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Research and Development

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# Prevention Reference Manual: Chemical Specific

## Volume 9. Control of Accidental Releases of Chlorine



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PREVENTION REFERENCE MANUAL:  
CHEMICAL SPECIFIC  
VOLUME 9: CONTROL OF ACCIDENTAL  
RELEASES OF CHLORINE

By:

D.S. Davis  
G.B. DeWolf  
J.D. Quass  
K.P. Wert  
Radian Corporation  
Austin, Texas 78766

Contract No. 68-02-3994  
Work Assignment 94

EPA Project Officer

T. Kelly Janes  
Air and Energy Engineering Research Laboratory  
Research Triangle Park, North Carolina 27711

AIR AND ENERGY ENGINEERING RESEARCH LABORATORY  
OFFICE OF RESEARCH AND DEVELOPMENT  
U.S. ENVIRONMENTAL PROTECTION AGENCY  
RESEARCH TRIANGLE PARK, NC 27711

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## ABSTRACT

Recent headlines of accidental releases of toxic chemicals at Bhopal and Chernobyl have created the current public awareness of toxic release problems. As a result of other, perhaps less dramatic incidents in the past, portions of the chemical industry were aware of this problem long before these events. These same portions of the industry have made advances in this area. Interest in reducing the probability and consequences of accidental toxic chemical releases that might harm workers within a process facility and people in the surrounding community prompted the preparation of this manual and a planned series of companion manuals addressing accidental releases of toxic chemicals.

Chlorine has an IDLH (Immediately Dangerous to Life and Health) concentration of 25 ppm, which makes it a substantial acute toxic hazard.

Reducing the risk associated with an accidental release of chlorine involves identifying some of the potential causes of accidental releases that apply to the processes that use chlorine. In this manual examples of potential causes are identified as are specific measures that may be taken to reduce the accidental release risk. Such measures include recommendations on plant design practices, prevention, protection and mitigation technologies, and operation and maintenance practices. Conceptual cost estimates of possible prevention, protection, and mitigation measures are provided.

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## SECTION 1

### INTRODUCTION

#### 1.1 BACKGROUND

Increasing concern about the potentially disastrous consequences of accidental releases of toxic chemicals resulted from the Bhopal, India accident of December 3, 1984, which killed approximately 2,000 people and injured thousands more. A toxic cloud of methyl isocyanate was released. Concern about the safety of process facilities handling hazardous materials increased further after the accident at the Chernobyl nuclear power plant in the Soviet Union in April of 1986.

While headlines of these incidents have created the current awareness of toxic release problems, there have been other, perhaps less dramatic, incidents in the past. Interest in reducing the probability and consequences of accidental toxic chemical releases that might harm workers within a process facility and people in the surrounding community prompted the preparation of this manual and a planned series of companion manuals addressing accidental releases of toxic chemicals.

Historically, there have been a number of significant releases of chlorine both in the United States and in other areas of the globe. Between 1950 and 1976, 16 reported major chlorine releases caused a total of twelve fatalities and at least 633 injuries. The largest release occurred in 1967 in Newton, Alabama, when a rail tank car was punctured in a wreck. Over 50 tons of chlorine escaped, but no deaths occurred. The release with the highest fatalities occurred in 1952 in Wilson, West Germany, when a boiler which had been converted into a chlorine storage tank failed. Approximately 15 tons of chlorine escaped, killing seven people (1).

## 1.2 PURPOSE OF THIS MANUAL

The purpose of this manual is to provide technical information about the prevention of accidental releases of chlorine. The manual addresses technological and procedural issues related to release prevention, associated with the storage, handling, and process operations involving chlorine as it is used in the United States. This manual does not address uses of chlorine not encountered in the United States.

This manual is intended as a summary manual for persons charged with reviewing and evaluating the potential for releases at facilities that use, store, handle, or manufacture chlorine. It is not intended as a specification manual, and in fact refers the reader to additional technical manuals and other information sources for more complete information on the topics discussed. Other information sources include manufacturers and distributors of chlorine, and technical literature on design, operation, and loss prevention in facilities handling toxic chemicals.

## 1.3 USES OF CHLORINE

Chlorine ( $\text{Cl}_2$ ) is one of the major commodity chemicals used in industry. It is co-produced electrolytically with sodium hydroxide (caustic soda) from sodium chloride brine in specially designed cells. In 1979, the most productive year to date (1987), 12.3 million tons of chlorine gas and 7.3 million tons of liquid chlorine were produced as reported by the Chlorine Institute (2). In 1986, approximately 10.6 million tons of chlorine gas were produced (3).

The major industrial uses of chlorine include chemical synthesis of chlorinated chemicals, cooling tower water treatment, and disinfection of drinking water and wastewater. Approximately three-quarters of the total chlorine produced in the U.S. is consumed by the chemical industry (4).

Numerous references in the technical literature provide information on both the manufacture and uses of chlorine.

The predominant uses of chlorine in the U.S. include (2,4):

- Organic and inorganic chemical synthesis;
- Bleach manufacture;
- Cooling tower water treatment;
- Drinking water treatment;
- Wastewater disinfection; and
- Repackaging.

Major cooling tower water treatment users include oil refineries, power plants, and chemical plants. Wastewater disinfection and drinking water treatment are similar applications and take place predominantly in municipal or county facilities. General chemical synthesis includes the manufacture of chlorocarbons, chlorofluorocarbons, and a variety of other chlorinated organic and inorganic chemicals and products, including bleach products. Chlorine is also repackaged from bulk quantities into smaller cylinders for resale.

In the United States, chlorine is stored in small cylinders (e.g., 150 lb), one-ton cylinders, bulk storage tanks, railroad tank cars and tank trucks used for temporary stationary storage.

#### 1.4 ORGANIZATION OF THE MANUAL

Following this introductory section, the remainder of this manual presents technical information on specific hazards and categories of hazards for chlorine releases and their control. As stated previously, these are examples only and are representative of only some of the hazards that may be related to accidental releases.

Section 2 discusses physical, chemical and toxicological properties of chlorine. Section 3 describes the types of facilities which manufacture and use chlorine in the United States. Section 4 discusses process hazards associated with these facilities. Hazard prevention and control are discussed in Section 5. Costs of example storage and process facilities reflecting different levels of control are also presented in Section 5. The examples are for illustration only and do not necessarily represent a satisfactory alternative control option in all cases. Section 6 presents a reference list. Appendix A is a glossary of key technical terms that might not be familiar to all users of the manual and Appendix B presents selected conversion factors between metric (SI) and English measurement units.

## SECTION 2

### CHEMICAL CHARACTERISTICS

This section of the report describes the physical, chemical and toxicological properties of chlorine as they relate to accidental release hazards.

#### 2.1 PHYSICAL PROPERTIES

Chlorine is an elemental chemical which exists as a gas at ambient conditions, but liquifies at moderate pressures. Some of its common physical properties are listed in Table 2-1.

Chlorine is slightly water soluble. The yellow-green gas has a strong characteristic odor. Because chlorine gas is about 2.5 times more dense than air, it tends to stay close to the ground when released into the atmosphere. Liquid chlorine has a clear amber color; one volume of liquid can vaporize to about 460 volumes of gas.

Liquid chlorine has a large coefficient of thermal expansion as shown in Figure 2-1. As a result, liquid-full equipment can pose a special hazard. A liquid-full vessel is a vessel that is not vented and is filled with liquid chlorine with little or no vapor space present above the liquid. A liquid-full line is a section of pipe that is sealed off at both ends and is full of liquid chlorine with little or no vapor space. In these situations, there is no room for thermal expansion of the liquid, and temperature increases can result in containment failure.

#### 2.2 CHEMICAL PROPERTIES AND REACTIVITY

Chlorine is considered to be neither explosive nor flammable in the normal sense. However, chlorine is an oxidizer which will, like oxygen,

TABLE 2-1. PHYSICAL PROPERTIES OF CHLORINE

		Reference
CAS Registry Number	07782-50-5	
Chemical Formula	Cl <sub>2</sub>	
Molecular Weight	70.914	
Normal Boiling Point	-29.3 °F @ 14.7 psia	5
Melting Point	-149.8 °F	5
Liquid Specific Gravity (H <sub>2</sub> O = 1)	1.41 @ 68 °F	2
Vapor Specific Gravity (air = 1)	2.5 @ 68 °F	2
Vapor Pressure	93 psia @ 68 °F	6
Vapor Pressure Equation		7
$\log P_v = A - \frac{B}{T+C}$		
where: P <sub>v</sub> = vapor pressure, mmHg T = temperature, °C A = 6.93790, a constant B = 861.34, a constant C = 246.33, a constant		
Liquid Viscosity	0.345 centipoise	2
Solubility in Water	6.08 lb/100 gal @ 68 °F and 14.7 psia	2
Specific Heat at Constant Volume (Vapor)	0.085 Btu/(lb-°F) @ 59 °F	2
Specific Heat at Constant Pressure (Vapor)	0.115 Btu/(lb-°F)	2
Specific Heat at Constant Pressure (Liquid)	0.226 Btu/(lb-°F)	2

(Continued)

TABLE 2-1 (Continued)

		Reference
Latent Heat of Vaporization	123.8 Btu/lb @ -29.3 °F	2
Liquid Surface Tension	25.4 dynes/cm @ -22 °F	8
Average Coefficient of Thermal Expansion, 0-60 °F	0.00110/ °F	6
Additional properties useful in determining other properties from physical property correlations:		
Critical Temperature	291.2 °F	2
Critical Pressure	1118.36 psia	2
Critical Density	35.77 lb/ft <sup>3</sup>	8
Energy of Molecular Interaction	357 K	9
Effective Molecular Diameter	4.115 Angstroms	9

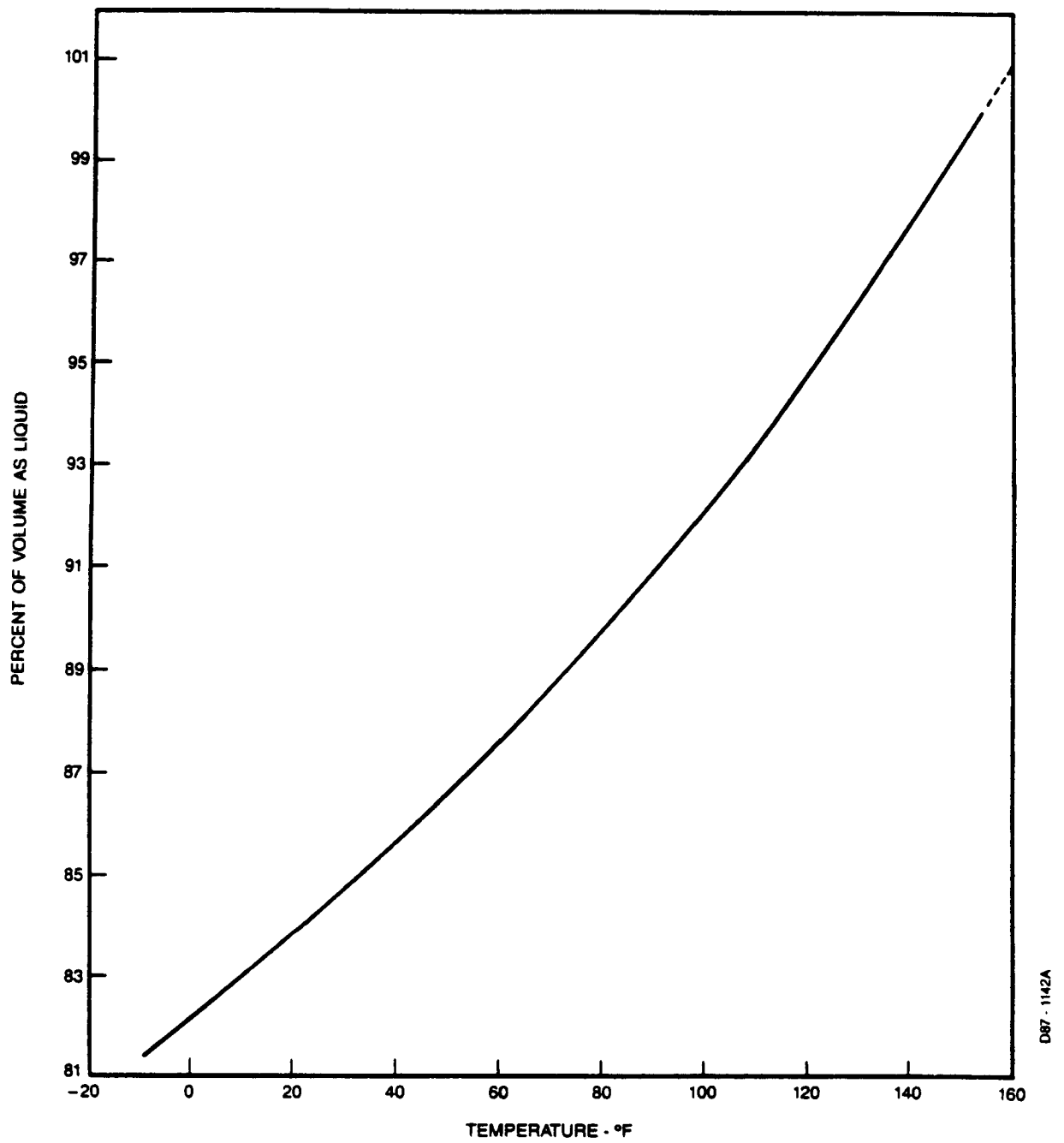


Figure 2-1. Volume - temperature relation of liquid chlorine in a container loaded to its authorized limit.

Source: Adapted from Reference 6.

support the burning of most combustible materials. Because chlorine is a strong oxidizer, it reacts readily with reducing agents. Chlorine will react with metals and other elements as well as inorganic and organic compounds. The most significant chemical properties contributing to the potential for accidental releases are as follows:

- As a result of hydrolysis, moist chlorine contains hydrochloric and hypochlorous acids which are very corrosive to most common metals. Dry chlorine, however, tends not to react with metals until an activation temperature specific to the metal has been reached. Above this temperature, the reaction proceeds rapidly; carbon steel, for example, ignites in chlorine at 483°F (10). Titanium ignites upon contact with dry chlorine at ambient temperatures. Chlorine also can react explosively with powdered metals.
- Under certain conditions, chlorine will react rapidly with most of the elements. It will, for example, react violently with hydrogen to form hydrogen chloride. This explosive reaction can take place if either component is present at concentrations greater than approximately 15 percent in a mixture (11).
- Because of its great affinity for hydrogen, chlorine tends to remove hydrogen atoms from other compounds. For example, chlorine reacts with hydrogen sulfide to form hydrogen chloride and sulfur. Chlorine combines with carbon monoxide to form phosgene and with sulfur dioxide to form sulfuryl chloride. Both of these reaction products are toxic and corrosive. Chlorine reacts with ammonia or ammonium compounds to form various mixtures of chloramines, depending on the conditions. One of these chloramines is nitrogen trichloride which becomes highly explosive, even at relatively low concentrations in the range of a few percent.

- Chlorine dissolves rapidly in strong alkali solutions to produce hypochlorite solution. When chlorine is absorbed in alkali solutions, excess chlorine causes an acid condition which promotes the release of large quantities of chlorine and oxygen. This decomposition can occur with explosive force (11).
- The strong oxidizing ability of chlorine allows it to react vigorously with organics to form chlorinated derivatives and hydrogen chloride. Flammable gases and vapors can form explosive mixtures with chlorine. Some of these compounds include gasoline, alcohols, ethers, acetylene, oils, greases, organic solvents, and other hydrocarbons.

### 2.3 TOXICOLOGICAL AND HEALTH EFFECTS

Chlorine is a highly toxic, severe skin and lung irritant. The toxicological effects of chlorine have been well documented, both through animal studies and accidental human exposure (12,13).

Exposure to low concentration of chlorine causes a stinging or burning sensation in the eyes, nose, and throat; choking; and sometimes headache due to irritation of the accessory nasal sinuses. There may be redness of the face, tearing, sneezing, coughing, and huskiness or loss of voice. Bleeding of the nose may occur and sputum from the larynx and trachea may be blood-tinged. Inhalation of chlorine in higher concentrations affects both the upper and lower respiratory tract and also produces pulmonary edema. The most pronounced symptoms are suffocation, constriction in the chest, and tightness in the throat. A concentration of 833 parts per million (ppm) breathed for 30 to 60 minutes has caused death (12). Skin contact with the liquid or vapor may result in ulceration and necrosis. Table 2-2 presents a summary of some of the relevant exposure limits for chlorine. Table 2-3 presents a summary of predicted human health effects of exposure to various concentrations of chlorine.

TABLE 2-2. EXPOSURE LIMITS FOR CHLORINE

Limit	Concentration (ppm)	Description	Reference
IDLH	25	The concentration defined as posing an immediate danger to life and health (i.e. causes irreversible toxic effects for a 30-minute exposure).	14
PEL	1	A time-weighted 8-hour exposure to this concentration, as set by the Occupational Safety and Health Administration (OSHA), should result in no adverse effects for the average worker.	13
TCLo	15	This concentration is the lowest published concentration causing toxic effects (irritation) for a 1-minute exposure.	13
LCLo	430	This concentration is the lowest published lethal concentration for a human over a 30-minute exposure.	13

TABLE 2-3. PREDICTED HUMAN HEALTH EFFECTS OF EXPOSURE TO VARIOUS CONCENTRATIONS OF CHLORINE

ppm	Predicted Effect
3.5	Odor threshold
4	Maximum concentration tolerated without serious effects for a 1-hour exposure
30	Minimum concentration known to cause coughing.
40-60	May be dangerous in 30 minutes.
1,000	Likely to be fatal after only a few deep breaths.

Source: Reference 2.

### SECTION 3

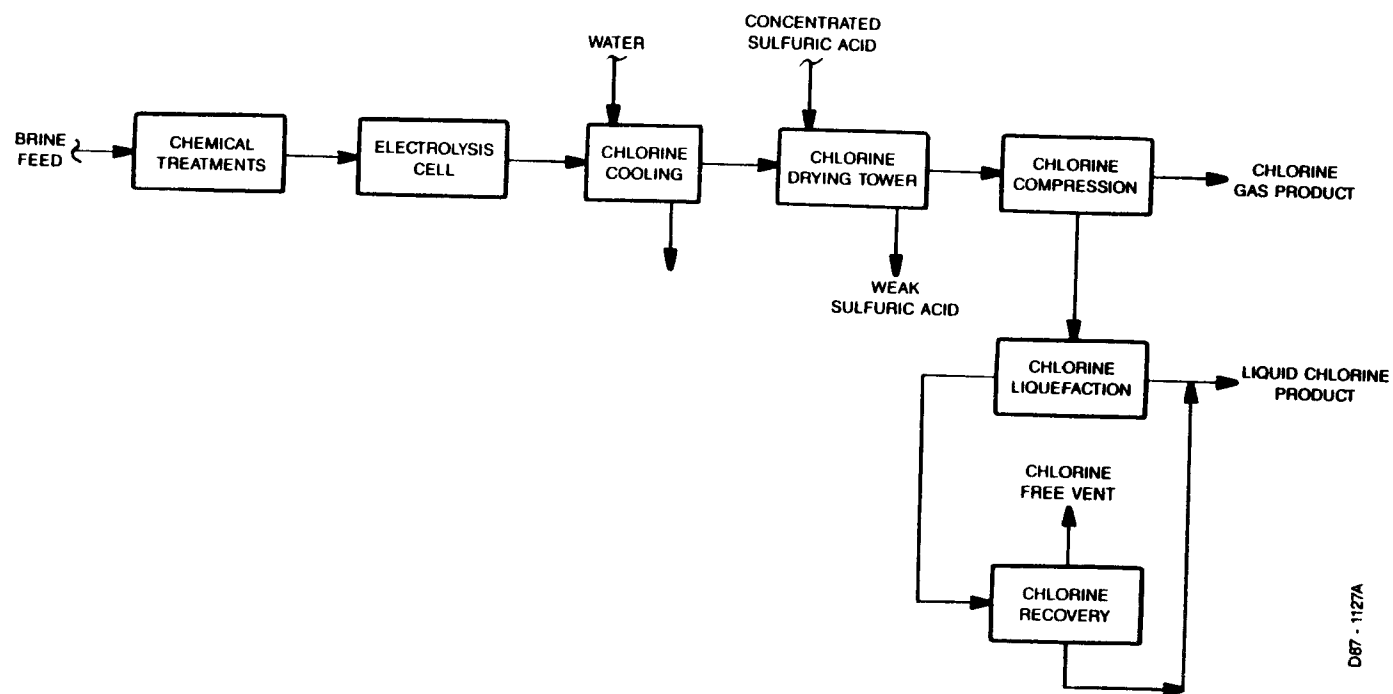
#### FACILITY DESCRIPTIONS

This section provides brief descriptions of the manufacture and uses of chlorine in the United States. Major hazards of these processes associated with accidental releases are discussed in Section 4. Preventive measures associated with these hazards are discussed in Section 5.

#### 3.1 CHLORINE MANUFACTURE

Chlorine is manufactured primarily by electrolysis of brine in three types of cells: diaphragm, mercury, and membrane. Approximately 95 percent of U.S. chlorine is produced in such cells, with diaphragm cells being the predominant method (4). Other methods of production including the electrolysis and the oxidation of hydrochloric acid are also used on a limited scale. Such methods are not a major source of chlorine. A flow diagram of a typical chlorine manufacturing process using a diaphragm cell is shown in Figure 3-1.

In a typical diaphragm cell, sodium or potassium chloride brine is electrolyzed to chlorine gas at a graphite, impregnated carbon, or titanium or tantalum based dimensionally stable (DSA®) anode. Sodium or potassium ions from the brine migrate through an asbestos diaphragm to the cathode, where sodium or potassium hydroxide is formed and hydrogen gas is liberated. The diaphragm cell typically operates at a temperature in the range of 176-210°F (15). The electrolyte is heated by the passage of current through the cell resistance. The gas leaving the anode is highly corrosive wet chlorine containing oxygen, nitrogen, hydrogen, and/or carbon dioxide, depending on the exact cell type used. The wet chlorine is cooled either in titanium heat exchangers or by direct contact with water in a packed tower and then dried by countercurrent scrubbing with sulfuric acid in a contact tower. The dried



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Figure 3-1. Conceptual process diagram of typical chlorine manufacturing process.

chlorine is either transported as a gas by pipeline to point of use or is compressed, liquified, and pumped to storage tanks.

The membrane cell process is similar to the diaphragm cell in that chlorine and hydrogen are co-produced by the electrolysis of a saturated brine solution. However, an ion exchange polymer membrane serves to prevent chlorine and hydrogen from coming in contact.

The mercury cell process differs from the diaphragm cell in that the cathode is a moving bed of mercury. As in the diaphragm cell, chlorine accumulates at the anode, but the sodium or potassium ions form an amalgam with mercury at the cathode. The dilute amalgam is then fed to a decomposer (packed-bed reactor) where it reacts with water to form sodium hydroxide, hydrogen, and mercury. The mercury is then recycled to the electrolysis cell.

High hazard areas in chlorine manufacture, excluding bulk storage and transfer, which are discussed separately in Section 3, include the following:

- Electrolysis cell,
- Chlorine cooling,
- Acid scrubber,
- Chlorine compressor, and
- Chlorine liquefaction.

The electrolysis cell is a critical area of the process since a potentially hazardous situation exists as a result of combination of chlorine and hydrogen, and hydrogen and oxygen present in the same manufacturing system. If the gases are allowed to contact, a highly explosive mixture could result. When the concentrations of both chlorine and hydrogen are both greater than approximately fifteen percent, the mixture can explode when initiated thermally or by U.V. radiation (11). Likewise, combination of hydrogen with air at hydrogen levels above four percent can also lead to fire and/or explosions. Additionally, since wet chlorine is produced in the cell, corrosion leading to

equipment failure is possible. A properly designed system should use materials which take this into account.

The cooling section of the process is subject to the corrosive attack of wet chlorine. A properly designed system should use materials of construction, such as titanium, which take this corrosion potential into account. Undetected corrosion could eventually result in equipment failure and release of chlorine. Overpressure and release of chlorine through a relief valve could occur with loss of cooling. In addition, loss of cooling could result in insufficient drying in the acid scrubber since this operation is temperature sensitive, requiring more acid at higher temperatures (see below).

Proper operation of the sulfuric acid scrubber is important in preventing a hazardous release. Since the scrubber is used to dry the chlorine, a loss of or insufficient flow of sulfuric acid would result in corrosive wet chlorine being sent to downstream processing with possible equipment failure from corrosive attack. If packed towers are used, an additional hazard can result from sulfuric acid reacting with residual caustic soda present in the chlorine gas to form solid sodium sulfate over a long period of time. This could eventually lead to plugging of the packing or process piping and result in overpressure.

The chlorine compression section presents hazards of overpressure of a pressurized gas system and possible compressor failure from corrosion caused by insufficient water removal from the chlorine gas.

One potentially hazardous by-product of chlorine manufacture is nitrogen trichloride. Nitrogen trichloride is unstable and highly explosive. It can be formed from a combination of chlorine with nitrogen compounds in the brine feed, ammonia in the water used in direct-contact cooling, or nitrogen compounds in sulfuric acid used in chlorine drying. If chlorine containing nitrogen trichloride is evaporated, explosive concentrations of nitrogen trichloride may be reached.

An additional consideration in chlorine manufacture is the potential presence of various noncondensable gases (i.e., carbon dioxide, oxygen, air, hydrogen) in the raw chlorine from the electrolysis cell. As the chlorine is condensed from the system during the liquefaction stage, the amount of noncondensibles in the liquefaction equipment increases. These must be purged in order to prevent overpressure. Liquefaction is controlled so that the hydrogen gas concentration in the residual gas stream is maintained below 5%. This level of hydrogen is reported to be safe from explosion under all conditions of operation (i.e., temperature, pressure, and composition) (16).

### 3.2 CHLORINE CONSUMPTION

The most important industrial uses of chlorine are based on its general reactivity and its properties as an oxidizer. Table 3-1 presents a listing of some of the end uses of chlorine. Aliphatic organic compounds are chlorinated through addition and substitution reactions; aromatic organic compounds are chlorinated in a substitution process. Chlorine is also used to produce a wide variety of inorganic chemicals; bleach production is a major use of chlorine. The primary application for chlorine is based on its oxidizing properties for water treatment. This includes drinking water, wastewater and sewage, and cooling tower water where chlorination kills microorganisms and oxidizes some organic compounds.

This subsection summarizes the major technical features, related to release hazards, of typical chlorine processing facilities that might be found in the United States.

#### 3.2.1 Drinking Water, Wastewater, and Cooling Tower Chlorination

Conventional chlorination facilities are composed of three parts: chlorine supply, metering system, and injector system. A typical water chlorination system is shown in Figure 3-2. In some systems, chlorine gas is

TABLE 3-1. TYPICAL USES OF CHLORINE

## o Organic Chemical Manufacture

allyl chloride

amyl chloride

benzene hexachloride

carbon tetrachloride

chloral

chlorinated naphthalenes

chlorinated paraffins

chlorinated waxes

chloroacetic acid

chloroacetyl chloride

chloroanilines

chloroanthraquinone

chlorobenzene

chlorofluoro hydrocarbons

chloroform

chlorophenols

chloroprene

chlorosulfonic acid

chlorotoluenes

dichlorobenzenes

2-4-dichlorophenoxyacetic acid

dichloropropane

dichloropropenes

ethyl chloride

ethylene dichloride

hexachlorocyclopentadiene

hexachloroethane

methallyl chloride

methyl chloride

methylene chloride

perchloroethylene

perchloromethyl mercaptan

phosgene

polychlorinated biphenyls

tetrachlorobenzene

tetrachlorophthalic anhydride

trichlorobenzene

1,1,1-trichloroethane

1,1,2-trichloroethane

trichloroethylene

2,4,5-trichlorophenoxy-acetic acid

## o Inorganic Chemical Manufacture

anhydrous aluminum chloride

antimony pentachloride

antimony trichloride

arsenic trichloride

bismuth trichloride

chlorinated isocyanurates

chlorine trifluoride

ferric chloride

hydrochloric acid

iodine monochloride

iodine trichloride

mercuric chloride

mercurous chloride

molybdenum pentachloride

phosphorus oxychloride

phosphorus pentachloride

phosphorus trichloride

silicon tetrachloride

sulfur dichloride

sulfur monochloride

sulfuryl chloride

stannous chloride

titanium tetrachloride

titanium trichloride

zinc chloride

## o Bleach Manufacture

## o Sanitizing and Disinfecting Agent

(e.g., for municipal water supplies, swimming pools)

## o Waste and Sewage Treatment

## o Slimicide

Source: Adapted from Reference 17.

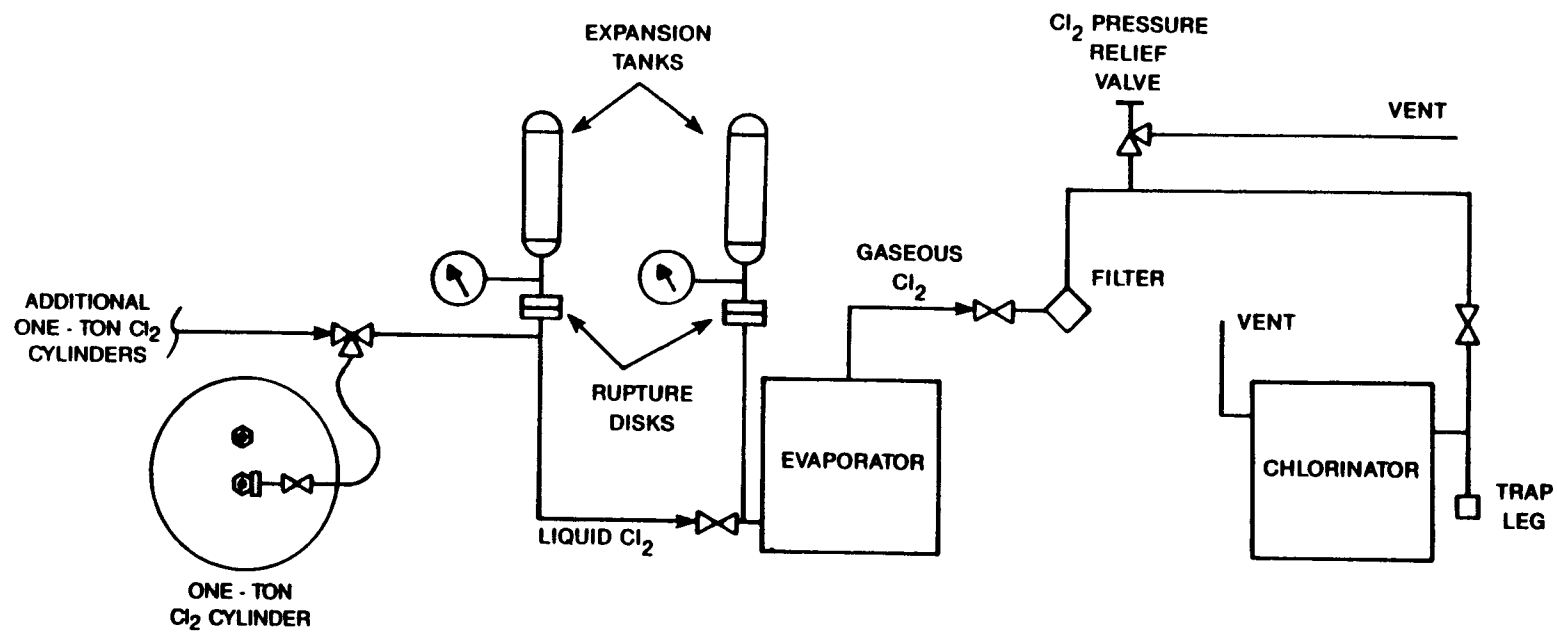


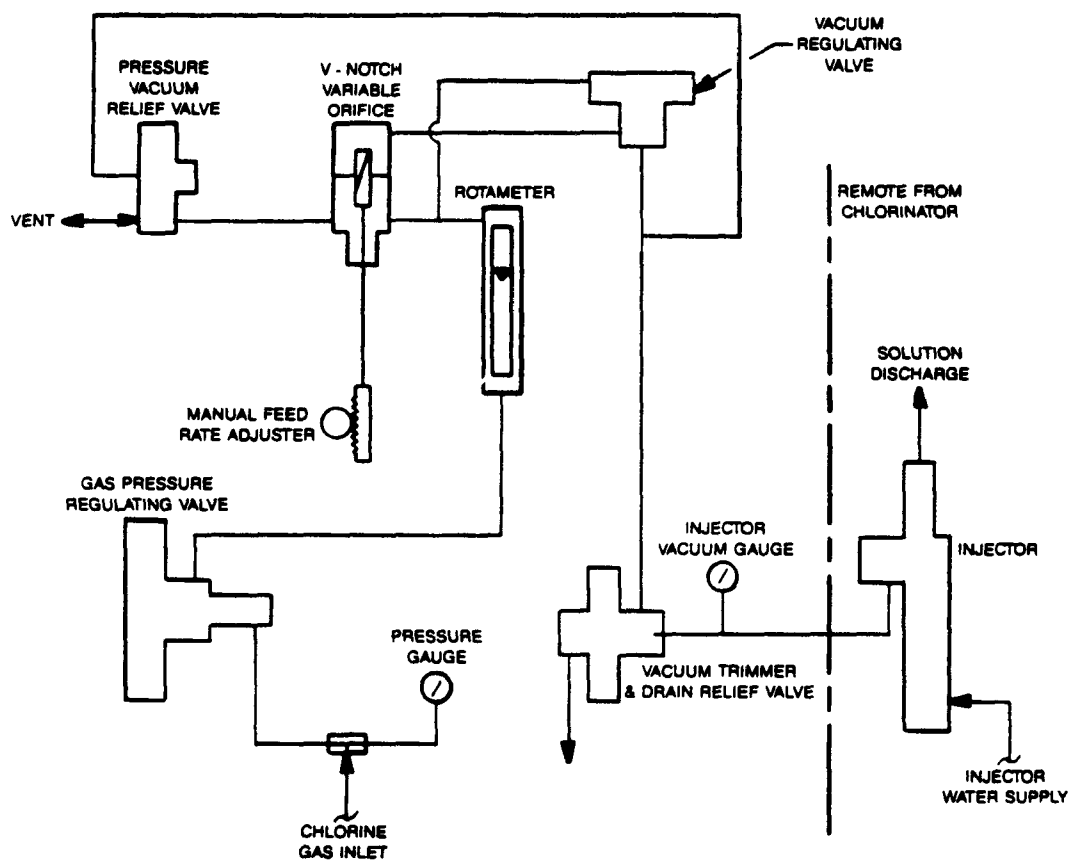
Figure 3-2. Conceptual process diagram of typical liquid chlorine feed water chlorination system.

fed directly to the chlorinator instead of a liquid feed-evaporator system as shown.

For chlorine supply, most facilities use chlorine packaged in containers ranging from 150-pound cylinders to single unit tank cars.

The chlorine gas metering system in a chlorination facility is known as the chlorinator. As shown in Figure 3-3, it consists of an inlet chlorine pressure regulating valve, a rotameter, a chlorine orifice, a manual feed rate adjuster, a vacuum differential regulating valve, a pressure-vacuum relief valve, and an injector. The vacuum created as water flows through the injector first opens the differential regulating valve, then the vacuum relief valve. This allows air to enter the system. This vacuum is also exerted on the inlet chlorine pressure regulating valve, allowing it to open, so that when the chlorine supply is open, the gas will flow through to the injector. As soon as the gas satisfies the vacuum created by the injector, the vacuum relief valve automatically closes, stopping the flow of air into the chlorinator. The following items are required for the safe control and operation of a chlorinator:

- Inlet chlorine pressure-reducing valve to reduce the cylinder pressure to a constant downstream pressure less than atmospheric;
- Manually and automatically adjustable chlorine metering orifice;
- Automatic pressure vacuum relief device;
- Rotameter for indicating chlorine feed rate;
- Differential vacuum regulating valve; and



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Figure 3-3. Conceptual diagram of typical chlorinator.

Source: Adapted from Reference 2.

- Chlorine pressure and injector vacuum gauges.

The injector is the primary functional component of the chlorinator. It develops the vacuum which causes the chlorine to flow from the storage supply through the chlorinator and then into itself. At the injector, the chlorine dissolves in water to form hypochlorous acid. This solution flows in the lines to the point of application. The injector system is usually composed of the following items:

- Water pressure gauge;
- Back pressure gauge located immediately downstream from the injector;
- Water pressure switch for the low water pressure alarm; and
- Water flow meters.

Remotely located injectors usually have a vacuum gauge and a vacuum line shutoff valve.

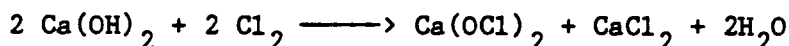
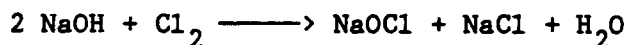
Additional information concerning the various types of chlorination facilities, equipment used, and specific design considerations is available from White (2).

The primary hazards associated with chlorination systems arise from the large inventory of stored chlorine and the chlorine evaporator. Excess feed to the evaporator or overheating could lead to overpressure and a possible release. The possibility of liquid chlorine feed lines being blocked while liquid full also presents a possibility of chlorine release.

Hazards associated with handling and hookup of chlorine cylinders or containers include human errors that could cause damage, or faulty connections that could lead to a release. A chlorine container that is improperly connected to the feed system could result in backflow of water into the cylinder, and internal corrosion which might go undetected until a failure occurs. Nitrogen is sometimes used for padding a chlorine feed tank or cylinder. The possibility exists for chlorine to enter a nitrogen line if the system is not designed correctly.

### 3.2.2 Bleach Production

Bleach is a hypochlorite solution prepared by chlorination of sodium hydroxide or calcium hydroxide. The respective reactions are as follows.

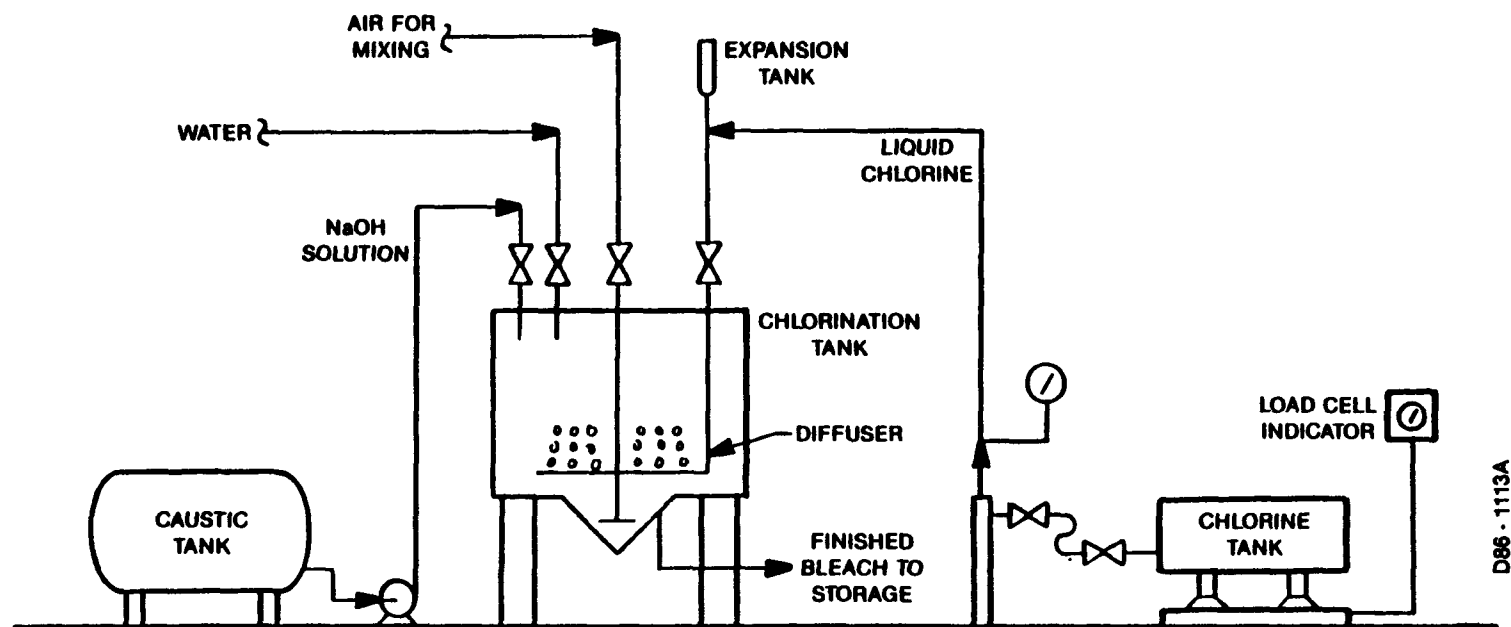


In both processes, chlorine is injected through sparge tubes into the caustic or lime solution. Sodium hypochlorite is referred to as liquid bleach; calcium hypochlorite is commonly called bleach liquor.

Liquid bleach is produced in stirred tank reactors, both batch and continuous, as well as continuous packed-tube reactors. Typical stirred tank reactor systems are shown in Figure 3-4 and Figure 3-5. Bleach liquor is also produced by both methods, but continuous production is preferred because of lower maintenance requirements.

Bleach production processes may include the following areas in which problems can lead to highly hazardous conditions:

- Reaction stability (a function of solution pH);
- Chlorine feed rate control system;



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Figure 3-4. Conceptual process diagram of typical batch sodium hypochlorite process.

Source: Adapted from Reference 18.

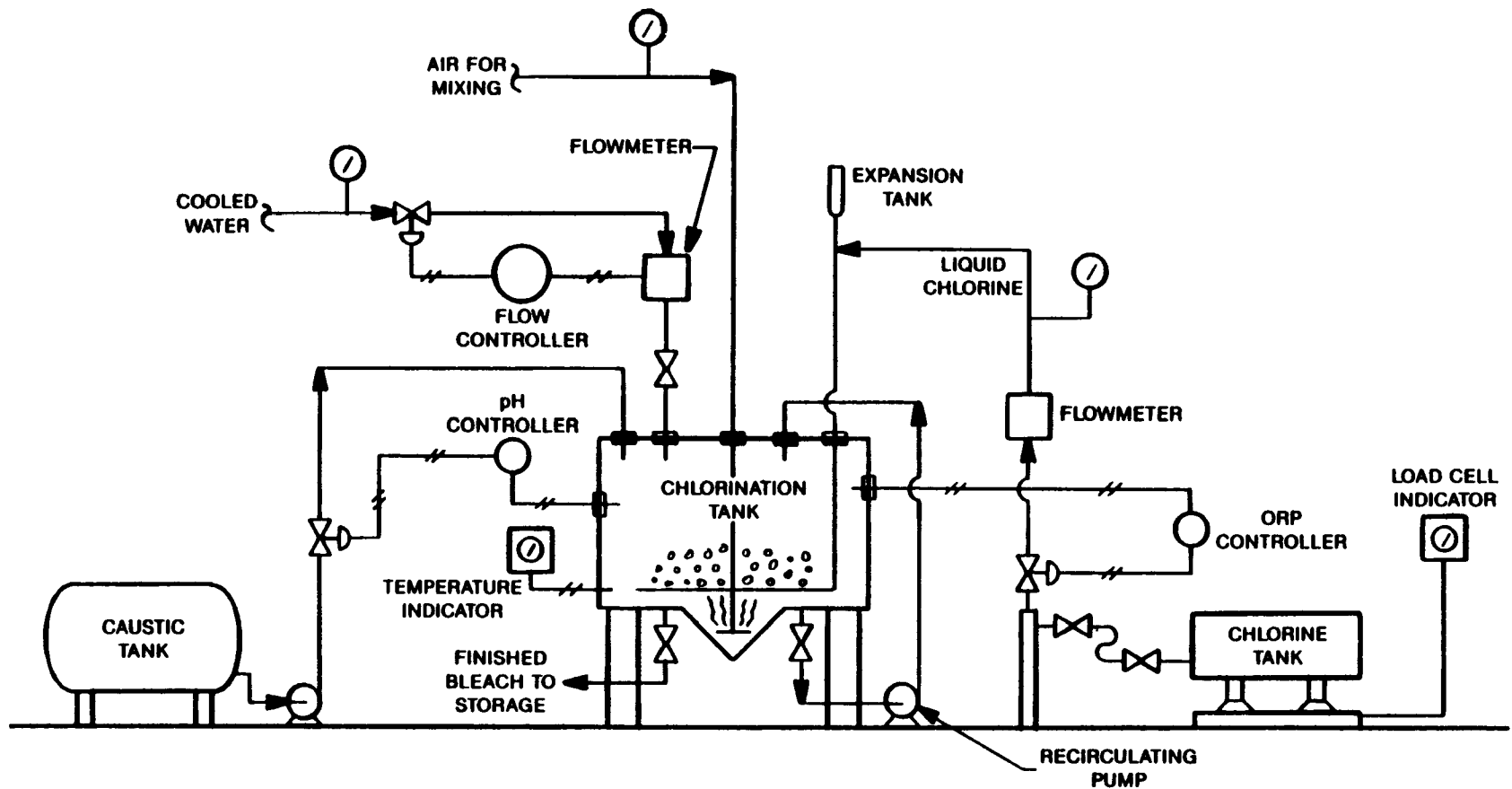


Figure 3-5. Conceptual process diagram of typical continuous sodium hypochlorite manufacturing process.

Source: Adapted from Reference 18.

- Reactor cooling system; and
- Batch reactor agitation.

When chlorine is absorbed in alkali solutions, the stability of the process is pH dependent. The pH of the solution should be monitored to ensure that there is free alkali present, since excess chlorine can promote an acid condition causing the release of chlorine and oxygen. This decomposition can occur explosively (11). Poor control of the chlorine feed rate could cause such a process failure.

Chlorination of caustics is exothermic and liberates 24.65 kcal/mol when chlorine gas is used. Reactor cooling is required, which is partially achieved using liquid chlorine feed. Thorough agitation is necessary to prevent local overchlorination as well as to improve the effectiveness of both the cooling system and the oxidation potentiometer used to monitor the reaction (11). The primary hazard is a runaway reaction from an excess chlorine feed rate, cooling system failure, or loss of agitation.

### 3.2.3 Chlorohydrocarbon Manufacture

Chlorohydrocarbons (chlorocarbons) are manufactured by the chlorination of hydrocarbon feedstock. A typical chlorocarbon manufacturing process is presented in Figure 3-6.

The dominant types of chlorination processes are:

- Thermal chlorination,
- Photochemical chlorination, and
- Catalytic chlorination.

Table 3-2 presents a list of typical organic chemicals prepared by these processes and brief details about the specific systems used.

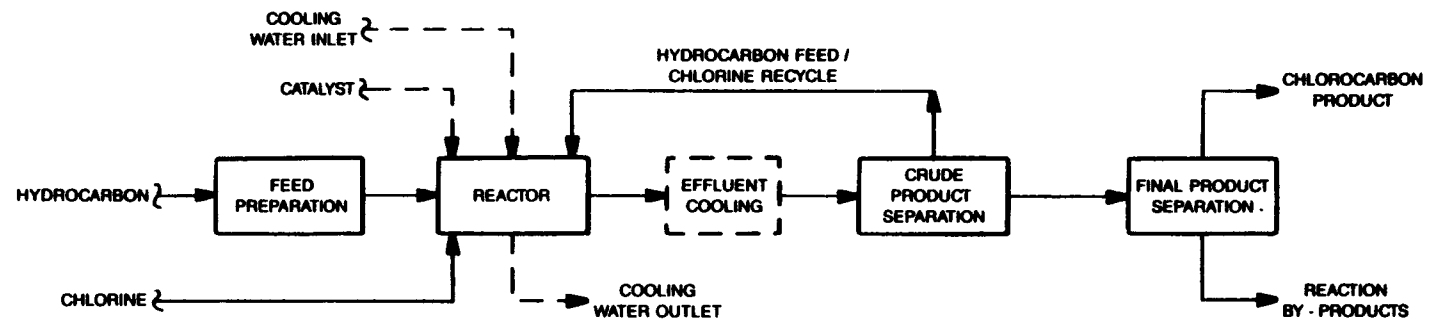


Figure 3-6. Conceptual process diagram of typical chlorohydrocarbon manufacturing process.

TABLE 3-2. TYPICAL CHLOROHYDROCARBONS MANUFACTURED FROM CHLORINE AND HYDROCARBON FEEDSTOCKS

Organic Chemical	Chlorination Type	Reaction Phase	Reactants	Reactor Temperature [°F]	Reactor Pressure [psig]
Allyl Chloride	Thermal	Vapor	Chlorine, propylene	932-950	15
Ethyl Chloride	Thermal	Vapor	Chlorine ethane	716-824	15
Trichloroethylene	Heterogeneous Catalytic	Vapor	Chlorine, dichloroethane	536-842	-
Benzyl Chloride	Thermal or Photochemical	Liquid	Chlorine, toluene	149-212	-
Benzene Hexachloride	Photochemical	Liquid	Chlorine, benzene	59-77	0
Chlorobenzene	Homogeneous Catalytic	Liquid	Chlorine, benzene ferric chloride (catalyst)	-	-
Chlorinated Paraffins	Photochemical	Liquid	Chlorine, liquid paraffin	194-212	-
Methyl Chloride	Thermal	Vapor	Chlorine, methane	752	-
Methylene Chloride	Thermal	Vapor	Chlorine, methane	905-950	-
Perchloroethylene	Thermal	Vapor	Chlorine, ethylene	1,022-1,292	-
	Heterogeneous Catalytic	Vapor	Chlorine, methane Fuller's earth (catalyst)	572	-

(Continued)

TABLE 3-2. TYPICAL CHLOROHYDROCARBONS MANUFACTURED FROM CHLORINE AND HYDROCARBON FEEDSTOCKS (Con't)

Organic Chemical	Chlorination Type	Reaction Phase	Reactants	Reactor Temperature [°F]	Reactor Pressure [psig]
Carbon Tetrachloride	Thermal	Vapor	Chlorine, methane	914-1,292	-
	Heterogeneous Catalytic	Vapor	Chlorine, methane Fuller's earth (catalyst)	572	-
Chloroform	Thermal	Vapor	Chlorine, methane	905-950	-
Tetrachloroethylene	Thermal Heterogeneous Catalytic	Vapor	Chlorine, ethane/ propane, ethylene dichloride, chlorine, steam, oxygen	1,022-1,292	-
				797	5-15
Chloroprene	Thermal	Vapor	Chlorine, butadiene	554-626	-
Ethylene Dichloride	Homogeneous Catalytic	Liquid	Chlorine, ethylene, ferric chloride (catalyst)	122-149	-
Hexachloroethane	Homogeneous Catalytic	Liquid	Chlorine, tetrachlo- roethylene, ferric chloride (catalyst)	212-284	-

Source: Reference (11).

### Thermal Chlorination--

Thermal chlorination uses thermal energy to initiate and carry out the reaction between chlorine and a hydrocarbon feedstock. Thermal chlorination reactions are typically gas phase reactions in continuous tubular or fluidized bed reactors. Operating temperatures in excess of 482°F are required for such reactions (11).

### Photochemical Chlorination--

Photochemical chlorination uses ultraviolet light as the energy source for reacting chlorine with a hydrocarbon feedstock. Photochemical chlorination reactions are typically carried out at temperatures ranging from 32-257°F (11). Photochemical reactors can be batch or continuously operated. Figure 3-7 shows examples of both batch and continuous reactors. A typical batch reactor consists of a large, stirred, jacketed vessel with lamps inserted through the top. The lamps are usually nitrogen blanketed and water cooled. A typical continuous reactor is tubular, with individual lamps positioned along its longitudinal axis.

### Catalytic Chlorination--

Catalytic chlorination uses a catalyst to enhance the chlorination reaction rate between chlorine and a hydrocarbon feedstock. Catalytic chlorination can be homogeneous or heterogeneous.

Homogeneous Catalytic Chlorination--in homogeneous catalytic chlorination the catalyst is dissolved in a liquid reaction medium. Homogeneous catalytic reaction systems can be batch or continuous. Batch reactors are typically stirred tanks and continuous reactors are either stirred tank or tubular reactors.

Heterogeneous Catalytic Chlorination--Heterogeneous catalytic chlorination processes use a solid catalyst with reactants in a gas or liquid phase. Heterogeneous catalytic reactors are typically continuous fixed bed (packed bed) or fluidized bed reactors.

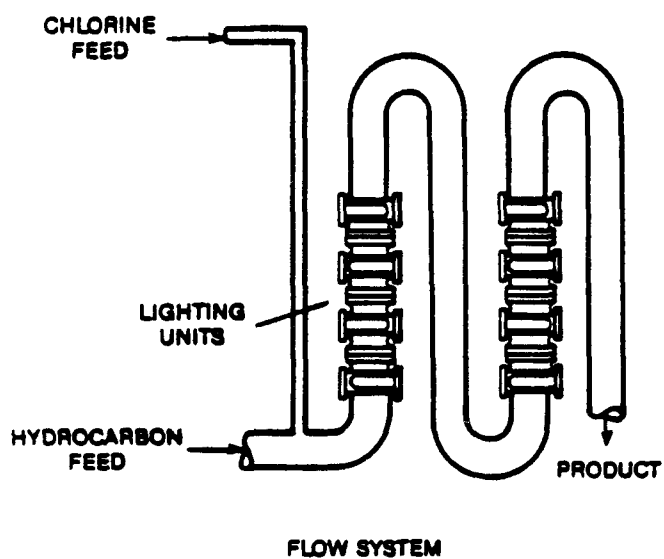
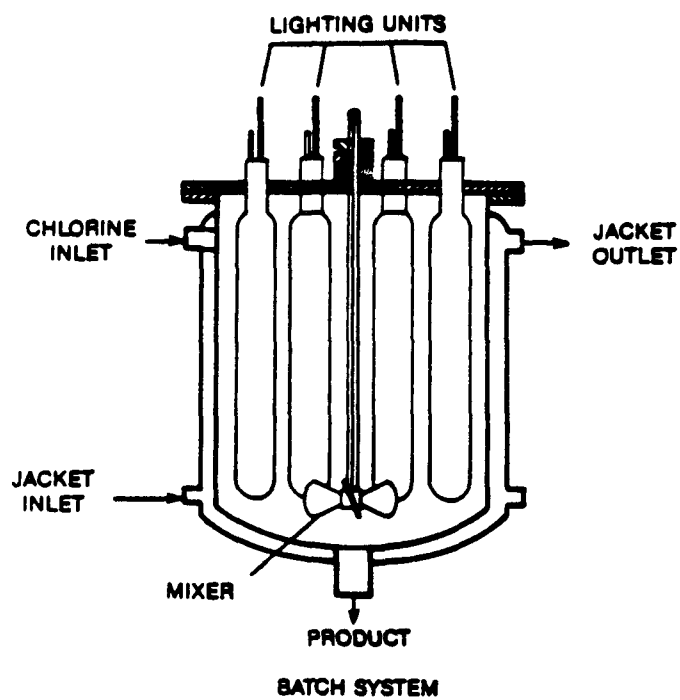


Figure 3-7. Photochlorination reactors.

Source: Adapted from Reference 11

High hazard areas in these processes include:

- Chlorine feed rate control,
- High temperature reactors,
- Reactor cooling system,
- Cooling of lamps (in photochemical processes),
- Mixing of reactants,
- Seals on the reactor head or stirrer shaft, and
- Chlorine recycle circuits.

An excessively high chlorine feed rate could result in overpressurizing the reactor or cause unreacted chlorine to pass through the reactor to downstream processing where it might cause a process upset leading to overpressure or emergency venting. In addition, in fluidized bed reactors, carry over of solid particles could also cause a process upset downstream.

Since chlorination of hydrocarbons is often exothermic, failure of the reactor cooling system could lead to a runaway reaction. In addition, localized hot spots could occur in catalytic reactions resulting in equipment failure.

An additional hazard with tubular or jacketed reactions is the potential for leakage of the cooling medium into the reactor section or reactor contents into the cooling medium section of the reactor system. Since water is often used as a cooling medium, undetected corrosion from wet chlorine could lead to equipment failure.

Failures to cool the reactor lamps in a photochemical reactor could cause the reaction rate to diminish, again resulting in a buildup of excessive chlorine.

A failure of agitation in stirred tank processes could have a similar result, or could result in local overheating leading to equipment failure. In

addition, a loss of mixing in any system could lead to overchlorination or undesired by-products to pass to downstream processes where they might cause a process upset leading to overpressure or emergency venting.

Chlorine recycle circuits are subject to corrosion, with general vessel, piping, valve, or pump failure. Where chlorine is recycled, traces of moisture may enter the system and concentrate in the recycle stream, thus contributing to corrosion.

### 3.2.4 Phosgene Manufacture

Phosgene is manufactured by the reaction of chlorine and carbon monoxide over a highly absorptive activated charcoal catalyst in a tubular reactor. Figure 3-8 presents a block diagram of a typical phosgene production process. The reactor typically operates at 392°F under a slight positive pressure (11). The reaction is exothermic and liberates 26.22 kcal/mole (11,19). The reactor is water cooled to remove the excess heat and maintain the reactor temperature below 572°F, since phosgene decomposes above this temperature (19). Carbon monoxide and chlorine are fed to the reactor in either equimolar proportions or with a small excess of carbon monoxide to ensure complete conversion of chlorine.

High hazard areas in the process include:

- Chlorine feed rate control; and
- Reactor cooling systems.

Concerns for these hazard areas are the same as those discussed in Section 3.2.3 for catalytic chlorination reactions.

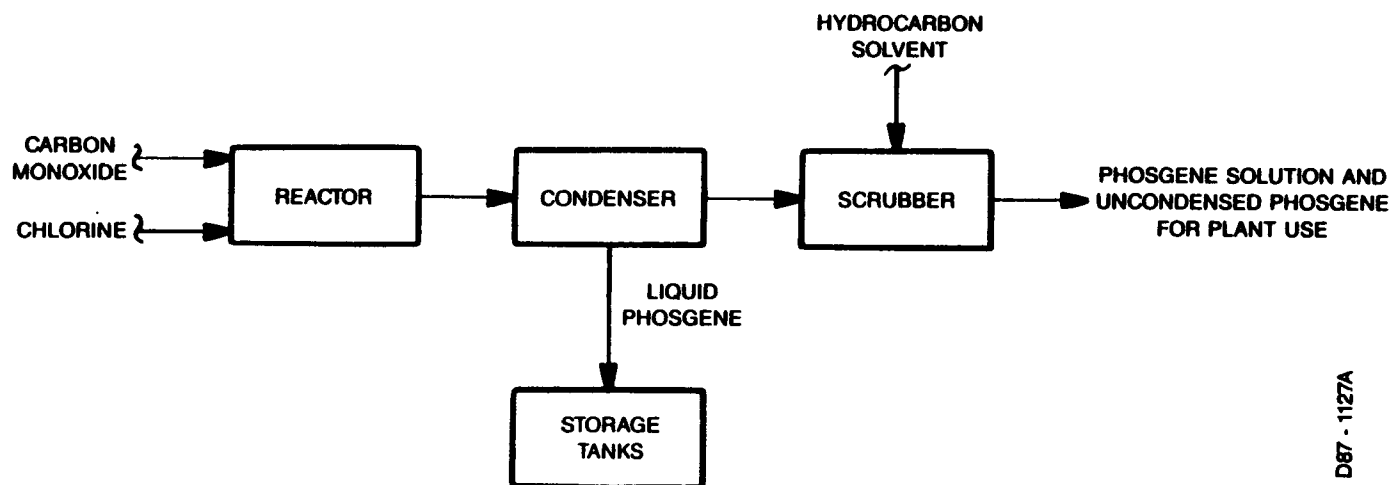


Figure 3-8. Conceptual diagram of typical phosgene manufacturing process.

### 3.2.5 Chlorofluorocarbon Manufacture

Chlorofluorination is one of the primary methods used in the manufacture of chlorofluorocarbons. This process differs from other chlorofluorocarbon processes in that hydrocarbon feedstocks are simultaneously chlorinated and fluorinated within the reactor system using chlorine and fluorine reactants, in place of just chlorinated hydrocarbon and fluorine feedstocks.

As shown in Figure 3-9, hydrocarbon reacts with chlorine and hydrogen fluoride in the presence of a catalyst. The reaction is carried out adiabatically in the vapor phase using a fluidized bed reactor. The reactor typically operates at temperatures in the range of 698°F to 842°F and pressures of 40 to 70 psig (16). A large recycle stream of chlorocarbon and fluorocarbon compounds serves as a heat sink to prevent the temperature from exceeding 842°F. This is to avoid overfluorination and excessive carbon formation (16). Carbonaceous deposits can reduce the catalyst activity and result in incomplete reaction. Crude product vapors evolved from the reactor are fed to an enriching column for further processing.

The exit gas stream from the enriching column is sent to a refrigerated condenser. The uncondensed vapor is sent to a caustic vent scrubber for removal of any residual chlorine before venting.

High hazard areas in the process include:

- Feed treatment to remove water from hydrocarbon feed,
- Chlorine feed rate control,
- Reactor cooling system,
- Enriching column, and
- Vent gas scrubber.

The feed treatment process to remove water is a critical area of the process because water in the process system promotes corrosion. Water and

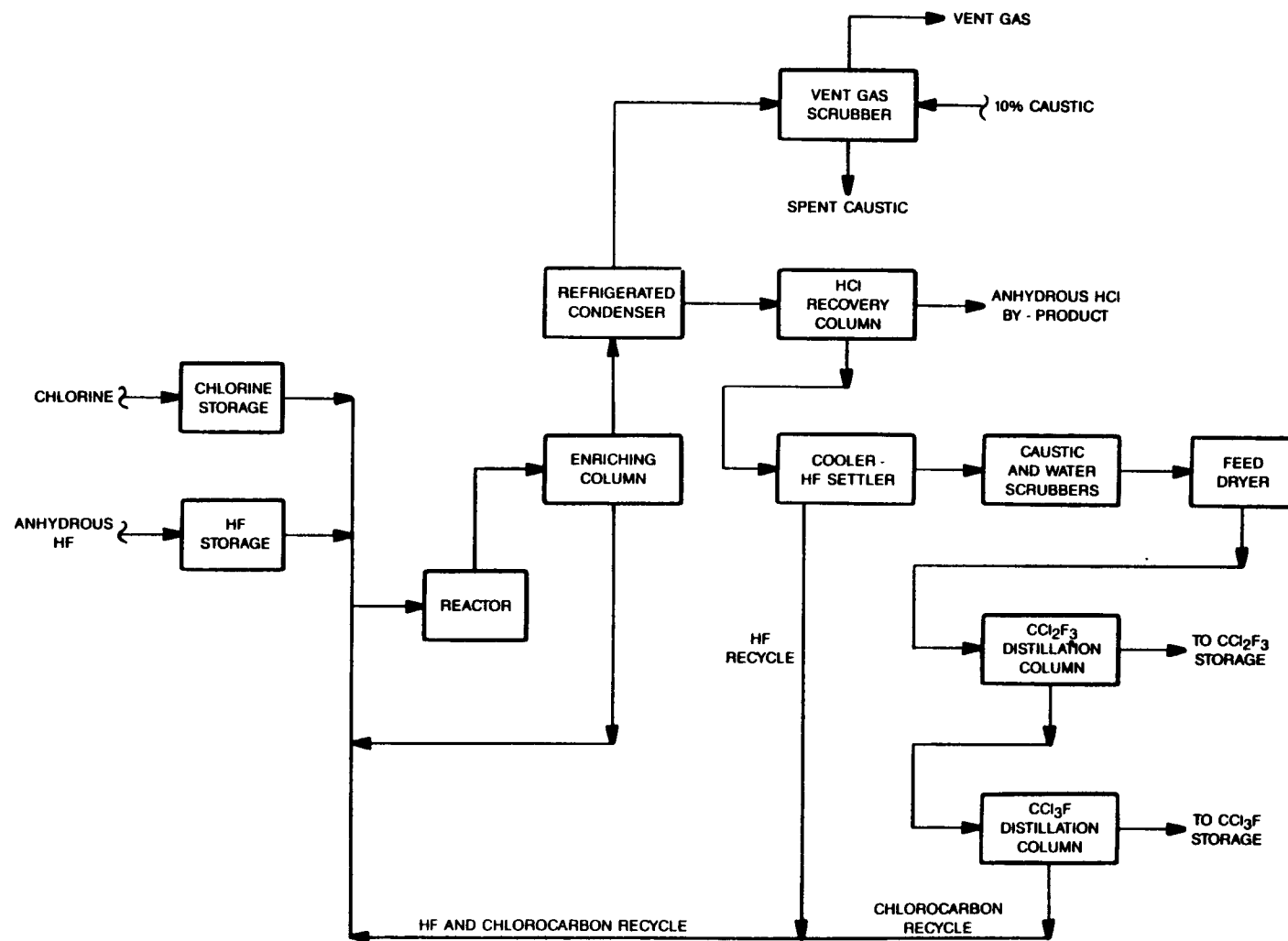


Figure 3-9. Conceptual diagram of chlorofluorination process.

chlorine combine to form hydrochloric and hypochlorous acids which rapidly attack many materials including carbon steel. A properly designed system should use materials of construction which take this corrosion potential into account and allow a certain moisture concentration to be maintained. Deficiencies could lead to protracted corrosion problem resulting eventually in equipment failure.

Concerns for chlorine feed rate and reactor cooling are the same as those discussed in Section 3.2.3 for catalytic chlorination reactions.

The enriching column is subject to potential overheating and overpressure. Loss of cooling in condensers could be a cause for overpressure. The reboiler and bottoms pump are potential weak points in these systems since operating conditions are severe.

A failure in the vent gas scrubber system could result in venting small quantities of residual chlorine along with the process off-gases. It should also be noted that a failure in the process train upstream from this scrubber could lead to a large release of chlorine unless the system has adequate safety controls as an inherent part of the process.

### 3.2.6 Propylene Oxide Manufacture

Propylene oxide is typically produced by the chlorohydrin process. A block diagram of the chlorohydrin process is shown in Figure 3-10.

Propylene and chlorine in approximately equal molar amounts are mixed with an excess of water in a stirred tank reactor. Because of the corrosive nature of the reactor, it is commonly constructed of brick, rubber, or lined with a plastic material (11). The reaction is carried out under atmospheric pressure at temperatures in the range of 104-194°F. Excess water is used to reduce the propylene chlorohydrin and chloride ion concentrations in the reactor, thereby minimizing the formation of by-product propylene dichloride.

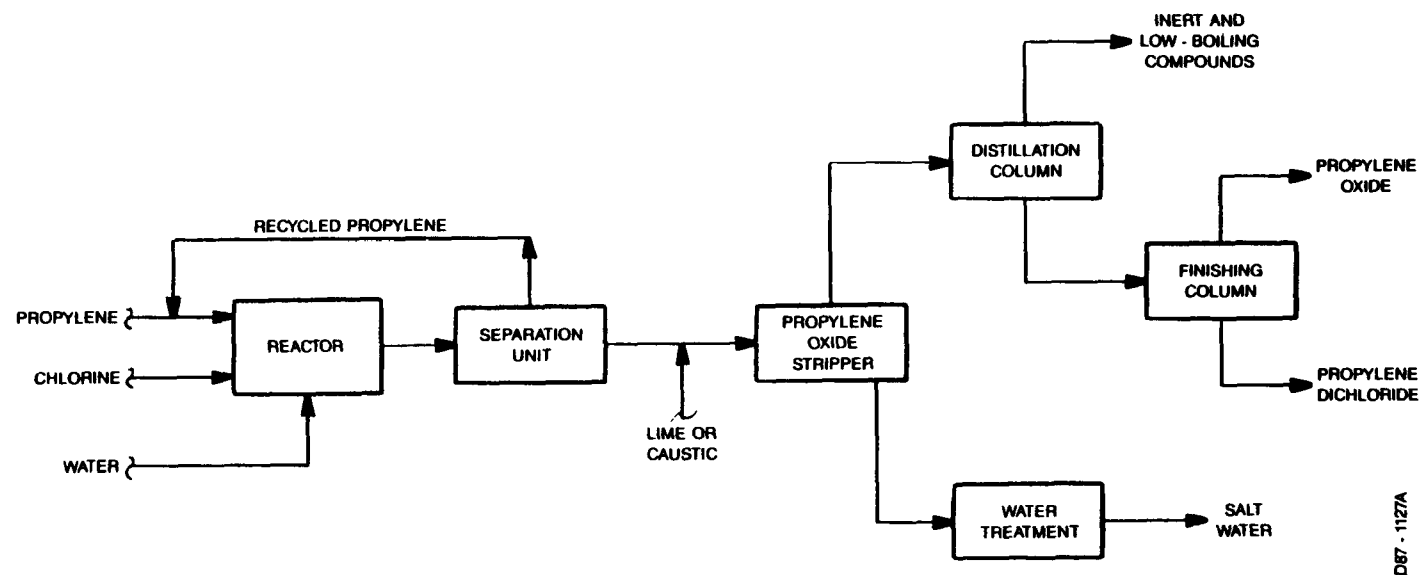


Figure 3-10. Conceptual process diagram of typical chlorohydrin process.

In addition, excess water also prevents formation of an organic phase of propylene dichloride with which chlorine and propylene react rapidly. The unreacted propylene is water-washed and recycled to the reactor.

The chlorohydrin product from the reactor is treated with aqueous base to produce crude propylene oxide. Propylene oxide is removed from alkaline solution in a stripping column and sent to a purification section for final treatment.

High hazard areas in this process include:

- Chlorine feed rate control,
- The propylene feed system and reactor,
- Water feed rate control, and
- Reactor cooling system.

Concerns for the chlorine feed rate control and reactor cooling system were discussed in Section 3.2.3. Of special concern in this process is the possible formation of explosive mixtures of propylene and air. Precautions must be taken to exclude any air from the propylene feed, recycle, and reaction systems. A propylene explosion or fire in the reactor area could cause a chlorine release.

Excess water is required to reduce the formation of the by-product propylene dichloride. If an organic phase of propylene dichloride were allowed to form in the reactor, propylene and chlorine would react rapidly resulting in a runaway reaction. Additionally, the water stream is used to maintain the temperature of the exothermic reaction constant.

The addition of water to a vessel containing chlorine can result in undetected corrosion. Such a system should be constructed of materials which take this corrosion potential into account to prevent possible equipment failure.

### 3.2.7 Hydrogen Chloride Manufacture

One method of hydrogen chloride manufacture is direct synthesis from chlorine and hydrogen. Figure 3-11 shows a typical hydrogen chloride manufacturing process.

Chlorine and hydrogen are fed to a vertical water-cooled combustion chamber constructed of karbate or impervious graphite (16). The reaction of hydrogen and chlorine is highly exothermic. The equilibrium flame temperature for adiabatic reaction is approximately 4,514°F (11). At this temperature, the gaseous mixture contains approximately 4.2 percent free chlorine gas by volume (11). However, as the gases are cooled, the free hydrogen and chlorine rapidly combine and at a temperature of 392°F, the concentration of free chlorine is negligible (11). The feed to the burner is controlled so that the gas exiting the combustion chamber contains greater than 99 percent hydrogen chloride gas.

The hydrogen chloride gas is absorbed in water in an absorber/cooler to produce hydrochloric acid. The absorber/cooler is a vertical shell and tube heat exchanger constructed of impervious graphite (11). A tail-gas scrubber is used to remove any residual hydrogen chloride from the absorber weak gas stream before being released to the atmosphere.

High hazard areas of these processes include:

- Chlorine feed rate control,
- Hydrogen feed system,
- Reactor cooling system, and
- Scrubber.

Concerns for the chlorine feed rate control and reactor cooling system were discussed previously in Section 3.2.3. In addition, if the hydrogen feed system were to fail and the chlorine flow was not shut off, then chlorine

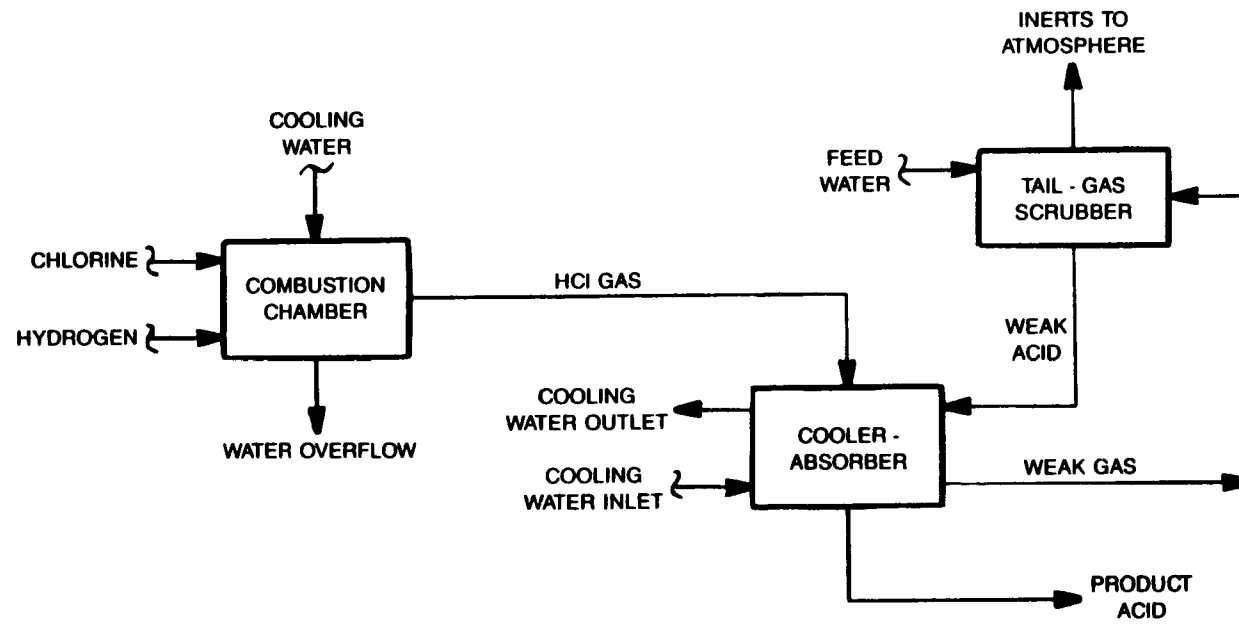


Figure 3-11. Conceptual process diagram of typical hydrogen chloride manufacturing process.

could go through the system and out the tail gas scrubber or product acid lines.

Caustic scrubbers are used to prevent the release of hydrogen chloride to the atmosphere. If the caustic feed to the scrubber were to fail, the possibility exists for a direct release of hydrogen chloride. In addition, improperly sized systems could also lead to a direct release in the event of a large quantity of chlorine in the vent stream. Additional concerns for scrubbing systems are discussed in Section 5.4 Protection Technologies.

### 3.2.8 Miscellaneous Inorganic Chemical Manufacture

Many inorganic chemicals are manufactured using chlorine as a reactant. This subsection briefly discusses the manufacturing processes associated with several of these chemicals. These processes are typical of the inorganic chloride chemicals in general.

High hazard areas of these processes include:

- Chlorine feed rate control, and
- Reactor cooling system.

Concerns for hazards associated with these operations were discussed previously in Section 3.2.3.

#### Aluminum Chloride--

Anhydrous aluminum chloride is manufactured by the direct chlorination of aluminum metal. Figure 3-12 presents a process diagram of a typical manufacturing scheme.

Scrap aluminum or a mixture of scrap and pig aluminum are fed to a refractory furnace in which the aluminum is melted. Dry chlorine gas is then passed into the molten aluminum to form aluminum chloride vapor, which leaves

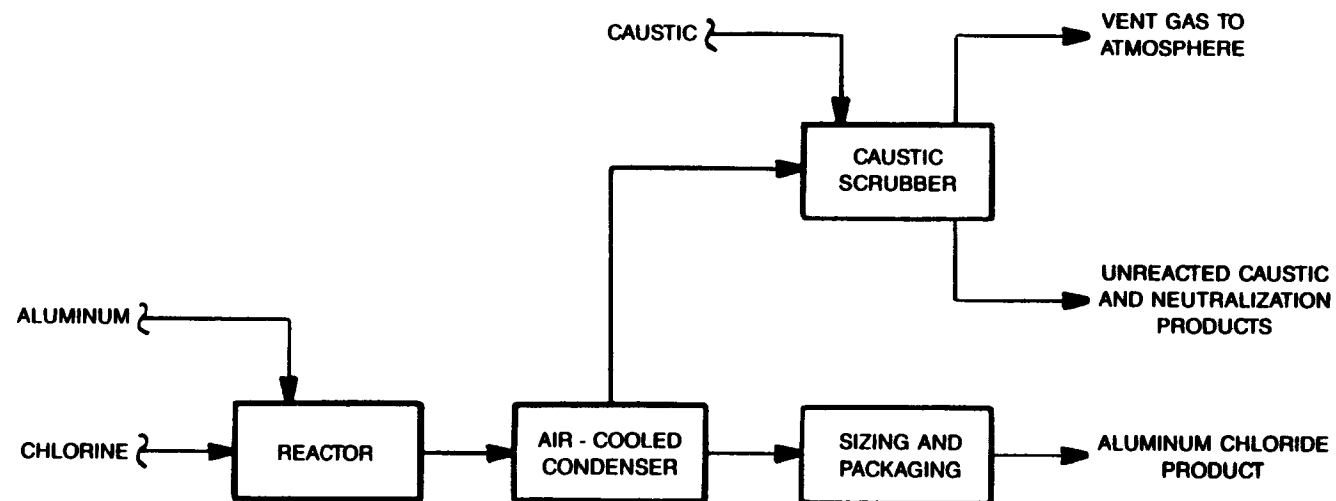


Figure 3-12. Conceptual process diagram of typical anhydrous aluminum chloride manufacturing process.

the furnace through a vapor duct. An air cooled condenser cools the vapor and collects the aluminum chloride, a crystalline solid, which is periodically removed from the condensers. A conveyor system transfers the aluminum chloride to sizing and packaging operations.

The chlorine feed rate is controlled so that unreacted chlorine is not present in the exit gases (16). However, a protective scrubber is commonly placed after the aluminum chloride condensers to collect any unreacted chlorine (16).

#### Mercuric Chloride--

Mercuric chloride is produced by the direct chlorination of mercury in a batch process.

The process consists of feeding mercury, by gravity, into a heated silica retort whose mouth is fitted into a large chamber constructed of chlorine-resistant materials (typically lead or tile-lined) (11). Gaseous chlorine, at a pressure slightly greater than atmospheric, is fed to the retort above the mercury surface. The mercury burns with a green flame, subliming a solid product which collects on the floor of the chamber. The chlorination reaction requires approximately 4-6 days and a slight excess of chlorine to assure complete conversion to the mercuric state (11). Following chlorination, dry compressed air is blown into the chamber to expel any excess chlorine, and is sent to a scrubber tower for chlorine removal. The material in the chamber is fed to a glass-lined or reinforced-plastic tank, slurried with water and washed several times by decantation.

The chamber must be large since cooling is accomplished by convection and heat dissipation by conduction through the walls of the chamber (11).

### Phosphorus Trichloride--

Phosphorous trichloride is manufactured by direct chlorination of phosphorus. Figure 3-13 presents a block diagram of a typical manufacturing scheme.

The reaction is carried out in a stirred tank reactor. Gaseous chlorine and liquid phosphorous are continuously fed to the reactor along with a precharge of phosphorous trichloride which is refluxed continuously. A portion of the phosphorous trichloride is sent to a distilling pot where it is contacted with additional chlorine to convert unreacted phosphorous. The crude phosphorous trichloride is purified by fractional distillation in a packed column and sent to storage.

### Sulfur Chloride--

Sulfur chloride is manufactured by direct chlorination of sulfur in batch processes.

The process consists of feeding liquid sulfur to a batch reactor containing sulfur chloride from a previous batch. Chlorine is introduced continuously into the liquid sulfur through a sparger tube. The chlorination reaction is slow and as a result, the chlorine addition rate is controlled to prevent excessive chlorine buildup and undesired sulfur product formation. The reaction is typically carried out at a temperature of 464°F and atmospheric pressure (11). The reaction is often catalyzed using iron, iodine, or a small amount of ferric chloride.

### Titanium Tetrachloride--

Titanium tetrachloride is manufactured by the chlorination of titanium compounds in the presence of coke which acts as a reducing agent. Mineral rutile, beneficiated ilmenite, and leucoxene are the most commonly used titanium compounds by industry (11). Figure 3-14 presents a process diagram of a typical titanium tetrachloride manufacturing process.

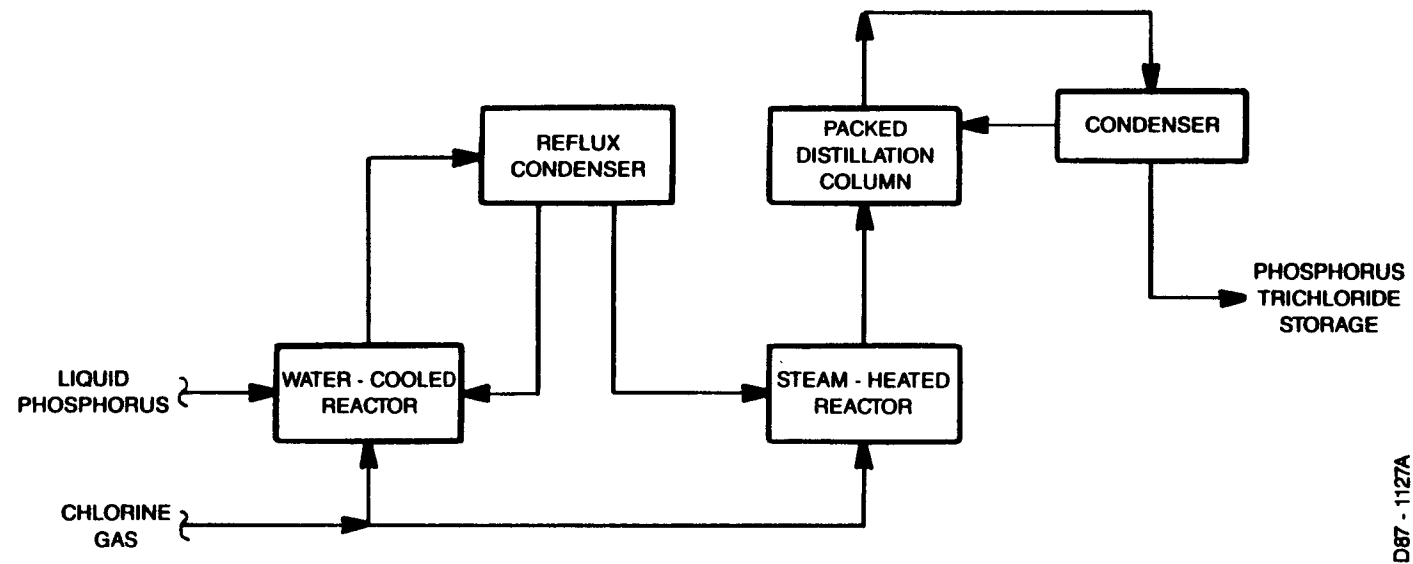


Figure 3-13. Conceptual process diagram of typical phosphorous trichloride manufacturing process.

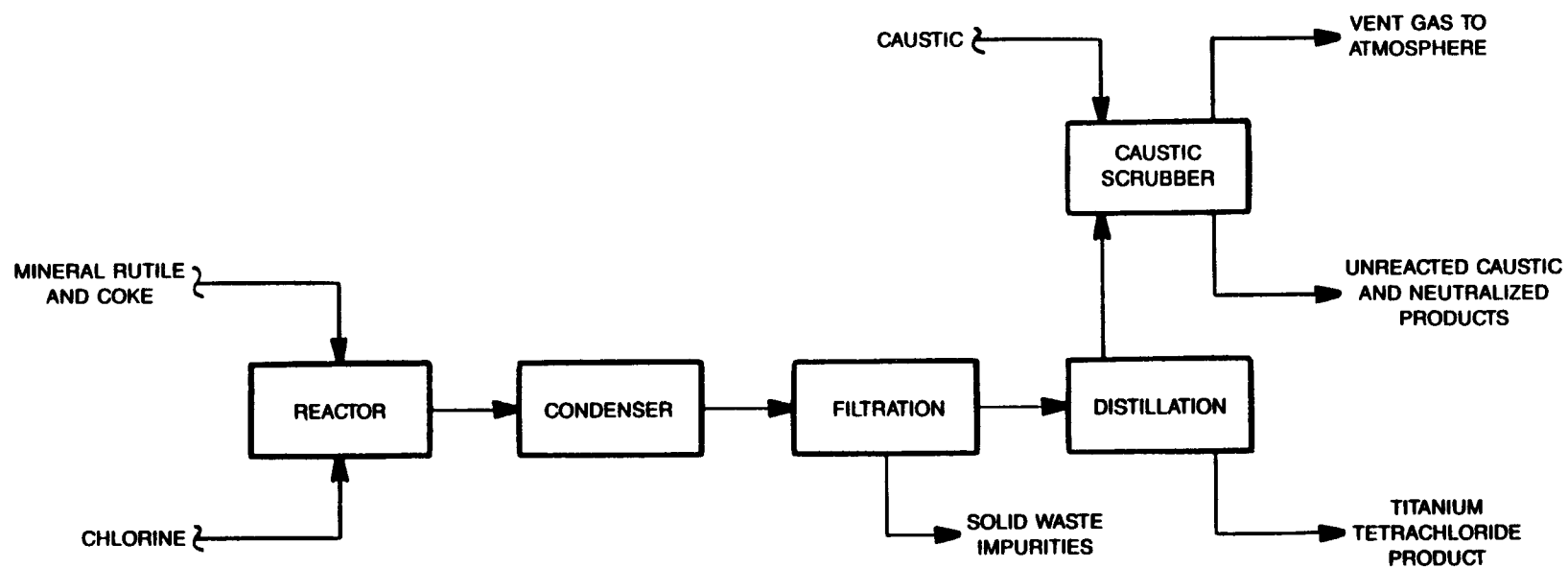


Figure 3-14. Conceptual process diagram of typical titanium tetrachloride manufacturing process.

The titanium ores can be chlorinated in batch furnaces, molten salt, or fluidized beds. However, the chlorination process is typically carried out as a continuous process in a fluid-bed reactor. The bed consists of a mixture of mineral rutile or other titanium compound and coke which are introduced at the top of the bed. Chlorine is used as the fluidizing medium and is fed to the bottom of the bed. The chlorine feed rate is such that fine reactant particles are not carried over by the product gases. The chlorination reactor operates at a temperature in the range of 1,472-1,832°F and at atmospheric pressure (20).

The exit stream from the reactor is condensed to a slurry containing impurities. The impurities are removed by filtration followed by fractional distillation (rectification) (20). The effluent gases are sent to a caustic scrubber to prevent release of chlorine to the atmosphere.

### 3.3 REPACKAGING

In many facilities, chlorine is repackaged for resale and further use. Chlorine is commonly repackaged into cylinders. Hazards associated with this operation include overpressure, overfilling, mechanical damage, fire exposure, and chemical contamination.

The Chlorine Institute Pamphlet 8 (21) provides an in-depth description of chlorine packaging operations. Equipment used in repackaging operations should be constructed from materials compatible with chlorine. Pressure relief systems are used to prevent possible equipment overpressure. In addition, care is taken to prevent overfilling of cylinders.

### 3.4 STORAGE AND TRANSFER

When a facility uses large quantities of chlorine, the chlorine is unloaded directly from a rail car or from a rail car to stationary storage.

The essential components of a typical storage tank and tank car unloading system include a storage tank with a weighing device and sun shield, air padding system, eductor, chlorine gas and liquid headers, unloading platform, gages, pressure switches and alarms, flexible connections, and expansion tanks. The Chlorine Institute Pamphlet 66 (22) provides detailed information on chlorine tank car unloading. Figure 3-15 shows a typical tank car unloading facility (6,23).

Hazards associated with chlorine storage facilities include overpressure, overfilling, and corrosion. An additional hazard is associated with contamination caused by backflow of process materials into the storage tank. Backflow not only jeopardizes raw material quality, it also poses an accidental release hazard. For example, if backflow were to occur in a bleach manufacturing operation, caustic solution might be introduced to the chlorine storage tank where it could react exothermically, causing overpressure and discharge through a relief valve. If the overpressure relief system failed to function, the storage tank could be ruptured by the pressure, resulting in a catastrophic release.

While the above concerns also apply to refrigerated liquid chlorine storage facilities, the refrigeration system poses an additional concern. Loss of refrigeration could result in overpressure and a release through pressure relief devices due to thermal expansion of both the liquid and gaseous chlorine. Failure of such relief devices would result in equipment failure and a direct release.

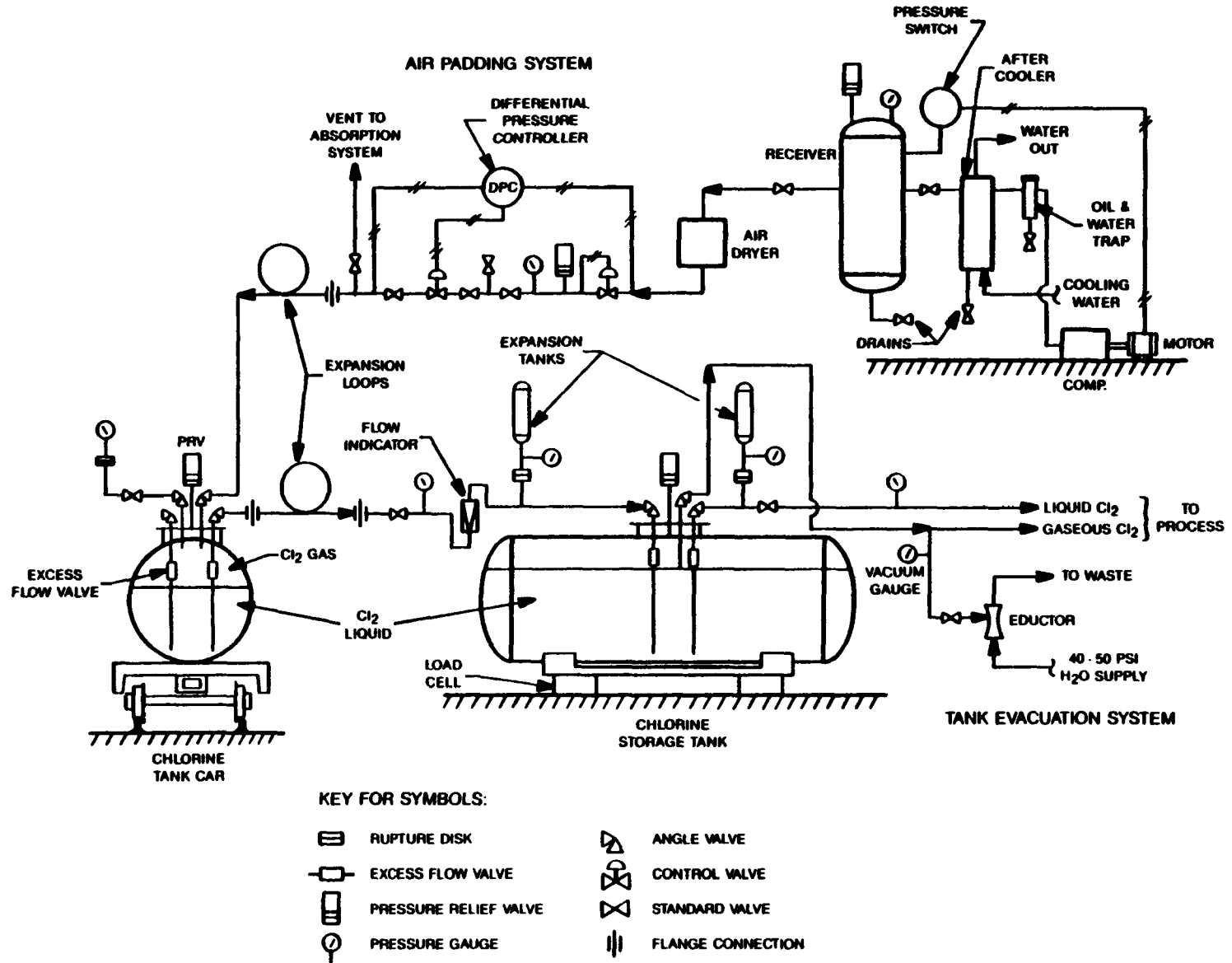


Figure 3-15. Typical bulk chlorine storage and tank car unloading system.

## SECTION 4

### PROCESS HAZARDS

Chlorine releases can originate from many sources including ruptures in process equipment, separated flanges, actuated relief valves or rupture discs, and failed pumps or compressors. In addition, losses may occur through leaks at joints and connections such as flanges, valves, and fittings where failure of gaskets or packing might occur.

Properties of chlorine which can promote equipment failure are its reactivity and its high liquid coefficient of thermal expansion. Reactivity manifested in corrosion is a likely general cause of equipment failure. Evaporators and metering and control equipment are especially sensitive if they are in intermittent use where moisture might enter the system.

Potential chlorine releases may be in the form of either liquid or vapor. Liquid spills can occur when chlorine is released at or below its boiling point of  $-29.3^{\circ}\text{F}$ , or when a sudden release of chlorine at temperatures above  $-29.3^{\circ}\text{F}$  results in vapor flashing, thus cooling at least part of the remaining material to  $-29.3^{\circ}\text{F}$ . Direct releases of vapor or gas can also occur.

#### 4.1 Potential Causes of Release

The extensive use of 150-pound cylinders and one-ton containers to store chlorine makes them a particular concern in the United States. A list compiled by the Chlorine Institute shows historical causes of chlorine emissions in order of a combined ranking of frequency and size (2):

1. Fire;
2. Flexible connection failure;
3. Fusible plug failure;

4. Human error;
5. Valve packing failure;
6. Gasket failure;
7. Piping failure;
8. Equipment failure;
9. Collision; and
10. Container failure.

Although fire is not the most frequent hazard, it may be the most serious. Fire can melt the fusible plug of a container at 158°F, causing the discharge of most of the chlorine in the container. Defective fusible plugs have also failed to melt, allowing a fire to rupture the container. A number of leaks have been caused by defective fusible plugs without a fire. Corrosion or poor bonding between the lead alloy plug and the plug retainer allows moisture accumulation and corrosion at the connection, leading to leakage of chlorine.

Probably the most frequent cause of chlorine emissions is failure of the copper tubes which are commonly used to connect cylinders and ton containers to process equipment. A corrosion cycle begins when the tube is disconnected for a container change. Moisture in the air enters the tube, promoting corrosion; repeated removal and reconnection of tubing will induce failure. Historically, other piping failures have been rare, but may have been caused by corrosion, thermal expansion of chlorine, or by impact damage.

Valve packing failure on the cylinders is usually a minor problem which can be corrected by tightening the packing nut. A potential hazard exists with overtightening if too large a wrench is used; a brass valve is easily damaged or broken. For serious leaks, the Chlorine Institute provides safety kits for each type of container (6).

Because of the strict standards and monitoring programs followed by chlorine packagers, container failures are very rare. In a period of 15 years, the Chlorine Institute accident reports indicate that approximately 15

million 68 kg (150-pound) and ton containers were shipped with only two reported failures (2). Collisions with containers are rare, but are a possible cause of a release (2).

Failures leading to accidental chlorine releases may be broadly classified as due to process, equipment, or operational causes. This classification is for convenience only. Causes discussed below are intended to be illustrative, not exhaustive.

#### 4.1.1 Process Causes

Process causes are related to the fundamentals of process chemistry, control, and general operation. Possible process causes of a chlorine release include:

- Excessively high chlorine feed rate to a bleach or chlorocarbon reactor leading to excessive exothermic reaction, combined with failure of the cooling system;
- Backflow of chlorination water to a chlorine cylinder;
- Loss of agitation in batch reactor systems;
- Excess chlorine feed leading to overfilling or overpressuring equipment;
- Photo-lamp failure in photochemical reactor; and
- Overpressure of chlorine storage vessel due to overheating from reactions. This situation may be caused by contamination, fire exposure, or unrelieved overfilling.

#### 4.1.2 Equipment Causes

Equipment causes of accidental releases result from hardware failure. Some possible causes include:

- Excessive stress due to improper fabrication, construction, or installation;
- Failure of vessels at normal operating conditions due to weakening of equipment from excessive stress, external loadings, or corrosion. Overheating is also a possibility, especially for chlorine evaporators and bleach reactors;
- Mechanical fatigue and shock in any equipment. Mechanical fatigue could result from age, vibration, or stress cycling, caused by pressure cycling, for example. Shock could occur from collisions with moving equipment such as cranes or other equipment in process or storage areas;
- Thermal fatigue and shock in bleach reactors and chlorine evaporation;
- Brittle fracture in any equipment, but especially in carbon steel equipment subjected to extensive corrosion. Equipment constructed of high alloys, especially high strength alloys selected to reduce the weight of major process equipment, might be especially sensitive where some corrosion has occurred, or severe operating conditions are encountered;

- Creep failure in equipment subjected to extreme operational upsets, especially excess temperature. This can occur in equipment subjected to a fire that may have caused damage before being brought under control; and
- All forms of corrosion, including external corrosion from fugitive emissions of chlorine, could lead to equipment weakening. Stress corrosion cracking is also a possibility since this is characteristic of certain metals exposed to halogens.

#### 4.1.3 Operational Causes

Operational causes of accidental releases are a result of incorrect operating and maintenance procedures or human errors (i.e., not following correct procedures). These causes include:

- Overfilled storage vessels;
- Errors in loading and unloading procedures;
- Inadequate maintenance in general, but especially on pressure relief systems and other preventive and protective systems;
- Lack of inspection and non-destructive testing of vessels and piping to detect corrosion weakening.
- Incomplete knowledge of the properties of a specific chemical; and
- Incomplete knowledge of the process or chemical system.

## SECTION 5

### HAZARD PREVENTION AND CONTROL

#### 5.1 BACKGROUND

Prevention of accidental releases relies on a combination of technological, administrative, and operational practices. These practices apply to the design, construction, and operation of facilities where chlorine is stored and used. Considerations in these areas can be grouped as follows:

- Process design considerations;
- Physical plant design considerations;
- Operating and maintenance practices; and
- Protective systems.

In each of these areas, consideration must be given to specific factors that could lead to a process upset or failure which could directly cause a release of chlorine to the environment, or result in an equipment failure which would cause the release. At a minimum, equipment and procedures should be examined to ensure that they are in accordance with applicable codes, standards, and regulations. In addition, stricter equipment and procedural specifications should be in place if extra protection against a release is considered appropriate.

The following subsections discuss some specific considerations regarding release prevention related to each of the areas mentioned above. In addition, illustrative cost estimates for different levels of control as applied to

storage and process facilities are also included. More detailed discussions will be found in a manual on control technologies, part of this manual series.

## 5.2 PROCESS DESIGN

Process design considerations involve the fundamental characteristics of the processes which use chlorine. These considerations include an evaluation of how deviations from expected process design considerations might initiate a series of events that could result in an accidental release. The primary focus is on how the process is controlled in terms of the basic process chemistry involved, and the variables of flow, pressure, temperature, composition, and level. Additional considerations may include quantity measuring systems, mixing systems, fire protection, and process control instrumentation. Modifications to enhance process integrity may result from review of these factors and would involve changes in quantities of materials used, process pressure and temperature conditions, the unit operations used, sequence of operations, the process control strategies, and instrumentation used.

Table 5-1 shows the relationship between some specific key process design considerations and the individual processes described in Section 3 of this manual. This does not mean that other factors should be ignored, nor does it mean that proper attention to the key considerations ensures a safe system. It does mean that the designated key considerations must be properly addressed if a system is to be safe.

The most significant process design considerations are aimed at preventing overheating and overpressuring systems containing chlorine. If chlorine is fed under its own vapor pressure, the primary cause of overpressure would be overheating. Where chlorine is fed by nitrogen padding of a storage vessel or through pumps or compressors, overpressuring could occur without overheating. Equipment failure without overpressure is possible if corrosion has weakened process equipment. Temperature monitoring is important, not only because of potential overpressure or equipment weakening due to overheating,

TABLE 5-1. KEY PROCESS DESIGN CONSIDERATIONS FOR CHLORINE PROCESSES

Process Design Consideration	Process or Unit Operation
Contamination (with water and organics especially)	A11
Flow control of chlorine feeds	A11
Temperature monitoring; heating media flow control	Chlorination reactors, chlorine vaporizer in any feed system
Adequate pressure relief	A11
pH control	Bleach process
Mixing	Bleach process, batch and continuous stirred tank chlorination
Temperature monitoring; cooling media flow control	Chlorination reactors, refrigerated storage
Corrosion monitoring	A11
Temperature monitoring	A11

but also because chlorine can react with many metals above a certain activation temperature. Conversely, chlorine can cool itself while off-gasing and potentially reach temperatures below the safe operating range for some metals. In addition, vessels containing liquid chlorine at room temperature or above should be designed to be in the leak before fracture region over the entire range of temperatures from the boiling point to maximum temperature and pressure of the vessel.

### 5.3 PHYSICAL PLANT DESIGN

Physical plant design considerations include equipment, siting and layout, and transfer/transport facilities. Vessels, piping and valves, process machinery, instrumentation, and factors such as location of systems and equipment must all be considered. The following subsections cover various aspects of physical plant design beginning with a discussion of materials of construction.

#### 5.3.1 Equipment

##### Materials of Construction--

The two most important considerations in selecting materials for chlorine service are the temperature and moisture content of the chlorine. The temperature is important because the corrosiveness of chlorine increases with increasing temperature, and most metals will ignite at a given temperature in the presence of chlorine. The moisture content is also critical because, though dry chlorine is noncorrosive (at normal to moderate temperatures), moist or wet chlorine is very corrosive to most metals.

Equipment construction materials must be chosen to prevent deterioration or product contamination. Steel, cast iron, wrought iron, most copper alloys, most nickel alloys, certain stainless steel, and lead are common materials of construction for chlorine processes (1). Other materials which are resistant to the corrosiveness of wet chlorine are titanium, nickel-copper and nickel-

chromium-molybdenum alloys, high silica iron, platinum, silver, tantalum, and zirconium. While titanium may be used with wet chlorine, it reacts rapidly, even violently, with dry chlorine. Tantalum is inert with both wet and dry chlorine up to 300°F (6). For handling wet chlorine at low pressures, suitable materials include hard rubber, unplasticized polyvinyl chloride, polyvinylidene chloride, fully-halogenated fluorocarbon resins, reinforced polyester resin, or certain other non-metallics (6,11). Before one of these materials is chosen the conditions and requirements of the chlorine system must be considered carefully. Many of the non-metals can be used as lining materials in higher pressure wet chlorine systems which require the strength of metals and the chemical resistance of polymers. Chlorination vessels and reactors are often constructed of fiberglass-reinforced plastic (FRP) or carbon steel lined with a polymeric material.

Table 5-2 compares the corrosion resistance of a number of common metals and alloys in the presence of dry chlorine (11). The usual material of construction for dry chlorine at moderate temperatures is mild steel. However, since wet chlorine attacks this metal severely, it is essential to exclude water from chlorine systems that use mild steel. The typical water content of commercial chlorine is 20-60 ppm; this is considered acceptable with the common materials of construction. The corrosiveness of chlorine on mild steel also is temperature dependent. Corrosion of mild steel is significant at 392°F and rapid at around 446°F. It is typical to restrict the use of mild steel to applications where the chlorine temperature is below about 248°F (1). Below 248°F, iron, copper, lead, nickel, platinum, steel, silver, and tantalum are chemically resistant to dry chlorine gas or liquid (11).

#### Vessels--

The predominant vessels that are involved in chlorine service in the U.S. include storage cylinders, fixed storage tanks, rail cars used for storage, evaporators, and chemical reactors. The role of these vessels in chlorine service was discussed in Section 3.

TABLE 5-2. CORROSION OF METALS IN DRY CHLORINE

Approximate temperature (°F) at which given corrosion rate is exceeded in short-time tests in dry Cl <sub>2</sub> <sup>a</sup>					
	0.0025 in. per month	0.005 in. per month	0.05 in. per month	0.05 in. per month	0.1 in. per month
nickel	950	1,000	1,100	1,200	1,250
Inconel	950	1,000	1,050	1,200	1,250
Hastelloy B	950	1,000	1,100	1,200	
Hastelloy C	900	1,000	1,050	1,200	
Hastelloy A	900	1,000	1,100	1,200	1,250
platinum	900	950	1,000	1,050	1,050
magnesium	850	900	950	1,000	1,050
Chromel A	850	900	1,000	1,150	
Monel	750	850	900	1,000	1,000
18-8-Mo stainless steel	600	650	750	850	900
18-8 stainless steel	550	600	650	750	850
Hastelloy D	400	450	550		
deoxidized copper	350	450	500	500	550 <sup>b</sup>
carbon steel	250	300	300	350	350 <sup>d</sup>
aluminum 2S	250	300	300	350	350 <sup>d</sup>
gold	250	300	350	400	400
cast iron	200	250	350	450	450 <sup>c</sup>
silver	100	150	150	450	500

<sup>a</sup>These values are based on short-time laboratory tests under controlled conditions. They should be interpreted only as being indicative of the limitations of the materials, and should not be used for estimation of the service life of equipment.

<sup>b</sup>Ignites at about 601°F.

<sup>c</sup>Ignites at 450-500°F.

<sup>d</sup>Ignites at 400-450°F.

Source: Adapted from Reference 10.

Chlorine storage vessels likely to be encountered in the U.S. range in size from 150-pound pressure cylinders to multi-thousand ton, spherical refrigerated chlorine storage tanks. Because of the relatively large inventories contained in chlorine storage vessels, they represent one of the most hazardous aspects of a chlorine system. The vessels most commonly used for transfer and storage of chlorine are well standardized and are described in detail in various Chlorine Institute literature (23,24,25). These containers include: cylinders up to 150-pound capacity, one-ton containers, 15-ton containers, single-unit tank cars (16, 30, 55, 85, and 90 tons capacity), 15- to 20-ton tank trucks, and 150- to 300-ton barge tanks. Up to about 450 tons of chlorine may be stored safely in high strength tanks as a liquid under pressure. Larger quantities are usually stored at atmospheric pressure as a refrigerated liquid in single and double-walled horizontal cylindrical or spherical vessels (6,11). Detailed design considerations are found in Chlorine Institute Pamphlet 78: "Refrigerated Liquid Chlorine Storage" (24).

Rail cars in chlorine service must meet Department of Transportation (DOT) Specifications (22).

Exact specifications for reactors used in bleach manufacture and organic and inorganic chlorination processes are unavailable, but at a minimum the reactors would be expected to conform to the ASME Unfired Pressure Vessel Code since they are subject to pressurization with a gas.

Vaporizing equipment for chlorine is available in capacities ranging from 400 lb/day to 10,000 lb/day (25). Several types of vaporizers, including electric heat, hot water, and steam types are used in chlorine service. Detailed design considerations are available in Chlorine Institute Pamphlet 9: "Chlorine Vaporizing Equipment" (25).

The Chlorine Institute specifies that chlorine vaporizing equipment must be protected by a pressure relief device (25). In addition, vaporizers must conform to the ASME Unified Pressure Vessel Code.

For most chlorine vessels, overpressure protection is provided by an adequate overpressure relief venting system which cannot be isolated from service. The relief system should be sized for flashing liquid caused by:

- Fire exposure (NFPA 30);
- Thermal expansion,
- Internal reaction/decomposition, and
- Excess supply rates

Release prevention considerations for all vessels include prevention of: overpressure, overfilling, overheating, and corrosion. With liquid chlorine, overfilling and overheating are especially important because of the high coefficient of thermal expansion associated with liquid chlorine.

Overpressure protection on vessels is provided by relief devices. These devices provide protection against catastrophic rupture or explosion by allowing a controlled release of overpressured contents. The types of devices used depend on the vessel service and potential causes of overpressure. Relief devices for overpressure caused by fire or other overheating of 150-pound cylinders and ton containers are usually fusible metal plugs which melt between 158°F and 165°F. The normal service seen by cylinders or ton containers does not usually require other overpressure protection on the cylinders or ton containers themselves. When cylinders are padded with nitrogen to pressure-feed chlorine at pressures above its vapor pressure, overpressure protection should be provided in the nitrogen feed system. This ensures that the nitrogen cannot exceed the working pressure of the chlorine vessels or any parts of the downstream system connected to these vessels. Chlorine cylinders and ton containers themselves are rated for several hundred pounds per square inch (6). In addition, a check valve should be installed on the nitrogen feed line to insure that no chlorine enters the nitrogen supply system.

Larger vessels are usually equipped with pressure relief valves and rupture disks. A rupture disk upstream of a relief valve is a common configuration in chlorine service since chlorine tends to corrode pressure relief valves. In addition to general provisions of good practices for the design and sizing of relief devices (1), these devices should be sized according to guidelines given by the Chlorine Institute as a minimum standard (26). These guidelines include materials of construction, flow capacity, connections, and relief system configuration.

Chlorine tank cars are equipped with spring-loaded safety relief devices which have a breaking pin assembly designed to function at a specified pressure. Tank trucks are similarly equipped.

It should be noted that while these devices are designed to prevent a catastrophic sudden release of vessel contents, a significant release of chlorine to the air could still occur. Protection from such an event might be achieved if the relief device discharge were routed to a caustic scrubber. Scrubber protection systems are discussed in Subsection 5.4 of this manual.

The pressure relief considerations discussed above also apply to chlorine evaporators and reactors except that there is a greater likelihood of two-phase flow in these cases. The effect of two-phase flow on relief device design should be taken into account and could result in a design different from that specified by the Chlorine Institute for relief devices on chlorine storage systems.

Prevention of overfilling can be accomplished using level sensing devices, pressure relief devices, and adequately trained personnel. Level sensing devices for chlorine service must be selected while taking into account the corrosiveness of chlorine, especially in contact with moisture. Relief devices for overfilling may be the same or similar to those used for gas pressure relief. The overfill relief would discharge to an overflow tank or other suitable receiver. Consideration should be given to two-phase flow

in the design of such relief systems. Protection against overpressure from a tank with a domed or arched roof filled with liquid chlorine with little or no vapor space can be provided by a short vented dip pipe. Relief from overpressure by liquid thermal expansion can be achieved with a relief device.

Because of the high coefficient of thermal expansion, the weight of chlorine in a tank must not exceed the nominal chlorine capacity of the tank or exceed 125% filling density (125% of the weight of water at 60°F that the tank will hold). The Chlorine Institute recommends having two tanks, each 20 percent larger than the shipping tank. This allows continuous operation and complete unloading of tank cars.

The Chlorine Institute provides guidelines on the materials of construction for stationary storage tanks (23). Except where the Institute indicates otherwise, the tanks should be constructed according to parts UW and UCS of the ASME Boiler and Pressure Vessel Code, Section VIII, Division 1. The tanks usually are constructed of normalized carbon steel. To allow for corrosion, the wall thickness should be 1/8 inch greater than that required by the design formula in the Code. The tank should be designed so that it can accept a tank car dome assembly. These assemblies can be purchased from chlorine tank car manufacturers. In the event of leakage, these assemblies allow the use of Chlorine Institute Emergency Kit "C" (6).

In addition to venting provisions, the containers should have valve arrangements which allow the vessel to be isolated from the process to which the chlorine is being fed. In addition, concerns about corrosion dictate that moisture be excluded from the tanks. Tanks should not be situated in standing water and care should be taken to prevent exposure to moist air such as applying a moisture proof material to the outside of the vessel. External corrosion can be as important as internal corrosion since air always contains moisture and minor leaks could lead to equipment failure.

A further concern is backflow of material into the storage vessels. When chlorine is being absorbed in a liquid, the potential exists for the liquid to be drawn back into the chlorine container. This has resulted in numerous accidents. Such backflow can be prevented by a vacuum-breaking device or a barometric leg, check valves, and positive displacement pumps, or combination of the above (6).

Careful attention should be given to vessel corrosion; vessels in chlorine service should be constructed of suitable materials of construction with adequate corrosion allowances. Special attention should be given to welds and to external corrosion under insulation.

#### Piping--

As with chlorine vessels, chlorine pipework design must reflect the pressure, temperature, and corrosion concerns associated with the use of chlorine. There are some general guidelines for both wet and dry chlorine piping systems. The first is simplicity of design; the number of joints and connections should be minimized. In addition to being securely supported, pipes should be sloped, with drainage provided at the low points. Piping should be constructed to allow room for thermal expansion of the pipe and should be protected from exposure to fire and high temperatures. Valves should be placed so that leaking pipes and equipment may be isolated, but no section of piping should be isolable from some form of overpressure relief or expansion chamber.

Piping and associated equipment should also be dry and grease- and oil-free since chlorine can react vigorously with organic compounds. Valves and instrumentation should be supplied by the manufacturer as "degreased and dried for chlorine duty."

For dry chlorine systems, carbon steel pipe is commonly used. Carbon steel such as ASTM A106 or seamless ASTM A53 is suitable in many cases. Materials which are not recommended include aluminum, titanium, tin, ordinary

grey iron, malleable iron fittings, general purpose valves, and porcelain valves.

Chlorine Institute Pamphlet 6, "Piping Systems for Dry Chlorine" (26) contains detailed information on materials of construction for pipes, fittings, flanges, valves, gaskets, nuts, bolts, unions, and other components of a dry chlorine system. Table 5-3 summarizes Chlorine Institute recommendations for piping materials for given operating temperature ranges.

A chief concern in liquid chlorine lines is overpressure due to thermal expansion of the chlorine, or pressure pulses caused by rapid valve closure. These pressures can rupture the pipes. Where applicable, an expansion chamber, such as the one shown in Figure 5-1, may be installed to prevent a rupture caused by thermal expansion. An expansion chamber device typically consists of a rupture disc and a receiver chamber which can hold about 20-30% of the capacity of the protected line. The chamber is equipped with a pressure indicator or alarm switch set to function upon rupture. The chamber should be constructed in accordance with Section VIII of the ASME Code for Unfired Pressure Vessels (23). Sudden pressure pulses can be avoided by selecting valves which do not close abruptly.

Another concern in liquid chlorine systems is low temperature toughness. Materials must be carefully selected when temperatures are significantly below ambient. The materials chosen should be resistant to brittle fracture over the entire range of process conditions. The Chlorine Institute Pamphlet 6 (26) provides additional information on materials of construction for low temperature operations.

The extremely corrosive nature of wet chlorine requires special corrosion resistant materials depending upon the requirements and operating conditions of the system. Wet chlorine is corrosive to all the common construction metals; however, nickel-copper and nickel-chromium-molybdenum alloys are widely used. Tantalum is inert to both wet and dry chlorine. Titanium can be

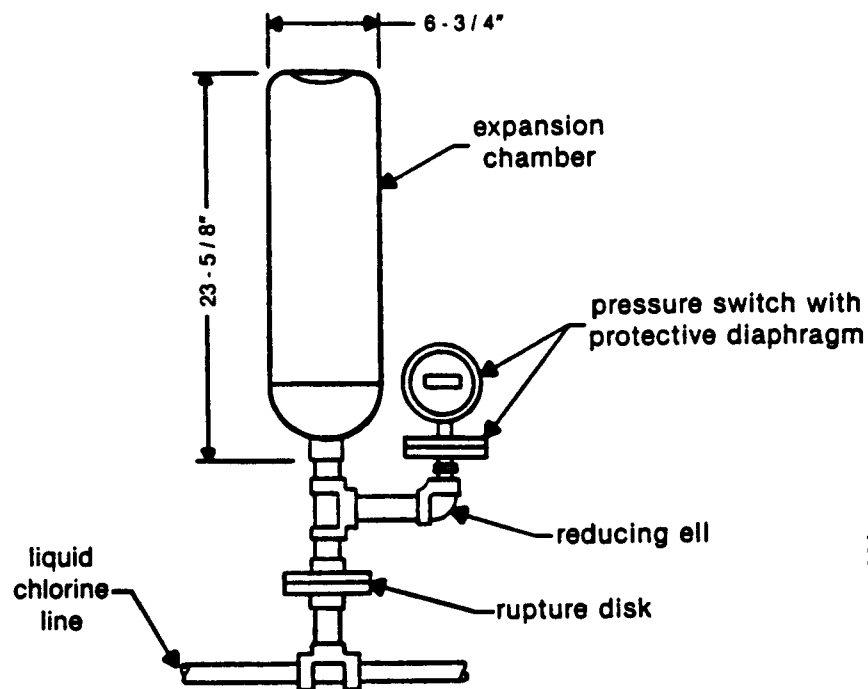
TABLE 5-3. SUMMARY OF CHLORINE INSTITUTE PIPING MATERIAL RECOMMENDATIONS

Phase	Temperature Range (°F)	Maximum Pressure (psia)	System	Pipe Specifications				
				Size	Sched- ule	ASTM	Grade	Type
Gas	-20 to 300	≤150	Class <sup>a</sup> 150, Carbon Steel	3/4 - 1-1/2 2 - 6	80 40	A53	A,B	S
Gas, Liquid	-20 to 300	≤300	Class <sup>a</sup> 300, Carbon Steel	3/4 - 1-1/2 2 - 6	80 80	A106 A53	A,B A,B	S S
Gas, Liquid	-50 to 300	≤300	Class 300, Alloy Steel	--	--	A333	1	
Gas, Liquid	-150 to 300	≤300	Class 300, Alloy Steel	--	--	A333	3	

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Source: Adapted from Reference 26.

<sup>a</sup>ANSI Class refers to pressure ratings at specified temperature as set by the American National Standards Institute (ANSI). For a carbon steel flange, Class 150 means a 150 psig pressure rating at 500°F, and Class 300 means a 300 psig pressure rating at 850°F.



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Figure 5-1. Liquid chlorine expansion chamber for liquid chlorine only. (Exact specifications for materials and fittings are provided in Reference 2. Substitutions should not be made without consultation with a recognized authority on chlorine system design and construction.)

used with wet chlorine, but reacts violently with dry chlorine. Lined pipes can be used if the lining materials are chosen according to the operating conditions. Some polymer lining materials which are inert to chlorine include: tetrafluoropolyethylene, polyvinylidene fluoride, and ethylene chlorotrifluoro-ethylene. Polymeric materials which may be used in chlorine service for limited purposes include polyvinylidene chloride, polyvinyl chloride, chlorinated polyvinyl chloride, acrylonitrile butadiene styrene, polyethylene, polypropylene fiberglass-reinforced polyester, and hard rubber (6,26). If lined pipes are used, it is important that the integrity of the lining be maintained. Penetration of chlorine through the liner could lead to insidious undetected pipe wall corrosion beneath the liner.

Many of the considerations for piping also apply to valves. Valves for chlorine service should be strong enough to withstand the expected pressure, resistant to corrosion, easy to remove and maintain, and should have a leak-tight gland or be leakproof such as a diaphragm or bellows-sealed valves. Table 5-4 provides a summary of guidelines for valve selection (26).

Ball and plug valves must be designed so that excess pressure in the body cavity (as well as in the ball or plug) will relieve spontaneously toward the high pressure side. This is accomplished by providing a relief hole in the valve body (or the ball or plug) which bypasses the upstream seat. Modified valves such as these must indicate the flow direction on the valve body. The valve stem seals should be externally adjustable to stop stem leakage, and the stem should not be removable while the valve is in service (26). All valves must be supplied and maintained dry as well as grease- and oil-free.

Because of the corrosiveness of chlorine, spring-loaded or gravity-operated check valves may not be suitable to prevent backflow. Instead, power-operated control valves with suitable instrumentation may be preferable for primary service with a check valve backup (26).

TABLE 5-4. SUMMARY OF CHLORINE INSTITUTE GUIDELINES FOR VALVES

Chlorine Phase	Temperature Range (°F)	Maximum Pressure (psia)	Valve Type	Rating (lb)	Class	Connection	Material
Gas	-20 to 300	≤300	Globe	800	-	Screwed	Forged Steel
			Ball	300	-	Screwed	Cast Steel
			Plug	300	-	Screwed	Ductile Iron
			Globe	-	150	Flanged	Cast Steel
			Ball	-	150	Flanged	Ductile Iron
			Plug	-	150	Flanged	Ductile Iron
			Globe	-	300	Flanged	Cast Steel
			Ball	-	300	Flanged	Cast Steel
			Plug	-	300	Flanged	Cast Steel
Gas, Liquid	-20 to 300	≤300	Globe	800	-	Screwed	Forged Steel
			Ball	800	-	Screwed	Cast Steel
			Plug	300	-	Screwed	Ductile Iron
			Globe	-	300	Flanged	Cast Steel
			Ball	-	300	Flanged	Cast Steel
			Plug	-	300	Flanged	Cast Steel
			Globe	-	300	Flanged	Cast Steel
			Ball	-	300	Flanged	Cast Steel
			Plug	-	300	Flanged	Cast Steel

Source: Adapted from Reference 26.

Excess flow valves are used in chlorine vessels, tank cars, and areas where unintentional high liquid discharge rates need to be prevented. In the event that a liquid discharge line is broken, the resulting high flow rate would cause the valve to close off, restricting the escape of chlorine. The Chlorine Institute has detailed information on valve materials, designs, and size for excess flow valves (22).

For maintenance and emergencies, it is often useful to be able to isolate vessels and other chlorine process equipment. In some cases, however, a single valve is insufficient to ensure complete isolation, and the use of slip plates or a double block and bleed arrangement may be necessary. Because of the potential for releasing trapped chlorine, proper training is essential to ensure safe operation of these isolation techniques.

#### Process Machinery--

Process machinery refers to rotating or reciprocating equipment that may be used in the transfer or processing of chlorine. This includes pumps and compressors which may be used to move liquid or gaseous chlorine where gas pressure padding is insufficient or inappropriate.

Pumps--Many of the concerns and considerations for chlorine piping and valves also apply to pumps. To assure that a given pump is suitable for chlorine service, the system designer should obtain information from the pump manufacturer certifying that the pump will perform properly in this application.

Pumps should be constructed with materials which are resistant to chlorine at operating temperatures and pressures. They should be installed dry and oil-free. It is especially important that their design not allow chlorine or lubricating oil to enter seal chambers where they may contact one another. Net positive suction head (NPSH) considerations are especially important for chlorine since pumping the liquid near its boiling point may be common (chlorine is a gas at typical ambient conditions). The pump supply tank should

have high and low level alarms; the pump should be interlocked to shut off at low supply level or low discharge pressure. External pumps should be situated inside a diked area and should be accessible in the event of a tank leak.

In many cases, the potential for seal leakage rules out the use of rotating shaft seals. One solution is to use pump types which isolate the seals from the process stream. The seals are typically cartridge canister double type (27). The buffer fluid between the mechanical seal is commonly light oil. Another solution is to use pump types which eliminate shaft seals altogether such as canned-motor, vertical extended-spindle submersible, magnetically-coupled, and diaphragm pumps (27).

Canned motor pumps are centrifugal units in which the motor housing is interconnected with the pump casing. Here, the process liquid actually served as the bearing lubricant. An alternative concept is the vertical pump often used on storage tanks. Vertical pumps consist of a submerged impeller housing connected by an extended drive shaft to the motor. The advantages of this arrangement are that the shaft seal is above the maximum liquid level (and is therefore not made wet by the pumped liquid) and the pump is self priming because the liquid level is above the impeller.

The Chlorine Institute suggests that vertical pumps be provided with double packed seal chambers which are designed to prevent contact of chlorine and any reactive material. Seal gas should be dry, oil-free, and inert to chlorine. They recommend that the seal gas pressure be at least 10 psi over tank pressure, and that a seal gas back-up system be considered (26).

Magnetically-coupled pumps replace the drive shaft with a rotating magnetic field as the pump-motor coupling device. Diaphragm pumps are positive displacement units in which a reciprocating flexible diaphragm drives the fluid. This arrangement eliminates exposure of packing and seals to the pumped liquid.

Centrifugal pumps often have a recycle loop back to the feed container which prevents overheating in the event that the pump is deadheaded (i.e., the discharge valves close). This is an important consideration in chlorine systems since the corrosiveness of chlorine increases rapidly with increasing temperature. Deadheading also is a concern with positive displacement pumps. To prevent rupture, positive displacement pumps commonly have a pressure relief valve which bypasses to the pump suction. Because of the probability of eventual diaphragm failure, the use of diaphragm pumps should be carefully considered in view of this hazard potential.

Pumps are not always necessary; in many circumstances, liquid chlorine is moved by pressure padding. With chlorine cylinders and ton containers, the liquid may be displaced from the vessel by the force of chlorine vapor pressure. As discussed earlier, this process is temperature dependent. With other types of vessels, an inert gas such as dry nitrogen may be used to force liquid from the tank. Padding system designs must reflect the operating conditions and limitations (e.g., required flow rate) and therefore must be custom designed for a process.

Compressors--Chlorine compressors include reciprocating, centrifugal, liquid-ring rotary, and non-lubricated screw compressors. Detailed descriptions of these compressors may be found in the technical literature (5).

Like pumps, compressors have the potential for heat buildup and shaft seal leakage. Heat sources in a compressor include the heat of compression as well as the heat generated through mechanical friction. Heat buildup in chlorine compressors is a particular concern because chlorine corrosion increases with increasing temperature. Most multistaged compressors can be equipped with intercoolers which limit heat buildup and increase compressor efficiency by reducing the volume of gas going to the next compression stage. Both air and water cooling are used, but water systems must be designed to prevent leakage and mixing of water and chlorine gas.

While it is often possible to avoid using rotary shaft seals with chlorine pumps, compressors in chlorine service usually require special seals such as double labyrinth seals. These seals have a series of interlocking touch points which, by creating many incremental pressure drops, reduce total leakage. To further reduce leakage, dry air is injected into the seal. In the event of deadheading, a compressor discharge can have a pressure relief mechanism which vents to the compressor inlet or to a scrubber system. The former appears to be satisfactory for a short term downstream flow interruption. Where a sustained interruption might occur, relief to a scrubber system would be safer.

#### Miscellaneous Equipment--

Pressure Relief Devices--For transportation equipment, the Chlorine Institute has drawings and specifications for chlorine relief valves. For vessels, an acceptable relief valve is of angle body construction with a closed bonnet and a screwed cap over the adjusting screw. These valves normally are used in combination with a rupture disc or a breaking pin assembly. Typical valve construction materials include a cast carbon steel body; a nickel-plated steel spring; and nickel-copper or nickel-chromium-molybdenum alloy nozzle, disc adjusting ring, nozzle ring, and spindle guide. The inlet flange should be Class 300 and the outlet flange should be Class 150 or 300. Valves of this construction which also have Viton® "O" ring seat seals need not have a rupture disc or breaking pin. Other types of pressure relief devices are acceptable as long as they are constructed of materials suitable for chlorine service and meet the general requirements of the ASME boiler and Pressure Vessel Code, Section VIII, Division 1 (26).

Rupture discs are constructed of chlorine resistant materials such as silver, tantalum, or impervious graphite. Impervious graphite rupture discs fragment upon overpressure and therefore should not be used in conjunction with relief valves. Connections smaller than two inches can be screwed, flanged or socket-welded; connections two inches or larger should be flanged

or butt-welded. The flanges should be constructed of forged carbon steel and be rated in accordance with their associated piping system. Because operating pressures exceeding 70% of disc burst pressure may induce premature failure, a considerable margin should be allowed when sizing rupture discs. When it is possible to draw a vacuum on the disc, supports should be provided (25).

Measures should be taken to ensure that process equipment is not isolated from its relief system. To provide continuous pressure relief protection, when a device is out of service for maintenance, equipment may be provided with dual relief systems, each sized to provide the total required flow capacity. Piping and valves should be arranged so that one of the systems always provides protection. Stop valves installed between a vessel and its relief device should have a full port area that is at least equal to that of the pressure relief device inlet. These valves should be locked open or have handles removed when the protected vessel is in use. If the discharge is to be piped to a closed disposal system, such as a scrubber, the pressure drop caused by the additional piping must be considered and the relief device sized accordingly. Relief device sizing guidelines are provided in Chlorine Institute Pamphlet 5 (23).

Instrumentation--A primary consideration for instrumentation in chlorine service is corrosion resistance. Diaphragm pressure switches usually have a diaphragm constructed of silver, tantalum, or nickel-copper alloy. The upper body seal is steel, and the lower body seal is steel or nickel-copper alloy. Direct reading pressure gauges often have a nickel-copper alloy bourdon tube. The pressure range for both types of pressure measurement devices should be twice the operating pressure (26). Other instrumentation, such as temperature and flow measurement devices, also should be constructed of chlorine resistant materials.

### 5.3.2 Plant Siting and Layout

The siting and layout of a particular chlorine facility is a complex issue which requires careful consideration of numerous factors. These include: other processes in the area, the proximity of population centers, prevailing winds, local terrain, and potential natural external effects such as flooding. The rest of this subsection describes general considerations which might apply to siting and layout of chlorine facilities.

Siting of facilities or individual equipment items should be done in a manner that minimizes personnel exposure, both plant and public, in the event of a release. Since there are also other siting considerations, there may be trade-offs between this requirement and others. The site should provide ready ingress or egress in the event of an emergency and yet also take advantage of barriers, either man-made or natural, which could reduce the hazards of releases. Large distances between large inventories and sensitive receptors is desirable.

Layout refers to the placement and arrangement of equipment in the process facility. Some general layout considerations include the following:

- Large inventories of chlorine should be kept away from sources of fire or explosion hazard;
- Vehicular traffic should not go too near chlorine process or storage areas if this can be avoided;
- Where such traffic is necessary, precautions should be taken to reduce the chances for vehicular collisions with equipment, especially pipe racks carrying chlorine across or next to roadways;

- Chlorine piping preferably should not be located adjacent to other piping which is under high pressure or temperature, or which carries flammable materials;
- Storage facilities should be segregated from the main process unless the hazards of pipe transport are felt to outweigh the hazard of the storage tank for site-specific cases; and
- Storage should also be situated away from control rooms, offices, utilities, storage, and laboratory areas.

Various techniques are available for formally assessing a plant layout and should be considered when planning high hazard facilities handling chlorine (1). These techniques provide for a systematic evaluation of key siting and layout factors.

Because heat increases chlorine corrosiveness and causes thermal expansion of liquid chlorine, measures should be taken to situate piping, storage vessels, and other chlorine equipment to minimize heat exposure. Hot process piping, equipment, steam lines, and other sources of direct or radiant heat should be avoided. Storage should also be situated away from control rooms, offices, utilities, storage, and laboratory areas. Special precautions should be taken to keep chlorine storage vessels away from potential fire or explosion sources.

In the event of an emergency, there should be multiple means of access to the facility for emergency vehicles and crews. Storage vessel shut off valves should be readily accessible. Containment for liquid storage tanks can be provided by diking. Dikes reduce evaporation while containing the liquid. It is also possible to equip a diked area to allow drainage to an underground containment sump. This sump would be vented to a scrubber system for safe discharge. A full containment system using a specially constructed building

vented to a scrubber is another possible option. This type of secondary containment could be considered for large volume, liquid chlorine storage tanks. However, secondary hazards abound with such a system, and extreme care in layout and design are required to protect the operators.

### 5.3.3 Transfer and Transport Facilities

Transfer and transport facilities where both road and rail tankers are loaded or unloaded are likely accident areas because of vehicle movement and the intermittent nature of the operations. Therefore, special attention should be given to the design of these facilities.

As mentioned in the previous section, tank car and tank truck facilities should be located away from potential sources of heat, fire, and explosion. Equipment in these areas should also be protected from impact by vehicles and other moving equipment. These tank vehicles should be securely moored during transfer operations; an interlocked barrier system is commonly used. Sufficient space should be available to avoid congestion of vehicles or personnel during loading and unloading operations. Vehicles, especially trucks, should be able to move into and out of the area without reversing. High curbs around transfer areas and barriers around equipment should be provided to protect equipment from vehicle collisions.

When possible, the transfer of chlorine should be made using fixed rigid piping. In situations which require flexible hoses or tubes, precautions must be taken to ensure sound connections. The use of breakaway valves with autoclosing shutoff valves should also be considered to prevent pullaway type accidents. Avoiding cross contamination of chemical materials is also a key concern which is sometimes addressed by having dedicated pipe lines or hoses designed so that interconnections with inappropriate lines are not possible.

## 5.4 PROTECTION TECHNOLOGIES

This subsection describes two types of protection technologies for containment and neutralization. These are:

- Enclosures; and
- Scrubbers.

A presentation of more detailed information on these systems is planned in other portions of the prevention reference manual series.

### 5.4.1 Enclosures

Enclosures refer to containment structures which capture any chlorine spilled or vented from storage or process equipment, thereby preventing immediate discharge of the chemical to the environment. The enclosures contain the spilled liquid or gas until it can be transferred to other containment, discharged at a controlled rate which would not be injurious to people or the environment, or transferred at a controlled rate to scrubbers for neutralization.

The use of specially designed enclosures for either chlorine storage or process equipment does not appear to be widely practiced. The location of toxic operations in the open air has been mentioned favorably in the literature, along with the opposing idea that sometimes enclosure may be appropriate (1). The desirability of enclosure depends partly on the frequency with which personnel must be involved with the equipment. A common design rationale for not having an enclosure where toxic materials are used is to prevent the accumulation of toxic concentrations of a chemical within a work area. However, if the issue is protecting the community from accidental releases, then total enclosure may be appropriate. Enclosures should be equipped with continuous monitoring equipment and alarms. Alarms should sound whenever lethal or flammable concentrations are detected.

Care must be taken when an enclosure is built around pressurized equipment. It would not be practical to design an enclosure to withstand the pressures associated with the sudden release of a pressurized vessel. An enclosure would probably fail as a result of the pressure created from such a release and could create an additional hazard. In these situations, it may be determined that an enclosure is not appropriate. If an enclosure is built around pressurized equipment then it should be equipped with some type of explosion protection, such as rupture plates that are designed to fail before the entire structure fails.

The type of containment structures that appear to be suitable for chlorine are concrete block or concrete sheet buildings, or bunkers. Chlorine reactivity may preclude buildings of metal or wood. An enclosure would have a ventilation system designed to draw in air when the building is vented to a scrubber. The bottom section of a building used for stationary storage containers should be liquid tight to retain any liquid chlorine that might be spilled. Buildings around rail tank cars used for storage do not lend themselves well to effective liquid containment. However, containment could be accomplished if the floor of the building is excavated several feet below the track level while the tracks are supported at grade in the center.

While the use of enclosures for secondary containment of chlorine spills or releases is not known to be widely used, it can be considered as a possible protection technology for areas near especially sensitive receptors.

#### 5.4.2 Scrubbers

Scrubbers are a traditional method for absorbing toxic gases from process streams. These devices can be used to control chlorine releases from vents and pressure relief discharges from storage equipment, process equipment, or secondary containment enclosures.

Chlorine discharges could be contacted with an aqueous scrubbing medium in any of several types of scrubbing devices. An alkaline solution is required to achieve effective absorption because absorption rates with water alone would require unreasonably high liquid-to-gas ratios. However, water scrubbing could be used in a make-shift scrubber in an emergency if an alkaline solution were not available. Typical alkaline solutions for an emergency scrubber are presented in Table 5-5.

Types of scrubbers that might be appropriate include spray towers, packed bed scrubbers, and venturists. Other types of special designs might be suitable, but complex internals subject to corrosion do not seem, to be advisable. Whichever type of scrubber is selected, a key consideration for emergency systems is the design flow rate to be used. A conservative design would use the maximum rate that would be expected from an emergency. Some typical absorption data for a packed scrubber used for chlorine are presented in Table 5-6.

Whatever type of scrubber is selected, a complete system would include the scrubber itself, a liquid feed system, and reagent makeup equipment. If such a system is used as protection against emergency releases, consideration must be given to how it would be activated in time to respond to an emergency load. One approach used in some process facilities is to maintain a continuous circulation of scrubbing liquor through the system. This may be practical where the emergency scrubber also serves as a routine vent scrubber. For many facilities this would not be practical, and the scrubber system might be tied into a trip system which would turn it on when needed. However, with this system a quantity of chlorine would be released prior to actuation of the scrubber (i.e., starting up a blower and turning on the flow of liquid).

The scrubbing system must be designed so as not to present excessive resistance to the flow of an emergency discharge. The pressure drop should be only a small fraction of the total pressure drop through the emergency discharge system. In general, at the liquid-to-gas ratios required for effective scrubbing, spray towers have the lowest, and venturists the highest pressure

TABLE 5-5. TYPICAL ALKALINE SOLUTION FOR CHLORINE SCRUBBING

Container Capacity (lb)	Caustic Soda		Soda Ash		Hydrated Lime <sup>a</sup>	
	100% (lb)	Water, (gal)	(lb)	Water, (gal)	(lb)	Water, (gal)
100	125	40	300	100	125	125
150	188	60	450	150	188	188
2,000	2,500	800	6,000	2,000	2,500	2,500

Source: Reference 6

<sup>a</sup> Hydrated lime solution must be continuously agitated to ensure aqueous mixture.

TABLE 5-6. TYPICAL CHLORINE ABSORPTION DATA

Size of Packed Tower	Liquid Rate [lb/(hr-ft <sup>2</sup> )]	Overall Mass Transfer Coefficient	Height of Transfer Unit H <sub>OL</sub> (ft)
		$K_L^a$ (lb-mole)/[hr-ft <sup>3</sup> - mole fraction solute in liquid]	
4-inch diameter	1,000	14	1.3
	2,000	20	1.7
	4,000	30	2.3
	6,000	38	2.6
	10,000	50	3.2
	15,000	61	3.6
	20,000	74	4.2
14-inch diameter	1,000	11	1.6
	2,000	16	2.1
	4,000	24	2.8
	6,000	30	3.3
	10,000	40	4.0
	15,000	48	4.6
	20,000	59	5.5

Basis: Packed tower, 1-inch rings, operating at 70°F.

Source: Adapted from Reference 28.

drops. While packed beds may have intermediate pressure drops at proper liquid-to-gas ratios, excessive ratios or plugging can increase the pressure drop substantially. However, packed beds have higher removal efficiencies than spray towers or venturists.

In addition, the scrubber system must be designed to handle the "shock wave" generated during the initial stages of the release. This is particularly important for packed bed scrubbers since there is a maximum pressure with which the gas can enter the packed section without damaging the scrubber internals.

Design of emergency scrubbers can follow standard techniques discussed in the literature, carefully taking into account the additional considerations just mentioned. An example of the sizing of an emergency packed bed scrubber is presented in Table 5-7. This example provides some idea of the size of a typical emergency scrubber for various flow rates. This is an example only and should not be used as the basis for an actual system which might differ based on site specific requirements.

Another approach is the drowning tank, where the chlorine vent is routed to the bottom of a large tank of uncirculating caustic. The drowning tank does not have the high contact efficiency of the other scrubber types. However, it can provide substantial capacity on demand as long as the back pressure of the hydrostatic head does not create a secondary hazard, by impeding an overpressure relief discharge, for example. In addition, precautions must be taken to prevent backflow of the scrubbing liquid through the lines to a chlorine containing vessel since explosions can occur. Such an event could occur as a result from overflowing of the scrubber.

## 5.5 MITIGATION TECHNOLOGIES

If, in spite of all precautions, a large release of chlorine were to occur, the first priority would be to rescue workers in the immediate vicinity of the accident and evacuate persons from downwind areas. The source of the

TABLE 5-7. EXAMPLE OF PERFORMANCE CHARACTERISTICS FOR AN EMERGENCY  
PACKED BED SCRUBBER FOR CHLORINE

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Basis: Inlet stream of 50% Cl<sub>2</sub> in 50% air.<sup>2</sup> Constant gas flow per unit  
cross-sectional area of 290 scfm/ft<sup>2</sup>.

Packing: 2-inch plastic Intalox® saddles.

Pressure Drop: 0.5-inch water column

Scrubbing Medium: 8% (wt) NaOH solution

Removal Efficiency, %	50	90
Liquid-to-Gas Ratio (gal/thousand scf)		
--at flooding	240	240
--operating	144	144
Packed Height, ft.	1.3	4.4

Column Diameter and Cooresponding Gas Flow Rates for Both Removal Efficiencies

Column Diameter (ft)	Flow Rate (scfm)
0.5	60
1.0	240
2.0	960
6.6	10,000

---

release should be determined, and the leak should be stopped., if this is possible. The next primary concern become reducing the consequences of the released chemical to the plant and the surrounding community. Reducing the consequences of an accidental release of a hazardous chemical is referred to as mitigation. Mitigation technologies include such measures as physical barriers, water sprays and fogs, and foams where applicable. The purpose of a mitigation technique is to divert, limit, or disperse the chemical that has been spilled or released to the atmosphere in order to reduce the atmospheric concentration and the area affected by the chemical. The mitigation technology chosen for a particular chemical depends on the specific properties of the chemical including its flammability, toxicity, reactivity, and those properties which determine its dispersion characteristics in the atmosphere.

If a release occurs from a pressurized chlorine storage tank above the boiling point, a quantity of liquid will immediately flash off as vapor, while the remaining liquid will be cooled to the normal boiling point of  $-29.3^{\circ}\text{F}$ . Heat transfer from the air and ground will result in further vaporization of the released liquid. Since the chlorine accidentally released from a refrigerated storage tank is already at or below its normal boiling point, a comparable quantity of vapor will not flash off, as with the pressurized release discussed above, but heat transfer from the environment will cause evaporation and the formation of a vapor cloud. It is therefore desirable to minimize the area available for heat transfer to a liquid spill which in turn will minimize the rate of evaporation. Mitigation technologies which are used to reduce the rate of evaporation of a released liquified gas include secondary containment systems such as impounding basins and dikes.

A post release mitigation effort requires that the source of the release be accessible to trained plant personnel. Therefore, the availability of adequate personnel protection is essential. Personnel protection will typically include such items as portable breathing air and chemically resistant protective clothing.

### 5.5.1 Secondary Containment Systems

Specific types of secondary containment systems include excavated basins, natural basins, earth, steel, or concrete dikes, and high impounding walls. The type of containment system best suited for a particular storage tank or process unit will depend on the risk associated with an accidental release from that location. The inventory of chlorine and its proximity to other portions of the plant and to the community should be considered when selecting a secondary containment system. The secondary containment system should have the ability to contain spills with a minimum of damage to the facility and its surroundings with minimum potential for escalation of the event.

Secondary containment systems for chlorine storage facilities commonly consist of one of the following:

- An adequate drainage system underlying the storage vessels which terminates in an impounding basin having a capacity as large as the largest tank served; and
- A diked area, with a capacity as large as the largest tank served.

These measures are designed to prevent the accidental discharge of liquid chlorine from spreading to uncontrolled areas.

The most common type of containment system is a low wall dike surrounding one or more storage tanks. Generally, no more than three tanks are enclosed within one diked area to reduce risk. Dike heights usually range from three to twelve feet depending on the area available to achieve the required volumetric capacity. The dike walls should be liquid tight and able to withstand the hydrostatic pressure and temperature of a spill. Low wall dikes may be constructed of steel, concrete or earth. If earthen dikes are used, the dike wall must be constructed and maintained to prevent leakage through the dike. Piping should be routed over dike walls, and penetrations through the walls should be avoided if possible. Vapor fences may be situated on top of the

dikes to provide additional vapor containment. If there is more than one tank in the diked areas, the tanks should be situated on berms above the maximum liquid level attainable in the impoundment.

A low wall dike can effectively contain the liquid portion of an accidental release and keep the liquid from entering uncontrolled areas. By preventing the liquid from spreading, the low wall dike can reduce the surface area of the spill. Reducing the surface area will reduce the rate of evaporation. The low wall dike will partially protect the spill from wind; this can reduce the rate of evaporation. A dike with a vapor fence will provide extra protection from wind and will be even more effective at reducing the rate of evaporation.

A low wall dike will not reduce the impact of a gaseous chlorine release. A dike also creates the potential for chlorine and trapped water to mix in the dike, which may accelerate the rate of evaporation and form highly corrosive hydrochloric and hydrochlorous acids. If materials that would react violently with chlorine are stored within the same diked area then the dike will increase the potential for mixing the materials in the event of a simultaneous leak. A dike also limits access to the tank during a spill.

A remote impounding basin is well suited to storage systems where more than one tank is served and a relatively large site is available. The flow from a chlorine spill is directed to the basin by dikes and channels under the storage tanks which are designed to minimize contact of the liquid with other tanks and surrounding facilities. Because of the high vapor pressure of chlorine, the trenches that lead to the remote impounding basin as well as the basin itself should be covered to reduce the rate of evaporation. Additionally, the impounding basin should be located near the tank area to minimize the amount of chlorine that evaporates as it travels to the basin.

This type of system has several advantages. The spilled liquid is removed from the immediate tank area. This allows access to the tank during the spill and reduces the probability that the spilled liquid will damage the tank,

pipng, electrical equipment, pumps or other equipment. In addition, the covered impoundment will reduce the rate of evaporation from the spill by protecting the spill from wind or heating from sunlight.

A limitation of a remote impounding basin is that there is still the potential for water or other incompatible materials to be trapped in the impoundment and mix with the incoming chlorine. Remote impounding basins do not reduce the impact of a gaseous chlorine release.

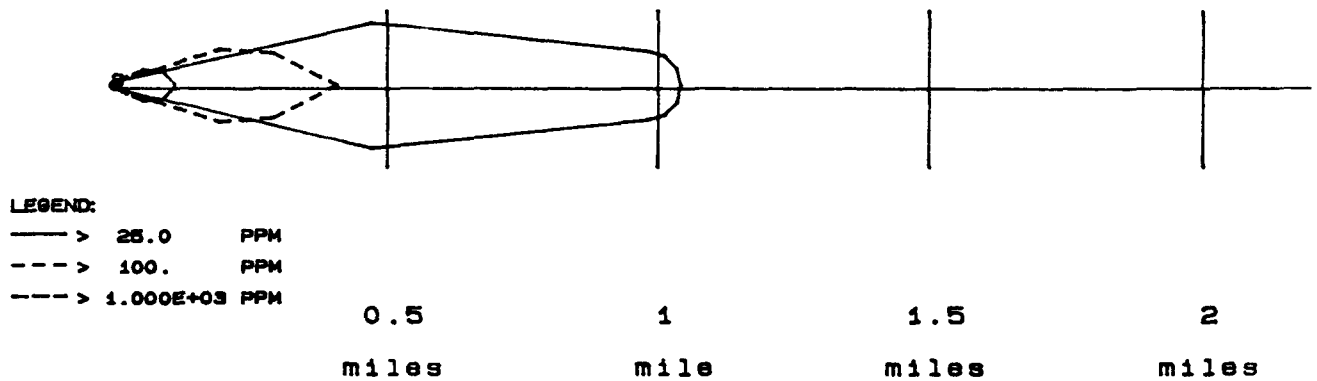
Although few authorities for chlorine facilities require them, high wall impoundments may be a good secondary containment choice for selected systems. Circumstances which may warrant their use include limited storage site area, the need to minimize vapor generation rates, and/or the tank must be protected from external hazards. Maximum vapor generation rates will generally be lower for a high wall impoundment than for low wall dikes or remote impoundments because of the reduced surface contact area. These rates can be further reduced with the use of insulation on the wall and floor in the annular space. High impounding walls may be constructed of low temperature steel, reinforced concrete, or prestressed concrete. A weather shield may be provided between the tank and wall with the annular space remaining open to the atmosphere. The available area surrounding the storage tank will dictate the minimum height of the wall. For high wall impoundments, the walls may be designed with a volumetric capacity greater than that of the tank to provide vapor containment. Increasing the height of the wall also raises the elevation of any released vapor.

One disadvantage of these dikes is that the high walls around a tank may hinder routine external observation. Furthermore, the closer the wall is to the tank, the more difficult it becomes to access the tank for inspection and maintenance. As with low wall dikes, piping should be routed over the wall if possible. The closeness of the wall to the tank may necessitate placement of the pump outside of the wall, in which case the outlet (suction) line will have to pass through the wall. In such a situation, a low dike encompassing the pip penetration and pump may be provided, or a low dike may be placed around the entire wall.

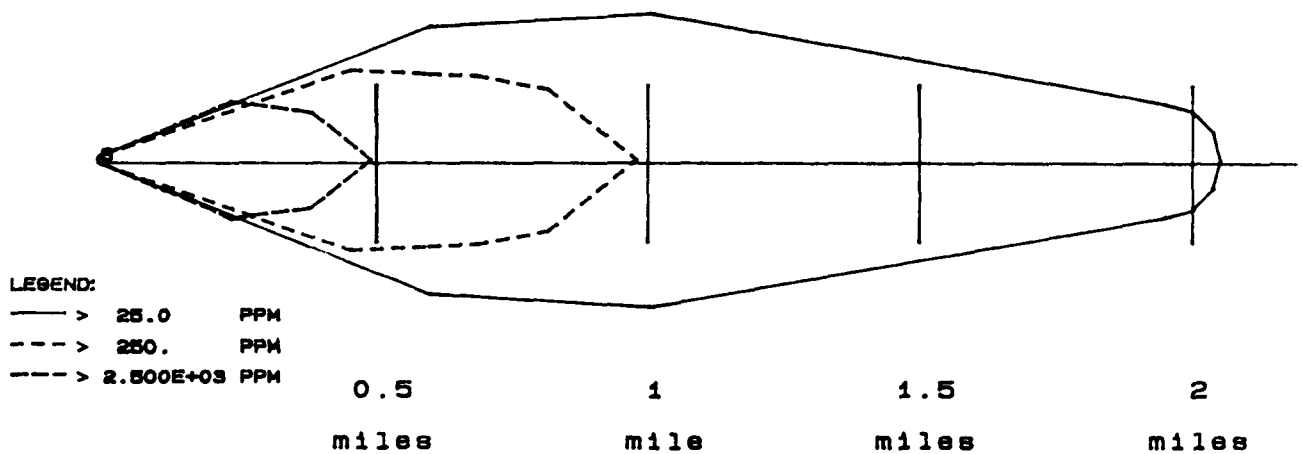
An example of the effect of diking as predicted by one vapor dispersion model is shown in Figure 5-2 (29). With diking, the predicted maximum IDLH exposure occurs at a distance of 1,195 feet at 6 minutes after release. Without diking, the predicted maximum IDLH exposure occurs at a distance of 2,802 feet at 12 minutes after exposure.

One further type of secondary containment system is one which is structurally integrated with the primary system and forms a vapor tight enclosure around the primary container. Many types of arrangements are possible. A double walled tank is an example of such an enclosure. These systems may be considered where protection of the primary container and containment of vapor for events not involving foundation or wall penetration failure are of greatest concern. Drawbacks of an integrated system are the greater complexity of the structure, the difficulty of access to certain components, and the fact that complete vapor containment cannot be guaranteed for all potential events.

Provision should be made for drainage of rainwater from diked areas. This will involve the use of sumps and separate drainage pumps, since direct drainage to stormwater sewers would presumably allow any spilled chlorine to follow the same route. Alternatively, a slope rain hood may be used over the diked area which could also serve to direct the rising vapors to a single release point (30). The ground within the enclosure should be graded to cause the spilled liquid to accumulate at one side or in one corner. This will help to minimize the area of ground to which the liquid is exposed and from which it may gain heat. In areas where it is critical to minimize vapor generation, surface insulation may be used in the diked area to further reduce heat transfer from the environment to the spilled liquid. the floor of an impoundment should be sealed with a clay blanket to prevent the chlorine from seeping into the ground; percolation into the ground causes the ground to cool more quickly, increasing the vapor generation rate. Absorption of the chlorine into water in the soil would also release additional heat.



Release from a tank surrounded by a 25 ft. diameter dike.  
Elapsed Time: 6 minutes



Release from a tank with no dike.  
Elapsed Time: 12 minutes

Common Release Conditions:

Storage Temperature = 29.3°F  
Storage Pressure = 14.7 psia  
Ambient Temperature = 85°F

Wind Speed = 10 mph  
Atmospheric Stability Class = C  
Quantity Released = 5,000 gallons  
through a 2-inch hole

Figure 5-2. Computer Model Simulation Showing the Effect of Diking on the Vapor Cloud Generated From a Release of Refrigerated Chlorine.

### 5.5.2 Flotation Devices and Foams

This subsection discusses the applicability, availability, and effectiveness of additional mitigation technologies for use in reducing the surface area of spilled chlorine and thereby minimizing the amount of toxic vapor released to the surrounding environment.

#### Flotation Devices--

Placing an impermeable flotation device over a spilled chemical is a direct approach for containing toxic vapors with nearly 100 percent efficiency. However, being able to use such devices requires acquisition in advance of a spill and storage until needed. In addition, deployment may be difficult in all but small spills.

Although such devices are potentially effective, no systems are currently available for use in mitigating chlorine spills. The primary deterrent to their use is the cost associated with material and dispersal equipment. Such a system would require the dispersal of a minimum of 280 particles per square foot of spill surface (30). Based on 1986 prices, material costs would be approximately \$100 per square foot, with dispersal equipment costs running 100 times this cost (31).

#### Foams--

One approach to a chlorine spill is dilution of chlorine with water. However, chlorine is only slightly soluble in water and a large quantity would be required for dilution. In addition, dilution of chlorine with water results in the formation of highly corrosive hydrochloric and hydrochlorous acids. As such, the Chlorine Institute states that water should never be sprayed directly on a chlorine leak since water will make the leak worse (6). A water-based foam cover provides an alternative means of diluting the chlorine.

The use of foams in vapor hazard control has been demonstrated for a broad range of volatile chemicals. Unfortunately, it is difficult to accurately quantify the benefits of foam systems because the effects will vary as

a function of the chemical spilled, foam type, spill size, and atmospheric conditions. With regard to liquified gases, it has been found that with some materials, foams have a net positive effect, but with others, foams may exaggerate the hazard.

Several studies of the effect of foam on chlorine have been conducted in the past (32,33). These studies have given mixed results. Although much information has yet to be determined, it has been shown that for the current grades of commercially available foam systems (i.e., protein-derived material and surfactant-based concentrates), application of foam to liquid chlorine results in rapid destruction of the foam along with a gross exaggeration of the boil-off rate (32,34). This effect may last through several successive applications depending on the type of foam, the expansion, and the rate of application.

As foam is applied, the interaction of the chlorine and the collapsing foam results in the formation of a layer of ice and chlorine hydrate that tends to float on the chlorine surface (34). As the foam application is continued, this layer eventually becomes continuous and a foam covering can then be built on top of the chlorine surface. When this occurs, a reduction in the downwind concentration can be achieved as a result of a slowing of the release rate of chlorine vapor (34).

Sufficient data are not presently available to define the variables needed to implement such a system (i.e., best foam type, expansion type, application rate, and duration of application). Based on preliminary research studies, medium expansion expansion foams (300 to 350:1) appear to work best, but low expansion foams have also shown some benefit (34). The results of a laboratory test program conducted by the Mine Safety Application (MSA) Research Corporation (32) to evaluate the applicability and effectiveness of various foams for various hazardous chemicals including chlorine is presented in Table 5-8 (32).

TABLE 5-8. FOAM CAPABILITIES TO SUPPRESS OR MINIMIZE THE RELEASE OF TOXIC VAPORS FROM A CHLORINE SPILL

Foam Type	Capability
Low-expansion surfactant	Acceptable in some situations
High-expansion surfactant	Acceptable in some situations
Protein	Acceptable in some situations
Fluoroprotein	Acceptable in some situations
Alcohol	Unsuitable
Aqueous film-forming foams (AFFF)	Unsuitable

Regardless of the type of foam used, the slower the drainage rate of the foam, the better its performance will be. A slow draining foam will collapse more slowly. The initial cost for a slow draining foam may be higher than for other foams, but a cost effective system will be realized in superior performance.

Even if the vaporization rate of chlorine is substantially reduced within a short time after a spill, a vapor cloud will still be formed which poses a serious threat to life and limb downwind. Dispersion and/or removal of the chlorine vapor in the atmosphere is the subject of the following section.

### 5.5.3 Mitigation Techniques for Chlorine Vapor

The extent to which the escaped chlorine vapor can be removed or dispersed in a timely manner will be a function of the quantity of vapor released, the ambient conditions, and the physical characteristics of the vapor cloud. The behavior and characteristics of the chlorine cloud will be dependent on a number of factors. These include the physical state of the chlorine before its release, the location of the release, and the atmospheric and environmental conditions. Many possibilities exist concerning the shape and motion of the vapor cloud, and a number of predictive models of dispersion have been developed. As a result of the higher specific gravity of pure chlorine, large accidental releases of chlorine will often result in the formation of chlorine-air mixtures which are denser than the surrounding atmosphere. This type of vapor cloud is especially hazardous, because it will spread laterally and remain close to the ground.

One possible means of dispersing as well as removing toxic vapors from the air is with the use of water sprays or fogs. The low solubility of chlorine in water, however, limits the effectiveness of such systems for chlorine removal from the air. An alternative is to use a mild aqueous alkaline spray system such as an ammonia injected water spray system which would act as a neutralizing agent. Although such systems do not appear to be widely used for the mitigation of chlorine vapor, they are used for other toxic chemicals of similar nature (35).

The spray medium is typically applied to the vapor cloud by means of hand-held hoses and/or stationary water-spray barriers. Important factors relating to the effectiveness of spray systems are the distance of the nozzle from the point of release, the fog pattern, nozzle flow rate, pressure, and nozzle rotation. If water sprays are used to mitigate chlorine vapors from a diked area containing spilled liquid chlorine, great care must be taken not to direct water into the liquid chlorine itself.

Several techniques have also been developed to effectively disperse toxic vapor resulting from major leaks in piping and equipment. One such technique has been developed by Beresford (36). Although such systems have not been used for the mitigation of chlorine vapor, they have been effectively used for other toxic chemicals of similar nature (36).

The method consists of coarse water sprays discharging upwards from the flat fan sprays and wide-angled spray monitors arranged so that a vent or chimney effect is created to completely surround the toxic vapor. Results have shown that the high velocity water droplets include large volumes of air at ground level as the water discharges upwards (36). The air is caused to move upwards through the chimney formed by the sprays. As the air moves over the ground, the heavier than air toxic gas is diluted and pushed up and out of the top of the chimney where it disperses safely. Design details are presented in Beresford (36). Both types of spray methods are incorporated into the design since the flat-fan sprays effectively stop the lateral spread of vapor and the monitors provide the required air movement for dilution and dispersal.

Another means of dispersing a vapor cloud is with the use of large fans or blowers which would direct the vapor away from populated or other sensitive areas. However, this method would only be feasible in very calm weather and in sheltered areas; it would not be effective in any wind and difficult to control if the release occupies a large open area. A large, mechanical blower would also be required which lowers the reliability of this mitigation technique compared to water fogs and sprays.

In general, techniques used to disperse or control vapor emissions should emphasize simplicity and reliability. In addition to the mitigation techniques discussed above, physical barriers such as buildings and rows of trees may help to contain the vapor cloud and control its movement. A presentation of additional information will be found in a manual on control technologies, part of this manual series.

## 5.6 OPERATION AND MAINTENANCE PRACTICES

Quality hardware, contained mechanical equipment, and protective devices all increase plant safety; however, they must be supported by the safety policies of management and by constraints on their operation and maintenance. This section describes how management policy and training, operation, and maintenance procedures relate to the prevention of accidental chlorine releases. Within the chlorine industry, these procedures and practices vary widely because of difference in the size and nature of the processes and because any determination of their adequacy is inherently subjective. For this reason, the following subsections focus primarily on fundamental principles and do not attempt to define specific policies and procedures.

### 5.6.1 Management Policy

Management is a key factor in the control of industrial hazards and the prevention of accidental releases. Management establishes the broad policies and procedures which influence the implementation and execution of specific hazard control measures. It is important that these management policies and procedures be designed to match the level of risk in the facilities where they will be used. Most organizations have a formal safety policy. Many make policy statements to the effect that safety must rank equally with other company functions such as production and sales. The effectiveness of any safety program, however, is determined by a company's commitment to it, as demonstrated throughout the management structure. Specific goals must be derived from the safety policy and supported by all levels of management. Safety and

loss prevention should be an explicit management objective. Ideally, management should establish the specific safety performance measures, provide incentives for attaining safety goals, and commit company resource to safety and hazard control. The advantages of an explicit policy are that it sets the standard by which existing programs can be judged, and it provides evidence that safety is viewed as a significant factor in company operations.

In the context of accident prevention, management is responsible for (1,37):

- Ensuring worker competency;
- Developing and enforcing standard operating procedures;
- Adequate documentation of policy and procedures;
- Communicating and promoting feedback regarding safety issues;
- Identification, assessment, and control of hazards; and
- Regular plant audits and provisions for independent checks.

Additional discussion on the responsibilities of management will be found in a manual on control technologies, part of this manual series.

#### 5.6.2 Operator Training

The performance of operating personnel is also a key factor in the prevention of accidental chlorine releases. Many case studies documenting industrial incidents note the contribution of human error to accidental releases (1). Release incidents may be caused by using improper routine operating procedures, by insufficient knowledge of process variables and equipment, by lack of knowledge about emergency or upset procedures, by failure to recognize critical situations, and in some cases by direct physical

mistake (e.g., turning the wrong valve). A comprehensive operator training program can decrease the potential for accidents resulting from such causes.

Operator training can include a wide range of activities and a broad spectrum of information. Training, however, is distinguished from education in that it is specific to particular tasks. While general education is important and beneficial, it is not a substitute for specific training. The content of a specific training program depends on the type of industry, the nature of the processes used, the operational skills required, the characteristics of the plant management system, and tradition.

Some general characteristics of quality industrial training programs include:

- Establishment of good working relations between management and personnel;
- Definition of trainer responsibilities and training program goals;
- Use of documentation, classroom instruction, and field training (in some cases supplemented with simulator training);
- Inclusion of procedures for normal startup and shutdown, routine operations, and upsets, emergencies, and accidental releases; and
- Frequent supplemental training and the use of up-to-date training materials.

In many instances, training is carried out jointly by plant managers and a training staff selected by management. In others, management is solely responsible for maintaining training programs. In either case, responsibilities should be explicitly designated to ensure that the quality and quantity

of training provided is adequate. Training requirements and practices can be expected to differ between small and large companies, partly because of resource needs and availability, and partly of differences in employee turnover.

A list of the aspects typically involved in the training of process operators for routine process operations is presented in Table 5-9.

Emergency training includes topics such as:

- Recognition of alarm signals;
- Performance of specific functions (e.g., shutdown switches);
- Use of specific equipment;
- Actions to be taken on instruction to evacuate;
- Fire fighting; and
- Rehearsal of emergency situations.

Aspects specifically addressed in safety training include (1,37):

- Hazard recognition and communication;
- Actions to be taken in particular situations;
- Available safety equipment and locations;
- When and how to use safety equipment;
- Use and familiarity with documentation such as,
  - plant design and operating manuals
  - company safety rules and procedures

TABLE 5-9. ASPECTS OF TRAINING PROGRAMS FOR ROUTINE PROCESS OPERATIONS

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Process goals, economics, constraints, and priorities  
Process flow diagrams  
Unit Operations  
Process reactions, thermal effects  
Control systems  
Process materials quality, yields  
Process effluents and wastes  
Plant equipment and instrumentation  
Equipment identification  
Equipment manipulation  
Operating procedures  
Equipment maintenance and cleaning  
Use of tools  
Permit systems  
Equipment failure, services failure  
Fault administration  
    Alarm monitoring  
    Fault diagnosis  
    Malfunction detection  
Communications, record-keeping, reporting

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Source: Reference 1.

- procedures relevant to fire, explosion, accident, and health hazards,
  - chemical property and handling information, and
- First aid and CPR.

Although emergency and safety programs typically focus on incidents such as fires, explosions, and personnel safety, it is important that prevention of accidental chemical releases and release responses be addressed as part of these programs.

Much of the type of training discussed above is also important for management personnel. Safety training gives management the perspective necessary to formulate good policies and procedures, and to make changes that will improve the quality of plant safety programs. Lees suggests that training programs applied to managers include or define (1):

- Overview of technical aspects of safety and loss prevention approach,
- Company systems and procedures,
- Division of labor between safety personnel and managers in , with respect to training, and
- Familiarity with documented materials used by workers.

### 5.6.3 Maintenance and Modification Practices

Plant maintenance is necessary to ensure the structural integrity of chemical processing equipment; modifications are often necessary to allow more effective production. However, since these activities are also a primary

source of accidental release incidents, proper maintenance and modification practices are an important part of accidental release prevention. Use of a formal system of controls is perhaps the most effective way of ensuring that maintenance and modification are conducted safely. In many cases, control systems have had a marked effect on the level of failures experienced (1).

Permit systems and up-to-date maintenance procedures minimize the potential for accidents during maintenance operations. Permit-to-work systems control maintenance activities by specifying the work to be done, defining individual responsibilities, eliminating or protecting against hazards, and ensuring that appropriate inspection and testing procedures are followed.

Maintenance permits originate with the operating staff. Permits may be issued in one or two stages. In one-stage systems, the operations supervisor issues permits to the maintenance supervisor, who is then responsible for his staff. Two-stage systems involves a second permit issued by the maintenance supervisor to his workforce (1).

Another form of maintenance control is the maintenance information system. Ideally, these systems should log the entire maintenance history of equipment, including preventative maintenance, inspection and testing, routine servicing, and breakdown or failure maintenance. This type of system is also used to track incidents caused by factors such as human error, leaks, and fires, including identification and quantification of failures responsible for hazardous conditions, failures responsible for downtime, and failures responsible for direct repair costs.

Accidental releases are frequently the result of some aspect of plant modification. Accidents result when equipment integrity and operation are not properly assessed following modification, or when modifications are made without updating corresponding operation and maintenance instructions. In these situations, it is important that careful assessment of the modification results has a priority equal to that of getting the plant on-line.

For effective modification control, there must be established procedures for authorization, work activities, inspection, and assessment, complete documentation of changes, including the updating of manuals, and additional training to familiarize operators with new equipment and procedures (1,37).

Formal procedures and checks on maintenance and modification practices must be established to ensure that such practices enhance rather than adversely affect plant safety. As with other plant practices, procedure development and complete documentation are necessary. However, training, attitude, and the degree to which the procedures are followed also significantly influence plant safety and release prevention.

The use and availability of clearly defined procedures collected in maintenance and operating manuals is crucial for the prevention of accidental releases. Well-written instructions should give enough information about a process that the worker with hands-on responsibility for operating or maintaining the process can do so safely, effectively, and economically. These instructions not only document the path to the desired results, but also are the basis for most industrial training programs (38,39). In the chemical industry, operating and maintenance manuals vary in content and detail. To some extent, this variation is a function of process type and complexity; however, in many cases it is a function of management policy. Because of their importance to the safe operation of a chemical process, these manuals must be as clear, straightforward, and complete as possible. In addition, standard procedures should be developed and documented before plant startup, and appropriate revisions should be made throughout plant operations.

Operation and maintenance may be combined or documented separately. Procedures should include startup, shutdown, hazard identification, upset conditions, emergency situations, inspection and testing, and modifications (1). Several authors think industrial plant operating manuals should include (1,37,38,39):

- Process descriptions,
- A comprehensive safety and occupational health section,
- Information regarding environmental controls,
- Detailed operating instructions, including startup and shutdown procedures,
- Upset and emergency procedures,
- Sampling instructions,
- Operating documents (e.g., logs, standard calculations),
- Procedures related to hazard identification,
- Information regarding safety equipment,
- Descriptions of job responsibilities, and
- Reference materials.

Plant maintenance manuals typically contain procedures not only for routine maintenance, but also for inspection and testing, preventive maintenance, and plant or process modifications. These procedures include specific items such as codes and supporting documentation for maintenance and modifications (e.g., permits-to-work, clearance certificates), equipment identification and location guides, inspection and lubrication schedules, information on lubricants, gaskets, valve packings and seals, maintenance stock requirements, standard repair times, equipment turnaround schedules, and specific inspection codes (e.g., for vessels and pressure systems) (1). Full

documentation of the maintenance required for protective devices is a particularly important aspect of formal maintenance systems.

The preparation of operating and maintenance manuals, their availability, and the familiarity of workers with their contents are all important to safe plant operations. The objective, however, is to maintain this safe practice throughout the life of the plant. Therefore, as processes and conditions are modified, documented procedures must also be modified.

## 5.7 CONTROL EFFECTIVENESS

It is difficult to quantify the control effectiveness of preventive and protective measures to reduce the probability and magnitude of accidental releases. Preventive measures, which may involve numerous combinations of process design, equipment design, and operational measures, are especially difficult to quantify because they reduce the probability of a release rather than a physical quantity of chemical. Protective measures are more analogous to traditional pollution control technologies. Thus, they may be easier to quantify in terms of their efficiency in reducing a quantity of chemical that could be released.

Preventive measures reduce the probability of an accidental release by increasing the reliability of process systems operations and equipment. Control effectiveness can thus be expressed for both of the qualitative improvements achieved and quantitative improvements as probabilities. Table 5-10 summarizes what appear to be major design, equipment, and operational measures applicable to the primary hazards identified for the chlorine applications in the United States. The items listed in Table 5-10 are for illustration only and do not necessarily represent satisfactory control options for all cases. These control options appear to reduce the risk associated with an accidental release when viewed from a broad perspective. However, there are undoubtedly specific cases where these control options will not be appropriate. Each case must be evaluated individually. A presentation of more

TABLE 5-10. EXAMPLES OF MAJOR PREVENTION AND PROTECTION MEASURES  
FOR CHLORINE RELEASES

Hazard Area	Prevention/Protection
External fire	Water sprays to cool exposed chlorine storage vessels; siting away from flammables; refrigeration systems; heat shield
Line, pipe, and valve failure	Replacement of copper with Monel in small lines; more frequent inspections and maintenance
Flexible connection failures	Minimized use; higher quality components; operator training in proper assembly
Fusible plug failure	Inspection/certification; storage in a containment building
Human error	Increased training and supervision; use of checklists; use of automatic systems
Container failure	Adequate pressure relief; inspection and maintenance; corrosion monitoring; siting away from fire and mechanical damage
Vehicular collisions	Location; physical barriers; warning signs; training
Water intrusion	Pad gas drying; backflow prevention; equipment purging with dry gas
Corrosion	Inspections, maintenance, and corrosion monitoring
Excess chlorine rates	Enhanced flow control; limited over-design of feed systems; fail-shut control valves
Overheated reactor	Redundant temperature sensing and alarms; interlocked chlorine feed shut-off; pH control for bleach reactor

(Continued)

TABLE 5-10 (Continued)

Hazard Area	Prevention/Protection
Heating media flow control	Enhanced flow control; redundant temperature sensing and alarm
Overpressure	Enhanced pressure relief (non-isolatable, adequate-sized, no discharge restrictions, safe discharge point)
Direct relief discharges to atmosphere	Emergency scrubber system; tank enclosures
Major tank or line rupture in storage	Diking; enclosure with scrubber; corrosion monitoring; overpressure protection; siting away from flammables and mechanical damage; inspection and non-destructive testing
Failure of mixing in bleach reaction	Interlock chlorine feed shut-off on loss of mixing power

information about reliability in terms of probabilities is planned in other volumes of the prevention reference manual series.

## 5.8 ILLUSTRATIVE COST ESTIMATES FOR CONTROLS

This section presents cost estimates for different levels of control and for specific release prevention and protection measures for chlorine storage and process facilities that might be found in the U.S..

### 5.8.1 Prevention and Protection Measures

Preventive measures reduce the probability of an accidental release from a process or storage facility by increasing the reliability of both process systems operations and equipment. Along with an increase in the reliability of a system is an increase in the capital and annual costs associated with incorporating prevention and protection measures into a system. Table 5-11 presents costs for some of the major design, equipment, and operational measures applicable to the primary hazards identified in Table 5-10 for chlorine applications in the U.S.

### 5.8.2 Levels of Control

Prevention of accidental releases relies on a combination of technological, administrative, and operational practices as they apply to the design, construction, and operation of facilities where hazardous chemicals are used and stored. Inherent in determining the degree to which these practices are carried out is their costs. At a minimum, equipment and procedures should be in accordance with applicable codes, standards, and regulations. However, additional measures can be taken to provide extra protection against an accidental release.

The levels of control concept provides a means of assigning costs to increased levels of prevention and protection. The minimum level is referred

TABLE 5-11. ESTIMATED TYPICAL COSTS OF SOME PREVENTION AND PROTECTION MEASURES FOR CHLORINE RELEASES<sup>a</sup>

Prevention/Protection Measure	Capital Cost (1986 \$)	Annual Cost (1986 \$/yr)
Replacement of copper lines with Monel®	150-200	20-25
Pressure relief.		
- relief valve	1,000-2,000	120-250
- rupture disk	1,000-1,200	120-150
Physical barriers		
- curbing	750-1,000	90-120
- 3 ft retaining wall	1,500-2,000	175-250
Flow control loop	4,000-6,000	500-750
Temperature sensor	250-400	30-50
pH control	7,500-10,000	900-1,300
Interlock system for feed shut-off	1,500-2,000	175-250
Alarm system	250-500	30-75
Diking		
- 3 ft high	1,200-1,500	150-175
- top of tank height	7,000-7,500	850-900
Corrosion monitoring <sup>b</sup>		200-400
Increased inspections and maintenance <sup>c</sup>		250-500

<sup>a</sup>Based on a 10,000-gallon fixed chlorine storage tank system and a 2,000-gallon continuous sodium hypochlorite bleach reactor system.

<sup>b</sup>Based on 10-20 hr @ \$20/hr.

<sup>c</sup>Based on 12.5-25 hr @ \$20/hr.

to as the "Baseline" system. This system consists of the elements required for normal safe operation and basic prevention of an accidental release of hazardous material.

The second level of control is "Level 1". "Level 1" includes the baseline system with added modifications such as improved materials of construction, additional controls, and generally more extensive release prevention measures. The costs associated with this level are higher than the baseline system costs.

The third level of control is "Level 2". This system incorporates both the "Baseline" and "Level 1" systems with additional modifications such as alarm and interlock systems designed specifically for the prevention of an accidental release. The extra accidental release prevention measures incorporated into "Level 2" are reflected in its cost, which is much higher than that of the baseline system.

When comparing the costs of the various levels of control, it is important to realize that higher costs do not necessarily imply improved safety. The measures must be applied correctly. Inappropriate modifications or add-ons may not make a system safer. Each added control option increases the complexity of a system. In some cases the hazards associated with the increased complexity may outweigh the benefits derived from the particular control option. Proper design and construction along with proper operational practices are needed to assure safe operation.

These estimates are for illustrative purposes only. It is doubtful that any specific installation would find all of the control options listed in these tables appropriate for their purposes. An actual system is likely to incorporate some items from each of the levels of control and also some control options not listed here. The purpose of these estimates is to illustrate the relationship between cost and control, and is not to provide an equipment check list.

Levels-of-control cost estimates were prepared for a 42 ton fixed chlorine storage tank system with a 10,000 gal capacity and a sodium hypochlorite bleach batch reactor system with 2,000 gal capacity. These systems are representative of storage and process facilities that might be found in the SCAQMD.

#### 5.8.3 Cost Summaries

Table 5-12 presents a summary of the total capital and annual costs for each of the three levels of controls for the chlorine storage system and the chlorine bleach reactor system. The costs presented correspond to the systems described in Table 5-13 and Table 5-14. Each of the level costs include the cost of the basic system plus any added controls. Specific cost information and breakdown for each level of control for both the storage and process facilities are presented in Tables 5-13 through 5-20.

#### 5.8.4 Equipment Specifications and Detailed Costs

Equipment specifications and details of the capital cost estimates for the chlorine storage and the chlorine bleach reactor systems are presented in Tables 5-21 through 5-28.

#### 5.8.5 Methodology

##### Format for Presenting Cost Estimates--

Tables are provided for control schemes associated with storage and process facilities for chlorine showing capital, operating, and total annual costs. The tables are broken down into subsections comprising vessels, piping and valves, process machinery, instrumentation, and procedures and practice. The presentation of the costs in this manner allows for easy comparison of costs for specific items, different levels, and different systems.

TABLE 5-12. SUMMARY COST ESTIMATES OF POTENTIAL LEVELS OF CONTROLS FOR CHLORINE STORAGE TANK AND HYPOCHLORITE BLEACH REACTOR

	Level of Control	Total Capital Cost (1986 \$)	Total Annual Cost (1986 \$/yr)
Chlorine Storage Tank; 60 ton Fixed Chlorine Tank with 10,000 gal Capacity	Baseline	208,000	25,000
	Level No. 1	510,000	60,000
	Level No. 2	786,000	92,000
Continuous Sodium Hypochlorite Bleach Reactor System With 2,000 gal Chlorination Tank	Baseline	105,000	13,000
	Level No. 1	123,000	16,000
	Level No. 2	130,000	17,000

TABLE 5-13 EXAMPLE OF LEVELS OF CONTROL FOR CHLORINE STORAGE TANK<sup>a</sup>

Process: 60 ton fixed chlorine storage tank  
10,000 gal

Controls	Baseline	Level No. 1	Level No. 2
Process:	None	None	None
Flow:	Single check-valve on tank-process feed line	Add second check valve.	Add a reduced-pressure device <sup>b</sup> with internal air gap and relief vent to scrubber.
Temperature:	None	None	Add temperature indicator.
Pressure:	Single pressure relief valve, vent to atmosphere, provide local pressure indicator.	Add second relief valve, secure non-isolatable installation; vent to scrubber.	Add rupture disks under relief valves; provide local pressure indication on space between disk and valves; vent to scrubber.
Quantity:	Local level indicator.	Add remote level indicator.	Add level alarm. Add high-low level interlock shut-off for both inlet and outlet lines.
Location:	Away from traffic, flammables, and other hazardous processes.	Away from traffic, flammables, and other hazardous processes.	Away from traffic, flammables, and other hazardous processes.
Materials of Construction:	Carbon steel.	Carbon steel with increased corrosion allowances. (1/8 inch)	Kynar® lined carbon steel.
Vessel:	Tank pressure specification 225 psig.	Tank pressure specification 300 psig.	Tank pressure specification 375 psig.

(continued)

TABLE 5-13 (Continued)

Process: 60 ton fixed chlorine storage tank  
10,000 gal

Controls	Baseline	Level No. 1	Level No. 2
Piping:	Sch. 80 carbon steel	Sch. 80 Kynar® lined carbon steel.	Sch. 80 Monel®.
Process Machinery:	Centrifugal pump, carbon steel, stuffing box seal.	Centrifugal pump, Kynar® lined steel, double mechanical seal.	Magnetically-coupled centrifugal pump Kynar® lined steel.
Enclosures:	None	Steel building.	Concrete building.
Diking:	None	3 ft high dike.	Top of tank height, 10 ft.
Scrubbers:	None	Water scrubber for relief and building vents.	Alkaline scrubber for relief and building vents.
Mitigation:	None	Water sprays.	Alkaline water sprays and barriers.

<sup>a</sup> The examples in this table are appropriate for many, but not all applications. This is only an exemplary system. Design must be suited to fit the specific service.

<sup>b</sup> A reduced pressure device is a modified double check valve.

TABLE 5-14. EXAMPLE OF LEVELS OF CONTROL FOR CHLORINE BLEACH REACTOR<sup>a</sup>  
Process: Continuous Sodium Hypochlorite Production

Controls	Baseline	Tier #1	Tier #2
Process:	Adequate cooling system.	Limited over-design of feed systems.	Interlock systems on feed systems.
Temperature:	Local temperature indicator.	Add redundant sensing and alarm. Add remote indicator.	Add temperature switch to shut off Cl <sub>2</sub> feed when temp. rises above a certain set point.
Pressure:	Single pressure relief valve. Vent to atmosphere. Expansion tank on chlorine feed line.	Add local pressure indicator on tank. Vent relief valve to scrubber.	Add rupture disk and provide local pressure indication on space between disk and valve.
Flow:	Local flow indicator on Cl <sub>2</sub> feed line.	Add remote indicator.	Add flow switch to shut off chlorine feed on loss of cooling medium.
Quantity:	None	None	Level alarm.
Mixing:	Provide adequate mixing.	Add alarm on loss of recirculating pump.	Interlock chlorine feed on loss of mixing.
Composition:	pH monitoring and control.	Same	Same

(Continued)

TABLE 5-14(Continued)

Controls	Baseline	Tier #1	Tier #2
Material of Construction:	Fiberglass-reinforced plastic - epoxy lined.	Same	Same
Vessel:	Atmospheric tank.	Same	Same
Piping:	Sch. 40 CPVC for bleach solutions.	Sch. 80 CPVC for bleach solutions.	Same
Process Machinery:	Centrifugal pump, Hastelloy C construction, stuffing box.	Same	Same
Enclosure:	None	Steel building.	Concrete building
Diking:	None	Curbing around process area.	Retaining wall around process area.

<sup>a</sup> The examples in this table are appropriate for many, but not all applications. This is only an exemplary system. Design must be suited to fit the specific service.

TABLE 5-15. ESTIMATED TYPICAL CAPITAL AND ANNUAL COSTS ASSOCIATED WITH  
BASELINE CHLORINE STORAGE SYSTEM

	Capital Cost (1986 \$)	Annual Cost (1986 \$/yr)
<b>Vessels:</b>		
Storage tank	170,000	20,000
Expansion tanks (3)	6,500	760
<b>Piping and Valves:</b>		
Pipework	2,300	270
Expansion loop	160	20
Check valve	280	35
Ball valves (5)	3,200	370
Excess flow valves (2)	500	60
Angle valves (2)	2,100	250
Relief valve	2,000	230
<b>Process Machinery:</b>		
Centrifugal pump	4,000	470
<b>Instrumentation:</b>		
Pressure gauges (4)	1,500	180
Load cell	16,000	1,800
<b>Procedures and Practices:</b>		
Visual tank inspection (external)		15
Visual tank inspection (internal)		60
Relief valve inspection		15
Piping inspection		300
Piping maintenance		120
Valve inspection		30
Valve maintenance		350
<b>Total Costs</b>	<b>208,000</b>	<b>25,000</b>

TABLE 5-16. ESTIMATED TYPICAL CAPITAL AND ANNUAL COSTS ASSOCIATED WITH  
LEVEL 1 CHLORINE STORAGE SYSTEM

	Capital Cost (1986 \$)	Annual Cost (1986 \$/yr)
<b>Vessels:</b>		
Storage tank	220,000	26,000
Expansion tanks (3)	6,500	760
<b>Piping and Valves:</b>		
Pipework	5,900	690
Expansion loop	160	20
Check valve	570	65
Ball valves (5)	3,200	370
Excess flow valves (2)	500	60
Angle valves (2)	2,100	250
Relief valve	4,000	470
<b>Process Machinery:</b>		
Centrifugal pump	6,400	750
<b>Instrumentation:</b>		
Pressure gauges (4)	1,500	180
Flow indicator	3,700	430
Load cell	16,000	1,800
Remote level indicator	1,900	220
<b>Enclosures:</b>		
Steel building	10,000	1,200
<b>Scrubbers:</b>		
Water scrubber	226,000	26,000
<b>Diking:</b>		
3 ft high concrete diking	1,400	160
		(Continued)

TABLE 5-16 (Continued)

	Capital Cost (1986 \$)	Annual Cost (1986 \$/yr)
Procedures and Practices:		
Visual tank inspection (external)		15
Visual tank inspection (internal)		60
Relief valve inspection		30
Piping inspection		300
Piping maintenance		120
Valve inspection		35
Valve maintenance		400
Total Costs	510,000	60,000

TABLE 5-17. ESTIMATED TYPICAL CAPITAL AND ANNUAL COSTS ASSOCIATED WITH  
LEVEL 2 CHLORINE STORAGE SYSTEM

	Capital Cost (1986 \$)	Annual Cost (1986 \$/yr)
<b>Vessels:</b>		
Storage tank	411,000	48,000
Expansion tanks (3)	6,500	760
<b>Piping and Valves:</b>		
Pipework	12,000	1,500
Expansion loop	160	20
Reduced pressure device	1,500	180
Ball valves (5)	3,200	370
Excess flow valves (2)	500	60
Angle valves (2)	2,100	250
Relief valve	4,000	470
Rupture disks (2)	1,100	130
<b>Process Machinery:</b>		
Centrifugal pump	8,500	1,000
<b>Instrumentation:</b>		
Temperature indicator	2,200	260
Pressure gauges (6)	2,200	260
Flow indicator	3,700	430
Load cell	16,000	1,800
Remote level indicator	1,900	220
Level alarm	380	45
High-low level shutoff	1,900	220
<b>Enclosures:</b>		
Concrete building	19,000	2,200
<b>Scrubbers:</b>		
Alkaline scrubber	280,000	33,000
<b>Diking:</b>		
10 ft high concrete diking	7,600	880

(Continued)

TABLE 5-17 (Continued)

	Capital Cost (1986 \$)	Annual Cost (1986 \$/yr)
Procedures and Practices:		
Visual tank inspection (external)		15
Visual tank inspection (internal)		60
Relief valve inspection		50
Piping inspection		300
Piping maintenance		120
Valve inspection		35
Valve maintenance		400
Total Costs	786,000	92,000

TABLE 5-18. ESTIMATED TYPICAL CAPITAL AND ANNUAL COSTS ASSOCIATED WITH  
BASELINE CONTINUOUS SODIUM HYPOCHLORITE PRODUCTION

	Capital Cost (1986 \$)	Annual Cost (1986 \$/yr)
<b>Vessels:</b>		
Chlorination tank	34,000	4,100
Expansion tank	2,200	260
<b>Piping and Valves:</b>		
Pipework	7,300	870
Ball and globe valves (8)	1,800	220
Relief valve	2,000	235
<b>Process Machinery:</b>		
Centrifugal pumps (2)	21,000	2,500
<b>Instrumentation:</b>		
Pressure gauges (3)	1,110	130
Temperature control		
- Controller	1,800	220
- Sensor	180	20
- Control valve	2,700	330
pH Control		
- Controller	1,800	220
- pH detector	7,300	870
- Control valve	2,700	330
Composition control		
- Controller	1,800	220
- ORP sensing cell	7,300	870
- control valve	3,600	430
Flow control		
- Controller	1,800	220
- Flowmeter	2,300	280
- Control valve	2,700	330

(Continued)

TABLE 5-18 (Continued)

	Capital Cost (1986 \$)	Annual Cost (1986 \$/yr)
Procedures and Practices:		
Visual tank inspection (external)		15
Visual tank inspection (internal)		60
Relief valve inspection		15
Piping inspection		600
Piping maintenance		250
Valve inspection		40
Valve maintenance		400
Total Costs	105,000	13,000

TABLE 5-19. ESTIMATED TYPICAL CAPITAL AND ANNUAL COSTS ASSOCIATED WITH  
LEVEL 1 CONTINUOUS SODIUM HYPOCHLORITE PRODUCTION

	Capital Cost (1986 \$)	Annual Cost (1986 \$/yr)
<b>Vessels:</b>		
Chlorination tank	34,000	4,100
Expansion tank	2,200	260
<b>Piping and Valves:</b>		
Pipework	9,100	1,100
Ball and globe valves (8)	1,800	220
Relief valve	2,000	230
<b>Process Machinery:</b>		
Centrifugal pumps (2)	21,000	2,500
<b>Instrumentation:</b>		
Pressure gauges (4)	1,400	180
Flow indicator	3,600	430
Local temp. indicator	2,200	260
Temperature alarm	360	45
Temperature control		
- Controller	1,800	220
- Sensor	360	45
- Control valve	2,700	330
pH Control		
- Controller	1,800	220
- pH detector	7,300	870
- Control valve	2,700	330
Composition control		
- Controller	1,800	220
- ORP sensing cell	7,300	870
- Control valve	3,600	430

(Continued)

TABLE 5-19 (Continued)

	Capital Cost (1986 \$)	Annual Cost (1986 \$/yr)
Flow control		
- Controller	1,800	220
- Flowmeter	2,300	280
- Control valve	2,700	330
Diking:		
Curbing around reactor	910	110
Enclosure:		
Steel building	8,300	1,000
Procedures and Practices:		
Visual tank inspection (external)		15
Visual tank inspection (internal)		60
Relief valve inspection		15
Piping inspection		600
Piping maintenance		250
Valve inspection		40
Valve maintenance		400
Total Costs	123,000	16,000

TABLE 5-20. ESTIMATED TYPICAL CAPITAL AND ANNUAL COSTS ASSOCIATED WITH  
LEVEL 2 CONTINUOUS SODIUM HYPOCHLORITE PRODUCTION

	Capital Cost (1986 \$)	Annual Cost (1986 \$/yr)
<b>Vessels:</b>		
Chlorination tank	34,000	4,100
Expansion tank	2,200	260
<b>Piping and Valves:</b>		
Pipework	9,100	1,100
Ball and globe valves (8)	1,800	220
Relief valve	2,000	230
<b>Process Machinery:</b>		
Centrifugal pumps (2)	21,000	2,500
<b>Instrumentation:</b>		
Level alarm	360	45
Mixing interlock system	1,800	220
Pressure gauges (4)	1,400	180
Flow interlock system	1,800	220
Flow indicator	3,600	430
Flow control		
- Controller	1,800	220
- Flowmeter	2,300	280
- Control valve	2,700	330
Local temp. indicator	2,200	260
Temperature alarm	360	45
Temperature control		
- Controller	1,800	220
- Sensors (2)	360	45
- Control valve	2,700	330
pH Control		
- Controller	1,800	229
- pH detector	7,300	870
- Control valve	2,700	330
Composition control		
- Controller	1,800	220
- ORP sensing cell	7,300	870
- control valve	3,600	430

(Continued)

TABLE 5-20 (Continued)

	Capital Cost (1986 \$)	Annual Cost (1986 \$/yr)
Diking:		
3 ft retaining wall	1,300	200
Enclosure:		
Concrete building	11,000	1,300
Procedures and Practices:		
Visual tank inspection (external)		15
Visual tank inspection (internal)		60
Relief valve inspection		20
Piping inspection		600
Piping maintenance		120
Valve inspection		40
Valve maintenance		400
Total Costs	130,000	17,000

TABLE 5-21. EQUIPMENT SPECIFICATIONS ASSOCIATED WITH CHLORINE STORAGE SYSTEM

Equipment Item	Equipment Specification	Reference
<b>Vessels:</b>		
Storage tank	Baseline: 10,000 gal. carbon steel, 225 psig rating Level 1: 10,000 gal. carbon steel with 1/8 in. corrosion protection, 300 psig rating Level 2: 10,000 gal. Kynar® lined carbon steel, 375 psig rating	40,41,42,43
Expansion tank	Standard carbon steel pressure vessel with rupture disk and pressure gauge	40,41
<b>Piping and Valves:</b>		
Pipework	Baseline: 1 in. schedule 80 carbon steel Level 1: 1 in. schedule 80 Kynar® lined carbon steel Level 2: 1 in. schedule 80 Monel®	44
Check valve	1 in. vertical left check valve, Monel® trim	41,45
Ball valve	300 lb., screwed, cast steel body, Monel® ball and stem, reinforced PTFE seat, PTFE seals	40,41,45
Excess flow valve	1.25 in. standard valve	41
Angle valve	1 in. carbon steel, cast	46
Relief valve	1 in. x 2 in., class 300 inlet and outlet flange, angle body closed bonnet with screwed cap, carbon steel body, Monel® trim	41

(Continued)

TABLE 5-21 (Continued)

Equipment Item	Equipment Specification	Reference
Reduced pressure device	Double check valve type device with internal air gap and relief valve	40
Rupture disk	1 in. Monel® disk and carbon steel holder	42,47,48
Process Machinery:		
Centrifugal pump	Baseline: single stage, carbon steel construction, Level 1: single stage, Kynar® lined, double mechanical seal	5,41
	Level 2: Magnetically-coupled, Monel® construction.	5,41
Instrumentation:		
Temperature indicator	Thermocouple, thermowell, electronic indicator	40,41,49
Pressure gauge	Diaphragm sealed, Monel® diaphragm, (0-1,000 psi)	40,41,49
Flow indicator	Differential pressure cell, transmitter, associated flowmeter	40,49
Load cell	Electrically operated load cell with electronic indicator	40,49,50
Level alarm	Indicating and audible alarm	41,46,51
High-low level shutoff	Solenoid valve, switch, and relay system	40,41,46,49

(Continued)

TABLE 5-21 (Continued)

Equipment Item	Equipment Specification	Reference
Enclosure:		
Building	Level 1: 26 gauge steel walls and roof, door, ventilation system Level 2: 10 in. concrete walls, 26 gauge steel roof, door	46
Scrubber:	Level 1: Spray tower, Monel® construction, water sprays, 6 ft. x 18 ft. Level 2: Spray tower, Monel® construction, alkaline sprays	52
Diking:	Level 1: 6 in. concrete walls, high Level 2: 10 in. concrete walls, top of tank height	46

TABLE 5-22. MATERIAL AND LABOR COSTS ASSOCIATED WITH BASELINE CHLORINE STORAGE SYSTEM

	Materials Cost	Labor Cost	Direct Costs (1986 \$)	Indirect Costs	Capital Cost
<b>Vessels:</b>					
Storage tank	79,000	35,000	114,000	40,000	170,000
Expansion tanks (3)	3,500	880	4,380	1,500	6,500
<b>Piping and Valves:</b>					
Pipework	550	1,000	1,550	542	2,300
Expansion loop	75	35	110	40	160
Check valves	160	30	190	65	280
Ball valves (5)	2,000	150	2,150	750	3,200
Excess flow valves (2)	300	40	340	120	500
Angle valves (2)	1,400	40	1,440	500	2,100
Relief valve	1,300	50	1,350	470	2,000
<b>Process Machinery:</b>					
Centrifugal pump	1,900	800	2,700	950	4,000
<b>Instrumentation:</b>					
Pressure gauges (4)	800	200	1,000	350	1,500
Load cell	8,400	2,100	10,500	3,700	16,000
<b>Total Costs</b>	<b>99,000</b>	<b>41,000</b>	<b>140,000</b>	<b>49,000</b>	<b>208,000</b>

TABLE 5-23. MATERIAL AND LABOR COSTS ASSOCIATED WITH LEVEL 1 CHLORINE STORAGE SYSTEM

	Materials Cost	Labor Cost	Direct Costs (1986 \$)	Indirect Costs	Capital Cost
<b>Vessels:</b>					
Storage tank	102,000	46,000	148,000	52,000	220,000
Expansion tanks (3)	3,500	880	4,380	1,500	6,500
<b>Piping and Valves:</b>					
Pipework	3,300	680	3,980	1,400	5,900
Expansion loop	75	35	110	40	160
Check valves	320	60	380	140	570
Ball valves (5)	2,000	150	2,150	750	3,200
Excess flow valves (2)	300	40	340	120	500
Angle valves (2)	1,400	40	1,440	500	2,100
Relief valve	2,600	100	2,700	950	4,000
<b>Process Machinery:</b>					
Centrifugal pump	3,000	1,300	4,300	1,500	6,400
<b>Instrumentation:</b>					
Pressure gauges (4)	800	200	1,000	350	1,500
Flow indicator	2,000	500	2,500	880	3,700
Load cell	8,400	2,100	10,500	3,700	16,000
Remote level indicator	1,000	250	1,250	440	1,900

(Continued)

TABLE 5-23 (Continued)

	Materials Cost	Labor Cost	Direct Costs (1986 \$)	Indirect Costs	Capital Cost
<b>Enclosures:</b>					
Steel building	4,600	2,300	6,900	2,400	10,000
<b>Scrubbers:</b>					
Water scrubber	105,000	47,000	152,000	53,000	226,000
<b>Diking:</b>					
3 ft high concrete diking	390	520	910	320	1,400
<b>Total Costs</b>	<b>241,000</b>	<b>102,000</b>	<b>343,000</b>	<b>120,000</b>	<b>510,000</b>

TABLE 5-24. MATERIAL AND LABOR COSTS ASSOCIATED WITH LEVEL 2 CHLORINE STORAGE SYSTEM

	Materials Cost	Labor Cost	Direct Costs (1986 \$)	Indirect Costs	Capital Cost
<b>Vessels:</b>					
Storage tank	191,000	86,000	277,000	97,000	411,000
Expansion tanks (3)	3,500	880	4,380	1,500	6,500
<b>Piping and Valves:</b>					
Pipework	4,800	3,500	8,300	2,900	12,000
Expansion loop	75	35	110	40	160
Reduced pressure device	800	200	1,000	350	1,500
Ball valves (5)	2,000	150	2,150	750	3,200
Excess flow valves (2)	300	40	340	120	500
Angle valves (2)	1,400	40	1,440	500	2,100
Relief valve	2,600	100	2,700	950	4,000
Rupture disks (2)	650	75	725	260	1,100
<b>Process Machinery:</b>					
Centrifugal pump	4,000	1,700	5,700	2,000	8,500
<b>Instrumentation:</b>					
Temperature indicator	1,200	300	1,500	530	2,200
Pressure gauges (6)	1,200	300	1,500	530	2,200
Flow indicator	2,000	500	2,500	880	3,700
Load cell	8,400	2,100	10,500	3,700	16,000
Remote level indicator	1,000	250	1,250	440	1,900
Level alarm	200	50	250	90	380
High-low level shutoff	1,000	250	1,250	440	1,900

(Continued)

TABLE 5-24 (Continued)

	Materials Cost	Labor Cost	Direct Costs (1986 \$)	Indirect Costs	Capital Cost
Enclosures:					
Concrete building	6,100	6,600	12,700	4,400	19,000
Scrubbers:					
Alkaline scrubber	130,000	59,000	189,000	66,000	280,000
Diking:					
10 ft high concrete dike	2,200	2,900	5,100	1,800	7,600
Total Costs	365,000	165,000	529,000	186,000	786,000

TABLE 5-25. EQUIPMENT SPECIFICATIONS ASSOCIATED WITH CHLORINE BLEACH REACTOR SYSTEM

Equipment Item	Equipment Specification	Reference
<b>Vessels:</b>		
Chlorination tank	2,000 gal. fiber-reinforced plastic tank	5
Expansion tank	Standard carbon steel pressure vessel with rupture disk and pressure gauge	40,41
<b>Piping and Valves:</b>		
Pipework	Baseline: 1 in. schedule 80 Monel®, chlorine feed line 2 in. schedule 40 CPVC for bleach solutions Levels 1 & 2: 2 in. schedule 80 CPVC for bleach solutions	41,44
Ball valves	300 lb., screwed, cast steel body, Monel® ball and trim,	40,41,45
Glove valves	Class 150, flanged, cast steel, Monel® disk and seat	40,41,45
Relief valve	1 in. x 2 in., class 300 inlet and outlet flange, angle body, closed bonnet with screwed cap, carbon steel body, Monel® trim	41
<b>Process Machinery:</b>		
Centrifugal pump	Hastelloy C construction, stuffing box	5
<b>Instrumentation:</b>		
Level alarm	Indicating and audible alarm	41,46,51
Interlock system	Solenoid valve, switch, and relay system	40,41,46,49

(Continued)

TABLE 5-25 (Continued)

Equipment Item	Equipment Specification	Reference
Pressure gauge	Diaphragm sealed, Monel® diaphragm, 0-500 psi	40,41,49
Flowmeter	D/P cell and transmitter and associated flow indicator	40,41,49
Control valve	1 in. and 1 in. globe valves, Monel® trim	40,53
Controller	Standard PID controller	40,54,55
Temperature indicator	Thermocouple, thermowell, and electronic indicator	40,41,49
Temp. sensor	Thermocouple and associated thermowell	40,41,49
pH detector	Electrode, electrode chamber, amplifier-transducer and indicator	40,50
ORP sensing cell	Standard calomel oxidation-reduction potential sensing cell	40,50
Diking:	Level 1: 6 in concrete curbing Level 2: 3 ft. high retaining wall	46
Enclosure:	Level 1: 26 gauge steel walls and roof, door, ventilation system Level 2: 10 in. concrete walls, 26 gauge steel roof, door	46

TABLE 5-26. MATERIAL AND LABOR COSTS ASSOCIATED WITH BASELINE CONTINUOUS  
SODIUM HYPOCHLORIDE PRODUCTION

	Materials Cost	Labor Cost	Direct Costs (1986 \$)	Indirect Costs	Capital Cost
<b>Vessels:</b>					
Chlorination tank	16,000	7,440	23,440	5,900	34,000
Expansion tank	1,200	300	1,500	380	2,200
<b>Piping and Valves:</b>					
Pipework	3,000	2,000	5,000	1,300	7,300
Ball and globe valves (8)	1,000	250	1,250	320	1,800
Relief valve	1,300	50	1,350	340	2,000
<b>Process Machinery:</b>					
Centrifugal pumps (2)	10,000	4,300	14,300	3,600	21,000
<b>Instrumentation:</b>					
Pressure gauges (3)	600	150	750	190	1,100
Temperature control					
- Controller	1,000	250	1,250	320	1,800
- Sensor	100	25	125	30	180
- Control valve	1,500	380	1,880	470	2,700
pH Control					
- Controller	1,000	250	1,250	430	1,800
- pH detector	4,000	1,000	5,000	1,300	7,300
- Control valve	1,500	380	1,880	470	2,700

(Continued)

TABLE 5-26 (Continued)

	Materials Cost	Labor Cost	Direct Costs (1986 \$)	Indirect Costs	Capital Cost
Composition control					
- Controller	1,000	250	1,250	320	1,800
- ORP sensing cell	4,000	1,000	5,000	1,300	7,300
- Control valve	2,000	500	2,500	630	3,600
Flow control					
- Controller	1,000	250	1,250	320	1,800
- Flowmeter	1,300	300	1,600	400	2,300
- Control valve	1,500	380	1,880	470	2,700
Total Costs	53,000	20,000	73,000	18,000	105,000

TABLE 5-27. MATERIAL AND LABOR COSTS ASSOCIATED WITH LEVEL 1 CONTINUOUS  
SODIUM HYPOCHLORIDE PRODUCTION

	Materials Cost	Labor Cost	Direct Costs (1986 \$)	Indirect Costs	Capital Cost
<b>Vessels:</b>					
Chlorination tank	16,000	7,400	23,400	5,900	34,000
Expansion tank	1,200	300	1,500	380	2,200
<b>Piping and Valves:</b>					
Pipework	3,800	2,500	6,300	1,600	9,100
Ball and globe valves (8)	1,000	250	1,250	320	1,800
Relief valve	1,300	50	1,350	340	2,000
<b>Process Machinery:</b>					
Centrifugal pumps (2)	10,000	4,300	14,300	3,600	21,000
<b>Instrumentation:</b>					
Pressure gauges (4)	800	200	1,000	250	1,400
Flow indicator	2,000	500	2,500	630	3,600
Local temperature indicator	1,200	300	1,500	380	2,200
Temperature alarm	200	50	250	60	360
Temperature control					
- Controller	1,000	250	1,250	320	1,800
- Sensors (2)	200	50	250	60	360
- Control valve	1,500	380	1,880	470	2,700

(Continued)

TABLE 5-27 (Continued)

	Materials Cost	Labor Cost	Direct Costs (1986 \$)	Indirect Costs	Capital Cost
pH Control					
- Controller	1,000	250	1,250	320	1,800
- pH detector	4,000	1,000	5,000	1,300	7,300
- Control valve	1,500	380	1,880	470	2,700
Composition control					
- Controller	1,000	250	1,250	320	1,800
- ORP sensing cell	4,000	1,000	5,000	1,300	7,300
- Control valve	2,000	500	2,500	630	3,600
Flow control					
- Controller	1,000	250	1,250	320	1,800
- Flowmeter	1,300	325	1,600	400	2,300
- Control valve	1,500	375	1,880	470	2,700
Diking:					
Curbing around reactor	500	130	630	160	910
Enclosure:					
Steel building	4,600	1,200	5,800	1,500	8,300
Total Costs	63,000	22,000	85,000	21,000	123,000

TABLE 5-28. MATERIAL AND LABOR COSTS ASSOCIATED WITH LEVEL 2 CONTINUOUS  
SODIUM HYPOCHLORITE PRODUCTION

	Materials Cost	Labor Cost	Direct Costs (1986 \$)	Indirect Costs	Capital Cost
<b>Vessels:</b>					
Chlorination tank	16,000	7,400	23,400	5,900	34,000
Expansion tank	1,200	300	1,500	380	2,200
<b>Piping and Valves:</b>					
Pipework	3,800	2,500	6,300	1,600	9,100
Ball and globe valves (8)	1,000	250	1,250	320	1,800
Relief valve	1,300	50	1,350	330	2,000
<b>Process Machinery:</b>					
Centrifugal pumps (2)	1,000	4,300	14,300	3,600	21,000
<b>Instrumentation:</b>					
Level alarm	200	50	250	60	360
Mixing interlock system	10,000	250	10,250	320	1,800
Pressure gauges (4)	800	200	1,000	250	1,400
Flow interlock system	1,000	250	1,250	320	1,800
Flow indicator	2,000	500	2,500	630	3,600
Flow control					
- Controller	1,000	250	1,250	320	1,800
- Flowmeter	1,300	300	1,600	400	2,300
- Control valve	1,500	380	1,880	470	2,700

(Continued)

TABLE 5-28 (Continued)

	Materials Cost	Labor Cost	Direct Costs (1986 \$)	Indirect Costs	Capital Cost
Local temp. indicator	1,200	300	1,500	380	2,200
Temperature alarm	200	50	250	60	360
Temperature control					
- Controller	1,000	250	1,250	320	1,800
- Sensors (2)	200	50	250	60	360
- Control valve	1,500	380	1,880	470	2,700
pH Control					
- Controller	1,000	250	1,250	320	1,800
- pH detector	4,000	1,000	5,000	1,300	7,300
- Control valve	1,500	380	1,880	470	2,700
Composition control					
- Controller	1,000	250	1,250	320	1,800
- ORP sensing cell	4,000	1,000	5,000	1,300	7,300
- Control valve	2,000	500	2,500	630	3,600
Diking:					
3 ft retaining wall	900	230	1,130	290	1,600
Enclosure:					
Concrete building	6,100	1,500	7,600	1,900	11,000
Total Costs	67,000	23,000	90,000	23,000	130,000

Capital Cost--All capital costs presented in this report are shown as total fixed capital costs. Table 5-29 defines the cost elements comprising total fixed capital as it is used here.

The computation of total fixed capital as shown in Table 5-29 begins with the total direct cost for the system under consideration. This total direct cost is the total direct installed cost of all capital equipment comprising the system. Depending on the specific equipment item involved, the direct capital cost was available or was derived from uninstalled equipment costs by computing costs of installation separately. To obtain the total fixed capital cost, other costs obtained by utilizing factors are added to the total direct costs.

The first group of other cost elements is indirect costs. These include engineering and supervision, construction expenses, and various other expenses such as administration expenses, for example. These costs are computed by multiplying total direct costs by a factor shown in Table 5-29. The factor is approximate, is obtained from the cost literature, and is based on previous experience with capital projects of a similar nature. Factors can have a range of values and vary according to technology area and for individual technologies within an area. Appropriate factors were selected for use in this report based on judgement and experience.

When the indirect costs are added to the total direct costs, total bare module cost is obtained. Some additional cost elements such as contractor's fee and contingency are calculated by applying and adding appropriate factors to the total bare module cost as shown in Table 5-29 to obtain the total fixed capital cost.

Annual Cost--Annual costs are obtained for each of the equipment items by applying a factor for both capital recovery and for maintenance expenses to the direct cost of each equipment item. Table 5-30 defines the cost elements and appropriate factors comprising these costs. Additional annual costs are

TABLE 5-29. FORMAT FOR TOTAL FIXED CAPITAL COST

Item No.	Item	Cost
1	Total Material Cost	-
2	Total Labor Cost	-
3	Total Direct Cost	Items 1 + 2
4	Indirect Cost Items (Engineering & Construction Expenses)	$0.35 \times \text{Item } 3^a$
5	Total Bare Module Cost	Items (3 + 4)
6	Contingency	$(0.05 \times \text{Item } 5)^b$
7	Contractor's Fee	$0.05 \times \text{Item } 5$
8	Total Fixed Capital Cost	Items (5 + 6 + 7)

<sup>a</sup> For storage facilities, the indirect cost factor is 0.35. For process facilities, the indirect cost factor is 0.25.

<sup>b</sup> For storage facilities, the contingency cost factor is 0.05. For process facilities, the contingency cost factor is 0.10.

TABLE 5-30. FORMAT FOR TOTAL ANNUAL COST

Item No.	Item	Cost
1	Total Direct Cost	-
2	Capital Recovery on Equipment Items	$0.163 \times \text{Item 1}$
3	Maintenance Expense on Equipment Items	$0.01 \times \text{Item 1}$
4	Total Procedural Items	-
5	Total Annual Cost	Items (2 + 3 + 4)

\* Based on a recovery factor at 10% cost of capital for 10 years.

incurred for procedural items such as valve and vessel inspections, for example. When all of these individual costs are added, the total annual cost is obtained.

#### Sources of Information--

The costs presented in this report are derived from cost information in existing published sources and also from recent vendor information. It was the objective of this effort to present cost levels for chlorine process and storage facilities using the best costs for available sources. The primary sources of cost information are Peters and Timmerhaus (40), Chemical Engineering (56), and Valle-Riestra (57) supplemented by other sources and references where necessary. Adjustments were made to update all costs to a June 1986 dollar basis. In addition, for some equipment items, well-documented costs were not available and they had to be developed from component costs.

Costs in this document reflect the "typical" or "average" representation for specific equipment items. This restricts the use of data in this report to:

- Preliminary estimates used for policy planning;
- Comparison of relative costs of different levels or systems;  
and
- Approximations of costs that might be incurred for a specific application.

The costs in this report are considered to be "order of magnitude" with a +50 percent margin. This is because the costs are based on preliminary estimates and many are updated from literature sources. Large departures from the design basis of a particular system presented in this manual or the advent of a different technology might cause the system cost to vary by a greater

extent than this. If used as intended, however, this document will provide a reasonable source of preliminary cost information for the facilities covered.

When comparing costs in this manual to costs from other references, the user should be sure the design bases are comparable and that the capital and annual costs as defined here are the same as the costs being compared.

#### Cost Updating--

All costs in this report are expressed in June 1986 dollars. Costs reported in the literature were updated using cost indices for materials and labor.

Costs expressed in base year dollars may be adjusted to dollars for another year by applying cost indices as shown in the following equation:

$$\text{new base year cost} = \text{old base year cost} \times \frac{\text{new base year index}}{\text{old base year index}}$$

The Chemical Engineering (CE) Plant Cost Index was used in updating cost for this report. For June 1986, the index is 316.3.

#### Equipment Costs--

Most of the equipment costs presented in this manual were obtained directly from literature sources of vendor information and correspond to a specific design standard. Special cost estimating techniques, however, were used in determining the costs associated with vessels, piping systems, scrubbers, diking, and enclosures. The techniques used are presented in the following subsections of this manual.

Vessels--The total purchased cost for a vessel, as dollars per pound of weight of fabricated unit free-on-board based freight basis (f.o.b.) with carbon steel as the basis (January 1979 dollars) were determined using the following equation from Peters and Timmerhaus (40):

$$\text{Cost} = [50(\text{Weight of Vessel in Pounds})^{-0.34}]$$

The vessel weight is determined using appropriate design equations as given by Peters and Timmerhaus (40) which allow for all thickness adjustments for corrosion allowances, for example. The vessel weight is increased by a factor of 0.15 for horizontal vessels and 0.20 for vertical vessels to account for the added weight due to nozzles, manholes, and skirts or saddles. Appropriate factors are applied for different materials of construction as given in Peters and Timmerhaus (40). The vessel costs are updated using cost factors. Finally, a shipping cost amounting to 10 percent of the purchased cost is added to obtain the delivered equipment cost.

Piping--Piping costs were obtained using cost information and data presented by Yamartino (44). A simplified approach is used in which it is assumed that a certain length of piping containing a given number of valves, flanges, and fittings is contained in the storage or process facility. The data presented by Yamartino (44) permit cost determinations for various lengths, sizes, and types of piping systems. Using these factors, a representative estimate can be obtained for each of the storage and process facilities.

Diking--Diking costs were estimated using Mean's Manual (46) for reinforced concrete walls. The following assumptions were made in determining the costs. The dike contains the entire contents of a tank in the event of a leak or release. Two dike sizes are possible: a three-foot high dike, six-inches thick and a top-of-tank height dike ten inches thick. The tanks are raised off the ground and are not volumetrically included in the volume enclosed by the diking. These assumptions facilitate cost determination for any size diking system.

Enclosures--Enclosure costs were estimated using Mean's Manual (46) for both reinforced concrete and steel-walled buildings. The buildings are assumed to enclose the same area and volume as the top-of-tank height dikes.

The concrete building is ten-inches thick with a 26-gauge steel roof and a metal door. The steel building has 26 gauge roofing and siding and metal door. The cost of a ventilation system was determined using a typical 1,000 scfm unit and doubling the cost to account for duct work and requirements for the safe enclosure of hazardous chemicals.

Scrubbers--Scrubber costs were estimated using the following equation from the Gard (52) manual for spray towers based on the actual cubic feet per minute of flow at a chamber velocity of 600 feet/minute.

$$\text{Costs} = 0.235 \times (\text{ACFM} + 43,000)$$

A release rate of 10,000 ft<sup>3</sup>/minute was assumed for the storage vessel systems and an appropriate rate was determined for process system based on the quantity of hazardous chemicals present in the system at any one time. For the chlorine bleach reactor system, a release rate of 10,000 ft<sup>3</sup>/minute was assumed. In addition to the spray tower, the costs also include pumps and a storage tank for the scrubbing medium. The costs presented are updated to June 1986 dollars.

#### Installation Factors--

Installation costs were developed for all equipment items included in both the process and storage systems. The costs include both the material and labor costs for installation of a particular piece of equipment. The costs were obtained directly from literature sources and vendor information or indirectly by assuming a certain percentage of the purchased equipment cost through the use of estimating factors obtained from Peters and Timmerhaus (40) and Valle-Riestra (57). Table 5-31 lists the cost factors used or the reference from which the cost was obtained directly. Many of the costs obtained from the literature were updated to June 1986 dollars using a 10 percent per year rate of increase for labor and cost indices for materials associated with installation.

TABLE 5-31. FORMAT FOR INSTALLATION COSTS

Equipment Item	Factor or Reference
Vessels:	
Storage Tank	0.45
Expansion Tank	0.25
Piping and Valves:	
Pipework	Ref. 44
Expansion Loop	Ref. 41
Reduced Pressure Device	Ref. 41
Check Valves	Ref. 41
Gate Valves	Ref. 41
Ball Valves	Ref. 41
Excess Flow Valves	Ref. 41
Angle Valves	Ref. 46
Relief Valves	Ref. 41
Rupture Disks	Ref. 49
Process Machinery:	
Centrifugal Pump	0.43
Gear Pump	0.43
Instrumentation:	
All Instrumentation Items	0.25
Enclosures:	Ref. 46
Diking:	Ref. 46
Scrubbers:	0.45

## SECTION 6

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## APPENDIX A

### GLOSSARY

This glossary defines selected terms used in the text of this manual which might be unfamiliar to some users or which might be used differently by different authors.

Accidental release: The unintentional spilling, leaking, pumping, purging, emitting, emptying, discharging, escaping, dumping, or disposing of a toxic material into the environment in a manner that is not in compliance with a plant's federal, state, or local environmental permits and results in toxic concentrations in the air that are a potential health threat to the surrounding community.

Assessment: The process whereby the hazards which have been identified are evaluated in order to provide an estimate for the level of risk.

Cavitation: The formation and collapse of vapor bubbles in a flowing liquid. Specifically the formation and collapse of vapor cavities in a pump when there is sufficient resistance to flow at the inlet side.

Chlorofluorocarbons: Organic compounds containing chlorine and/or fluorine atoms within the molecule.

Containment/control: A system to which toxic emissions from safety relief discharges are routed to be controlled. A caustic scrubber and/or flare can be containment/control devices. These systems may serve the dual function of destructing continuous process exhaust gas emissions.

Creep failure: Failure of a piece of metal as a result of creep. Creep is time dependent deformation as a result of stress. Metals will deform when exposed to stress. High levels of stress can result in rapid deformation and rapid failure. Lower levels of stress can result in slow deformation and protracted failure.

Deadheading: Closing or nearly closing or blocking the discharge outlet or piping of an operating pump or compressor.

Facility: A location at which a process or set of processes are used to produce, refine or repackage chemicals, or a location where a large enough inventory of chemicals are stored so that a significant accidental release of a toxic chemical is possible.

Hazard: A source of danger. The potential for death, injury or other forms of damage to life and property.

Hygroscopic: Readily absorbing and retaining moisture, usually in reference to readily absorbing moisture from the air.

Identification: The recognition of a situation, its causes and consequences relating to a defined potential, e.g. Hazard Identification.

Mild steel: Carbon steel containing a maximum of about 0.25% carbon. Mild steel is satisfactory for use where severe corrodants are not encountered or where protective coatings can be used to prevent or reduce corrosion rates to acceptable levels.

Mitigation: Any measure taken to reduce the severity of the adverse effects associated with the accidental release of a hazardous chemical.

Passivation film: A layer of oxide or other chemical compound of a metal on its surface that acts as a protective barrier against corrosion or further chemical reaction.

Plant: A location at which a process or set of processes are used to produce, refine, or repackage, chemicals.

Prevention: Design and operating measures applied to a process to ensure that primary containment of toxic chemicals is maintained. Primary containment means confinement of toxic chemicals within the equipment intended for normal operating conditions.

Primary Containment: The containment provided by the piping, vessels and machinery used in a facility for handling chemicals under normal operating conditions.

Probability/potential: A measure, either qualitative or quantitative, that an event will occur within some unit of time.

Process: The sequence of physical and chemical operations for the production, refining, repackaging or storage of chemicals.

Process machinery: Process equipment, such as pumps, compressors, heaters, or agitators, that would not be categorized as piping and vessels.

Protection: Measures taken to capture or destroy a toxic chemical that has breached primary containment, but before an uncontrolled release to the environment has occurred.

Qualitative Evaluation: Assessing the risk of an accidental release at a facility in relative terms; the end result of the assessment being a verbal description of the risk.

Quantitative Evaluation: Assessing the risk of an accidental release at a facility in numerical terms; the end result of the assessment being some type of number reflects risk, such as faults per year or mean time between failure.

Reactivity: The ability of one chemical to undergo a chemical reaction with another chemical. Reactivity of one chemical is always measured in reference to the potential for reaction with itself or with another chemical. A chemical is sometimes said to be "reactive", or have high "reactivity", without reference to another chemical. Usually this means that the chemical has the ability to react with common materials such as water, or common materials of construction such as carbon steel.

Redundancy: For control systems, redundancy is the presence of a second piece of control equipment where only one would be required. The second piece of equipment is installed to act as a backup in the event that the primary piece of equipment fails. Redundant equipment can be installed to backup all or selected portions of a control system.

Risk: The probability that a hazard may be realized at any specified level in a given span of time.

Secondary Containment: Process equipment specifically designed to contain material that has breached primary containment before the material is released to the environment and becomes an accidental release. A vent duct and scrubber that are attached to the outlet of a pressure relief device are examples of secondary containment.

Toxicity: A measure of the adverse health effects of exposure to a chemical.

APPENDIX B  
TABLE B-1. METRIC (SI) CONVERSION FACTORS

Quantity	To Convert From	To	Multiply By
Length:	in	cm	2.54
	ft	m	0.3048
Area:	in <sup>2</sup>	cm <sup>2</sup>	6.4516
	ft <sup>2</sup>	m <sup>2</sup>	0.0929
Volume:	in <sup>3</sup>	cm <sup>3</sup>	16.39
	ft <sup>3</sup>	m <sup>3</sup>	0.0283
	gal	m <sup>3</sup>	0.0038
Mass (weight):	lb	kg	0.4536
	short ton (ton)	Mg	0.9072
	short ton (ton)	metric ton (t)	0.9072
Pressure:	atm	kPa	101.3
	mm Hg	kPa	0.133
	psia	kPa	6.895
	psig	kPa*	(psig +14.696) x (6.895)
Temperature:	°F	°C*	(5/9) x (°F-32)
	°C	K*	°C+273.15
Caloric Value;	Btu/lb	kJ/kg	2.326
Enthalpy:	Btu/lbmol	kJ/kgmol	2.326
	kcal/gmol	kJ/kgmol	4.184
Specific-Heat Capacity:	Btu/lb-°F	kJ/kg-°C	4.1868
Density:	lb/ft <sup>3</sup>	kg/m <sup>3</sup>	16.02
	lb/gal	kg/m <sup>3</sup>	119.8
Concentration:	oz/gal	kg/m <sup>3</sup>	7.490
	quarts/gal	cm <sup>3</sup> /m <sup>3</sup>	25,000
Flowrate:	gal/min	m <sup>3</sup> /min	0.0038
	gal/day	m <sup>3</sup> /day	0.0038
	ft <sup>3</sup> /min	m <sup>3</sup> /min	0.0283
Velocity:	ft/min	m/min	0.3048
	ft/sec	m/sec	0.3048
Viscosity:	centipoise (CP)	Pa-s (kg/m-s)	0.001

\*Calculate as indicated