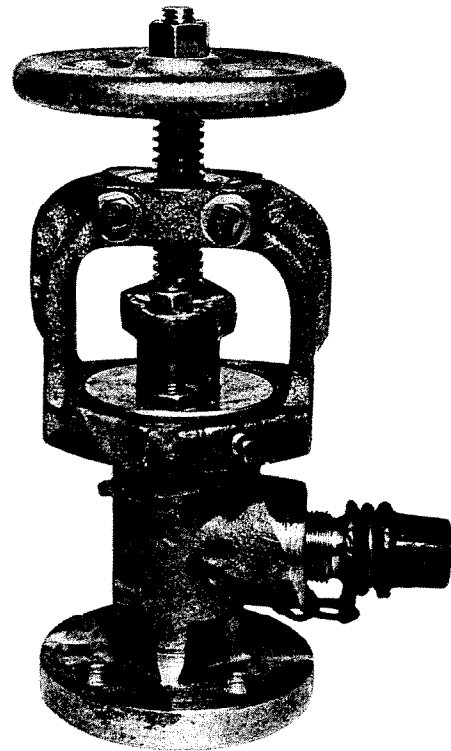


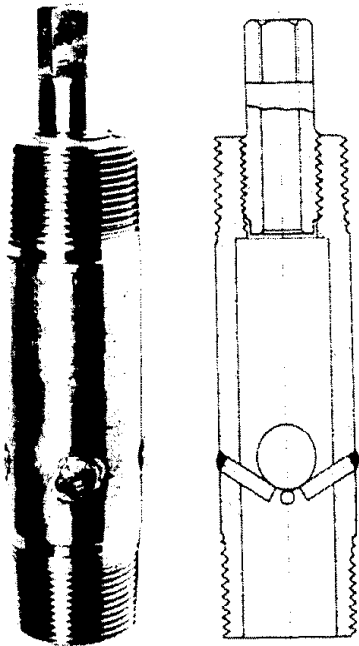
Figure 3.3 Standard Angle Valve

Institute standard angle valve, but may have different design features, e.g., replacement outlet port, bellows-seals, stem packing arrangements.

Chlorine tank cars may also be equipped with pneumatically operated valves (POVs). The manway cover for tank cars equipped with POVs is different. The POV is a dual valve system consisting of an external bellows seal, angle globe valve, and a spring loaded ball check valve with a top-mounted pneumatic actuator, including provisions for a manual override. Actuating the valve simultaneously operates the spring loaded check valve mounted beneath the angle globe valve. The valves are designed to be opened or closed pneumatically and are of a fail-safe/fail-closed design with a loss of pneumatic pressure. The valve also may be opened manually with a specially designed device that mounts on top of the angle globe valve. The device may be attached to a cord allowing the valve to be tripped safe/closed. See Pamphlet 93.

### 3.2.3.3 Excess Flow Valves

Except for tank cars equipped with pneumatically operated valves, under each liquid valve there is an excess-flow valve (Fig. 3.4). The excess-flow valve consists of a rising ball which closes when the rate of flow exceeds a predetermined value. It does not respond to pressure in the car. It is designed to close automatically against the flow of liquid chlorine if the angle valve is broken off in transit. It may close if a catastrophic leak

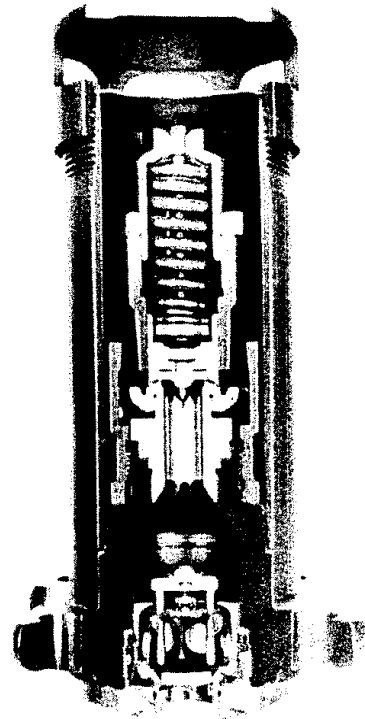


**Figure 3.4 Excess-Flow Valve**

involving a broken connection occurs but it is not designed to act as an emergency shut-off device during transfer. The excess-flow valves have a maximum operating flow rate of 7,000 lb/hr (3,200 kg/hr), 11,000 lb/hr (5,000 kg/hr) or 15,000 lb/hr (6,800 kg/hr). Tank cars equipped with POVs are equipped with a ball check valve under both the liquid and vapor outlets.

### 3.2.3.4 Eduction Pipes

Liquid chlorine is withdrawn through 1¼-inch eduction pipes (Fig. 3.2). (Bottom outlets are not permitted in chlorine cars.) The eduction pipes are attached to the excess-flow valves, or directly to the bottom of the tank car dome if equipped with POVs, and extend to the bottom of the car. One or both eduction pipes may be used to unload the car.



**Figure 3.5 Standard Pressure Relief Device**

### 3.2.3.5 Pressure Relief Device

In the center of the manway cover is a spring loaded pressure relief device (Fig. 3.5). The device is set to start-to-discharge at a gage

pressure of 225 psig (1551 kPag) on cars stenciled 105J300W or 105S300W or at a gage pressure of 375 psig (2586 kPag) on cars stenciled 105J500W or 105S500W.

### 3.2.4 Transfer Operations

The following is general information. For more detailed information, refer to Pamphlet 66.

#### 3.2.4.1 Precautions

- Every site handling chlorine should have an on-going safety program. Special attention should be directed to the appropriateness of emergency procedures and to equipment to be used in an emergency.

- All personnel responsible for transfer operations should be knowledgeable about the facility's emergency response plan for handling spills and leaks of products.

- DOT, OSHA and TC have specific training requirements applicable to handling of hazardous materials. Chlorine transfer operations must be performed only by personnel who are trained as required by applicable hazardous material regulations.

- Chlorine tank cars must be loaded or unloaded on a private track or siding.

- Chlorine transfer operations should incorporate an emergency shut-off system to reduce the possibility of a major release. See Pamphlet 57.

- It is recommended that chlorine tank cars be loaded on a track scale.

- The transfer operation area should be adequately illuminated during transfer operations.

- During all times when the tank car(s) is connected for transfer of product:

- Tank car brakes must be set and wheels chocked.

- Caution signs (blue flags or lights) must be so placed on the track to give necessary warning to persons approaching the tank cars from the open end(s) of the siding.

- Derail devices should be placed at the open end(s) of the siding not less than approximately

one car length from the car(s) being transferred, unless the tank car(s) is protected by a closed and locked switch.

- Before the transfer valves are opened, the loading/unloading connections must be attached securely to the tank car connections. All connections should be leak-checked. See Section 4.4.2.

- The transfer area should be checked to make sure all safety equipment (e.g., self-contained breathing apparatus, emergency kits, eye wash fountains) is in its proper place and operable.

- A suitable operating platform should be provided at the transfer station for easy access to the protective housing, for connection of lines, for the operation of valves and for rapid escape, if required. See Pamphlet 66.

#### 3.2.4.2 Connections

Transfer operations should be done through a suitable flexible connector to permit the movement of the tank car on its springs. Recommended specifications for chlorine transfer hose as well as more detailed information pertaining to piping and other components are contained in Pamphlet 6.

Nipples for insertion into the tank car angle valve should have clean, sharp threads. A non-reactive lubricating pipe dope or PTFE tape should be used to prevent galling of the threads. It should be applied in such a manner as to prevent its entry into the piping. After the connections are tight, add a small amount of chlorine to the system by slightly opening the liquid angle valve for a second or two to pressurize the piping with chlorine gas and test for leaks. See Section 4.4.2.

During unloading, if the liquid angle valve is opened too rapidly or an unusually high flow rate is established, the excess-flow valve will close. If this situation occurs, the angle valve should be closed until the metal ball in the excess-flow valve drops back into place. A click will be heard when the ball drops.

If this action is unsuccessful, the manway cover next to the valve may be tapped sharply with a hammer.

**Note: The valve must never be directly struck.**

If the ball in the excess flow valve is still not dislodged, nitrogen from a cylinder, or some other non-reactive gas, may be applied to the down-stream side of the excess flow valve. Do not exceed the design pressure of the piping system. Liquid angle valve(s) must never be used to regulate the flow rate of chlorine. These valves, if opened, should be kept completely open.

#### 3.2.4.3 Pressure Padding

Liquid chlorine usually is unloaded by tank car pressure. See Pamphlet 66. The vapor pressure of the chlorine is frequently augmented by a "pad" of dry air or non-reactive gas. It is essential that the air used for padding be free from oil and foreign matter and be dried to a dew point -40°F (-40°C) or below.

Air for padding should be supplied by a separate air compressor which is not used for any other purpose. To minimize the potential of a chlorine-hydrocarbon oil reaction, either a non-lubricated compressor or a compressor lubricated with a non-reactive synthetic oil, should be utilized. Filters ahead of the dryers are required to ensure oil free dry air if a lubricated compressor is used.

The air pad system should be designed to prevent the backflow of chlorine vapors from the car. Lack of a positive backflow protection with a hydrocarbon lubricated compressor may result in a violent reaction of chlorine and oil. A check valve alone should not be considered adequate to prevent back flow. See Pamphlet #6.

#### 3.2.4.4 Monitoring

Current DOT and TC regulations require that throughout the entire period the tank car is connected, the car must be attended by the operator. There may be exceptions to this

general rule. It is the responsibility of each transfer site to ensure all applicable regulations are followed. See Pamphlet 66.

#### 3.2.4.5 Disconnecting

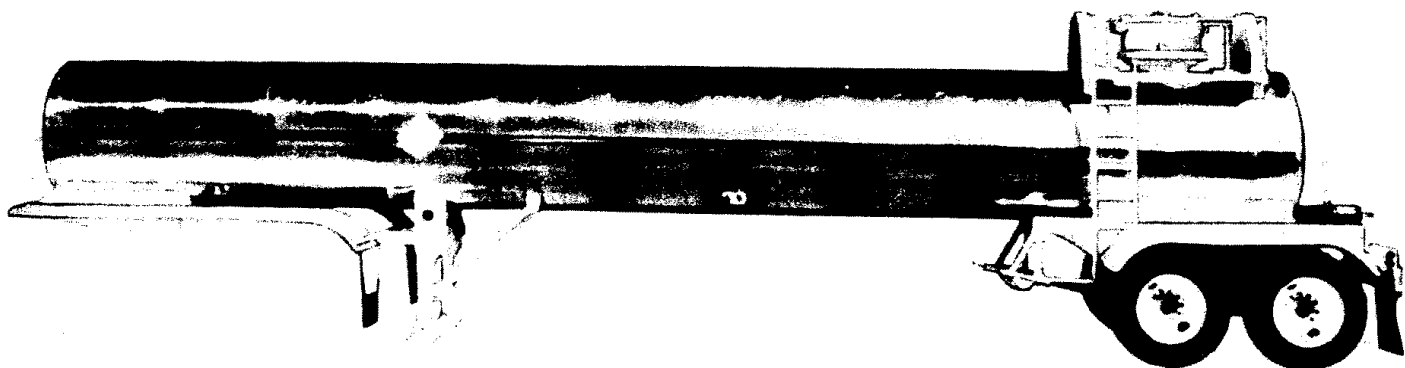
A noticeable drop in tank car pressure usually indicates that the tank car is empty. It is desirable to discharge as much of the residual chlorine as possible to the process. Chlorine lines should be purged with dry air or non-reactive gas to an absorption system or vented to a vacuum system before disconnecting.

After the transfer lines have been disconnected, the valve outlet plugs should be installed immediately. This is essential to prevent corrosion of the threads by atmospheric moisture. After checking for leaks the protective housing cover must be closed. After unloading, the DOT placards must indicate the car last contained chlorine. The open end of the chlorine transfer lines should also be protected from atmospheric moisture with suitable closures.

### 3.3 Tank Motor Vehicles

#### 3.3.1 General

The following is generalized information on chlorine tank motor vehicles. For more detailed information, see Pamphlet 49. In North America they usually have a capacity ranging from 15 to 22 tons (13,600 kg to 20,000 kg) with certain exceptions (Fig. 3.6). DOT specifications apply only to the tank; such "cargo tanks" comply with specification MC331 including the special requirements for chlorine, but tanks built to specification MC330 maybe continued in service.



**Figure 3.6 Chlorine Tank Truck**

### 3.3.2 Manway Arrangement

#### 3.3.2.1 General

The manway arrangement is the same as that on chlorine tank cars (see Section 3.2.3.1) except that special excess-flow valves are required under the gas valves.

#### 3.3.2.2 Angle Valves

The angle valves are the same as those on tank cars (see Section 3.2.3.2). Angle valves must be tested before installation and every two years.

#### 3.3.2.3 Excess-Flow Valves

Under each liquid angle valve there is an excess-flow valve with a maximum operating flow rate of 7,000 lb/hr (3,200 kg/hr). There are eduction pipes connected to the two liquid excess-flow valves as in a tank car.

In addition under each gas angle valve there is an excess-flow valve of different design; these valves have a removable basket so that the ball can be removed and the interior of the tank inspected.

#### 3.3.2.4 Pressure Relief Device

The pressure relief device is the same type as that used on tank cars (see Section 3.2.3.5). On all cargo tanks the start-to-discharge pressure is 225 psig (1,551 kPag).

### 3.3.3 Transfer Operations

Procedures for transferring chlorine to/ from tank trucks are essentially the same as for tank cars. There is, however, more variation in facilities and conditions at customers' plants, and these may require modifications of methods and equipment.

#### 3.3.3.1 Precautions

The engine should be shut off, hand brakes must be set and wheel chocks must be in place during transfer. The tank motor vehicle must not be left unattended. The tank motor vehicle must not be moved when loading or unloading connections are attached to the vehicle (see discussion of tank car transfer, Section 3.2.4.1, for additional, applicable precautions.)

#### 3.3.3.2 Emergency Equipment

Approved respiratory equipment is required on the transport vehicle. In the U.S., all personnel authorized to use the equipment must meet the medical and training requirements of OSHA 29 CFR 1910.134. An Emergency Kit "C" must be on the transport vehicle.

It also is recommended that the transport vehicle have 2-way communication equipment of radio transmitter type or cellular phone.

### 3.3.3.3 Connections/Disconnecting

See discussion for tank cars (Sections 3.2.4.2 and 3.2.4.5).

The driver should recheck all equipment by a general visual inspection before starting the vehicle.

### 3.3.3.4 Pressure Padding

See discussion for tank cars (Section 3.2.4.3).

## 3.4 Portable Tanks

Tanks suitable for multi-modal transportation (road, rail and water) of chlorine should be built under the provisions of DOT 51 and special provisions for chlorine. See Pamphlet 49.

## 3.5 Tank Barges

### 3.5.1 General

The following is generalized information on chlorine tank barges. For more detailed information, see Pamphlet 79.

Chlorine barge design is dependent upon its geographical operating pattern – inland river or ocean service. The inland river units are designed solely for chlorine transportation with either 4 or 6 independent, cylindrical uninsulated pressure tanks mounted longitudinally.

The ocean units are multi-product designed vessels with chlorine in cylindrical pressure deck tanks and sodium hydroxide, sodium chlorate, and/or sodium hypochlorite in center and wing tanks. Both barge types are subject to U.S. Coast Guard and Canadian Coast Guard regulations.

### 3.5.3 Manway Arrangement

#### 3.5.2.1 General

Chlorine barge tanks may have one or more flanged openings on the top of the cargo tanks. No openings are allowed below the top surface. The arrangement of valving is not standardized. Depending on the tank cargo capacities, each tank has either two or three pressure relief devices and a varying number of angle valves located on the top manway openings.

#### 3.5.2.2 Angle Valves

Inland chlorine barge cargo tanks are normally equipped with 4 one-inch Chlorine Institute Standard Valves utilized for the pad gas and liquid discharge control. The ocean service barge cargo tanks are equipped with a similar number of two-inch valves.

#### 3.5.2.3 Excess-Flow Valves

Each liquid discharge tank assembly connection contains an excess flow valve which incorporates a ball check that will close when the discharge flow rate exceeds a pre-determined quantity. The gas tank connection also contains an excess flow valve. The gas flow valve may contain a removable basket which allows inspection of the cargo tank prior to loading. Excess flow valves are designed to close if a catastrophic leak occurs. However, they are not designed to serve as an emergency shut-off device during transfer.

#### 3.5.2.4 Eduction Pipes

Liquid chlorine is withdrawn through eduction pipes. The eduction pipes are attached to the excess-flow valves and extend to the bottom of the tank. One or both eduction pipes may be used to unload the tank.

### 3.5.2.5 Pressure Relief Devices

Depending on capacity, each barge tank has two or three pressure relief devices. These are designated 4 JQ and are designed to start-to-discharge pressure of 300 psig (2,070 kPa). See Pamphlet 41.

### 3.5.3 Transfer Operations

The following is general information. For more detailed information, see Pamphlet 79.

#### 3.5.3.1 General

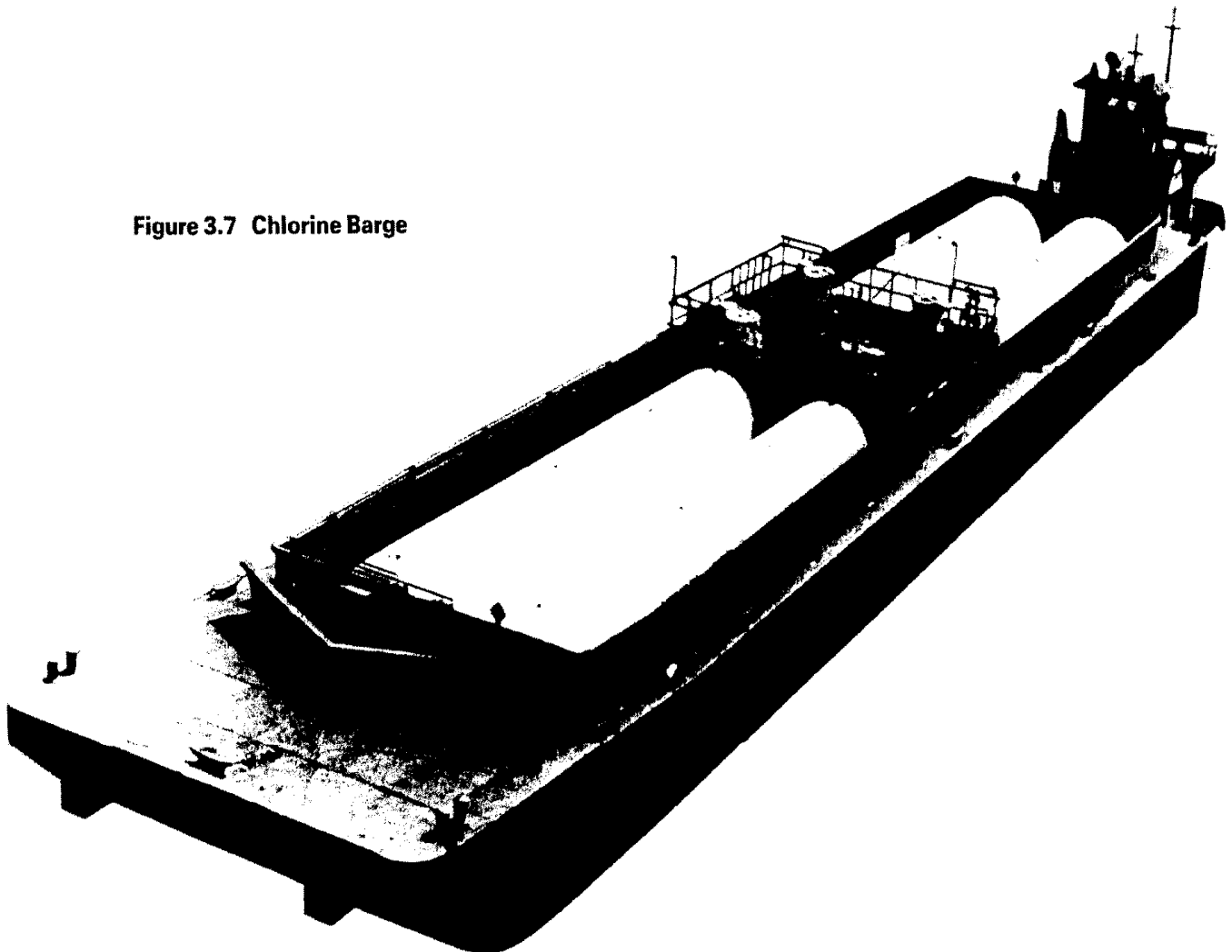
Loading and unloading of chlorine barges are subject to U.S. and Canadian Coast Guard

regulations. Chlorine transfers between a vessel and a marine terminal must be supervised by individuals who have been designated as the Person in Charge. Procedures for withdrawing chlorine from barges are essentially the same as for tank cars except that diagonal barge cargo tanks must be discharged together to prevent the barge from becoming unstable. Variation in facilities and conditions at customers' plants may require modifications of methods and equipment and should be considered before discharge is initiated.

#### 3.5.3.2 Personnel Protection

See Section 5-Employee Training and Safety

**Figure 3.7 Chlorine Barge**



# 4

# EMERGENCY MEASURES

## 4.1 General

A chlorine emergency may occur during manufacture, use or transportation. Trained employees, along with a comprehensive, written emergency response plan (Pamphlet 64), are necessary to mitigate the consequences of the emergency. Federal, state and provincial regulations, as well as various local fire and building codes, regulate chemical emergency preparedness and response. All persons handling, or responsible for the handling of chlorine, must be familiar with the contents of those varied requirements.

Regulatory requirements deal generally with preparation and response to chemical and other emergencies. This section is designed to provide additional information for use in chlorine emergencies. Help is also available from CHLOREP (see Sections 4.5.1 to 4.5.3) through CHEMTREC in the U.S. and through CANUTEC in Canada.

## 4.2 Response to a Chlorine Release

As soon as there is any indication of a chlorine release, immediate steps must be taken to correct the condition.

Chlorine leaks always get worse if they are not promptly corrected. When a chlorine leak occurs, authorized, trained personnel equipped with respiratory and appropriate other personal protective equipment (PPE) should investigate and take proper action. Personnel should not enter into atmospheres containing concentrations of chlorine in excess of the Immediately Dangerous to Life and Health Concentration (10 ppm) without appropriate personal protective equipment and back-up personnel.

Pamphlet 65 provides PPE recommendations for responders to a chlorine release. Keep unnecessary personnel away and isolate the hazard area. Persons potentially affected by a

chlorine release should be evacuated or sheltered in place as circumstances warrant.

Area chlorine monitors and wind direction indicators can supply timely information (e.g., escape routes) to help determine whether personnel are to be evacuated or sheltered in place.

When evacuation is utilized, potentially exposed persons should move to a point upwind of the leak. Because chlorine is heavier than air, higher elevations are preferable. To escape in the shortest time, persons already in a contaminated area should move crosswind.

When inside a building and sheltering in place is selected, shelter by closing all windows, doors and other openings, and turning off air conditioners and air intake systems. Personnel should move to the side of the building furthest from the release.

Care must be taken not to position personnel without an escape route. A safe position may be made hazardous by a change in wind direction. New leaks may occur or the existing leak may get larger.

If notification of local authorities is required, the following information should be provided:

- Company name, address, telephone number and the name of the person(s) to contact for further information
- Description of the emergency
- Travel directions to the site
- Type and size of container involved
- Corrective measure being applied
- Other pertinent information, i.e., weather conditions, injuries, etc.

## 4.3 Response to a Fire

If fire is present or imminent, chlorine containers and equipment should be moved away from the fire, if possible. If a non-leaking container or equipment cannot be moved, it should be kept cool by applying water on it.

Water should not be used directly on a chlorine leak. Chlorine and water react forming acids and the leak quickly will get worse. However, where several containers are involved and some are leaking, it may be prudent to use a water spray to help prevent over-pressurization of the non-leaking containers. Whenever containers have been exposed to flames, cooling water should be applied until well after the fire is out and the containers are cooled. Containers exposed to fire should be isolated and the supplier should be contacted as soon as possible.

## 4.4 Releases

### 4.4.1 General

Chlorine facilities should be designed and operated so that the risk of a chlorine release into the environment is minimized. However, accidental releases and leaks of chlorine may occur. The overall effects of such releases must be considered.

### 4.4.2 Detection of Minor Releases and Leaks

A plastic squeeze bottle containing 26<sup>0</sup>Baumé aqua ammonia can be used to detect a minor release or leak. If ammonia vapor is directed at a leak, a white cloud will form indicating the source of the leak. If a wash bottle is used, the dip tube should be cut off so that squeezing the bottle directs vapor, not liquid, out of the nozzle. Avoid contact of aqua ammonia with brass or copper. Portable electronic chlorine monitors can also be used to detect leaks. If a leak occurs in equipment or piping, the chlorine supply should be shut off, the pressure relieved and necessary repairs made.

Leaks around shipping container valve stems usually can be stopped by tightening the packing gland. If such tightening does not stop the leak, the container valve should be closed. Pamphlets 66 and 151 provide further details. If simple corrective measures are not sufficient, the appropriate Chlorine Institute Emergency Kit should be applied or the cylinder should be placed in a recovery vessel designed to contain

the leak, and the chlorine supplier notified. See Section 4.8.

### 4.4.3 Types of Releases

Chlorine releases can be classified as either instantaneous (puffs) or continuous. See Pamphlet 74.

#### 4.4.3.1 Instantaneous Release

An instantaneous release is characterized by the release of chlorine to the atmosphere in a relatively short period of time (a few minutes), resulting in a cloud which moves across the downwind range while growing in size and decreasing in concentration. Thus, the concentration of chlorine monitored at any given point downwind will vary over time depending on the position of the chlorine cloud.

#### 4.4.3.2 Continuous Release

A continuous release is characterized by the release of chlorine to the atmosphere over a longer period of time (usually more than 15 minutes), resulting in a continuous plume which reaches an equilibrium size and concentration gradient. Thus, the concentration of chlorine monitored at any given point downwind from the source will be constant over time for the duration of the release. The failure of a valve or fitting on a large container is an example of a continuous release.

### 4.4.4 Area Affected

The area affected by a chlorine release and the duration of the exposure depend upon the total quantity released, the rate of release, the height of the release point and weather conditions, as well as the physical form of the chlorine being released. These factors are difficult to evaluate in an emergency situation. Chlorine downwind can vary from barely detectable to high concentrations. Pamphlet 74 provides information on the area affected by specific chlorine release scenarios.

#### 4.4.5 Physical Form of the Chlorine Released

Chlorine occurs as a gas or a liquid depending on the pressure and temperature. Typically, chlorine is stored and transported as a liquid under pressure. Whether the release source is a liquid or gas significantly affects the downwind dispersion since liquid chlorine expands in volume by nearly 460 times when it vaporizes.

During a release, chlorine can escape as a gas, a liquid, or both. When pressurized liquid or gas is released from a container, the temperature and pressure inside the container will decrease thus reducing the release rate.

Escaping liquid may collect in a pool and may actually form a running stream. Chlorine will immediately cool to its boiling point (-29°F, -34°C) as it enters the atmosphere. Upon contact with any heat source — the air, the ground, or water— the heat will cause the chlorine to boil readily. Typically, the boiling-off rate will be relatively high initially and then decline as the heat source surrounding the chlorine is cooled.

Since water in bulk provides a vast heat source for evaporating liquid chlorine, any liquid falling into water should be assumed to vaporize. For this reason, water should be prevented from coming in contact with a liquid chlorine pool, and chlorine should be prevented from flowing into water drains.

#### 4.4.6 Effect of Chlorine on the Environment

##### 4.4.6.1 Vegetation

Chlorine causes bleached spots on leafy plants due to attack on chlorophyll in leaves. Mature leaves are most susceptible to chlorine injury. Usually the plant itself is not destroyed although yield or growth rate may be retarded.

##### 4.4.6.2 Animals

The U.S. National Institute for Occupational Safety and Health 1980 "Registry of Toxic Effects of Chemical Substances" lists the following inhalation LC<sub>50</sub>s (concentration of chlorine in air lethal to 50% of the test

population of the defined animal, exposed over the specified time period):

Human	840ppm/30 minutes
Rat	293ppm/60 minutes
Mouse	137ppm/60 minutes

The lowest concentration of chlorine in air (other than LC<sub>50</sub>) which has been reported to cause death in humans or animals is listed as 500ppm/5 minutes.

##### 4.4.6.3 Aquatic Life

Chlorine is only slightly soluble in water and there would be little absorption from a cloud of chlorine gas. Many forms of aquatic life are adversely affected by chlorine in concentrations well below 0.1 ppm. Chlorine is listed as a marine pollutant by DOT.

### 4.5 Transportation Emergencies

DOT and TC require that any person who offers chlorine for transportation must provide a staffed 24-hour emergency response telephone number that can be called in the event of an emergency involving chlorine. For emergencies involving the transportation of chlorine, the Chlorine Institute's CHLOREP, the Chlorine Emergency Plan, can provide assistance.

#### 4.5.1 CHLOREP

The Chlorine Emergency Plan (CHLOREP) was established in January 1973 by the Institute as an industry-wide program to improve the speed and effectiveness of response to chlorine emergencies in the United States and Canada.

The primary purpose of the formalized plan is to minimize the risk of injury arising from the actual or potential release of chlorine during emergencies occurring in the course of transportation, at distribution points, or at chlorine user locations. Under this plan, the United States and Canada have been divided into regional sectors where trained emergency teams from producing, packaging, distribution and consuming plants are on constant alert on a 24-hour basis to handle possible or actual chlorine releases.

During a chlorine emergency, any carrier, customer, or civil authority can obtain basic emergency information and be put in contact with the closest chlorine emergency group through either CHEMTREC (U.S.) or CANUTEC (Canada). CHEMTREC and CANUTEC can be contacted as indicated in the next section.

#### 4.52 CHEMTREC, CANUTEC, & CECOM

In the United States, the Chemical Transportation Emergency Center (CHEMTREC), in Arlington, VA is the dispatch agency which is utilized. CHEMTREC operates around the clock, 24 hours a day, 7 days per week, to receive direct dial toll free calls from any point in the continental United States at 1-800-424-9300. The number for Alaska and Hawaii and for calls from marine radio telephones is 703-527-3887.

CHEMTREC provides immediate advice for those at the scene of emergencies, then promptly contacts the appropriate responder group as required. In many cases, this will be the shipper. However, in some cases the designated response group is called and then the shipper is notified.

In Canada, the Canadian Transport Emergency Center (CANUTEC) in Ottawa, is the dispatch agency. Its telephone number is 613-996-6666. It may be called collect. CANUTEC, administered by Transport Canada, operates similarly to CHEMTREC.

In Mexico, Centro de Comunicaciones de la Direccion General de Proteccion Civil (CECOM) is the dispatch agency and operates similarly to CHEMTREC and CANUTEC. Its telephone number is 91-800-70-226. For calls originating in Mexico City and the metropolitan area, the telephone number is 7-04-11-69 or 7-05-31-48. If a chlorine leak develops in transit through a populated area, appropriate emergency measures should be taken as quickly as possible. If a vehicle transporting chlorine cylinders or ton containers is disabled and there is any possibility of fire, the containers should be removed from the vehicle.

If a tank car or cargo tank trailer is disabled and chlorine is leaking, appropriate emergency

procedures should be instituted in consultation with local authorities. Clearing of track or highway should not be started until safe working conditions are established. See Section 4.3 for action to take if a fire occurs.

These additional specific actions may be taken to contain or reduce leaks:

- If a container is leaking chlorine, turn it, if possible, so that gas instead of liquid escapes. The quantity of chlorine that escapes from a gas leak is much less than the amount that escapes from a liquid leak through the same size hole.
- If practical, reduce pressure in the container by removing the chlorine as gas (not as liquid) to process or a disposal system as described below.
- It may be desirable to move the container to an isolated spot where the consequences will be mitigated.
- Apply the appropriate Chlorine Institute Emergency Kit or place the cylinder in a recovery vessel designed to contain the leak (see Section 4.8).

A leaking chlorine container must not be immersed or thrown into a body of water; the leak will be aggravated and the container may float when still partially full of liquid chlorine allowing gas evolution at the surface.

Regulations prohibit the normal shipment of a leaking chlorine container or a container which has been exposed to fire, whether full or partially full. It may be necessary in some instances to ship a defective chlorine container. In such cases special arrangements are required and the chlorine supplier should be consulted first.

#### 4.6 Disposal of Chlorine

If a leak occurs at a consuming location, it may be best to dispose of the chlorine through the regular consuming process or to run a temporary line to the consuming point. If the consuming process cannot handle chlorine under emergency conditions, a standby alkali absorption system should be considered. It must be recognized that systems consuming liquid chlorine at low rates will not significantly reduce pressure in the supply container.

In order to reduce pressure in the supply container, chlorine must be removed as a gas at a rate high enough to cause cooling of the remaining liquid. See Section 2.8.2.

#### 4.7 Absorption Systems

A simple absorption system consists of a suitable tank capable of holding the required alkaline solution. The alkali should be stored in a form such that a solution can readily be prepared when needed. After the solution is prepared, the chlorine can be passed from the container into the solution through a connection weighted to hold the outlet of the transfer hose or pipe beneath the level of the solution. Do not immerse the container. See Tables 4.1A and 4.1B for recommended solution (the recommended alkali quantities provide 20% excess).

**Note: When absorbing chlorine in alkaline solutions, the heat of reaction is substantial. Caustic solutions can cause burns to personnel.**

The process should be monitored to ensure the absorption is controlled as to heat and reaction. Do not boil the solution or exceed the capacity of the reaction.

#### 4.8 Emergency Kits and Recovery Vessels

Chlorine Institute Emergency Kits and cylinder recovery vessels are designed to contain most leaks which may be encountered in chlorine shipping containers. The

following kits and recovery vessels (Figure 4.1) are available.

- Kit A - for 100 lb and 150 lb cylinders
- Kit B - for ton containers.
- Kit C - for tank cars and tank trucks.
- Recovery vessels for cylinders.

These kits operate on the principle of containing valve leaks by applying hoods and gaskets. For cylinders and ton containers, patches are provided for sealing off a small hole in the side wall. Capping devices are provided for fusible plugs in ton containers.

<b>Table 4.1A</b>				
<b>Recommended Alkaline Solutions for Absorption</b>				
<b>U.S. UNITS</b>				
Chlorine Container Capacity	20 Weight % Sodium Hydroxide Solution		10 Weight % Sodium Carbonate Solution	
	100% NaOH lb.	Water gal.	100% Na <sub>2</sub> CO <sub>3</sub> lb.	Water gal.
100	135	65	359	390
150	203	98	538	585
2000	2708	1300	7176	7800

<b>Table 4.1B</b>				
<b>Recommended Alkaline Solutions for Absorption</b>				
<b>METRIC UNITS</b>				
Chlorine Container Capacity	20 Weight % Sodium Hydroxide Solution		10 Weight % Sodium Carbonate Solution	
	100% NaOH kg.	Water liters	100% Na <sub>2</sub> CO <sub>3</sub> kg.	Water liters
45.4	61.5	246	163	1470
68	92	370	244	2200
907	1230	4920	3260	29,350



**Figure 4.1 Chlorine Institute Emergency Kit A for Chlorine Cylinders**

The kits contain step-by-step instructions for the use of the devices. The necessary tools are included, but personal protective equipment is not included. Pamphlets IB/A, IB/B, and IB/C provide information on these kits and their use.

Many chlorine consumers incorporate plans for the use of these kits in their emergency programs. Further information on the utility, availability and purchase of kits, kit components and audio visual training aids is available from the Institute.

Chlorine recovery vessels are commercially available equipment designed to hold an entire cylinder. Pamphlet IB/RV provides detailed information on recovery vessels for 100- and 150- lb. cylinders. A leaking cylinder can be placed in a recovery vessel which is then closed, thus containing the leak. The chlorine can then be recaptured from the recovery vessel.

It is the responsibility of the user to provide instruction in the use of kits and recovery vessels and to properly maintain them. The chlorine supplier can provide assistance in these matters.

Chlorine use or storage locations should either have the appropriate Institute emergency kit(s) or containment vessel(s) readily available

with emergency responders trained in their use or have a formal arrangement with an outside emergency response group that can respond to emergencies using such equipment.

#### **4.9 Reporting**

Most governmental agencies have reporting requirements for chlorine releases. Producers, transporters and users of chlorine should be aware of the "reportable quantity" and of all relevant requirements. In the U.S., any chlorine release of 10 pounds or more within a twenty-four hour period not specifically allowed by an operating permit must be reported immediately to the National Response Center at 1-800-424-8802 or 202-426-2675.

A written follow-up report is required within 30 days. See 49 CFR 171.16.

# 5 EMPLOYEE TRAINING AND SAFETY

## 5.1 Employee Training

Safety in handling chlorine depends, to a great extent, upon the effectiveness of employee training, proper safety instructions and the use of suitable equipment. It is the responsibility of the employer to train its employees and to document such training as appropriate and as required by regulation. It is the responsibility of employees to carry out correct operating procedures safely and to properly use the safety equipment provided.

Employee training should include:

- Instruction and periodic refresher courses in operation of chlorine equipment and handling of chlorine containers.
- Instruction in the properties and physiological effects of chlorine. A Material Safety Data Sheet (MSDS) for chlorine is available from chlorine suppliers.
- Instruction to report to the proper authority all equipment failures and chlorine leaks.
- Instruction and periodic drills regarding:
  - Locations, purpose, and use of chlorine emergency equipment, fire fighting equipment, fire alarms and shut-down equipment such as valves and switches.
  - Use of emergency kits, such as the Chlorine Institute Emergency Kits A, B, or C and the recovery vessel, if they are part of emergency equipment and planning at the location. Training should include the actual installation of kits on containers.
  - Locations, purpose, and use of personal protective equipment.
  - Locations, purpose, and use of safety showers, eye baths, bubbler fountains or the closest source of water for use in emergencies.
  - Locations, purpose, and use of specialized first aid equipment.

## 5.2 Personal Protective Equipment

### 5.2.1 Availability and Use

Exposure to chlorine can occur whenever chlorine is handled or used. Personal protective equipment (PPE) for emergency use should be available away from areas of likely contamination. If chlorine is used in widely separated locations, personal protective equipment should be available near each use point. Pamphlet 65 provides recommendations for specific tasks including loading/unloading, initial line entry, material sampling, and emergency response.

### 5.2.2 Respiratory Equipment

All personnel entering areas where chlorine is stored or handled should carry or have immediately available an escape type respirator. Respiratory equipment should be selected based on evaluation of hazards and degree of potential exposure. For example, when tank cars, ton containers or cylinders are connected to or disconnected from plant piping, small releases of chlorine can occur. The need for respiratory protection during such operations should be determined. See Pamphlets 65 and 75.

Chemical cartridge respirators or full face canister gas masks offer adequate temporary protection provided the oxygen content in the air is greater than 19.5% and the chlorine concentration does not exceed the rated capability of the respirator. The need to protect the eyes from chlorine should be part of the evaluation of appropriate respiratory equipment. Pressure-demand self-contained breathing apparatus (SCBA), with full face piece, is required for performing tasks when chlorine may be present unless air sampling verifies the chlorine concentration is such that a lower level of respiratory protection provides protection.

## CONFINED SPACE ENTRY TIPS

- Suitable respiratory and other protective equipment for *anyone* entering confined space;
- Safety harness and life line for *all workers* in a confined space;
- Supervision of the operation from *outside* the confined space at all times;
- No entry for rescues without appropriate respiratory protection, safety harness, life line, and back-up personnel;
- See OSHA standard 29 CFR 1910.164.

Self-contained breathing apparatuses should be located on site near the chlorine storage and use areas readily accessible to the trained responders. Documented, regularly scheduled training is required to assure competency with self-contained breathing apparatuses. If arrangements have been made to use an approved outside emergency response group, then emergency responders and the self-contained breathing apparatuses may be located off-site.

Fit testing and regular maintenance programs for respirator equipment are necessary.

### 5.2.3 Other Personal Protective Equipment

Specialized personal protective equipment is not required for performing many routine plant operations. However, plant practice may dictate the need for eye and head protection as well as long pants, shirts, and safety shoes.

### 5.3 Confined Space Entry

Confined space entry procedures must comply with all applicable local codes and regulations. The OSHA standard 29 CFR 1910.146 must be adhered to by most facilities in the United States.

Some key points to be considered:

- Workers entering the confined space must be equipped with suitable respiratory and other protective equipment;
- Workers must be equipped with a safety harness and life line;
- A person must oversee the operation from outside the confined space at all times;
- Neither the overseer nor any other person should enter the confined space to rescue a victim without appropriate respiratory protection, safety harness, life line, and backup personnel.

### 5.4 Personal Exposure Monitoring

The characteristic odor of chlorine makes its presence known at concentrations well below the permissible exposure level (PEL). Because the odor of chlorine in itself is an inadequate indicator of concentration, it is essential that some quantitative measure of exposure be determined. This is necessary to insure that the health of workers is not impaired and to determine compliance with any applicable regulations.

The OSHA PEL is 1 ppm, expressed as a “ceiling” exposure level. The American Conference of Governmental Industrial Hygienists (ACGIH) has set the following threshold limit values (TLVs): TLV-TWA (8 hours) at 0.5 ppm and the TLV-STEL (15 minutes) at 1.0 ppm.

# 6 MEDICAL ASPECTS AND FIRST AID

## 6.1 Hazards to Health

### 6.1.1 General

Chlorine gas is primarily a respiratory irritant. It is so intensely irritating that low concentrations in air (well below 1 ppm) are readily detectable by most people. At low concentrations chlorine gas has an odor similar to household bleach. As the concentrations increase from the level of detection by smell so does symptomatology in the exposed individual. At chlorine concentrations above 5 ppm the gas is very irritating and it is unlikely that any person would remain in such an exposure for more than a very brief time unless the person is trapped or unconscious. The effects of exposure to chlorine may become more severe for up to 36 hours after the incident. Close observation of exposed individuals should be a part of the medical response program. See Pamphlets 63 and 90 and the video "Health Effects from Short-Term Chlorine Exposure."

### 6.1.2 Acute Toxicity

In concentrations near the threshold of smell, chlorine gas will, after several hours of exposure, cause mild irritation of the eyes and of the mucous membrane of the respiratory tract. As concentrations increase there is an increase in the irritating effect on the eyes, coughing mechanism and on the upper and lower respiratory tract with eventual difficulty in breathing. As the duration of exposure and/or the concentration increase, the affected individual may become apprehensive and restless with coughing accompanied by throat irritation, sneezing, and excess salivation. At higher levels there is vomiting associated with labored breathing. In extreme cases difficulty in breathing can progress to the point of death through suffocation. An exposed person with pre-existing medical/cardiovascular condition can have an exaggerated response.

Liquid chlorine in contact with the eyes or skin will cause local irritation and/or burns. All symptoms and signs result directly or indirectly

from its direct irritating action. There are no known systemic effects.

### 6.1.3 Chronic Toxicity

Most studies indicate no significant connection between adverse health effects and chronic exposure to low concentrations of chlorine. A 1983 Finish study (Reference 10.18.14) did show an increase in chronic coughs and a tendency for hypersecretion of mucous among workers. However, these workers showed no abnormal pulmonary function in tests or chest x-rays.

In December 1993, the Chemical Industry Institute of Toxicology issued its report on a study on the chronic inhalation of chlorine in rats and mice (Reference 10.17.1). Rats and mice were exposed to chlorine gas at 0.4, 1.0 or 2.5 ppm for up to 6 hours a day and 3-5 days/week for up to 2 years. There was no evidence of cancer. Exposure to chlorine at all levels produced nasal lesions. Because rodents are obligatory nasal breathers, how these results should be interpreted for humans is not clear.

## 6.2 Preventive Health Measures

### 6.2.1 Physical Examinations

The Institute recommends that chlor-alkali producers provide baseline and periodic medical examinations for employees potentially exposed to chlorine. The examination should consist of a complete medical history and physical examination, including chest x-ray (14 inch x 17 inch) and baseline respiratory function studies (FVC, FEV1). Specific reference to respiratory allergies, congenital or acquired pulmonary and/or cardiac disease is necessary. Chronic eye conditions (i.e. chronic conjunctivitis) should be ascertained. It should be determined that the employee is physically capable of wearing respiratory protection equipment. See Pamphlet 126.

Chlorine users should adopt a medical surveillance program suitable to their needs.

## 6.3 First Aid

First aid is the immediate temporary treatment given to an exposed individual before the services or recommendations of a physician are obtained. Prompt action is essential. Firmness and assurance will help to alleviate anxiety. Medical assistance must be obtained as soon as possible. Never give anything by mouth to an unconscious or convulsing person.

### 6.3.1 Inhalation

#### 6.3.1.1 Respiratory Assistance

In all cases, first move the victim to an area free of chlorine. If breathing has apparently ceased, the victim should be given cardiopulmonary resuscitation (CPR) immediately. If breathing has not ceased, the exposed individual should be placed in a comfortable position. In severe cases, the patient should lie down with the head and trunk elevated to a 45-60 degree position. Slow, deep breathing should be encouraged. Trained personnel should administer humidified oxygen by inhalation as soon as possible.

#### 6.3.1.2 Oxygen Administration

Oxygen should be administered by first aid attendants trained in the use of the specific oxygen equipment. Suitable equipment for the administration of oxygen should be available either on site or at a nearby facility. Such equipment should be periodically tested. More sophisticated inhalation equipment is available in most emergency facilities. Humidified oxygen should be used whenever possible.

### 6.3.2 Contact With Skin

If liquid chlorine has contaminated the skin or clothing, an emergency shower should be used immediately and contaminated clothing should be removed under the shower. Flush contaminated skin with copious amounts of running water for 15 minutes or longer. Thermal burns, due to the cold temperature of liquid chlorine, may be more damaging than any chemical reaction of chlorine and the skin. Exposure to gaseous chlorine can irritate the

skin. Do not attempt chemical neutralization or apply any salves or ointments to damaged skin. Refer to a physician if irritation persists after irrigation or if skin is broken or blistered.

### 6.3.3 Contact With The Eyes

If the eyes have been exposed to any concentration of chlorine in excess of the PEL, they should be flushed immediately with copious quantities of tepid running water or a direct stream of water for at least 15 minutes.

**Note: Never attempt to neutralize with chemicals.**

The eyelids should be held apart during this period to ensure contact of water with all accessible tissue of the eyes and lids. Medical assistance must be obtained as soon as possible. If such assistance is not immediately available, eye irrigation should be continued for a second 15-minute period. Nothing but water should be applied unless ordered by a qualified health care provider.

## 6.4 Medical Management of Chlorine Exposures

### 6.4.1 General Principles

- All individuals who have developed symptoms as a result of an acute overexposure to chlorine gas by inhalation should be placed under the supervision of medical personnel trained in the treatment of chlorine exposure.
- There is no known specific antidote for acute chlorine exposure. However, prompt medical assessment and supportive measures are necessary to obtain good therapeutic results.
- If individual is unconscious and vomiting, take steps necessary to protect the airway from obstruction.
- Alleviate anxiety by communicating with the patient the various procedures undertaken and elicit his/her cooperation, especially in breathing exercises.
- Position patient in chair; in severe cases have the patient lie down with the head and trunk elevated to a 45-60 degree position.
- Encourage slow, regular respiration.
- Humidify air.

## 6.4.2 Therapy for Specific Physiological Disturbances

**Note: The following notes regarding therapy are intended for general guidance only. Final determination of specific medical intervention(s) should only be made by skilled medical personnel upon full consideration of each patient's overall medical condition. Provision of any treatment without full medical assessment by competent personnel is not recommended.**

### 6.4.2.1 Pulmonary Edema

- Administer 60 to 100% humidified oxygen at 6 liters per minute.
- Intermittent use of positive pressure breathing apparatus may be valuable in reducing edema. Caution is required if there are coexisting medical conditions (e.g., peripheral circulatory collapse) which may be a contra-indication to its use.
  - Test arterial blood gases for pulmonary status.
  - Chest X-rays: Baseline and follow-up are indicated (pulmonary edema may not be evident for up to 36 hours after exposure).
    - Cardiac monitoring should be employed.
    - A diuretic furosemide (lasix) may be used.
- There is inconclusive evidence regarding the use of corticosteroids to prevent or alleviate pulmonary edema. The dosage and frequency of administration of any steroid therapy should only be determined by a qualified physician in keeping with clinical findings of a medical assessment.
  - The use of antibiotics may be considered to protect against secondary pulmonary infection.

### 6.4.2.2 Bronchospasm

Systemic bronchodilators administered either by subcutaneous injection, intravenously or nebulized into the inspiratory air may be beneficial if patient is conscious and when spasm is present.

### 6.4.2.3 Increased Mucus Secretion

Positive pressure treatment and nebulized detergents may be beneficial. Care should be taken to maintain the patient's hydration and to humidify the inspired air.

### 6.4.2.4 Excitement Phenomenon

- This occurs as a result of central stimulation and emotional disturbances.
- Reassurance is best accomplished without the use of sedatives.
- Use of sedatives should only be considered by qualified medical personnel following medical assessment and only employed under close supervision of respiratory function to monitor progress.

## 6.4.3 Delayed Effects

The inhalation of any irritating gas may lead to delayed reactions such as pulmonary edema. Since physical exercise appears to have some relation with the incidence of delayed reaction, it is recommended that any patient who has had severe inhalation exposure should be kept at rest for a period of observation. The length of observation will depend on the clinical assessment of the exposed individual. Observation may be required up to several days after exposure. Excitement, apprehension and/or emotional distress may persist after a period of observation following a severe exposure.

# 7 ENGINEERING DESIGN AND MAINTENANCE

## 7.1 Structures

Buildings and structures to house chlorine equipment or containers should conform with local building and fire codes, and with this document. Any building used to house chlorine equipment or containers should be designed and constructed to protect all elements of the chlorine system from fire hazards. If flammable materials are stored or used in the same building, then a fire wall should be erected to separate the two areas. Non-combustible construction is recommended.

Chlorine monitoring equipment which continuously samples the air and detects the presence of chlorine is available and should be considered in any storage or operating area where chlorine can be released. See Pamphlet 73.

At least two exits should be provided from each separate room or building in which chlorine is stored, handled or used. Exit doors should not be locked and should open outward. Platforms should be designed to facilitate egress and two or more access stairways or ladders should be considered. Steel structures should be protected to prevent corrosion.

## 7.2 Ventilation

### 7.2.1 General

All ventilation systems for buildings that house equipment or containers should conform with applicable building code requirements, American Conference of Governmental Industrial Hygienists (ACGIH) recommendations (Reference 10.4.2) and with this manual. The building ventilation system should provide fresh air for normal operation and should take into consideration the possibility of a leak. In some cases natural ventilation may be adequate; otherwise, mechanical ventilation systems should be provided.

Previously, the Institute has recommended that the building ventilation allow for a complete

change of air with fresh air in less than four minutes. The Institute now believes such a recommendation may not be compatible with current design philosophies as follows:

Section 8003.1.8.2 of the 1994 *Uniform Fire Code* (see Section 8.6) requires mechanical ventilation at the rate of not less than one (1) ft<sup>3</sup>/minute per square foot for floor area for storage buildings.

*Industrial Ventilation* (10.4.2) cautions in Section 7.7 that "Air changes per hour is a poor basis for ventilation criteria where environmental control of hazards, heat, and/or odors is required ... there is little relationship between 'air changes' and the required contaminant control."

The Institute now recommends that ventilation requirements be determined on a site-specific basis. Safeguards should be in place to insure that persons do not remain in nor enter buildings where chlorine is present due to a leak or equipment failure without the appropriate personal protective equipment.

### 7.2.2 Air Openings

Chlorine gas is heavier than air and has a tendency to collect at floor level. The exhaust air intake should be located at or near floor level. An elevated fresh air inlet must be provided and should be located for adequate cross ventilation. Multiple fresh air inlets and fans may be necessary to facilitate adequate ventilation. Fans, if used, should be made to start and stop from a safe, remote location.

Alternatively, it maybe desirable to pressurize an installation with fresh air and to exhaust the contaminated air through outlets at floor level.

### 7.2.3 Heating

Rooms containing chlorinator feed equip-

ment should be maintained at a normal indoor temperature of about 60 - 70°F (about 15 - 20°C) to facilitate gas discharge rates from the container.

### **7.3 Material for Processing Equipment**

#### **7.3.1 General**

Commercial liquid chlorine contains only minor amounts of impurities and is dry enough to be handled in carbon steel equipment. In the manufacturing process, certain properties unique to chlorine should be considered when considering the materials of construction.

#### **7.3.2 Water**

Wet chlorine may be safely handled with a variety of materials which can be chosen to suit the process conditions. Some materials, such as titanium, are suitable for wet chlorine but not for dry chlorine. Titanium reacts violently with dry chlorine. Reference 10.18.13 indicates that titanium is a safe material in wet gaseous chlorine provided the partial pressure of water component is greater than 14 mbar (0.20 psi) and the temperature is between 15°C (59°F) and 70°C (158°F).

#### **7.3.3 Temperature**

Carbon steel used in the handling of dry chlorine must be kept within definite temperature limits. Where process temperatures are expected to exceed 300°F (149°C), the material used should be more resistant than carbon steel to high temperature corrosion by chlorine. Above 392°F (200°C) chlorine rapidly attacks steel. Above 483°F (251°C) the reaction is immediate as carbon steel flames in the presence of chlorine. Impurities in the chlorine and/or a high surface area of the steel may significantly lower the auto-ignition temperature of chlorine and steel.

There is also a possibility of brittle fracturing in certain chlorine processing equipment and storage tanks. Where this is the case, a type of steel should be used that can withstand the lowest temperatures possible in the process.

#### **7.3.4 Chemicals**

Several chemicals are normally involved in the manufacture of chlorine, including sulfuric acid, mercury, certain salts, oxygen and various products of their reaction with chlorine. Materials of construction should be selected to guard against these corrosive or hazardous materials that are present in the manufacturing process.

#### **7.3.5 Alternative Materials**

Other than steel, a wide variety of materials may be used in chlorine handling. A number of them, particularly plastics, are suitable but have pressure and temperature limitations that must be considered. Care must be taken to prevent external mechanical damage.

### **7.4 Electrolyzers (Cells)**

#### **7.4.1 General**

Chlorine can be produced electrolytically by either membrane electrolyzers, diaphragm cells, or mercury cells. Reference 10.18.7 provides a detailed discussion of the electrolytic methods of chlorine manufacture.

#### **7.4.2 Membrane Electrolyzers**

The membrane electrolyzer is the newest technology for producing chlorine electrolytically. Sheets of perfluorinated polymer ion exchange membrane separate the anodes and cathodes within the electrolyzer. Ultra-pure sodium chloride solution (brine) is fed to the anode compartments, where chloride ions are oxidized to form chlorine gas. The membranes are cation selective resulting in predominantly sodium ions and water migrating across the membranes to the cathode compartments. Water is reduced to form hydrogen gas and hydroxide ions at the cathodes. In the cathode compartment, hydroxide ions and sodium ions combine to form sodium hydroxide.

Membrane electrolyzers typically produce 30% to 35% sodium hydroxide, containing less than 50 ppm of sodium chloride. The sodium hydroxide can be concentrated further, typically to 50%, in an evaporation system.

#### 7.4.3 Diaphragm Cells

Currently in North America, more than 75% of chlorine production is from diaphragm cell technology. The products of this type of cell are chlorine gas, hydrogen gas, and cell liquor composed of sodium hydroxide and sodium chloride solution.

An almost saturated brine solution enters the diaphragm cell anolyte compartment and flows through the diaphragm to the cathode section.

Chloride ions are oxidized at the anode to produce chlorine gas.

Hydrogen gas and hydroxide ions are produced at the cathode. Sodium ions migrate across the diaphragm from the anode compartment to the cathode side to produce cell liquor containing 10% to 12% sodium hydroxide. Chloride ions also migrate across the diaphragm resulting in the cell liquor also containing about 16% sodium chloride. The cell liquor is typically concentrated to 50% sodium hydroxide by an evaporation process. The salt recovered in the evaporation process is returned to the brine systems for reuse.

#### 7.4.4 Mercury Cells

In a mercury cell, the cathode is a stream of mercury flowing along the bottom of the electrolyzer. The anodes are suspended parallel to the base of the cell, a few millimeters above the flowing mercury. Brine is fed into one end of the cell box and flows by gravity between the anodes and the cathode. Chlorine gas is evolved and released at the anode.

The sodium ions are deposited along the surface of the flowing mercury cathode. The alkali metal dissolves in the mercury, forming a liquid amalgam. The amalgam flows, by gravity, from the electrolyzer to the carbon-filled decomposer, where deionized water is added. The water chemically strips the alkali metal from

the mercury, producing hydrogen and 50% sodium hydroxide. (In the decomposer, the amalgam is the anode and the graphite packing is the cathode.) The stripped mercury is then pumped back to the cell box, where the electrolysis process is repeated.

### 7.5 Chlorinators

Chlorine gas feeding equipment must be carefully selected. Vacuum operated equipment offers the safest operation for low capacities. For higher capacities a pressure-vacuum system may be required. Pressure piping and connections should be minimized to decrease the possibility of a leak. Equipment manufacturers can recommend optimum system design.

### 7.6 Vaporizers

High capacity chlorine gas feed systems may need a chlorine vaporizer (evaporator). Vaporizers are usually water-jacketed or steam-heated. Careful attention must be given to the design and operation of such systems. See Pamphlet 9.

### 7.7 Support Equipment

#### 7.7.1 General

Some key support equipment used in chlorine service are included in this section. Equipment used in chlorine must be designed either for dry chlorine or for wet chlorine so that proper materials of construction are selected. Most equipment used in chlorine service is built to a specific design code or regulation. Such codes or regulations include ANSI, API, ASME and TEMA standards and OSHA regulations.

#### 7.7.2 Vessels

Materials of construction for vessels used in wet chlorine applications include certain plastic-lined or rubber-lined steel, reinforced polyesters,

and titanium. Vessels used in dry chlorine service are usually carbon steel.

The minimum fabrication standard for metal vessels operating at greater than 15 psig is that given in the ASME Code (Reference 10.5.1) for pressure vessels. Vessels operating at less than 15 psig have no ASME code requirements, but should be designed according to a manufacturer's specification. Vessels in vacuum service require special designs to prevent collapse.

### 7.7.3 Heat Exchangers

Metallic shell-and-tube heat exchangers should be designed and fabricated in accordance with the TEMA Standard and proper ASME material classifications and codes. Titanium is usually the choice for "wet chlorine", and carbon steel is normally used for "dry chlorine." See Section 7.3.2.

### 7.7.4 Pumps

Pumps for aqueous solutions containing chlorine are constructed of a wide range of materials such as certain plastic-lined or rubber-lined steel, reinforced polyester, and titanium. Pumps for dry liquid chlorine are special items and a supplier of these pumps should be contacted before use.

### 7.7.5 Compressors

Compressors used in dry chlorine service include centrifugal, non-lubricated reciprocating, and liquid-ring sealed (sulfuric acid). Compressors should be built in accordance with the applicable ASME Code and supplier specifications proper for the application. Aluminum, copper, and copper alloys must be avoided.

Fans are sometimes used to boost pressure or move chlorine gas in vent or scrubber systems. In wet chlorine service, rubber-lined, fiberglass reinforced polyester or titanium are normally used. In dry chlorine service, carbon

steel is normally used.

### 7.7.6 Scrubbers

While scrubbers are an effective means of absorbing chlorine, the need for a scrubber should be based on a site specific hazard assessment that considers factors such as the quantity of chlorine on site, the likelihood of a release, and the consequences of a release. See Pamphlet 89.

## 7.8 Piping Systems for Dry Chlorine

Piping as described in this section pertains only to above ground fixed piping. For more detailed information on piping systems for dry chlorine, see Pamphlet 6.

### 7.8.1 Materials

In general, carbon steel piping is recommended for handling dry chlorine. Stainless steels of the 300 series have useful properties for low temperature service but can fail due to chloride stress corrosion cracking, particularly in the presence of moisture at ambient or elevated temperatures.

### 7.8.2 Design and Installation

#### 7.8.2.1 General Design

Piping arrangements should be routed for the shortest distance practical with respect to flexibility, line expansion and good engineering practice. Piping systems should be properly supported, adequately sloped to allow drainage, and low spots should be minimized.

Avoid installing lines next to steam lines, acid lines, etc. that could cause corrosion of the chlorine line. Protect chlorine piping from all risks of excessive heat or fire.

Sprinklers are not needed for chlorine storage or use areas that have been constructed and

maintained per Institute recommendations. In such situations, no combustible or flammable materials should be present. If sprinklers are installed, they should be used only to suppress fires and/or cool containers threatened by fire.

#### 7.8.2.2 Liquid Expansion

Liquid chlorine has a high coefficient of thermal expansion. See Figure 9.2. If liquid chlorine is trapped between two valves, an increase in temperature of the trapped liquid will result in high pressures potentially leading to a rupture of the line. The causes of possible rupture must be considered in the design of any piping systems. Protection may be either a suitably designed, operated and maintained expansion chamber, a pressure relief valve, or a rupture disc.

#### 7.8.2.3 Condensation

Condensation or reliquefaction of chlorine may occur in chlorine gas lines which pass through areas where the temperature is below the temperature-pressure equilibrium indicated in the vapor pressure curve (Fig. 9.1).

Condensation can usually be prevented by the use of a pressure reducing valve or heat tracing and insulating the line. Any heat tracing installation should be designed such that the surface temperature of the pipe shall not exceed 300°F (149°C) to limit the possibility of a chlorine - carbon steel reaction.

#### 7.8.2.4 Installation

Joints in chlorine piping may be flanged, screwed or welded depending on pipe size. Flanged and screwed joints should be kept to a minimum. If screwed joints are used, extreme care should be taken to obtain clean, sharp threads. A thread sealant compatible with chlorine should be used.

Before cutting or welding on a chlorine line, a determination must be made that the system is chlorine free. Dry chlorine can support combustion of carbon steel, nickel and other

materials.

### 7.8.3 Preparation of Systems for Use

#### 7.8.3.1 Cleaning

All portions of new piping systems must be cleaned before use because chlorine can react violently with cutting oil, grease, and other foreign materials. Cleaning must not be done with hydrocarbons or alcohols, since chlorine may react violently with many solvents. New valves or other equipment received in an oily condition should be dismantled and cleaned before use. See Pamphlet 6.

#### 7.8.3.2 Pressure Testing

New chlorine piping systems should be tested according to one of the methods recommended in Pamphlet 6. Components which may be damaged during testing should be removed or blocked off. After testing, all moisture-absorbing gaskets and valve packings should be replaced; it is essential that chlorine systems be dried as described below prior to being placed into service.

#### 7.8.3.3 Drying

Chlorine piping systems must always be dried prior to use. Even if water has not been purposely introduced into the system from hydrostatic testing or cleaning, drying is still required due to the introduction of moisture from the atmosphere or other sources during maintenance and new construction.

Drying can be facilitated as the system is cleaned by passing steam through the lines from the high end until the lines are heated. While steaming, the condensate and foreign matter is drained out. The steam supply then should be disconnected and all the pockets and low spots in the line drained. While the line is still warm, dry air or inert gas (e.g., nitrogen) having a dew point of -40°F (-40°C) or below should be blown

through the line until the discharge gas is also at a dew point of  $-40^{\circ}\text{F}$  ( $-40^{\circ}\text{C}$ ) or below.

If steam or dry utility system air are not available, particular care must be taken in cleaning sections of pipe and other equipment before assembly, and careful inspection is necessary as construction proceeds. The final assembled system should be purged with dry cylinder air or nitrogen until the discharge gas is at a dew point of  $-40^{\circ}\text{F}$  ( $-40^{\circ}\text{C}$ ) or below.

#### 7.8.3.4 Leak Testing

After drying, the system should be leak-tested with dry air or nitrogen. A soap solution should be utilized to test for leaks at piping joints. Chlorine gas may then be introduced gradually and the system further tested for leaks with  $20^{\circ}$  Baume aqua ammonia vapor. Care must be taken that chlorine has diffused throughout the piping systems before testing for leaks. Never attempt to repair leaks by welding until all chlorine has been purged from the system. When leaks have been repaired, the line should be retested.

### 7.9 Piping Systems for Wet Chlorine

Wet chlorine is very corrosive to all of the more common construction metals. At low pressures wet chlorine can be handled in chemical stoneware, glass or porcelain equipment and in certain alloys. Hard rubber, unplasticized polyvinyl chloride, fiberglass reinforced polyester, polyvinylidene chloride or fluoride and fully halogenated fluorocarbon resins have been used successfully. All of these materials must be selected with care. For higher pressures, lined metallic or compatible metallic systems should be used.

In the metallic systems, Hastelloy<sup>®</sup> C, titanium and tantalum have been used. Within limits, titanium may be used with wet chlorine but must not be used with dry chlorine under any circumstances, as it burns spontaneously on contact. Tantalum is inert to wet and dry chlorine at temperatures up to  $300^{\circ}\text{F}$  ( $149^{\circ}\text{C}$ ).

### 7.10 Stationary Storage

Consumers receiving chlorine in barges, tank cars or trucks may require stationary storage facilities. The facilities should be properly designed and should be operated and periodically inspected in accordance with Institute recommendations. See Pamphlets 5 and 78.

A tank should not be filled beyond its rated chlorine capacity because liquid chlorine will expand as it warms. At normal storage temperatures, the thermal-expansion rate of liquid chlorine is high and, if room for expansion is not provided, could increase the hydrostatic pressure enough to rupture the tank. The maximum chlorine level should be determined by the filling density as discussed in Section 1.5.12.

### 7.11 Equipment Maintenance

#### 7.11.1 General

Maintenance of chlorine equipment and tanks should be under the direction of trained personnel. All precautions pertaining to safety education, protective equipment, health and fire hazards should be reviewed and understood. Workers should not attempt to repair chlorine piping or other equipment while it is in service. When a chlorine system is to be cleaned or repaired, tanks, piping and other equipment should always be purged with dry air or non-reactive gas.

Decontamination is especially important where cutting or welding operations are undertaken because iron and steel will ignite in chlorine near  $483^{\circ}\text{F}$  ( $251^{\circ}\text{C}$ ). Immediate drying of a chlorine pipe or container into which water has been introduced or which has been opened for repairs or cleaning is essential to prevent corrosion.

### 7.11.2 Cleaning of Piping and Other Equipment

If moisture enters a chlorine system containing metallic components, such as when connections are being made or broken at a chlorine container or while maintenance is being performed, ferric chloride, already present in small amounts, will absorb moisture and change to a corrosive, brown, viscous liquid. If not removed, this viscous liquid will continue to corrode the metal and can rapidly plug chlorine lines and equipment such as vaporizers. This hydrated ferric chloride is corrosive to many metals including Hastelloy<sup>®</sup> C.

Steam or hot water rapidly dissolves ferric chloride. However, lines or equipment cleaned in this manner must be dried carefully before they are put back in service. Steam should not be used on plastic equipment unless it is known that the specific plastic material can stand the temperature. Any in-line instrumentation should be protected during the cleaning process. Cleaning of piping and various other equipment is addressed in Pamphlet 6.

### 7.11.3 Entering Tanks

Chlorine tank inspection, cleaning and repair, are discussed in Pamphlet 5. All piping to the tank should be disconnected and blanked before entering. See Section 5.3.

## 7.12 Chlorine Neutralization

If a chlorine consuming process involves the discharge of a waste containing chlorine, special processes may be required. All governmental regulations regarding health and safety or the pollution of natural resources must be followed.

A system should be provided to neutralize any chlorine vented for maintenance preparation or process upset, such as a sudden failure of the chlorine compressor, trouble during the start-up of a circuit, or a breakdown of the tail gas handling system.

The neutralization is usually accomplished by causing the chlorine to react with sodium hydroxide solution or, in certain situations, with another alkaline compound. Neutralization can take place in an appropriately designed tank or in a scrubber. The sodium hydroxide concentration should be less than 20% to prevent precipitation of sodium chloride crystals (salting-out) and excessive heat of reaction. See Pamphlet 89.

# 8

# KEY REGULATIONS AND CODES

**Note: The purpose of this section is to provide a list of some of the key OSHA, EPA, and DOT regulations that significantly affect the production, storage, packaging, distribution, or use of chlorine in the United States.**

**Additionally, information is provided on some of the Fire Codes that similarly affect chlorine. This section is not meant to cover all such regulations affecting chlorine.**

## **8.1 Occupational Safety and Health Regulations -29 CFR**

### 8.1.1 Part 1904 - Recordkeeping

Requirements for recordkeeping.

### 8.1.2 Section 1910.20 - Access to Exposure and Medical Records

Requirements for employee access to exposure and medical records.

### 8.1.3 Section 1910.38 – Employee Emergency Plans and Fire Protection Plans

Requirements for emergency action plans when such plans are required by a specific OSHA regulation.

### 8.1.4 Section 1910.95 - Occupational Noise Exposure

Requirements for protection against high noise levels.

### 8.1.5 Section 1910.119 - Process Safety Management of Highly Hazardous Chemicals

Required management practices for preventing or minimizing the consequences of catastrophic release of toxic, reactive, flammable, or explosive chemicals.

### 8.1.6 Section 1910.120 - Hazardous Waste Operations and Emergency Response

Requirements for responding to a chemical emergency.

### 8.1.7 Sections 1910.132 to .139 - Personal Protective Equipment

Requirements for personal protective equipment for personnel potentially exposed to chemical or other hazards.

### 8.1.8 Section 1910.134 - Respiratory Equipment

Requirements for respiratory use for personnel potentially exposed to chemical hazards.

### 8.1.9 Section 1910.146 - Confined Space Entry

Requirements for entry into permit required confined spaces.

### 8.1.10 Section 1910.147 - Control of Hazardous Energy (Lockout/Tagout)

Requirements for locking out electrical equipment.

### 8.1.11 Section 1910.151 - First Aid/Medical Service

Requirements for first aid/medical service providers.

### 8.1.12 Sections 1910.331 to 335 – Electrical Safety

Requirements for cell house electrical safety.

### 8.1.13 Section 1910.1000 - Air Contaminants

Exposure limits to chemicals.

- 8.1.14 Section 1910.1200 - Hazard Communications  
Requirements for transmitting information about hazardous chemicals to employees.
- 8.2 Navigation and Navigable Water Regulations -33 CFR**
- 8.2.1 Parts 1 to 26, Subchapter A - General delegation of authority, rulemaking procedures and enforcement regulations.
- 8.2.2 Part 126 - Handling Explosives or Other Dangerous Cargoes Within or Contiguous to Waterfront Facilities  
Requirements for waterfront facilities that handle hazardous materials.
- 8.2.3 Part 127 - Waterfront Facilities Handling Liquefied Hazardous Gas  
Requirements in addition to those in Part 126 for waterfront facilities that handle liquefied hazardous gases including chlorine.
- 8.2.4 Part 130 - Financial Responsibility for Water Pollution  
Requirements for vessel operators to demonstrate the ability to meet financial liability resulting from the discharge of oil or hazardous substance(s).
- 8.2.5 Part 153 -Control of Pollution by Oil and Hazardous Substances;  
Discharge Removal  
Requirements concerning notification of the Coast Guard of the discharge of oil or hazardous substances.
- 8.2.6 Part 154 - Facilities Transferring Oil or Hazardous Materials in Bulk  
Requirements intended to prevent and mitigate pollution and assure safe operations at facilities during marine transfers.
- 8.2.7 Part 155 - Oil or Hazardous Material Pollution Prevention Regulations for Vessels  
Requirements to prevent and mitigate pollution from vessels while in navigable waters.
- 8.2.8 Part 156-Oil and Hazardous Material Transfer Operations  
Requirements for the operational control of the transfer of oil or hazardous materials between vessels and marine terminals.
- 8.2.9 Parts 160 to 167, Subchapter P - Ports and Waterways Safety  
Requirements for traffic management, port arrival notification, vessel navigational equipment
- 8.3 Environmental Regulations - 40 CFR**
- 8.3.1 Part 61 - National Emissions Standards for Hazardous Air Pollutants  
Emission standards for chlorine manufacturing facilities.
- 8.3.2 Part 68 - Clean Air Act/Accidental Releases  
Requirements to prevent or mitigate the consequences of hazardous materials with off-site effects.
- 8.3.3 Part 82 - Protection of Stratospheric Ozone  
Requirements for the use of ozone depleting substances and labeling of products using such substances.

- 8.3.4 Part 141 - Safe Drinking Water  
Requirements for limiting contaminants in drinking water.
- 8.3.5 Part 152-Pesticide Registration  
Requirements for the registration of materials used as pesticides.
- 8.3.6 Parts 260 to 269 - Hazardous Waste Management System  
Requirements for the classification, handling, treatment, and disposal of hazardous wastes.
- 8.3.7 Parts 302 and 355 - Release of Hazardous Substances, Emergency Planning and Notification  
Requirements for the planning, reporting, and notification of hazardous and highly hazardous substances.
- 8.3.8 Parts 370 and 372-Hazardous Chemicals Reporting: Community Right to Know  
Requirements for providing the public with information on hazardous chemicals.
- 8.3.9 Part 415, Subpart F - Effluent Guidelines/Chlor-Alkali Production  
Effluent guidelines for chlorine production facilities.
- 8.3.10 Subchapter R, Parts 700 to 799 -Toxic Substances Control Act  
Requirements for recordkeeping and reporting for various chemical substances.

**8.4 Shipping Regulations - 46 CFR (Water Transportation)**

- 8.4.1 Part 2 - Vessel Inspections  
Requirements and procedures for obtaining vessel certification and approvals.
- 8.4.2 Parts 10 to 12-Licensing and Certification of Maritime Personnel  
Requirements for licensing and certification of maritime personnel including eligibility, fees, procedures for renewals, and the certification of tankermen. Provides authorization for an individual to act as the person in charge on the vessel of a marine transfer of an oil or hazardous material.
- 8.4.3 Part 15 - Manning Requirements  
Requirements for the minimum manning of vessels.
- 8.4.4 Parts 30 to 40, Subchapter D - Tank Vessels  
Requirements for vessels carrying flammable or combustible liquid cargoes. Subchapter regulates vessel design, operation, fire fighting and life saving equipment and equipment testing. Generally, vessels carrying nonflammable hazardous materials are also regulated under this subchapter.
- 8.4.5 Part 151 - Barges Carrying Bulk Liquid Hazardous Materials Cargoes  
Requirements for vessels carrying hazardous materials in barges. Regulations include barge design, saving equipment, equipment testing and special requirements for specific hazardous cargoes including chlorine.

## 8.5 Transportation Regulations - 49 CFR

### 8.5.1 Part 106 - Rulemaking Procedures

General rulemaking procedures for issuing, amending, and repealing regulations.

### 8.5.2 Part 107 - Hazardous Materials Program Procedures

Requirements for exemptions, preemptions, enforcement, compliance orders, civil and criminal penalties, registration of cargo tank manufacturers and repairers, registration and fees.

### 8.5.3 Part 171 - General Information, Regulations, Definitions

Use and applicability of transportation regulations within and outside the U.S. and reporting requirements for hazardous material incidents.

### 8.5.4 Part 172 - Hazardous Materials Table, Special Provisions, Hazardous Materials Communications, Emergency Response Information, and Training Requirements

Requirements for shipping papers, marking, labeling and placarding and the training of hazmat employees.

### 8.5.5 Part 173 - Shippers - General Requirements for Shipments and Packagings

Definitions of hazardous materials for transportation purposes. Requirements for preparing hazardous materials shipments, for container inspections, testing and retesting.

### 8.5.6 Part 174 - Carriage by Rail

Requirements for handling, loading, unloading and storage of tank cars.

### 8.5.7 Part 176 - Carriage by Vessel

Requirements for packaged hazardous materials transported by vessel.

### 8.5.8 Part 177 - Carriage by Public Highway

Requirements on the handling, transportation, loading and unloading and segregation of hazardous materials.

### 8.5.9 Part 178 - Specifications for Packagings

Specifications for cylinders, portable tanks and cargo tanks.

### 8.5.10 Part 179 - Specifications for Tank Cars

Design requirements and specifications for bulk rail tank cars.

### 8.5.11 Part 180 - Continuing Qualifications and Maintenance of Packagings

Requirements for qualifying existing cargo tanks for hazardous materials.

### 8.5.12 Part 190 - Pipeline Safety Program Procedures

Enforcement regulations pursuant to the Natural Gas Pipeline Safety Act, the Hazardous Liquid Pipeline Safety Act and the Hazardous Materials Transportation Act as amended.

### 8.5.13 Part 191 - Transportation of Natural and Other Gas by Pipeline; Annual Reports, Incident Reports and Safety Related Condition Reports

Requirements for reporting incidents, safety related conditions, and pipeline data.

### 8.5.14 Part 192 - Transportation of Natural and other Gas by Pipeline: Minimum Federal Safety Standards

Requirements for pipeline facilities and the transportation of gases.

#### 8.5.15 Part 195 - Transportation of Hazardous Liquids by Pipeline

Safety standards and reporting requirements for pipeline facilities used in the transportation of hazardous liquids or carbon dioxide. While the regulations do not currently include chlorine, the Institute recommends adhering to these requirements.

### 8.6 Fire Codes

Numerous fire and building codes exist that affect chlorine production, storage, packaging, distribution and use. Code requirements may include, but are not limited to minimum separation distance between classes of chemicals, design of piping systems, secondary containment, need for treatment systems or gas detectors, emergency response requirements and the need for sprinklers.

To properly address these codes, the local government (e.g., city or county) should be contacted. Determine what specific fire and building codes, including the code year, were passed by the governing jurisdiction.

Some local or state authorities develop their own codes. However, many jurisdictions adopt a model code or reference National Fire Protection Association (NFPA) Standards. Either of these may serve as the local code(s).

The model codes are modified annually and yearly supplements are issued. Completely new editions of the codes are published every third year. Therefore, the code year is important in determining which code is applicable. The specific requirements are contained in the applicable code.

The NFPA Standards and the major model building and fire codes can be obtained from these organizations:

#### 1. NFPA Standards or Codes

National Fire Protection Association  
1 Batterymarch Park  
PO Box 9101  
Quincy, MA 02269-9101  
Phone (800) 344-3555

#### 2. The BOCA National Fire Prevention Code or the BOCA National Building Code

Building Officials & Code Administrators International, Inc.  
4051 W. Flossmoor Road  
Country Club Hills, IL 60478-5 795  
Phone (708) 799-2300

#### 3. Standard Fire Prevention Code or Standard Building Code

Southern Building Code Congress International, Inc.  
900 Montclair Road  
Birmingham, AL 35213-1206  
Phone (205) 591-1853

#### 4. Uniform Building Code

International Conference of Building Officials  
5360 Workman Mill Road  
Whittier, CA 90601-2298  
Phone (310) 699-0541

#### 5. Uniform Fire Code

International Fire Code Institute  
9300 Jollyville Road, Suite 105  
Austin, TX 78759-7455

# 9 TECHNICAL DATA

## 9.1 General

Chlorine has a characteristic penetrating and irritating odor. The gas is greenish yellow in color and the liquid is clear amber. The data on physical properties of chlorine as determined by different investigators show some variations. Values for physical properties below are taken from Pamphlet 72.

## 9.2 Atomic and Molecular Properties

Atomic Symbol - Cl  
Atomic Weight - 35.453  
Atomic Number - 17  
Molecular Weight - 70.906

Elemental chlorine exists in the form of two naturally occurring isotopes with mass numbers of 35 and 37. Ordinary molecular chlorine consists of a mixture of about 76% chlorine 35 and 24% chlorine 37. There are also at least 13 artificially produced isotopes of chlorine.

## 9.3 Chemical Properties

### 9.3.1 Flammability

Chlorine, gas or liquid, is non-explosive and non-flammable; however, like oxygen, it is an oxidizer and is capable of supporting combustion of certain substances. Many organic chemicals react readily with chlorine, sometimes violently.

### 9.3.2 Valence

Chlorine usually forms compounds with a valence of -1 but it can combine with a valence of +1, +2, +3, +4, +5 or +7.

### 9.3.3 Chemical Reactions

#### 9.3.3.1 Reactions With Water

Chlorine is only slightly soluble in water.

When it reacts with pure water, a weak solution of hydrochloric and hypochlorous acids is formed. Chlorine hydrate ( $\text{Cl}_2 \cdot 8\text{H}_2\text{O}$ ) may crystallize below 49.3°F (9.6°C) at atmospheric pressure and higher temperatures at increased pressures.

#### 9.3.3.2 Reactions With Metals

The reaction rate of dry chlorine with most metals increases rapidly above a temperature which is characteristic for the metal. Below 250°F (121°C) iron, copper, steel, lead, nickel, platinum, silver and tantalum are resistant to dry chlorine, gas or liquid. At ordinary temperatures dry chlorine, gas or liquid, reacts with aluminum, arsenic, gold, mercury, selenium, tellurium, and tin. Dry chlorine reacts violently with titanium. At certain temperatures, sodium and potassium burn in chlorine gas. Carbon steel ignites near 483°F (251 °C) depending on its physical form. For piping recommendations, see Pamphlet 6. Moist chlorine, primarily because of the hydrochloric and hypochlorous acids formed through hydrolysis, is very corrosive to most common metals. Platinum, silver, tantalum and titanium are resistant.

#### 9.3.3.3 Reactions With Other Elements

Chlorine unites under specific conditions with most of the elements; these reactions may be extremely rapid. At its boiling point chlorine reacts with sulfur. It does not react directly with oxygen or nitrogen; the oxides and nitrogen compounds are well known but can only be prepared by indirect methods. Mixtures of hydrogen and chlorine can react violently. Ignition limits depend on temperature, pressure and concentration. Between 70° and 80°F (21° and 27°C) the ignition limits range from 3% to 93% by volume of hydrogen. Ignition can be initiated by direct sunlight, other source(s) of ultraviolet light, static electricity, or sharp impact.

### 9.3.3.4 Reactions With Inorganic Compounds

The preparation of soda and lime bleaches (sodium and calcium hypochlorite) are typical reactions of chlorine with the alkali and alkaline earth metal hydroxides; the hypochlorites formed are powerful oxidizing agents. Because of its great affinity for hydrogen, chlorine removes hydrogen from some compounds such as the reaction with hydrogen sulfide to form hydrochloric acid and sulfur. Chlorine, as the hypochlorous ion, reacts with ammonium ions to form various mixtures of chloramines. At low pH the predominant chloramine formed is explosive nitrogen trichloride ( $\text{NCl}_3$ ).

### 9.3.3.5 Reactions With Organic Compounds

Chlorine reacts with many organic compounds to form chlorinated derivatives. Hydrogen chloride is often formed as a by-product of the reaction. Some reactions can be extremely violent, especially those with hydrocarbons, alcohols and ethers. Proper methods must be followed, whether in laboratory or plant, when organic materials are reacted with chlorine.

## 9.4 Physical Properties

The following properties are for pure chlorine. "Standard conditions," where referenced, are  $32^\circ\text{F}$  ( $0^\circ\text{C}$ ) and an absolute pressure of 14.696 psi (101.325 kPa).

### 9.4.1 Boiling Point (Liquefying Point)

$-29.15^\circ\text{F}$  ( $-33.97^\circ\text{C}$ ) -The temperature at which liquid chlorine vaporizes under one atmosphere pressure (101.325 kPa).

### 9.4.2 Critical Properties

#### 9.4.2.1 Critical Density

$35.77 \text{ lb/ft}^3$  ( $573.0 \text{ kg/m}^3$ ) - The mass of a unit volume of chlorine at the critical pressure and temperature.

#### 9.4.2.2 Critical Pressure

1157.0 psia (7977 kPa) -The vapor pressure of liquid chloride at the critical temperature.

### 9.4.2.3 Critical Temperature

$290.75^\circ\text{F}$  ( $143.75^\circ\text{C}$ ) -The temperature above which chlorine exists only as a gas no matter how great the pressure.

### 9.4.2.4 Critical Volume

$0.02795 \text{ ft}^3/\text{lb}$  ( $0.001745 \text{ m}^3/\text{kg}$ ) -The volume of a unit mass of chlorine at the critical pressure and temperature.

### 9.43 Density

The mass of a unit volume of chlorine at specified conditions of temperature and pressure. See Figure 9.2.

#### 9.4.3.1 Gas at Standard Conditions

$0.2006 \text{ lb/ft}^3$  ( $3.213 \text{ kg/m}^3$ )

#### 9.4.3.2 Saturated Gas

At  $32^\circ\text{F}$  ( $0^\circ\text{C}$ )  $0.7632 \text{ lb/ft}^3$  ( $12.23 \text{ Kg/m}^3$ ). (Absolute pressure at  $32^\circ\text{F}$  ( $0^\circ\text{C}$ ) is 53.51 psi (368.9 kPa)).

#### 9.4.3.3 Saturated Liquid

$91.56 \text{ lb/ft}^3$  ( $1467 \text{ kg/m}^3$ ) at  $32^\circ\text{F}$  ( $0^\circ\text{C}$ );  $88.76 \text{ lb/ft}^3$  ( $11.87 \text{ lb/gal}$ ;  $1422 \text{ kg/m}^3$ ) at  $60^\circ\text{F}$  ( $15.6^\circ\text{C}$ ) - (Absolute pressure of liquid chlorine at  $60^\circ\text{F}$  is 86.58 psi (597.0 kPa)).

### 9.4.4 Freezing Point

See Melting Point, 9.4.7.

### 9.4.5 Latent Heat of Vaporization

123.9 Btu/lb (288.1 kJ/kg) at the normal boiling point - The heat required to evaporate a unit weight of chlorine.

### 9.4.6 Liquid-Gas Volume Relationship

At standard conditions the weight of one volume of liquid chlorine equals the weight of 456.5 volumes of chlorine gas.

### 9.4.7 Melting Point - Freezing Point

$-149.76^\circ\text{F}$  ( $-100.98^\circ\text{C}$ ) -The temperature at which solid chlorine melts or liquid chlorine solidifies at one atmosphere.

#### 9.4.8 Solubility in Water

The weight of chlorine which can be dissolved in a given amount of water at a given temperature when the total vapor pressure of chlorine and the water equals a designated value. See Fig. 9.3. At 60°F (15.6°C) and one atmosphere (101.325 kPa) it is 6.93 lbs/100 gals (8.30 kg/m<sup>3</sup>).

#### 9.4.9 Specific Gravity

##### 9.4.9.1 Gas

2.485 — The ratio of the density of chlorine gas at standard conditions to the density of air under the same conditions. (Density of air, free of moisture, at standard conditions is 1.2929 kg/m<sup>3</sup>.)

##### 9.4.9.2 Liquid

1.467 0/4°C — The ratio of the density of saturated liquid chlorine at 32°F (0°C) to the density of water at its maximum density (approximately 39°F (4°C)).

#### 9.4.10 Specific Heat

The heat required to raise the temperature of a unit weight of chlorine one degree.

##### 9.4.10.1 Saturated Gas

*At Constant Pressure (Cp)*

0.1244 Btu/lb·°F (0.521 kJ/kg·°K) at 32°F (0°C); 0.1347 Btu/lb·°F (0.564 kJ/kg·°K) at 77°F (25°C).

##### 9.4.10.2 Saturated Gas

*At Constant Volume (Cv)*

0.088 87 Btu/lb·°F (0.372 1 kJ/kg·°K) at 32°F (0°C); 0.093 03 Btu/lb·°F (0.3895 kJ/kg·°K) at 77°F (25°C).

##### 9.4.10.3 Saturated Liquid

0.2264 Btu/lb·°F (0.948 kJ/kg·°K) at 32°F (0°C); 0.2329 Btu/lb·°F (0.975 kJ/kg·°K) at 77°F (25°C).

##### 9.4.10.4 Ratio

Ratio of gas specific heat at constant pressure to gas specific heat at constant volume, Cp/Cv. 1.400 for saturated gas at 32°F (0°C); 1.448 for saturated gas at 77°F (25°C).

#### 9.4.11 Specific Volume

The volume of a unit mass of chlorine at specified conditions of temperature and pressure.

##### 9.4.11.1 Gas at Standard Conditions

4.986 ft<sup>3</sup>/lb (0.3113 m<sup>3</sup>/kg).

##### 9.4.11.2 Saturated Gas at 32°F (0°C)

1.310 ft<sup>3</sup>/lb (0.08179 m<sup>3</sup>/kg).

##### 9.4.11.3 Saturated Liquid at 32°F (0°C)

0.01092 ft<sup>3</sup>/lb (0.000 681 8 m<sup>3</sup>/kg.).

#### 9.4.12 Vapor Pressure

The absolute pressure of chlorine gas above liquid chlorine when they are in equilibrium. 53.51 psi (368.9 kPa) at 32°F (0°C); 112.95 psi (778.8 kPa) at 77°F (25°C). See Fig. 9.1.

#### 9.4.13 Viscosity

The measure of internal molecular friction when chlorine molecules are in motion.

##### 9.4.13.1 Saturated Gas

0.0125 centipoise (0.0125 mPa·s) at 32°F (0°C); 0.0132 centipoise (0.0132 mPa·s) at 60°F (15.6°C)

##### 9.4.13.2 Liquid

0.3863 centipoise (0.3863 mPa·s) at 32°F (0°C); 0.3538 centipoise (0.3538 mPa·s) at 60°F (15.6°C).

#### 9.4.14 Volume - Temperature Relation of Liquid Chlorine in a Container Loaded to its Authorized Limit

See Figure 9.4

#### 9.4.15 Solubility of Water in Liquid Chlorine

See Figures 9.5 and 9.6

FIGURE 9.1  
VAPOR PRESSURE OF LIQUID CHLORINE

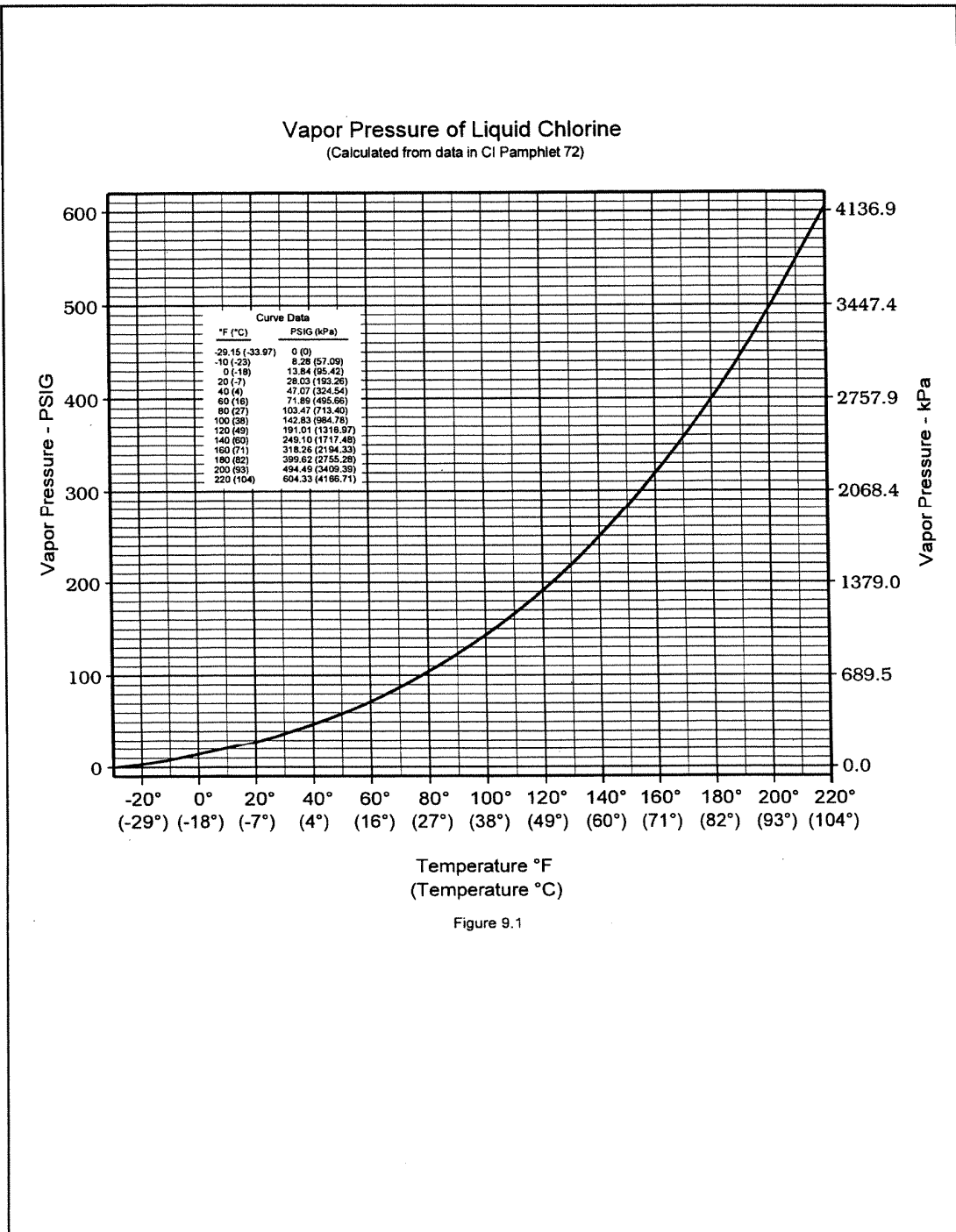


FIGURE 9.2  
TEMPERATURE-DENSITY RELATION OF LIQUID CHLORINE

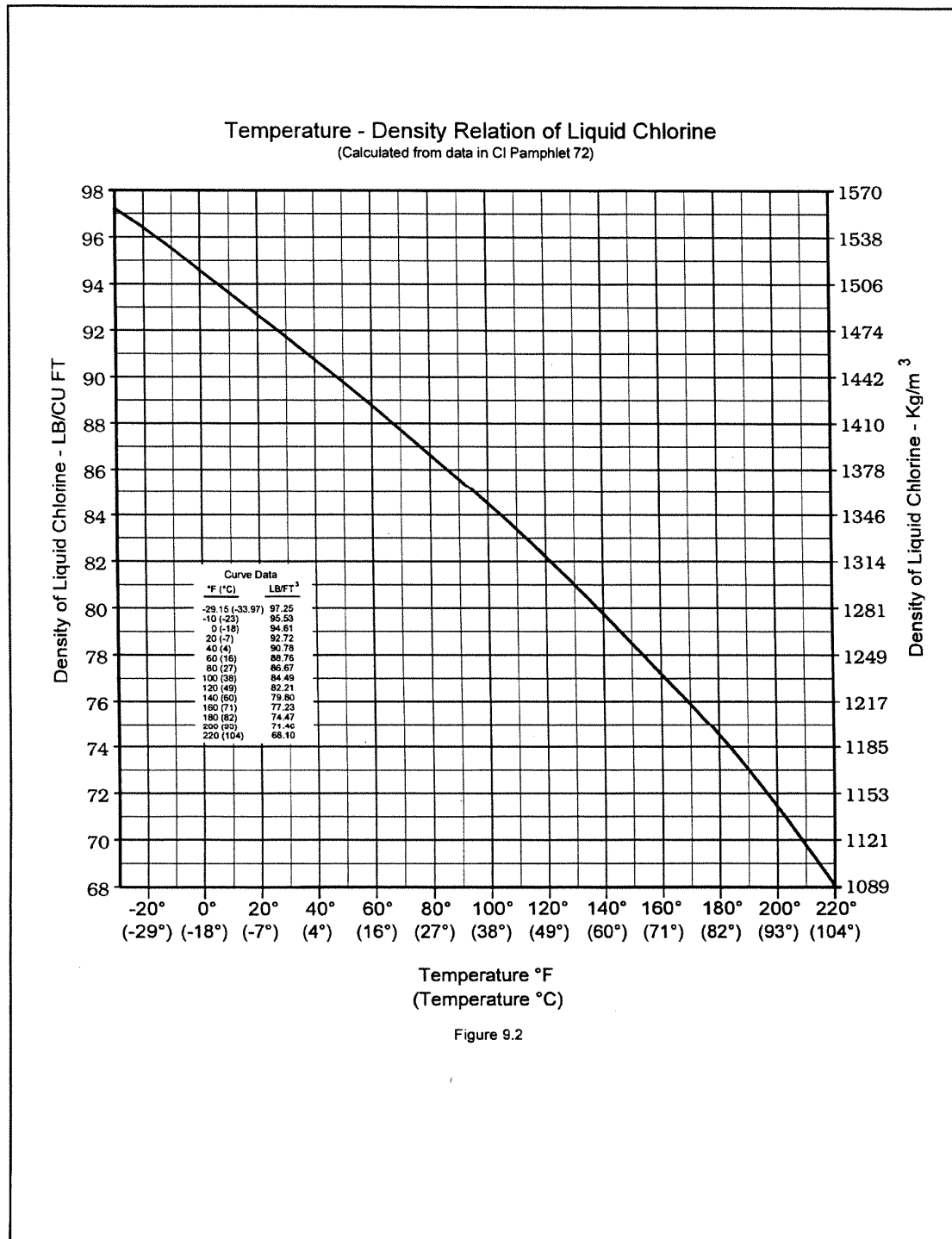


Figure 9.2

**FIGURE 9.3**  
**EQUILIBRIUM SOLUBILITY OF CHLORINE IN WATER**

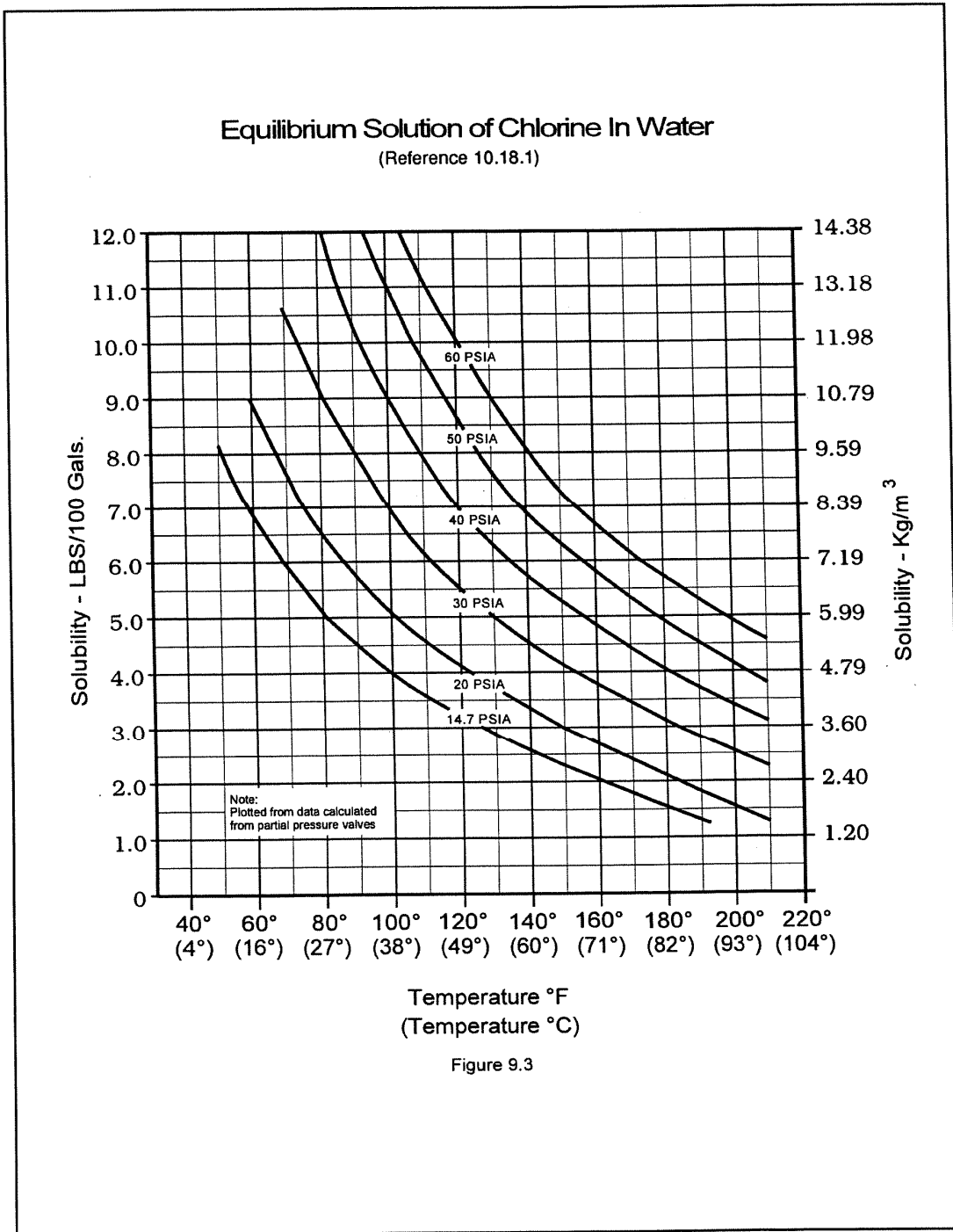


FIGURE 9.4  
 VOLUME-TEMPERATURE RELATION OF LIQUID CHLORINE  
 IN A CONTAINER LOADED TO ITS AUTHORIZED LIMIT

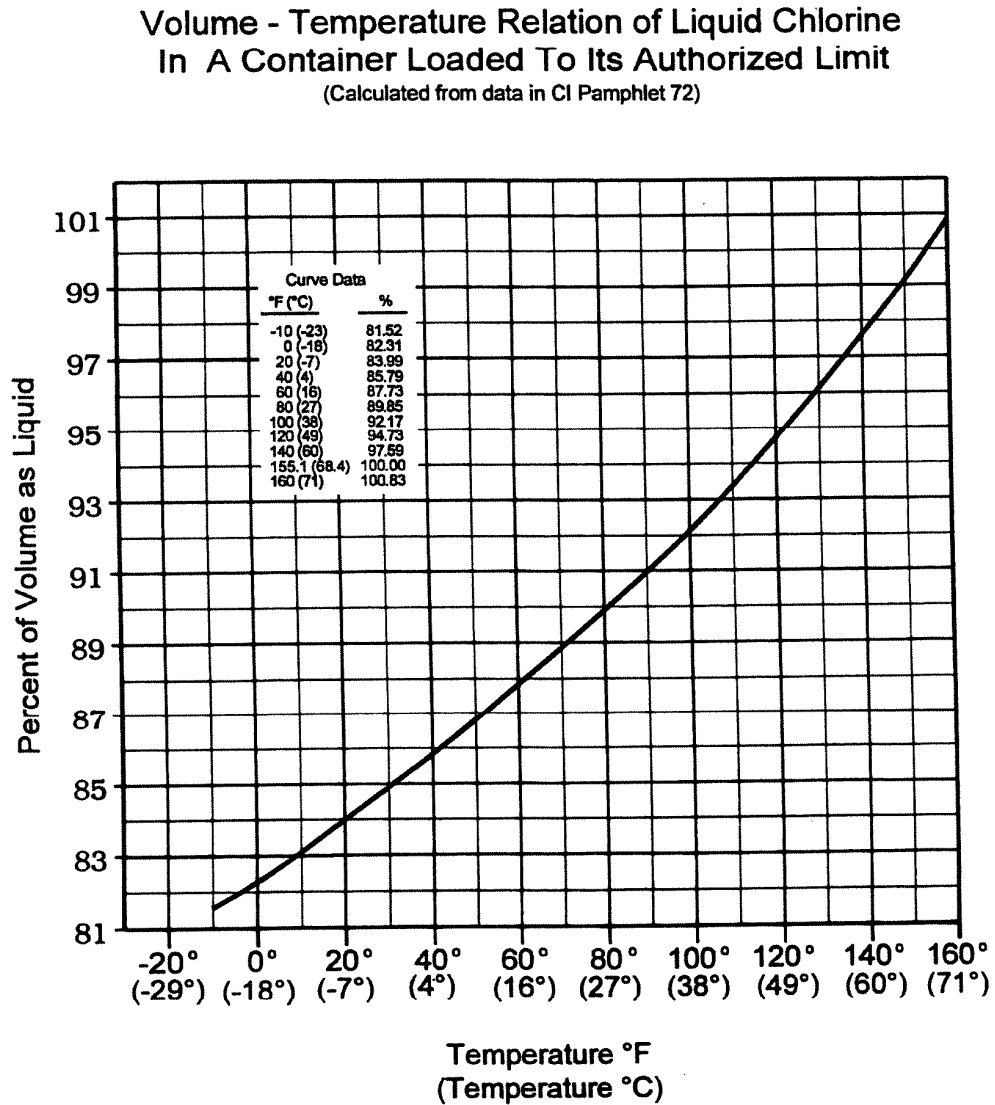


Figure 9.4

FIGURE 9.5  
 SOLUBILITY OF WATER IN LIQUID CHLORINE

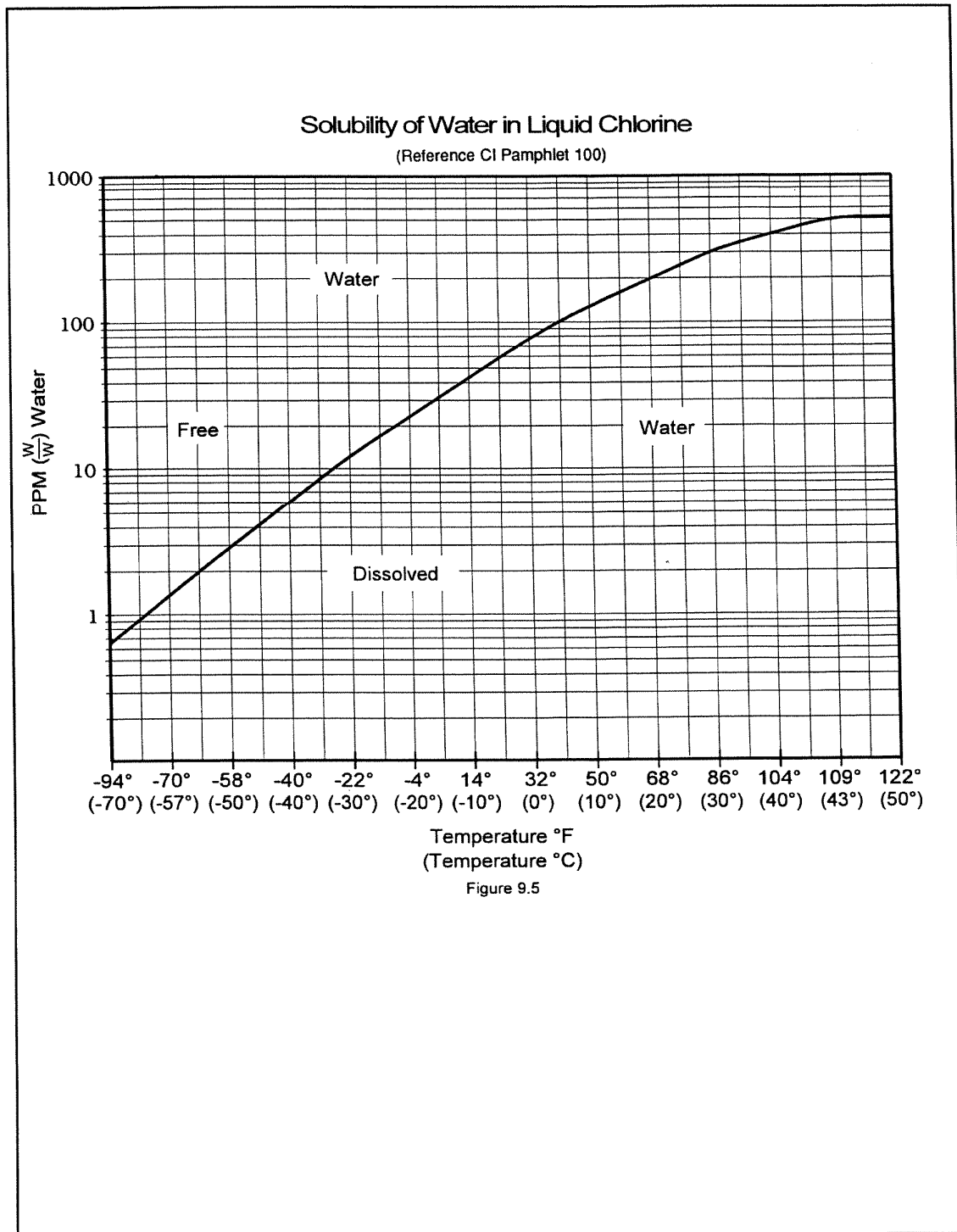
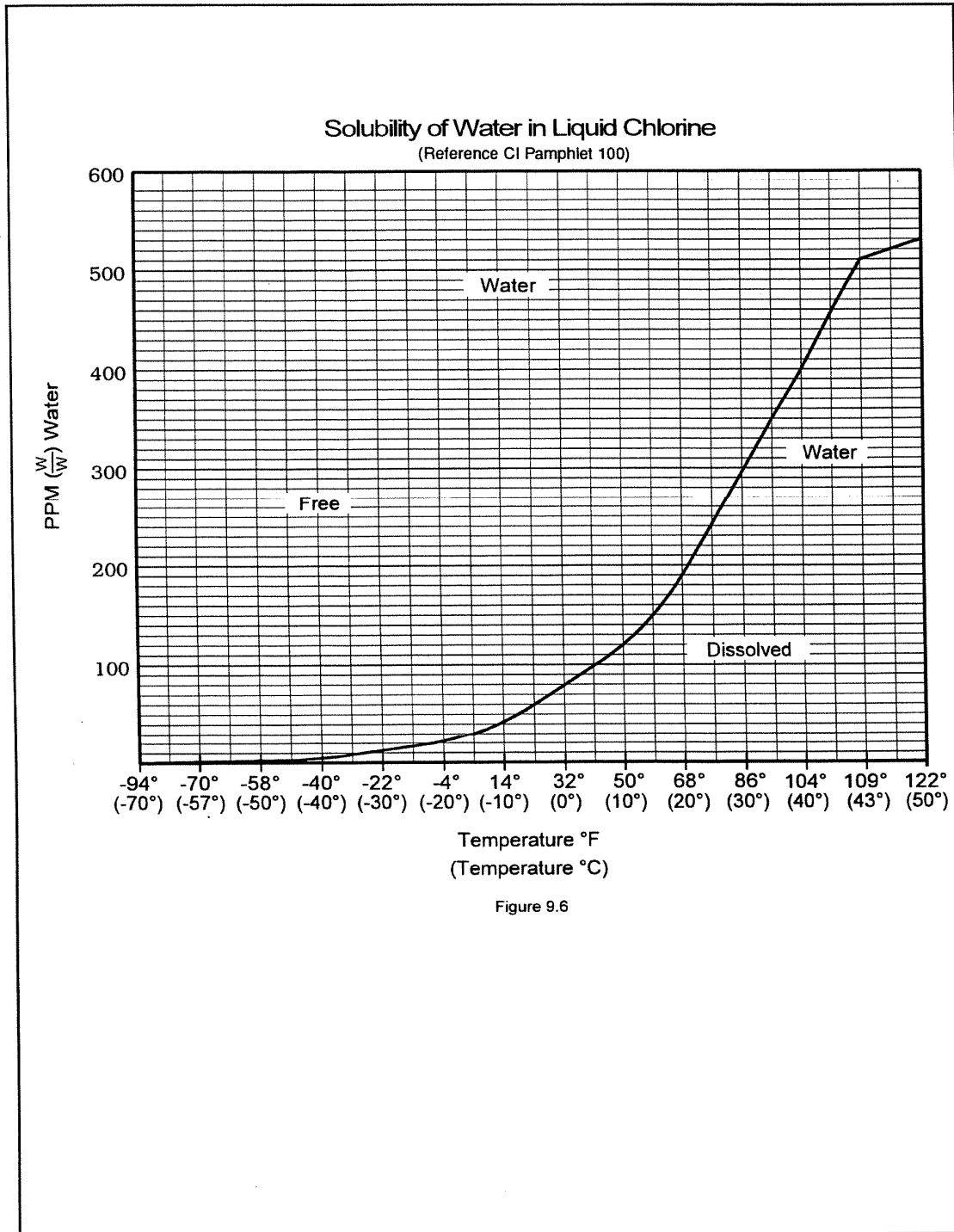


FIGURE 9.6  
 SOLUBILITY OF WATER IN LIQUID CHLORINE



# 10 SELECTED REFERENCES

Many of the following references are cited in the text. Such references are to the editions current at the date of publication of this manual. The reader should be aware that changing technology or regulations may require a change in the reference cited.

## 10.1 U.S. Government Regulations and Specifications

All U.S. regulations and specifications are available from the Superintendent of Documents, U.S. Government Printing Office, Washington, D.C. 20402.

10.1.1 Code of Federal Regulations (CFR), Various Sections

10.1.2 Chlorine Technical, Liquid; Federal Specification BB-C 120 C.

## 10.2 Canadian Regulations

Most Canadian regulations can be obtained from the Canadian Government Publishing Center, Supply and Services Canada, Ottawa, Canada K1A 0S9.

## 10.3 Chlorine Institute References

10.3.1 Pamphlets and Instructional Booklets

5 *Non-Refrigerated Liquid Chlorine Storage*

5 *Piping Systems for Dry Chlorine*

9 *Chlorine Vaporizing Systems*

17 *Cylinder and Ton Container Procedures for Chlorine Packaging*

21 *Nitrogen Trichloride - A Collection of Reports and Papers*

39 *Maintenance Instructions for Chlorine Institute Standard Safety Valves, Type 1-1/2JQ*

40 *Maintenance Instructions for Chlorine Institute Standard Angle Valve*

41 *Maintenance Instructions for Chlorine Institute Standard Safety Valves, Type 4 JQ*

42 *Maintenance Instructions for Chlorine Institute Standard Excess Flow Valves*

49 *Handling Chlorine Tank Motor Vehicles*

57 *Emergency Shut-Off Facilities for Tank Car/Tank Truck Transfer of Chlorine*

60 *Chlorine Pipelines*

63 *First Aid and Medical Management of Chlorine Exposures*

64 *Emergency Response Plans for Chlorine Facilities*

65 *Personal Protective Equipment for Chlorine and Sodium Hydroxide*

66 *Recommended Practices for Handling Chlorine Tank Cars*

72 *Properties of Chlorine in SI Units*

73 *Atmospheric Monitoring Equipment for Chlorine*

74 *Estimating the Area Affected by a Chlorine Release*

- 75 *Respiratory Protection Guidelines for Chlor-Alkali Manufacturing Facilities*
- 76 *Guidelines for the Safe Motor Vehicular Transportation of Chlorine Containers*
- 77 *Sampling Liquid Chlorine*
- 78 *Refrigerated Liquid Chlorine Storage*
- 79 *Recommended Practices for Handling Chlorine Barges*
- 82 *Chlorine Safety at Non-Residential Swimming Pools*
- 84 *Environmental Fate of Chlorine in the Atmosphere*
- 85 *Recommendations for Prevention of Personnel Injuries for Chlorine Producer and User Facilities*
- 86 *Recommendations to Chlor-Alkali Manufacturing Facilities for the Prevention of Chlorine Releases*
- 89 *Chlorine Scrubbing Systems*
- 90 *Toxicity Summary for Chlorine and Hypochlorite and Chlorine in Drinking Water*
- 91 *Checklist for Chlorine Packaging Plants, Chlorine Distributors and Tank Car Users of Chlorine*
- 93 *Pneumatically Operated Valves for Use on Chlorine Tank Cars*
- 95 *Gaskets for Chlorine Service*
- 97 *Safety Guidelines for Swimming Pool Applicators*
- 100 *Dry Chlorine: Definitions and Analytical Issues*
- 121 *Explosive Properties of Gaseous Mixtures Containing Hydrogen and Chlorine*
- 126 *Guidelines: Medical Surveillance and Hygiene Monitoring Practices for Control of Worker Exposure to Chlorine in the Chlor-Alkali Industry*
- 134 *The Drying and Liquefaction of Chlorine and the Phase Diaphragm  $Cl_2 - H_2O$*
- 139 *Electrical Safety in Chlor-Alkali Cell Facilities*
- 151 *Training Guide for Distributors and End-Users of Packaged Chlorine*
- 152 *Safe Handling of Chlorine Containing Nitrogen Trichloride*
- IB/A *Instruction Booklet: Chlorine Institute Emergency Kit "A" for 100- and 150-lb. Chlorine Cylinders*
- IB/B *Instruction Booklet: Chlorine Institute Emergency Kit "B" for Chlorine Ton Containers*
- IB/C *Instruction Booklet: Chlorine Institute Emergency Kit "C" for Chlorine Tank Cars and Tank Trucks*
- IB/RV *Instruction Booklet: Cl Recovery Vessel for 100-and 150-lb. Chlorine Cylinders*
- VPC *The Vapor Pressure of Chlorine*

### 10.3.2 Drawings

The reader should refer to the current Institute catalog for a complete list of drawings.

- DWG 104 *Standard Chlorine Angle Valve Assembly*
- DWG 110 *Valve for Chlorine Cylinders and Ton Containers - Assembly*
- DWG 111 *Fusible Plugs for Chlorine Cylinders and Ton Containers*
- DWG 112 *Valves and Fusible Plugs for Chlorine Ton Containers*
- DWG 113 *Valves for Chlorine Cylinders and Ton Containers*
- DWG 114 *Excess Flow Valve with Removable Seat - 15,000 lb/hr*
- DWG 118 *Chlorine Tank Car Unloading Connections*
- DWG 121 *Limiting Dimensions for Chlorine Cylinders*
- DWG 122 *Ton Container Lifting Beam*
- DWG 130 *Standard Chlorine Cylinder and Ton Container Valve Adapter*
- DWG 131 *Chlorine Cylinder Valve Yoke*
- DWG 136 *Chlorine Expansion Chambers*
- DWG 162 *Excess Flow Valve with Removable Seat - 30,000 lb/hr*
- DWG 163 *Excess Flow Valve with Removable Seat - 11,000 lb/hr*
- DWG 167 *Chlorine Tank Car Marking*
- DWG 168 *Chlorine Cargo Tank Marking*
- DWG 181 *DOT 106A500X - Ton Container*
- DWG 183 *Manifolding Ton Containers for Liquid Chlorine Withdrawal*

DWG 188 *Chlorine Cylinder Recovery Vessel*

### 10.3.3 Audio/Visual Materials

H-VIDEO *Health Effects from Short-Term Chlorine Exposure*

## 10.4 American Conference of Governmental Industrial Hygienists

1330 Kemper Meadow Drive Cincinnati, OH 45240

10.4.1 *Threshold Limit Values and Biological Exposure Indices*, Published Annually

10.4.2 *Industrial Ventilation Manual: A Manual of Recommended Practices*, 22nd Edition, 1995.

10.5 **American Society of Mechanical Engineers**, United Engineering Center, 345 East 47th Street New York, NY 10017.

10.5.1 *Rules for Construction of Pressure Vessels*, Sections VIII, Division ASME Boiler and Pressure Vessel Code ANSI/ASME BPV-VIII- 1.

## 10.6 American Society for Testing Materials

1916 Race Street Philadelphia, PA 19103.

10.6.1 ASTM-E4 10-92, *Standard Method of Testing for Moisture and Residue in Liquid Chlorine*

10.6.2 ASTM-E4 12-86, *Standard Method of Assaying Liquid Chlorine (Zinc Amalgam Method)*

10.6.3 ASTM-E649-94, *Standard Test Method for Bromine in Chlorine*

10.6.4 ASTM-E806-93, *Standard Test Method for the Determination of Carbon Tetrachloride and Chloroform in Liquid*

*Chlorine by Direct Injection (Gas Chromatographic Procedure)*

- 10.6.5 ASTM-D2022-89, *Standard Methods of Sampling and Chemical Analysis of Chlorine-Containing Bleaches*
- 10.7 American Water Works Association**  
6666 West Quincy Avenue  
Denver, CO 80235.
- 10.8 Association of American Railroads**  
50 F St., NW  
Washington, DC 20001
- 10.9 Compressed Gas Association**  
1725 Jefferson Davis Highway, Suite  
1004 Arlington, VA 22202.
- 10.9.1 *Handbook of Compressed Gases* Van Nostrand Reinhold, New York, NY
- 10.9.2 Pamphlet C-1, *Methods for Hydrostatic Testing of Compressed Gas Cylinders*
- 10.9.3 Pamphlet C-6, *Standards for Visual Inspection of Compressed Gas Cylinders*
- 10.9.4 Pamphlet P-1, *Safe Handling of Compressed Gases in Containers*
- 10.9.5 Pamphlet V-1, *Compressed Gas Cylinder Valve Outlet and Inlet Connections* (This pamphlet is also designated as ANSI B57.1 and CSA b96.)
- 10.10 National Academy of Sciences**  
Printing and Publishing Office  
National Academy of Sciences  
2101 Constitution Avenue, NW  
Washington, DC 20418.
- 10.10.1 *Water Chemicals Codex*, 1982.
- 10.10.2 *Food Chemicals Codex II*,  
Fourth Edition, 1996
- 10.11 National Fire Protection Association**  
Batterymarch Park, Quincy, MA 02269.
- 10.12 National Institute of Occupational Safety and Health**
- 10.12.1 *Pocket Guide to Chemical Hazards U.S.*  
Department of Health  
and Human Services: 1994.
- 10.13 National Safety Council**  
444 North Michigan Avenue  
Chicago, IL 60610.
- 10.14 NSF International**  
3475 Plymouth Road  
Ann Arbor, MI 48113
- 10.14.1 *ANSI/NSF Standard 60  
-Drinking Water Additives-Health Effects;*  
updated annually.
- 10.15 Water Environment Foundation**  
601 Wythe Street  
Alexandria, VA 22314
- 10.16 World Health Organization**  
Distribution and Sales Service  
1211 Geneva 27, Switzerland
- 10.16.1 *Environmental Health Criteria 21  
Chlorine and Hydrogen Chloride*, 1982.

## 10.17 Chemical Industry Inst. of Toxicology

6 Davis Drive  
Research Triangle Park, NC 27709

10.17.1A *Chronic Inhalation Study of Chlorine in Female and Male B6C3J Mice and Fischer344 Rats*; Chemical Industry Institute of toxicology: 1993.

## 10.18 Other References

10.18.1 Adams, F. W.; Edmonds, R. G.; *I & EC*, 1937, 29, 447.

10.18.2 Ambrose, D.; Hall, D. J.; Lee, D. A.; Lewis, G. B.; Mash, C. J. J.; *Chemical Thermodynamics*, 1979, 11, 1089.

10.18.3 *Chlorine Bicentennial Symposium*; Jeffery, T.; Danna, P. A.; Holden, H. S., Eds.; Electrochemical Society: Princeton, NJ, 1974.

10.18.4 *Chlorine, Its Manufacture, Properties and Uses*; Sconce, J. S. ed.; ACS Monograph 154; Robert E. Krieger: Huntington, NY, 1972.

10.18.5 Heinemann, G.; Garrison, F.G.; Haber, P.A.; *I & EC*. 1946, 38, 497.

10.18.6 *Interpretive Review of the Potential Adverse Effects of Chlorinated Organic Chemicals on Human Health and the Environment, Report of an Expert Panel*; Coulston, F. and Kolbye, A.C., Eds.; Regulatory Toxicology and Pharmacology Journal; Academic Press: New York, NY, 1994.

10.18.7 *Alkali and Chlorine Products and Chlorine and Sodium Hydroxide*; Kirk-Othmer Encyclopedia of Chemical Technology; ed. 4; Editor: John Wiley & Sons, New York, NY, 1991.

10.18.8 Kowitz, T. A.; Reba, R. C.; Parker, R. T.; Spicer, W. S.; *Arch. of Environmental Health*, 1967, 14, 545.

10.18.9 *Modern Chlor-Alkali Technology*; Jackson, C., Ed.; Society of Chemical Industry; John Wiley & Sons: New York, NY, 1983; Vol. 2.

10.18.10 Patty, F. A.; *Industrial Hygiene and Toxicology*; Interscience: New York, NY.

10.18.11 Rotman, Harold H., et al.; *Journal of the American Physiological Society*, 1983, 1120, 983.

10.18.12 Weill, H.; George, R.; Schwartz, M.; Ziskind, M.; *Am. Review of Respiratory Diseases*, 1969, 29, 373.

10.18.13 Weston, P.C. *Modern Chlor-Alkali Technology*; Coulter, M.O., et al, Eds.; Society of Chemical Industry; Royal Society of Chemistry: Cambridge, 1994; Vol.6, pp 62-69.

10.18.14 Grenquist-Norden, B.; Institute of Occupational Health, 1983, pp 1-83.

# CHLORINE

## The Essential Element

Over 200 years ago, a young Swedish researcher, Carl Wilhelm Scheele, discovered chlorine. Because of its reactivity and bonding characteristics, chlorine has become a popular building block in chemistry and it is essential in everyone's life. Drinking water, agricultural abundance, disinfected waste water, essential industrial chemicals, bleaches and fuels all depend on chlorine. Pharmaceutical, plastics, dyes, cosmetics, coatings, electronics, adhesives, clothing and automobile parts are examples of product groups that depend on chlorine chemistry.

---

### APPLICATIONS OF CHLORINE

#### **Automotive**

Foam Seating  
Paints  
Plastic Bumpers Molding  
Instruments  
Floor Mats  
Fabric  
Seat Belts  
Tire Cords  
Dashboards  
Hoses

#### **Construction**

Carpeting  
Upholstery  
Wire Insulation  
Pipes  
Siding  
Flooring  
Paints  
Coatings

#### **Defense**

Bullet-Proof Vests  
Helmets  
Parachutes  
Water Repellant Fibers  
Shatter-Resistant Glass  
Titanium Aircraft

Jet Engines  
Missiles

#### **Electronics**

Semiconductors  
Computer Disks  
Wire Insulation

#### **Food Production & Handling**

Herbicides  
Vitamins B1 & B6  
Cleaners  
Disinfectants  
Thermal Insulation  
Sterile Packaging

#### **Health Care**

Electronic Instruments  
Sterile Packaging  
Surgical Equipment  
Cleaning Compounds  
Prescription Eye Wear  
Laboratory Reagents

#### **Medicines**

Antibiotics  
Cancer Treatment  
Pain Relievers  
Local Anesthetics

Antihistamines  
Decongestants

#### **Metal Production**

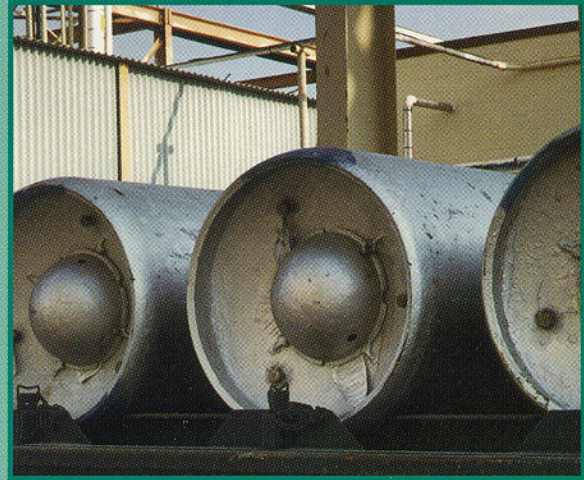
Magnesium  
Nickel  
Bismuth  
Titanium  
Zirconium  
Zinc

#### **Outdoor Recreation**

Neoprene Wet Suits  
Inflatable Rafts  
Golf Grip  
Surf Boards  
Nylon Ropes  
Tents  
Sleeping Bags  
Coats  
Backpacks  
Waterproof Clothing

#### **Water Treatment**

Safe Drinking Water  
Wastewater Treatment



Chlorine Institute Pamphlet 1, Edition 6 January 1997

Second Printing March 2000

**Topics in this manual include: CHLORINE and ...**

**BULK SHIPMENTS  
CONTAINERS  
EMERGENCIES  
EMPLOYEE SAFETY  
ENGINEERING  
ENVIRONMENT**



The Chlorine Institute, Inc.  
1300 Wilson Boulevard  
Arlington, VA 22209  
Phone: 703-741-5760  
Fax: 703-741-6068  
Web: <http://www.cl2.com>

**FIRST AID  
MAINTENANCE  
REFERENCES  
REGULATIONS  
TECHNICAL DATA  
TRAINING**

