



## Pamphlet 1 Chlorine Basics

Edition 7



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#### 1. INTRODUCTION

#### 1.1 CHLORINE BASICS

The first Chlorine Manual was published by The Chlorine Institute in 1947. It was a comprehensive compilation of information to assist chlorine producers, packagers, and end users in the safe handling, storage, shipment, and use of chlorine. In the years since the original Chlorine Manual was published, the Institute has developed numerous documents that provide more detailed information on safe chlorine management.

With this edition of Pamphlet 1, the Chlorine Manual has been re-named Chlorine Basics. This change reflects the fact that a single document can no longer adequately communicate the detailed information required to safely handle, store, transport, and use chlorine. This pamphlet remains a valued resource, providing overview and reference information to the many other resources available from The Chlorine Institute. For more detailed information, an on-line catalog is available on the Institute's website – www.chlorineinstitute.org.

#### 1.2 CHORINE INSTITUTE STEWARDSHIP PROGRAM

The Chlorine Institute, Inc. (CI) 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.

Chlorine Institute members are committed to adopting CI safety and stewardship initiatives including pamphlets, checklists, and incident sharing that will assist members in achieving measurable improvement. For more information on the Institute's stewardship program visit the CI website at <u>www.chlorineinstitute.org</u>.

#### 1.3 DISCLAIMER

The information in this pamphlet is drawn from sources believed to be reliable. The Institute and its members, jointly and severally, make no guarantee, and assume no liability, in connection with any of this information. Moreover, it should not be assumed that every acceptable procedure is included, or that special circumstances may not warrant modified or additional procedures. The user should be aware that changing technology or regulations may require changes in the recommendations contained herein. Appropriate steps should be taken to ensure that the information is current, when used. These recommendations should not be confused with federal, state, provincial, municipal regulations, insurance requirements, or with national safety codes.

#### 1.4 <u>APPROVAL</u>

The Institute's Customer Stewardship Issue Team approved Edition 7 of this pamphlet on October 7, 2008.

#### 1.5 <u>REVISIONS</u>

Suggestions for revisions should be directed to the Secretary of the Institute.

#### 1.6 CHECKLISTS

Several pamphlets contain checklists to assist members and non-members in selfaudits or other reviews.

Because Chlorine Basics only summarizes some of the information contained in other pamphlets, the reader should refer to specific referenced 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 checklists.

#### 1.7 <u>ABBREVIATIONS AND ACRONYMS</u>

AAR	Association of American Railroads		
ANSI	American National Standards Institute		
API	American Petroleum Institute		
ASME	American Society of Mechanical Engineers		
ASTM	ASTM International (Formerly American Society for Testing and Materials)		
AWWA	American Water Works Association		
CAS	Chemical Abstracts Service		
CFR	Code of Federal Regulations		
CGA	Compressed Gas Association		
CI	The Chlorine Institute, Inc.		
CIH	Chronic Inhalation Hazard		
CIIT	Chemical Industry Institute of Toxicology		
DHS	Department of Homeland Security		
DOL	Department of Labor		
DOT	Department of Transportation		
EPA	Environmental Protection Agency		

FIFRA Federal Insecticide, Fungicide and Rodenticide Act

IMDG	International Maritime Dangerous Goods Code		
kPa	kilopascal		
MSDS	Material Safety Data Sheet		
NAS	National Academy of Sciences		
NFPA	National Fire Protection Association		
NIOSH	National Institute of Occupational Safety and Health		
NSF	National Science Foundation		
OSHA	Occupational Safety and Health Administration		
PMRA	Pest Management Regulatory Agency, a division of Health Canada		
POV	Pneumatically Operated Valve		
ppm	Parts per million		
psia	Pounds per square inch, absolute pressure		
psig	Pounds per square inch, gauge pressure		
PSM	Process Safety Management		
RCRA	Resource Conservation and Recovery Act		
RMP	Risk Management Plan		
RTECS	Registry of Toxic Effects of Chemical Substances		
SSP	Site Security Plan		
SVA	Security Vulnerability Assessment		
тс	Transport Canada		
TDG	Transportation of Dangerous Goods Act and Regulations		
TEMA	Tubular Exchanger Manufacturers Association, Inc.		
TLV	Threshold Limit Value		
WEF	Water Environment Foundation		
WHMIS	Workplace Hazardous Materials Information System		
WHO	World Health Organization		

#### 1.8 <u>REFERENCES</u>

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

At the beginning of Section 11 – "Selected References," complete information about the Institute publications is provided. Other sources are referenced in this publication in the following manner: (Reference 11.4.1). Section 11 provides information on each of these references. In most cases, an address also is provided.

A number of pamphlets are available electronically from the CI website or can be ordered as hard copies. A free publications catalog can be obtained from the CI website or by contacting the Institute Publications Department, 1300 Wilson Boulevard, Arlington, VA 22209:

Ph: 703-741-5760 Fax: 703-741-6068 Web: www.chlorineinstitute.org

#### 2. GENERAL INFORMATION

For detailed information, refer to the following CI literature:

Pamphlet # <u>Title</u>	
10	North American Chlor-Alkali Industry Plants and Production Data Reports
21 Nitrogen Trichloride - A Collection of Reports and F	
100 Dry Chlorine: Definitions and Analytical Issues	
152 Safe Handling of Chlorine Containing Nitrogen Trichl	

#### 2.1 <u>WHAT IS CHLORINE?</u>

Chlorine is one of 90 natural elements, the basic building blocks of our world. Since it is highly reactive, it is usually found chemically bonded to other elements, such as sodium, forming sodium chloride which is common table salt.

Chlorine plays a vital role in many key uses and applications:

- Chlorine is used to control bacteria and viruses in drinking water that can cause devastating illnesses such as cholera and typhoid. Approximately 98% of modern drinking water systems in the US use chlorine chemistry to ensure the drinking water remains safe from bacterial contamination.
- 90% of all pharmaceuticals rely on chlorine chemistry, including medicines that treat heart disease, cancer, AIDS, and many other life-threatening diseases.
- Chlorine chemistry is involved in the production of over 96% of crop protection chemicals.

• Chlorine chemistry contributes more than \$46 billion to the U.S. economy each year, through sales of chlorine and other building block chemicals that are used to make thousands of essential products.

#### 2.2 CHLORINE MANUFACTURE

Most chlorine is manufactured electrolytically by the diaphragm, membrane, or mercury cell process. In each process, a salt solution (sodium or potassium chloride) is electrolyzed by the action of direct electric current which converts chloride ions to elemental chlorine. Chlorine is also produced in a number of other ways, for example, 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 (Reference 11.18.2).

$$\begin{aligned} Salt + Water + Electricity &\rightarrow Chlorine + Caustic + Hydrogen \\ NaCl + H_2O + e^- &\rightarrow \frac{1}{2}Cl_2 + NaOH + \frac{1}{2}H_2 \end{aligned}$$

Figure 1. Basic Chlor-Alkali Chemical Reaction Equation

Table 1	Chlorine Production		
Area	Million Short Tons		
Globally	65		
United States	13.8		
Canada	1.1		
Mexico	0.5		

Chlorine production for 2006 in short tons/year is estimated to be as follows:

#### 2.2.1 Diaphragm Cell Technology

Currently in North America, most 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.

A nearly saturated sodium chloride solution (brine) 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. Some chloride ions also migrate across the diaphragm resulting in the cell liquor 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 system for reuse.

#### 2.2.2 Membrane Cell Technology

Membrane cell technology uses sheets of perfluorinated polymer ion exchange membranes to separate the anodes and cathodes within the electrolyzer. Ultra-pure 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 100 ppm of sodium chloride. The sodium hydroxide can be concentrated further, typically to 50%, using evaporators.

#### 2.2.3 Mercury Cell Technology

Mercury Cell technology uses a stream of mercury flowing along the bottom of the electrolyzer as the cathode. 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. The mercury is then pumped back to the cell inlet, where the electrolysis process is repeated.

#### 2.3 CHLORINE TRANSPORTATION

#### 2.3.1 General

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

#### 2.4 OTHER REGULATORY ASPECTS

Chlorine manufacturers, packagers, and most consumers are subject to workplace regulations pertaining to chlorine.

#### 2.4.1 United States

There are many regulations at the federal, state, and local levels that apply to chlorine manufacture, transport, and use. Agencies such as OSHA, EPA, DOT, and DHS regulate various aspects of the chlorine industry and should be consulted. Refer to Section 9 of this pamphlet for more information.

Table 2	Chlorine Classification			
Country United States	Hazard Class Primary: 2	<b>Division</b> Primary: 2.3 Poison Gas	<b>Key Regulation</b> Land: 49 CFR Barge: 33 CFR and	Other Poison Zone B inhalation
	Secondary: 5, 8	Secondary: 5.1 Oxidizer	46 ČFR	hazard material rating.
		Secondary: 8 Corrosive		Various state and/or local regulations.
Canada	Primary: 2	Primary: 2.3 Poison Gas	Transportation of Dangerous Goods	Various provincial
	Secondary: 5	Secondary: 5.1 Oxidizer	Act and Regulations (TDG)	and/or local regulations
Mexico	Primary: 2	Primary: 2.3 Poison Gas	Regulation for Surface	Various state and/or local
	Secondary: 5	Secondary: 5.1 Oxidizer	Transportation of Hazardous Materials and Waste	regulations.
International			International Maritime Dangerous Goods Code (IMDG)	Designation for chlorine: UN1027

#### 2.4.2 Canada

There are many regulations at the federal, provincial, and local levels that apply to chlorine manufacture, transport, and use. Agencies such as Health Canada, Environment Canada, and Transport Canada regulate various aspects of the chlorine industry and should be consulted.

#### 2.5 <u>TERMINOLOGY</u>

2.5.1 Elemental Chlorine

Chlorine's symbol is Cl, its atomic number is 17, and its atomic weight is 35.453. Elemental chlorine almost always exists as a molecule with two chlorine atoms bound together as Cl<sub>2</sub>. Its molecular weight is 70.906. The CAS registry number is 7782-50-5.

#### 2.5.2 Liquid Chlorine

Chlorine  $(Cl_2)$  which has been cooled and compressed to a liquid form. Under atmospheric temperature and pressure, liquid chlorine evaporates quickly, with one pound of liquid forming about 5.4 cubic feet of chlorine gas.

Liquid chlorine is NOT the same as a hypochlorite or chlorine bleach solutions and this terminology should not be used to describe such solutions.

#### 2.5.3 Chlorine Gas

At atmospheric conditions, chlorine is a gas.

#### 2.5.4 Dry Chlorine/Wet Chlorine

DRY chlorine is defined as chlorine with its water content dissolved in solution. If a condition is reached anywhere in the system that will allow the water to exceed its solubility and form a second aqueous liquid phase, the chlorine is defined as WET chlorine. WET chlorine will form corrosive compounds affecting the safety and integrity of the system (See CI Pamphlet 100 and Figure 10.5 and Figure 10.6).

Dry Chlorine is NOT a dry chlorinating compound such as calcium hypochlorite or chloroisocyanurates and this terminology should not be used to describe such a substance.

2.5.5 Moist Chlorine

Synonymous with wet chlorine.

#### 2.5.6 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 does not describe or refer to the relative moisture content of the chlorine.

2.5.7 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 does not describe or refer to the relative moisture content of the chlorine.

2.5.8 Chlorine Solution (Chlorine Water)

A solution of chlorine in water (See Figure 10.3).

A chlorine solution is NOT the same as hypochlorite or chlorine bleach solutions and this terminology should not be used to describe such solutions.

2.5.9 Liquid Bleach

An aqueous solution of hypochlorite, usually sodium hypochlorite (NaOCI).

#### 2.5.10 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.

#### 2.5.11 Filling Density

By DOT and TC 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.

#### 2.5.12 Sodium Hydroxide

Normally sodium hydroxide (NaOH) is 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 or lye.

#### 2.5.13 Potassium Hydroxide

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

#### 2.6 SPECIFIC MANUFACTURING AND USE HAZARDS

#### 2.6.1 Hydrogen

Hydrogen  $(H_2)$  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 (See CI Pamphlet 121).

#### 2.6.2 Nitrogen Trichloride

Small quantities of nitrogen trichloride ( $NCl_3$ ), 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 concentrate to hazardous concentrations in the residue (See CI Pamphlets 21 and 152).

#### 2.6.3 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, pipe thread lubricants, as well as wood and rags from maintenance work.

#### 2.7 <u>OTHER HAZARDS</u>

#### 2.7.1 Fire

Chlorine is neither explosive nor flammable. Chlorine will support combustion under certain conditions. Many materials that burn in oxygen (air) atmospheres will also burn in chlorine atmospheres.

#### 2.7.2 Chemical Action/Reactions

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 10.3.3).

#### 2.7.3 Corrosive Action on Steel

At ambient 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 such as precipitation or humidity. If water is used on a chlorine leak, the resulting corrosive conditions will make the leak worse.

#### 2.7.4 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 10.4).

#### 3. CYLINDERS AND TON CONTAINERS

For detailed information, refer to the following CI literature:

#### Pamphlet # Title

- 6 Piping Systems for Dry Chlorine
- 17 Packaging Plant Safety and Operational Guidelines
- 65 Personal Protective Equipment for Chlor-Alkali Chemicals
- 76 Guidelines for the Safe Motor Vehicular Transportation of Chlorine Cylinders and Ton Containers
- 91 Checklist for Chlorine Packaging Plants, Chlorine Distributors and Tank Car Users of Chlorine
- 155 Water and Wastewater Operators Chlorine Handbook

#### Drawing # Title

Drawing 122 Ton Container Lifting Beam

Drawing 183 Manifolding Ton Containers for Liquid Chlorine Withdrawal

Drawing 189 Closed Yoke Chlorine Container Valve

Drawing 197 Chlorine Ton Containers

#### 3.1 CONTAINER DESCRIPTIONS

#### 3.1.1 General

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

In this document, "container" will be used to refer to any vessel that holds chlorine for the purpose of transporting the product. This may include cylinders, toncontainers, cargo tanks, tank cars, and barges. If the information provided is specific to the type of container, it will be specified.

Site chlorine inventories exceeding the threshold quantity are subject to such regulations as RMP and PSM. Check with federal, state, and provincial agencies for threshold requirements.

#### 3.1.2 Cylinders

Chlorine cylinders are of seamless construction with a capacity of 1 to 150 lb (0.45 to 68 kg); those of 100 and 150 lb (45.4 and 68 kg) capacity predominate. The only opening in the cylinder is the valve connection at the top of the cylinder. The steel valve protective housing should be utilized to cover the valve during shipment and storage. Care must be taken with the protective cap since the cylinder neck-ring to which it is attached is not physically welded to the cylinder.

#### 3.1.3 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). The sides are crimped inward at each end to form chimes which provide a substantial grip for lifting beams. The ton container valves are protected by a removable steel valve protective housing.

#### 3.2 CONTAINER VALVES

#### 3.2.1 Cylinder Valves

The typical cylinder is equipped with one valve. The valve outlet threads are not standard pipe threads, but are special straight threads. These outlet threads are intended for securing the valve outlet cap and not for connecting unloading connections or other devices. Typical cylinder connections are made with a yoke and adapter (See CI Pamphlet 17). The valve is also equipped with a fusible metal pressure relief device or, as more commonly named, a fusible plug.

#### 3.2.2 Ton Container Valves

Each ton container is equipped with two identical valves near the center of one end. They are different from the typical cylinder valve in that they have no fusible metal plug and usually have a larger internal passage. Each valve connects to an internal eduction tube (See CI Pamphlet 17).

#### 3.3 PRESSURE RELIEF DEVICES

#### 3.3.1 General

A metal relief device or fusible plug 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 designed to activate only in the event of a temperature increase and will not prevent over-pressurization due to overfilling.

3.3.2 Cylinders

Cylinder valves are equipped with one fusible metal relief device or fusible plug.

#### 3.3.3 Ton Containers

Ton containers are equipped with fusible metal pressure relief devices. Most have six fusible metal plugs, three in each end.

- 3.4 <u>CONTAINER SHIPPING</u>
- 3.4.1 Cylinders

Cylinders may be shipped by highway, rail, or water. Suitable restraints are necessary to prevent cylinders from shifting during transportation (See CI Pamphlet 76).

#### 3.4.2 Ton Containers

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

#### 3.5 CONTAINER MARKING/LABELING AND VEHICLE PLACARDING

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

#### 3.6 CONTAINER HANDLING

#### 3.6.1 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. Containers should be secured to prevent them from rolling (See CI Pamphlet 76).

#### 3.6.2 Cylinders

Cylinders can be moved using a properly balanced hand truck. The hand 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 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.

#### 3.6.3 Ton Containers

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

#### 3.7 CONTAINER STORAGE

Containers may be stored indoors or outdoors. The storage area should comply with federal and state regulations. See CI Pamphlets 17 and 155 for more detail on storage considerations.

#### 3.8 <u>CONTAINER USE</u>

#### 3.8.1 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.

#### 3.8.2 Gas Discharge

Chlorine gas discharge rates 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. See CI Pamphlet 155 for details.

If the gas discharge rate from a single container will not meet the flow requirements, two or more may be connected to a manifold. Alternately, liquid from one or more containers may be sent to a vaporizer for increasing the chlorine gas delivery rate (See Section 3.8.3).

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.

#### 3.8.3 Liquid Discharge

Discharging liquid chlorine has special design requirements (See CI Pamphlet 6).

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 ton 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 kPa gauge) is at least 400 lb/hr (181 kg/hr) for ton containers. When connected to a manifold, ton containers discharging liquid chlorine should include precautions to equalize the pressure. Drawing 183 depicts a system for equalizing pressures for gas valves connected to a manifold. 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.

#### 3.8.4 Weighing

Because chlorine is shipped as a compressed liquefied gas, the pressure in a container depends on the temperature of the chlorine (Figure 10.1). The pressure is not related to the amount of chlorine in the container. Container contents can be determined accurately only by weighing.

#### 3.8.5 Connections

A chlorine compatible flexible connection must be used between the container and a pressurized piping system. If a system is to remain in operation while containers are being connected or disconnected, auxiliary (isolating) container valves must be used. Flexible connections should be inspected and replaced on a regular basis. A flat gasket on the face of the valve is part of the connection. A new gasket should be used each time a connection is made (See CI Pamphlets 6 and 155 and Drawing 189).

#### 3.8.6 Opening Valves

The container valve is opened by turning the valve stem in a counter-clockwise direction. One full turn of the stem typically permits an appropriate feed rate. More stem turns should not be made unless recommended by the supplier. A wrench, no longer than 8 inches, should be used. Never use a wrench extension (cheater bar) as the valve may be damaged preventing gas-tight shut-off. Once the valve is opened, the wrench should be left in place so that the valve can be closed quickly. Do not loosen the packing nut unless authorized by the supplier.

Once connections have been made, pressurize the system with a small amount of chlorine, and check for leaks (See Section 5.4.2). If a leak is found, it must be remedied before proceeding (See CI Pamphlet 155).

#### 3.8.7 Closing Valves

Apply 25-30 foot-pounds to the valve stem. Check for leaks. If any leaks still exist, the torque may be increased up to 40 foot-pounds. If the leak has not stopped at 40 foot-pounds, increase the torque on the valve stem to 50 foot-pounds. If this fails to work, contact your supplier.

#### 3.8.8 Disconnecting Containers

As soon as a container is empty, the valve should be closed (See Section 3.8.7). Prior to disconnecting, reconfirm that the valve is closed and provide a means of removing the chlorine trapped in the flexible connecting line. 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. Personal Protective Equipment should be used as appropriate for the task (See CI Pamphlet 65). 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.

#### 4. BULK SHIPPING CONTAINERS

For detailed information, refer to the following CI literature:

#### Pamphlet # Title

- 6 Piping Systems for Dry Chlorine
- 49 Recommended Practices for Handling Chlorine Bulk Highway Transports
- 57 Emergency Shut-Off Systems for Bulk Transfer of Chlorine
- 60 Chlorine Pipelines

66	Recommended Practices for Handling Chlorine Tank Cars
166	Angle Valve Guidelines for Chlorine Bulk Transportation

#### Drawing # Title

Drawing 104 Standard Chlorine Angle Valve Assembly

4.1 <u>GENERAL</u>

Bulk chlorine is shipped by pipeline, tank cars, tank motor vehicles, portable tanks, and barge tanks.

- 4.2 TANK CARS
- 4.2.1 General

The following is generalized information on chlorine tank cars (See CI Pamphlet 66).

4.2.2 Specifications

The most commonly used tank cars have a chlorine capacity of 90 tons. By regulation, tank cars may not be loaded with chlorine in excess of the nominal weight.

Table 3	Key Government Specifications	
		_

 United States
 49 CFR 179.102-2
 49 CFR 176-314 (c) note 12

 Transport Canada
 79.102-2
 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 eduction pipes with approved excess flow valves to be used for liquid discharge. Tank cars must be thermally protected with four inches of insulating material.

- 4.2.3 Manway Arrangement
- 4.2.3.1 General

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

#### 4.2.3.2 Angle Valves

The manually operated angle valves for the standard manway arrangement should comply with CI Pamphlet 166. The two angle valves on the longitudinal centerline of the tank car are for liquid discharge. The angle valves on the transverse centerline are connected to the vapor space.

Chlorine tank cars may also be equipped with pneumatically operated valves (POVs).

#### 4.2.3.3 Excess Flow Valves

Except for tank cars equipped with pneumatically operated valves, under each liquid valve there is an excess-flow valve. 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 involving a broken connection occurs but it is not designed to act as an emergency shut-off device during transfer. Tank cars equipped with POVs are equipped with a ball check valve under both the liquid and vapor outlets.

#### 4.2.3.4 Eduction Pipes

Liquid chlorine is withdrawn through eduction pipes. 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.

#### 4.2.3.5 Pressure Relief Valve

In the center of the manway cover is a two-stage spring loaded pressure relief valve. The device is set to start-to-discharge at the pressure stenciled on the car.

#### 4.2.4 Transfer Operations

The following is general information (See CI Pamphlet 66).

#### 4.2.4.1 Precautions

Every site handling chlorine in bulk containers should have RMP and PSM programs.

Special attention should be directed to the appropriateness of emergency procedures and to equipment to be used in an emergency.

Chlorine transfer operations must be performed only by personnel who are trained as required by applicable hazardous material regulations.

DOT (49 CFR), OSHA (29 CFR) and TC (Sec. 10.2) have specific training requirements applicable to handling of hazardous materials.

All personnel responsible for transfer operations should be knowledgeable about the facility's emergency response plan for handling spills and leaks of products (See CI Pamphlet 66).

Before beginning transfer operations, a number of things should be considered. Details can be found in Pamphlet 66. A partial list of topics includes:

- Connections
- Pressure Padding
- Monitoring
- Disconnecting

#### 4.3 CARGO TANK MOTOR VEHICLES

4.3.1 General

The following is generalized information on chlorine cargo tank motor vehicles (See CI 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. DOT specifications apply only to the tank.

- 4.3.2 Manway Arrangement
- 4.3.2.1 General

The manway arrangement is the same as that on chlorine tank cars (see Section 4.2.3) except that special excess-flow valves are required under the gas valves.

4.3.2.2 Angle Valves

The angle valves are the same as those on tank cars (See Section 4.2.3.2).

4.3.2.3 Excess-Flow Valves

Under each liquid angle valve there is an excess-flow valve. There is an excessflow valve of different design under each gas angle valve. These valves have a removable basket so that the ball can be removed and the interior of the tank inspected.

4.3.2.4 Pressure Relief Valve

The pressure relief valve is the same type as that used on tank cars (See Section 4.2.3.5). On all cargo tanks, the start-to-discharge pressure is 225 psig (1,551 kPa gauge pressure).

#### 4.3.3 Transfer Operations

Procedures for transferring chlorine to/from cargo tanks 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.

#### 4.3.3.1 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 be attended at all times. 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 4.2.4.1, for additional, applicable precautions.)

#### 4.3.3.2 Emergency Equipment

Approved respiratory equipment is required on the transport vehicle. An Emergency Kit "C" must be on the transport vehicle. Proper training on the use of emergency equipment is required (OSHA 29 CFR 1910.134).

It also is required that the transport vehicle have 2-way communication such as a cell phone or radio.

4.3.3.3 Connections/Disconnecting

See discussion for tank cars (Section 4.2.4).

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

#### 4.3.3.4 Pressure Padding

See discussion for tank cars (Section 4.2.4).

#### 4.4 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 CI Pamphlet 49).

#### 4.5 TANK BARGES

Consult your supplier for information on chlorine barges.

#### 5. EMERGENCY MEASURES

For detailed information, refer to the following CI literature:

Pamphlet #	<u>Title</u>	
64	Emergency Response Plans for Chlor-Alkali, Sodium Hypochlorite and Hydrogen Chloride Facilities	
65	Personal Protective Equipment for Chlor-Alkali Chemicals	
66	Recommended Practices for Handling Chlorine Tank Cars	
74	Guidance on Complying with EPA Requirements Under the Clean Air Act by Estimating the Area Affected by Chlorine Release	
89	Chlorine Scrubbing Systems	
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	

#### 5.1 GENERAL

A chlorine emergency may occur during manufacture, use, or transportation. Trained employees, along with a comprehensive, written emergency response plan are necessary to mitigate the consequences of the emergency. Regular drills and reviews of emergency response plans with all involved organizations are encouraged (See CI Pamphlet 64). Federal, state and provincial regulations, as well as various local fire and building codes, regulate chemical emergency preparedness and response. All persons responsible for the handling of chlorine must be familiar with those requirements. Regulatory requirements deal generally with preparation and response to chemical and other emergencies (See CI Pamphlet 64). Help is also available from CHLOREP (see Sections 5.5.1 to 5.5.3) which can be accessed through the Institute and CHEMTREC (U.S.). In Canada, CANUTEC may provide advice, as well as contact information for the appropriate CHLOREP Team.

#### 5.2 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 PPE should investigate and take proper action. Personnel should not enter into atmospheres containing concentrations of chlorine in excess of the IDLH Concentration of 10 ppm without appropriate personal protective equipment and back-up personnel.

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

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.

There are specific government requirements for reporting a hazardous chemical release. Releases must be reported in a timely manner (See CI Pamphlet 64).

#### 5.3 RESPONSE TO A FIRE

If fire is present or imminent, chlorine containers and equipment should be moved away from the fire, if it is possible to do so safely. 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 will quickly get worse. However, where several containers are involved and some are leaking, it may be prudent to use a water spray to help cool 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.

- 5.4 <u>RELEASES</u>
- 5.4.1 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.

#### 5.4.2 Detection of Minor Releases and Leaks

A plastic squeeze bottle containing 26° 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 from 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. Leaks at the packing nut will always stop when the valve is closed (See CI Pamphlet 66). 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 5.8).

#### 5.4.3 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. CI Pamphlet 74 provides information on the area affected by specific chlorine release scenarios.

#### 5.4.4 Physical Form of the Chlorine Released

Typically, chlorine is stored and transported as a liquid under pressure. Liquid chlorine expands in volume by nearly 460 times when it vaporizes; therefore, a liquid chlorine leak can have significantly greater downwind effect than a gaseous chlorine leak.

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.

5.4.5 Effect of Chlorine on the Environment

#### 5.4.5.1 Vegetation

Plants in the path of a chlorine release may be damaged. Leaves may be bleached and browning and leaf loss may occur. Healthy plants will usually recover with time.

5.4.5.2 Animals

Seek medical attention for evaluation or treatment for pets and other animals that experience irritation or any signs of respiratory distress.

#### 5.4.5.3 Aquatic Life

Chlorine is only slightly soluble in water and there would be little absorption from a cloud of chlorine gas. If chlorine is released into a lake or stream, it may harm aquatic plants and animals until it dissipates.

#### 5.5 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. The MSDS, provided by the chlorine supplier, contains this contact information. This information may also be found on the bill of lading and the shipping container.

#### 5.5.1 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 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.

#### 5.5.2 CHEMTREC, CANUTEC, & SETIQ

During a chlorine emergency, any carrier, customer, or civil authority can obtain basic emergency information and contact information for the closest chlorine emergency group through CHEMTREC (U.S.), CANUTEC (Canada), SETIQ (Mexico), or their chlorine supplier. The emergency response call center, i.e. CHEMTREC and CANUTEC, provides immediate advice for those at the scene of emergencies. CHEMTREC will promptly contact the appropriate responder group as required. CANUTEC will provide contact information and participate on a call to the appropriate responder, which must be initiated by the incident scene contact. In many cases, the responder will be the shipper. However, in some cases, the designated response group is called and then the shipper is notified.

Table 4         Emergency Contact Information				
Dispatch Agency	Country	Phone Number		
CHEMTREC	Continental United States	1-800-424-9300		
CHEMTREC	Alaska and Hawaii	1-703-527-3887		
CHEMTREC	Marine radio telephone	1-703-527-3887		
CHEMTREC	Collect calls anywhere in the US	1-703-527-3887		
CANUTEC	Canada	1-613-996-6666		
		(collect calls accepted)		
SETIQ	Mexico	01-800-00214-00		
SETIQ	Mexico – from outside the	011-55-5-5591588		
	country			
	-			

#### 5.5.3 In Transit Emergency Response

If a chlorine leak develops in transit, 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 to a safe distance if possible.

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 5.3 for action to take if a fire occurs.

The specific actions taken by emergency responders will vary. Some items to consider acting upon are:

- Is it possible to safely turn the container 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.
- Is it possible to safely reduce the pressure in the container by removing the chlorine as gas (not as liquid) to a process or a disposal system? (See Sections 5.6 and 5.7).

- Can the container be safely moved to an isolated spot where the consequences can be minimized?
- Is it possible to safely apply the appropriate Chlorine Institute Emergency Kit or place the cylinder in a recovery vessel designed to contain the leak? (See Section 5.8).

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.

Specific government regulations must be followed for the shipment of a leaking chlorine container or a container which has been exposed to fire, whether full or partially full. In such cases, special arrangements are required and the chlorine supplier should be consulted first.

#### 5.6 CHLORINE LEAK AT A CONSUMING LOCATION

In addition to leak mitigation efforts, the following may be considered:

- It may be best to consume the chlorine through the regular process. If the consuming process cannot handle chlorine under emergency conditions, a standby alkali absorption system or a scrubber should be considered.
- It must be recognized that systems consuming liquid chlorine at low rates may 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 3.8.2).

#### 5.7 <u>ABSORPTION SYSTEMS</u>

Chlorine is readily absorbed in and reacted with an alkaline solution. The alkaline solution consists of water and sodium hydroxide, sodium carbonate, or potassium hydroxide. Contact your chlorine supplier and consult CI Pamphlet 89.

#### 5.8 EMERGENCY KITS AND RECOVERY VESSELS

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

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. CI Pamphlets IB/A, IB/B, and IB/C provide information on these kits and their use.

Chlorine recovery vessels are commercially available equipment designed to hold an entire cylinder. 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.

For chlorine barges, contact your supplier for information or equipment for leak mitigation.

Chlorine consumers should incorporate plans for the use of these kits in their emergency programs, provide instruction to the emergency responders, and properly maintain the equipment. Further information on the utility, availability, and purchase of kits, kit components, and audio visual training aids is available from the Institute or the chlorine supplier.

Chlorine use or storage locations should have either the appropriate 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.

#### 5.9 <u>REPORTING</u>

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.

#### 6. EMPLOYEE TRAINING AND SAFETY

For detailed information, refer to the following CI literature:

# Pamphlet #Title63First Aid, Medical Management/Surveillance and<br/>Occupational Hygiene Monitoring Practices for Chlorine65Personal Protective Equipment for Chlor-Alkali Chemicals

#### 6.1 <u>EMPLOYEE TRAINING</u>

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 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 but is not limited to:

- Instruction and periodic refresher courses in operation of chlorine equipment and handling of chlorine containers.
- Instruction in the properties and physiological effects of chlorine, including the information on the MSDS.
- A MSDS is provided by the chlorine supplier.
- 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 and installation 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.
- Locations, . purpose, and use of personal protective equipment.
- Locations, purpose, and use of safety showers, eye washes, or the closest source of water for use in emergencies.
- Locations, purpose, and use of any specialized first aid equipment.

#### 6.2 PERSONAL PROTECTIVE EQUIPMENT

#### 6.2.1 Availability and Use

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

#### 6.2.2 Respiratory Equipment

Respiratory equipment should be selected based on evaluation of hazards and degree of potential exposure. The need to protect the eyes from chlorine should be part of the evaluation of appropriate respiratory equipment (See CI Pamphlet 65).

All personnel entering areas where chlorine is stored or handled should carry or have immediately available appropriate respiratory protection.

A 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 is sufficient.

Fit testing and regular maintenance programs for respirator equipment are necessary. Documented, regularly scheduled training is required to assure competency with self-contained breathing apparatus (29 CFR 1910).

#### 6.3 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.

#### 6.4 PERSONAL EXPOSURE MONITORING

Because the odor of chlorine in itself is an inadequate indicator of concentration, it is essential that some quantitative measure of exposure be determined. Exposure guidelines are listed on the MSDS, including OSHA PEL and American Conference of Governmental Industrial Hygienists (ACGIH) TLV (Reference 11.4.1)

#### 7. MEDICAL ASPECTS AND FIRST AID

For detailed information, refer to the MSDS provided by the chlorine supplier.

#### Pamphlet # Title

63 First Aid, Medical Management/Surveillance and Occupational Hygiene Monitoring Practices for Chlorine

#### 7.1 <u>HAZARDS TO HEALTH</u>

Chlorine gas is primarily a respiratory irritant. At low concentrations, chlorine gas has an odor similar to household bleach. As the concentrations increase from the level of detection by smell, so do the symptoms in the exposed individual. Depending on the level of exposure to chlorine, the effects may become more severe for several days after the incident. Observations of exposed individuals should be considered part of the medical response program.

The following list is a compilation of potential chlorine exposure thresholds and potential responses in humans, with considerable variation among subjects:

Table 5	Chlorine Exposure Thresholds in ppm and Reported Responses
0.2 - 0.4	Odor threshold (decrease in odor perception occurs over time)
1 – 3	Mild mucous membrane irritation, tolerated up to 1 hour
5 – 15	Moderate irritation of the respiratory tract. 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
30	Immediate chest pain, vomiting, dyspnea, cough
40 - 60	Toxic pneumonitis and pulmonary edema
430	Lethal over 30 minutes
1000	Fatal within a few minutes.

#### 7.2 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. Reassurance to the individual 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.

If chlorine has saturated an exposed person's clothes or skin, decontamination should be done by removing affected clothing and showering as recommended on the MSDS.

CI Pamphlet 63 contains detailed guidance on first aid for chlorine exposure, including:

- Inhalation
- Respiratory Assistance
- Oxygen Administration
- Skin Contact
- Eye Contact
- Medical Management of Chlorine Exposures
- Delayed Effects

#### 8. ENGINEERING DESIGN AND MAINTENANCE

For detailed information, refer to the following CI literature:

Pamphlet #	Title
5	Bulk Storage of Liquid Chlorine
6	Piping Systems for Dry Chlorine
9	Chlorine Vaporizing Systems
17	Packaging Plant Safety and Operational Guidelines
65	Personal Protective Equipment for Chlor-Alkali Chemicals
73	Atmospheric Monitoring Equipment for Chlorine
89	Chlorine Scrubbing Systems
100	Dry Chlorine: Definitions and Analytical Issues
155	Water and Wastewater Operators Chlorine Handbook
164	Reactivity and Compatibility of Chlorine and Sodium Hydroxide with Various Materials

#### 8.1 <u>STRUCTURES</u>

Items to be considered include:

- Local building and fire codes;
- Avoid co-storage with other materials where possible, especially flammables;
- Chlorine monitoring equipment; and
- Means and locations of egress.

#### 8.2 <u>VENTILATION</u>

The ventilation requirements must be determined on a site-specific basis. The building ventilation system should provide fresh air for normal operation and should take into consideration the possibility of a chlorine leak. Safeguards should be in place to ensure that persons do not remain in nor enter buildings where chlorine is present in the atmosphere due to a leak or equipment failure without the appropriate personal protective equipment.

Chlorine gas is heavier than air and has a tendency to collect at floor level. This property must be considered when locating air openings.

#### 8.3 MATERIAL FOR PROCESSING EQUIPMENT

Materials of construction for handling dry chlorine and wet chlorine are very different. Temperature also plays an important role in material selection (See CI Pamphlets 6, 100, and 164).

Several other chemicals may be associated with the chlor-alkali process. These include hydrogen, 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.

#### 8.4 VAPORIZERS

High capacity chlorine gas feed systems may need a chlorine vaporizer (evaporator). Vaporizers are designed to convert liquid chlorine into chlorine gas. Steam or hot water jackets are used to provide the heat needed for vaporization. Temperature control is critical. Pressure relief through the use of a safety valve with a rupture disk is required for vaporizers. Careful attention must be given to the design and operation of such systems. Periodic cleaning is necessary and the manufacturer's recommendations should be followed (See CI Pamphlet 9).

#### 8.5 SUPPORT EQUIPMENT

#### 8.5.1 General

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.

#### 8.5.2 Vessels

The minimum fabrication standard for metal vessels operating at greater than 15 psig is that given in the ASME Code (Reference 11.5.1) for pressure vessels. Vessels operating at less than 15 psig have no ASME code requirements, but should be designed according to manufacturer's specification. Vessels in vacuum service require special designs to prevent collapse.

#### 8.5.3 Heat Exchangers

Heat exchangers should be designed and fabricated in accordance with the TEMA Standard and proper ASME material classifications and codes.

#### 8.5.4 Pumps

Pumps for chlor-alkali service are constructed of a wide range of materials. A supplier of such pumps should be contacted before use.

#### 8.5.5 Compressors and Blowers

Compressors and blowers should be built in accordance with the applicable ASME Code and supplier specifications.

#### 8.5.6 Scrubbers

While scrubbers are an effective means of absorbing chlorine, the need for a scrubber should be based on a site-specific hazard assessment. The design of the scrubber depends on the quantity of chlorine to be absorbed, the flow rate of air through the scrubber and the scrubbing liquid (See CI Pamphlet 89).

#### 8.6 <u>PIPING SYSTEMS FOR DRY CHLORINE</u>

Piping as described in this section pertains only to above ground fixed piping (See CI Pamphlet 6).

#### 8.6.1 Materials

In general, ASTM A106 Grade B Schedule 80 seamless carbon steel piping is recommended for handling dry chlorine when the process temperature range is from -20°F to 300°F (-29°C to 149°C). 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. Certain metal piping materials, including titanium, aluminum, gold, and tin, cannot be used with dry chlorine.

Some plastics can be used under certain conditions (See CI Pamphlet 6). Plastic piping can become brittle in chlorine service and has a limited service life. Periodic inspection and replacement is recommended.

- 8.6.2 Design and Installation
- 8.6.2.1 General Design

Piping arrangements should be routed for the shortest distance practical with respect to flexibility, line expansion, and good engineering practice.

Periodic inspection and replacement is recommended for all piping systems in chlorine service.

For detailed information on piping material selection and general design, see CI Pamphlet 6. Items that should be considered for piping design and are in CI Pamphlet 6 include:

- Liquid Expansion
- Condensation
- Installation
- Routing
- Valves
- Inspection and Maintenance
- Other Components
- Preparation of Systems for Use

#### 8.7 PIPING SYSTEMS FOR WET CHLORINE

Wet chlorine is very corrosive to all of the more common construction metals. Materials must be selected with care

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.

For higher pressures, lined metallic or compatible metallic systems should be used.

Hastelloy<sup>®</sup> C, titanium, and tantalum have been used.

Titanium may only be used with sufficiently 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°F (149°C).

#### 8.8 <u>STATIONARY STORAGE</u>

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 CI Pamphlet 5.

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 2.5.11.

#### 8.9 EQUIPMENT MAINTENANCE

#### 8.9.1 General

All chlorine piping and equipment should be carefully inspected on a regular basis. Inspections can be done using ultrasonic thickness testing, eddy current testing, magnetic flux testing, and other non destructive testing (See CI Pamphlet 6).

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. All significant piping or process changes must be followed by compliance with the "Management of Change" guidelines in the OSHA Process Safety Management (PSM) regulations.

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Decontamination is especially important where cutting or welding operations are undertaken because iron and steel will ignite in chlorine near 483°F (251°C). Immediate drying of chlorine equipment, piping, or containers into which water has been introduced or which has been opened for repairs or cleaning is essential to prevent corrosion.

Cleaning of piping and other equipment is addressed in CI Pamphlet 6.

8.9.2 Entering Tanks

Chlorine tank inspection, cleaning and repair are discussed in CI Pamphlet 5. OSHA has specific regulations concerning the entering of confined spaces. These regulations should be thoroughly understood and followed. See OSHA standard 29 CFR 1910.146.

## 9. U.S. REGULATIONS AND CODES

**Note**: The purpose of this section is to provide a list of some of the 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 regulations affecting chlorine.

- 9.1 OCCUPATIONAL SAFETY AND HEALTH REGULATIONS -29 CFR
- 9.1.1 Part 1904 Recording and Reporting Occupational Injuries and Illnesses
- 9.1.2 1910 Subpart E: Exit Routes, Emergency Action Plans, and Fire Prevention Plans
- 9.1.3 Section 1910.38 Emergency Action Plans
- 9.1.4 1910 Subpart G: Occupational Health and Environment Control
- 9.1.5 Section 1910.95 Occupational Noise Exposure.
- 9.1.6 1910 Subpart H: Hazardous Materials
- 9.1.7 Section 1910.119 Process Safety Management of Highly Hazardous Chemicals
- 9.1.8 Section 1910.120 Hazardous Waste Operations and Emergency Response
- 9.1.9 1910 Subpart I Personal Protective Equipment
- 9.1.10 1910.132 General Requirements
- 9.1.11 1910.133 Eye and Face Protection
- 9.1.12 1910.134 Respiratory Protection
- 9.1.13 1910.135 Head Protection

- 9.1.14 1910.136 Occupational Foot Protection
- 9.1.15 1910.137 Electrical Protection Devices
- 9.1.16 1910.138 Hand Protection
- 9.1.17 1910 Subpart J: General Environmental Controls
- 9.1.18 1910.146 Permit-Required Confined Space Entry
- 9.1.19 1910.147 The Control of Hazardous Energy (Lockout/tagout)
- 9.1.20 1910 Subpart K: Medical and First Aid
- 9.1.21 Section 1910.151 Medical Service and First Aid
- 9.1.22 1910 Subpart Z: Toxic and Hazardous Substances
- 9.1.23 Section 1910.1000 Air Contaminants
- 9.1.24 Section 1910.1020 Access to Employee Exposure and Medical Records
- 9.1.25 Section 1910.1200 Hazard Communications
- 9.2 NAVIGATION AND NAVIGABLE WATER REGULATIONS -33 CFR
- 9.2.1 Parts 1 to 26, Subchapter A General delegation of authority, rulemaking procedures, and enforcement regulations.
- 9.2.2 Part 126 Handling Explosives or Other Dangerous Cargoes Within or Contiguous to Waterfront Facilities

Requirements for waterfront facilities that handle hazardous materials.

9.2.3 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.

9.2.4 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).

9.2.5 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.

36	PAMPHLET 1
9.2.6	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.
9.2.7	Part 155 - Oil or Hazardous Material Pollution Prevention Regulations for Vessels
	Requirements to prevent and mitigate pollution from vessels while in navigable waters.
9.2.8	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.
9.2.9	Parts 160 to 167, Subchapter P - Ports and Waterways Safety
	Requirements for traffic management, port arrival notification, vessel navigational equipment
9.3	ENVIRONMENTAL REGULATIONS - 40 CFR: PROTECTION OF ENVIRONMENT
9.3.1	Part 61 - National Emissions Standards for Hazardous Air Pollutants
9.3.2	Part 68 - Chemical Accident Prevention Provisions
9.3.3	Part 82 - Protection of Stratospheric Ozone
9.3.4	Part 141 - National Primary Drinking Water Regulations
9.3.5	Part 152 - Pesticide Registration and Classification Procedures
9.3.6	Parts 260 to 269 - Hazardous Waste Management System
9.3.7	Part 261 - Identification and Listing of Hazardous Waste
9.3.8	Part 264 - Standards for Owners and Operators of Hazardous Waste Treatment
9.3.9	Part 265 - Interim Status Standards for Owners and Operators of Hazardous Waste
9.3.10	Part 266 - Standards for the Management of Specific Hazardous Wastes and Specific Types of Hazardous Waste Management Facilities.
9.3.11	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.

- 9.3.12 Parts 370 and 372 Hazardous Chemicals Reporting: Community Right to Know Requirements for providing the public with information on hazardous chemicals.
- 9.3.13 Part 415, Subpart F Effluent Guidelines/Chlor-Alkali Production

Effluent guidelines for chlorine production facilities.

9.3.14 Subchapter R, Parts 700 to 799 -Toxic Substances Control Act (TSCA)

Requirements for recordkeeping and reporting for various chemical substances.

- 9.4 Shipping Regulations 46 CFR (Water Transportation)
- 9.4.1 Part 2 Vessel Inspections

Requirements and procedures for obtaining vessel certification and approvals.

9.4.2 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. Requirements for the minimum manning of vessels.

9.4.3 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.

9.4.4 Part 151 - Barges Carrying Bulk Liquid Hazardous Materials Cargoes

Requirements for vessels carrying hazardous materials in barges. Regulations include barge design, equipment testing, and special requirements for specific hazardous cargoes including chlorine.

- 9.5 TRANSPORTATION REGULATIONS 49 CFR
- 9.5.1 Part 106 Rulemaking Procedures

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

9.5.2 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.

38	PAMPHLET 1
9.5.3	Part 171 - General Information, Regulations, Definitions
	Use and applicability of transportation regulations within and outside the U.S. in addition, reporting requirements for hazardous material incidents.
9.5.4	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.
9.5.5	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.
9.5.6	Part 174 - Carriage by Rail
	Requirements for handling, loading, unloading and storage of tank cars.
9.5.7	Part 176 - Carriage by Vessel
	Requirements for packaged hazardous materials transported by vessel.
9.5.8	Part 177 - Carriage by Public Highway
	Requirements on the handling, transportation, loading and unloading and segregation of hazardous materials.
9.5.9	Part 178 - Specifications for Packagings
	Specifications for cylinders, portable tanks, and cargo tanks.
9.5.10	Part 179 - Specifications for Tank Cars
	Design requirements and specifications for bulk rail tank cars.
9.5.11	Part 180 - Continuing Qualifications and Maintenance of Packagings
	Requirements for qualifying existing cargo tanks for hazardous materials.
9.5.12	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.
9.5.13	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.

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

Requirements for pipeline facilities and the transportation of gases.

9.5.15 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.

#### 9.6 DEPARTMENT OF HOMELAND SECURITY – 6 CFR

9.6.1 Part 27 - Chemical Facility Anti-Terrorism Standards

This rule establishes risk-based performance standards for the security of facilities producing, handling, storing, or using chemicals of concern. It requires covered chemical facilities to prepare Security Vulnerability Assessments (SVAs), which identify facility security vulnerabilities, and to develop and implement Site Security Plans (SSPs), which include measures that satisfy the identified risk-based performance standards.

#### 9.7 <u>FIRE CODES</u>

Numerous fire and building codes exist that affect chlorine production, storage, packaging, distribution, and use. To properly address these codes, the local government should be contacted to 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. New editions of the codes are published every third year. The code year is important in determining which code is applicable. The specific requirements are contained in the applicable code.

## 10. TECHNICAL DATA

For detailed information, refer to the following CI literature:

Pamphlet #	Title
6	Piping Systems for Dry Chlorine
72	Properties of Chlorine in SI Units
121	Explosive Properties of Gaseous Mixtures Containing Hydrogen and Chlorine

### 10.1 <u>General</u>

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.

10.2 ATOMIC AND MOLECULAR PROPERTIES

Atomic Symbol - Cl

Atomic Weight - 35.453

Atomic Number - 17

Molecular Weight of Cl<sub>2</sub> - 70.906

## 10.3 CHEMICAL PROPERTIES

## Table 6Physical Properties

	• •		
<b>Property</b> Boiling Point (Liquefying Point)	<b>Definition</b> The temperature at which liquid chlorine vaporizes	<b>Conditions</b> 14.696 psia (101.325 kPa)	<b>Value</b> -29.15°F (-33.97°C)
Critical Density	The mass of a unit volume of chlorine at the critical pressure and temperature		35.77 lb/ft <sup>3</sup> (573.0 kg/m <sup>3</sup> )
Critical Pressure	The vapor pressure of liquid chloride at the critical temperature		1157.0 psia (7977 kPa)
Critical Temperature	The temperature above which chlorine exists only as a gas no matter how great the pressure		290.75°F (143.75°C)
Critical Volume	The volume of a unit mass of chlorine at the critical pressure and temperature		0.02795 ft <sup>3</sup> /lb (0.001745 m <sup>3</sup> /kg)
Density	The mass of a unit volume of chlorine at specified conditions of temperature and pressure.		See Figure 10.2.
Density of Cl <sub>2</sub> Gas		32°F, 14.696 psia (0°C, 101.325 kPa)	0.2006 lb/ft <sup>3</sup> (3.213 kg/m <sup>3</sup> )
Density of Saturated Cl <sub>2</sub> Gas		32°F, 53.51 psia (0°C, 368.9 kPa)	0.7632lb/ft <sup>3</sup> (12.23 kg/m <sup>3</sup> )

Table 6	Physical Properties		
Property Density of Saturated Cl <sub>2</sub>	Definition	<b>Conditions</b> 32°F, 14.696 psia (0°C, 101.325 kPa)	<b>Value</b> 91.56 lb/ft <sup>3</sup> (1467 kg/m <sup>3</sup> )
Liquid		60°F, 86.58 psia	88.76 lb/ft <sup>3</sup> 11.87 lb/gal
		(15.6°C, 597.0 kPa)	(1422 kg/m <sup>3</sup> )
Latent Heat of Vaporization	The heat required to evaporate a unit weight of chlorine	At the normal boiling point	123.9 Btu/lb (288.1 kJ/kg)
Liquid-Gas Volume Relationship	The weight of one volume of liquid chlorine equals the weight of 456.5 volumes of chlorine gas.	32°F, 14.696 psia (0°C, 101.325 kPa)	
Melting Point (Freezing Point)	The temperature at which solid chlorine melts or liquid chlorine solidifies	14.696 psia (101.325 kPa)	-149.76°F (-100.98°C)
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.	60°F,14.696 psia (15.6°C,101.325 kPa)	6.93 lbs/100gal (8.30 kg/m <sup>3</sup> ) See Figure 10.3
Specific Gravity of Cl <sub>2</sub> Gas	The ratio of the density of chlorine gas at standard conditions to the density of air under the same conditions:	32°F, 14.696 psia (0°C, 101.325 kPa)	2.485 (Note: The density of air, free of moisture at the same conditions is 1.2929 kg/m <sup>3</sup> )
Specific Gravity of Cl <sub>2</sub> Liquid	The ratio of the density of saturated liquid chlorine to the density of water at its maximum density - 39°(4°C)	32°F (0°C)	1.467
Specific Heat	The heat required to raise the temperature of a unit weight of chlorine one degree.		
Saturated Gas at constant pressure		32°F (0°C) 77°F (25°C)	0.1244 Btu/lb·°F (0.521 kJ/kg·K) 0.1347 Btu/lb·°F (0.564 kJ/kg·K)

Table 6	Physical Properties		
<b>Property</b> Saturated Gas at constant volume	Definition	<b>Conditions</b> 32°F (0°C) 77°F (25°C)	Value 0.08887 Btu/lb·°F (0.372 kJ/kg·K) 0.09303 Btu/lb·°F (0.3895 kJ/kg·K)
Saturated Liquid		32°F (0°C) 77°F (25°C)	0.2264 Btu/lb•°F (0.948 kJ/kg•K) 0.2329 Btu/lb•°F (0.975 kJ/kg•K)
Ratio for Saturated Gas	Ratio of gas specific heat at constant pressure to gas specific heat at constant volume	32°F (0°C) 77°F (25°C)	1.400 1.448
Specific Volume	The volume of a unit mass of chlorine at specified conditions of temperature and pressure.		
Gas		32°F, 14.696 psia (0°C, 101.325 kPa)	4.986 ft <sup>3</sup> /lb (0.3113 m³/kg).
Saturated Gas		32°F (0°C)	1.310 ft <sup>3</sup> /lb (0.08179 m <sup>3</sup> /kg).
Saturated Liquid		32°F (0°C)	0.01092 ft <sup>3</sup> /lb (0.0006818 m <sup>3</sup> /kg)
Vapor Pressure	The absolute pressure of chlorine gas above liquid chlorine when they are in equilibrium	32°F (0°C) 77°F (25°C)	53.51 psia (368.9 kPa) 112.95 psia (778.8 kPa)
Viscosity	The measure of internal molecular friction when chlorine molecules are in motion		
Saturated Gas		32°F (0°C) 60°F (15.6°C)	0.0125 cP (0.0125 mPa•s) 0.0132 cP (0.0132 mPa•s)
Liquid		32°F (0°C) 60°F (15.6°C)	0.3863 cP (0.3863 mPa•s) 0.3538 cP (0.3538 mPa•s)

Table 6	Physical Properties		
<b>Property</b> Volume – Temperature Relationship	<b>Definition</b> Volume – Temperature relationship of liquid chlorine in a container loaded to its authorized limit	Conditions	<b>Value</b> Figure 10.4
Solubility of Water in liquid chlorine			Figure 10.5 and Figure 10.6

#### 10.3.1 Flammability

Chlorine is neither explosive nor flammable. Chlorine will support combustion under certain conditions. Many materials that burn in oxygen (air) atmospheres will also burn in chlorine atmospheres. Many organic chemicals react readily with chlorine, sometimes violently.

#### 10.3.2 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.

#### 10.3.3 Chemical Reactions

10.3.3.1 Reactions with Water

Chlorine is only slightly soluble in water (0.3% to 0.7%) depending on the water temperature.

#### 10.3.3.2 Reactions with Metals

The reaction rate of dry chlorine with most metals increases rapidly above a temperature which is characteristic for the metal. Consult CI Pamphlet 6 for detailed information on reactivity with metals.

10.3.3.3 Reactions with Other Elements

Chlorine unites under specific conditions with most of the elements; these reactions may be extremely rapid. Consult CI Pamphlet 121 for more information.

10.3.3.4 Reactions with Inorganic Compounds

See CI Pamphlet 21.

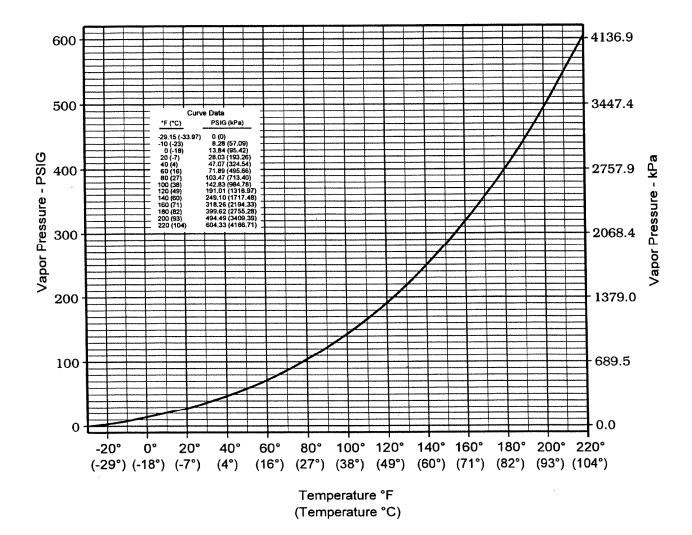
## 10.3.3.5 Reactions with Organic Compounds

Chlorine reacts with many organic compounds to form chlorinated derivatives. 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.

## 10.4 PHYSICAL PROPERTIES

Figure 10.1 through Figure 10.6 are for pure chlorine.

Figure 10.1 Vapor Pressure of Liquid Chorine (Calculated from data in CI Pamphlet 72)



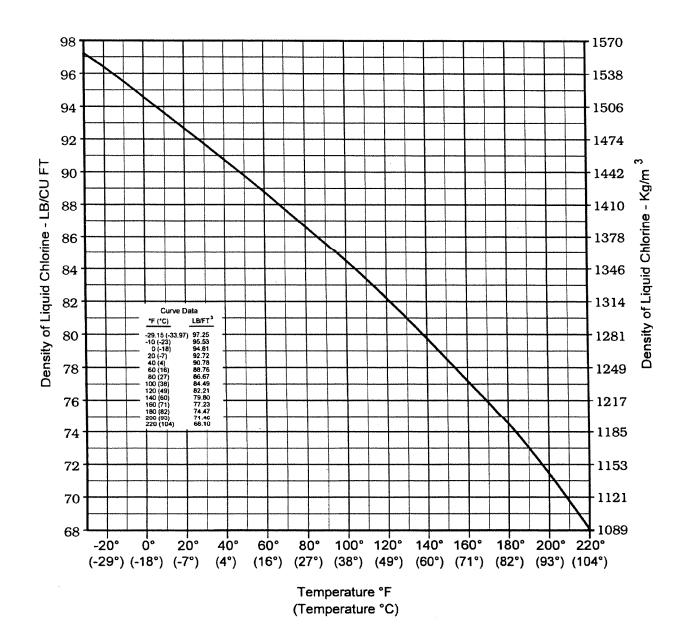


Figure 10.2 Temperature-Density Relation of Liquid Chlorine (Calculated from data in CI Pamphlet 72)

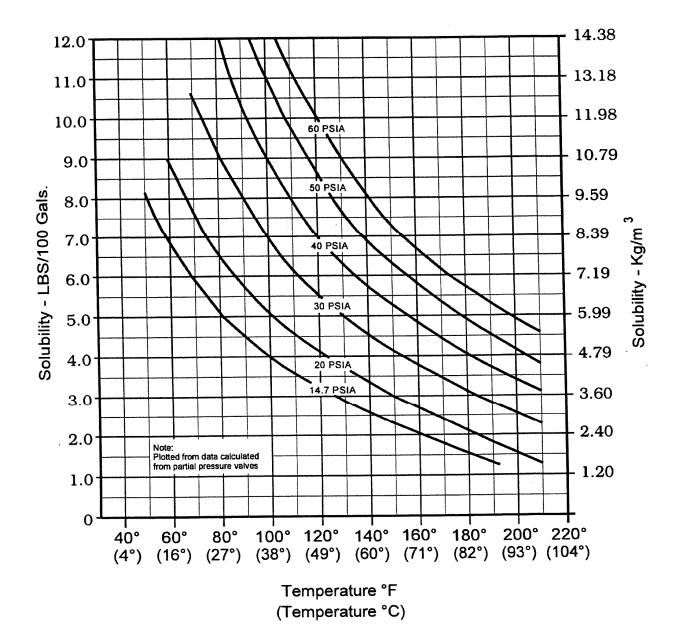


Figure 10.3 Equilibrium Solution of Chlorine In Water (Reference 11.18.1)

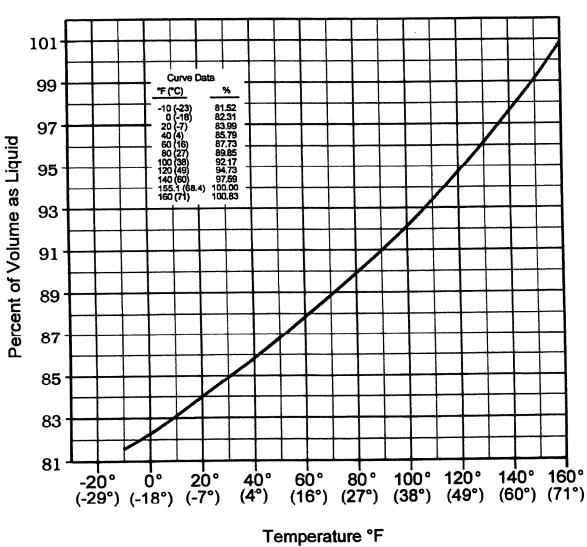


Figure 10.4 Volume-Temperature Relation of Liquid Chlorine in a Container Loaded to its Authorized Limit (Calculated from data in CI Pamphlet 72)

(Temperature °C)

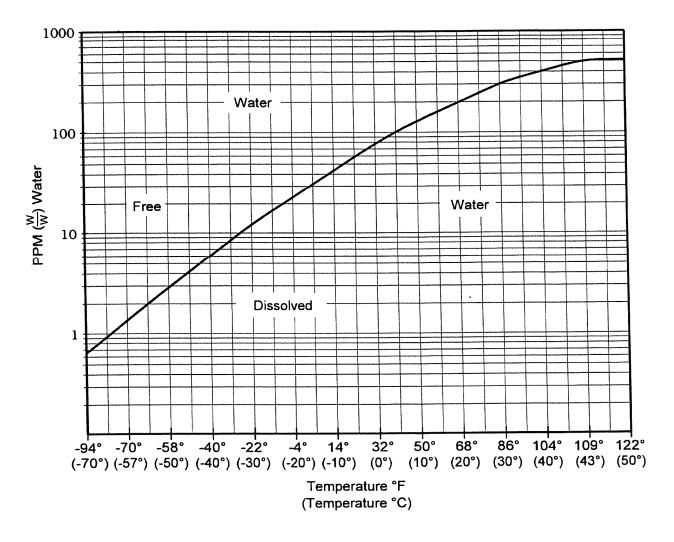


Figure 10.5 Solubility of Water in Liquid Chlorine (Reference CI Pamphlet 100)

Note: Above the curve, the chlorine is wet. Below the curve, the chlorine is dry.

The following are examples using this figure:

- Chlorine with a water content of 30 ppm at a temperature of 50°F (10°C) is dry. If this same chlorine 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.

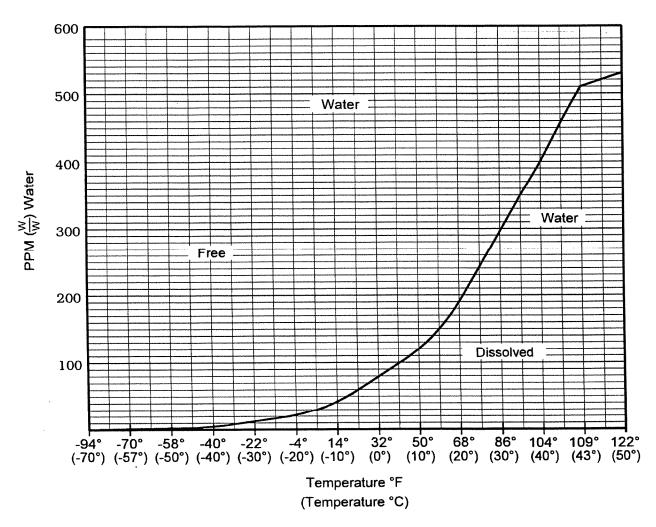


Figure 10.6 Solubility of Water in Liquid Chlorine (Reference CI Pamphlet 100)

**Note**: Above the curve, the chlorine is wet. Below the curve, the chlorine is dry. The following are examples using this figure:

- Chlorine with a water content of 30 ppm at a temperature of 50°F (10°C) is dry. If this same chlorine 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.

## 11. 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 pamphlet. The reader should be aware that changing technology or regulations may require a change in the reference cited.

## 11.1 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. <u>www.gpo.gov</u>

- 11.1.1 Code of Federal Regulations (CFR), Various Sections.
- 11.1.2 Chlorine Technical, Liquid; Federal Specification BB-C 120 C.

## 11.2 CANADIAN REGULATIONS

Most Canadian regulations can be obtained from the Canadian Government Publishing Center. <u>publications.gc.ca</u>

#### 11.3 CHLORINE INSTITUTE (CI)

1300 Wilson Boulevard Arlington, VA 22209 www.chlorineinstitute.org

## 11.3.1 Pamphlets and Instructional Booklets

Refer to the current CI catalog for a complete list of pamphlets.

#### Pamphlet # Title

- 5 Bulk Storage of Liquid Chlorine
- 6 Piping Systems for Dry Chlorine
- 9 Chlorine Vaporizing Systems
- 10 North American Chlor-Alkali Industry Plants and Production Data Reports
- 17 Packaging Plant Safety and Operational Guidelines
- 21 Nitrogen Trichloride A Collection of Reports and Papers
- 49 Recommended Practices for Handling Chlorine Bulk Highway Transports
- 57 Emergency Shut-Off Systems for Bulk Transfer of Chlorine
- 60 Chlorine Pipelines
- 63 First Aid, Medical Management/Surveillance and Occupational Hygiene Monitoring Practices for Chlorine

Pamphlet #	<u>Title</u>
64	Emergency Response Plans for Chlor-Alkali, Sodium Hypochlorite, and Hydrogen Chloride Facilities
65	Personal Protective Equipment for Chlor-Alkali Chemicals
66	Recommended Practices for Handling Chlorine Tank Cars
72	Properties of Chlorine in SI Units
73	Atmospheric Monitoring Equipment for Chlorine
74	Guidance on Complying with EPA Requirements under the Clean Air Act Estimating the Area Affected by a Chlorine Release
76	Guidelines for the Safe Motor Vehicular Transportation of Chlorine Cylinders and Ton Containers
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
91	Checklist for Chlorine Packaging Plants, Chlorine Distributors and Tank Car Users of Chlorine
95	Gaskets for Chlorine Service
100	Dry Chlorine: Definitions and Analytical Issues
121	Explosive Properties of Gaseous Mixtures Containing Hydrogen and Chlorine
139	Electrical Safety in Chlor-Alkali Cell Facilities
152	Safe Handling of Chlorine Containing Nitrogen Trichloride
155	Water and Wastewater Operators Chlorine Handbook
164	Reactivity and Compatibility of Chlorine and Sodium Hydroxide with Various Materials
165	Instrumentation for Chlorine Service
166	Angle Valve Guidelines for Chlorine Bulk Transportation
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

## 11.3.2 Drawings

Refer to the current CI catalog for a complete list of drawings.

11.3.3 Audio/Visual Materials

These materials are available in both English and Spanish (except H-VIDEO) and in both video and DVD format.

## Video/DVD Title

- A-VIDEO How to Use the Chlorine Institute Emergency Kit "A" for 100-lb. and 150-lb. Chlorine Cylinders
- B-VIDEO How to Use the Chlorine Institute Emergency Kit "B" for Chlorine Ton Containers
- C-VIDEO How to Use the Chlorine Institute Emergency Kit "C" for Chlorine Tank Cars and Tank Trucks
- H-VIDEO Health Effects from Short-Term Chlorine Exposure
- W-VIDEO Chlorine Safety for Water and Wastewater Operators

#### 11.4 AMERICAN CONFERENCE OF GOVERNMENTAL INDUSTRIAL HYGIENISTS (ACGIH)

1330 Kemper Meadow Drive Cincinnati, OH 45240 www.acgih.org

- 11.4.1 *Threshold Limit Values and Biological Exposure Indices*, Published Annually.
- 11.4.2 *Industrial Ventilation Manual: A Manual of Recommended Practices*, 22nd Edition, 1995.
- 11.5 AMERICAN SOCIETY OF MECHANICAL ENGINEERS (ASME)

3 Park Avenue New York, NY 10016-5990. www.asme.org

- 11.5.1 *Rules for Construction of Pressure Vessels*, Sections VIII, Division ASME Boiler, and Pressure Vessel Code ANSI/ASME BPV-VIII- 1.
- 11.6 ASTM INTERNATIONAL (ASTM)

(Formerly American Society for Testing and Materials) 100 Barr Harbor Drive P.O. Box C700 West Conshohocken, PA 19428-2959 www.astm.org

54	PAMPHLET 1	
11.6.1	ASTM-E4 10-92, Standard Method of Testing for Moisture and Residue in Liquid Chlorine.	
11.6.2	ASTM-E4 12-86, <i>Standard Method of Assaying Liquid Chlorine</i> (Zinc Amalgam Method).	
11.6.3	ASTM-E649-94, Standard Test Method for Bromine in Chlorine.	
11.6.4	ASTM-E806-93, Standard Test Method for the Determination of Carbon Tetrachloride and Chloroform in Liquid Chlorine by Direct Injection (Gas Chromatographic Procedure).	
11.6.5	ASTM-D2022-89, Standard Methods of Sampling and Chemical Analysis of Chlorine-Containing Bleaches.	
11.7	AMERICAN WATER WORKS ASSOCIATION (AWWA)	
	6666 West Quincy Avenue Denver, CO 80235. <u>www.awwa.org</u>	
11.8	ASSOCIATION OF AMERICAN RAILROADS (AAR)	
	50 F Street, NW Washington, DC 20001 <u>www.aar.org</u>	
11.9	COMPRESSED GAS ASSOCIATION (CGA)	
	4221 Walney Road, 5th Floor Chantilly, VA 20151 <u>www.cganet.com</u>	
11.9.1	Handbook of Compressed Gases Van Nostrand Reinhold, New York, NY.	
11.9.2	Pamphlet C-1, Methods for Hydrostatic Testing of Compressed Gas Cylinders.	
11.9.3	Pamphlet C-6, Standards for Visual Inspection of Compressed Gas Cylinders.	
11.9.4	Pamphlet P-1, Safe Handling of Compressed Gases in Containers.	
11.9.5	Pamphlet V-1, <i>Compressed Gas Cylinder Valve Outlet and Inlet Connections</i> (This pamphlet is also designated as ANSI B57.1 and CSA b96.)	
11.10	NATIONAL ACADEMY OF SCIENCES (NAS)	
	Printing and Publishing Office 500 Fifth Street, NW Washington, DC 20001 <u>www.nationalacademies.org</u>	

- 11.10.1 Water Chemicals Codex, 1982.
- 11.10.2 *Food Chemicals Codex V*, Fifth Edition, 2003.
- 11.11 NATIONAL FIRE PROTECTION ASSOCIATION (NFPA)

Batterymarch Park Quincy, MA 02169 www.nfpa.org

#### 11.12 NATIONAL INSTITUTE OF OCCUPATIONAL SAFETY AND HEALTH (NIOSH)

1600 Clifton Road Atlanta, GA 30333 www.cdc.gov/niosh/

Pocket Guide to Chemical Hazards, U.S. Department of Health and Human Services: 1994.

11.13 NATIONAL SAFETY COUNCIL

1121 Spring Lake Drive Itasca, IL 60143-3201 www.nsc.org

11.14 NSF INTERNATIONAL

789 N. Dixboro Road Ann Arbor, MI 48105 www.nsf.org

ANSI/NSF Standard 60 - Drinking Water Additives-Health Effects; updated annually.

11.15 THE HAMNER INSTITUTES FOR HEALTH SCIENCES

6 Davis Drive Research Triangle Park, NC 27709 www.thehamner.org

11.16 WATER ENVIRONMENT FEDERATION (WEF)

601 Wythe Street Alexandria, VA 22314 www.wef.org

11.17 WORLD HEALTH ORGANIZATION (WHO)

Avenue Appia 20 1211 Geneva 27, Switzerland www.who.int

Environmental Health Criteria 21 Chlorine and Hydrogen Chloride, 1982.

## 11.18 OTHER REFERENCES

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# 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 CancerTreatment 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





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