

CHLORINE DIOXIDE

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## 1.0 SCOPE

This data sheet applies to the manufacture and use of chlorine dioxide (ClO<sub>2</sub>), an unstable gas used primarily as a bleaching agent in the pulp and paper industry. It now includes information on the latest chlorine dioxide generation processes.

### 1.1 Changes

January 2012. Terminology related to ignitable liquids has been revised to provide increased clarity and consistency with regard to FM Global's loss prevention recommendations for ignitable liquid hazards.

## 2.0 LOSS PREVENTION RECOMMENDATIONS

### 2.1 Protection

#### 2.1.1 Fire Protection

2.1.1.1 Provide automatic sprinkler protection at the ceiling of buildings of combustible construction. Buildings containing significant amounts of glass-fiber-reinforced plastic equipment or construction should be protected in accordance with Data Sheet 1-57, *Plastics in Construction*.

2.1.1.2 Provide internal and external sprinklers in ducts of high value, high importance to production or unusually large size. Refer to Data Sheet 7-78, *Industrial Exhaust Systems*, for protection guidelines.

2.1.1.3 Provide protection for methanol (see Solvay and ERCO R8 Processes) storage and piping as outlined in Data Sheet 7-32, *Ignitable Liquid Operations*, and Data Sheet 7-88, *Ignitable Liquid Storage Tanks*.

#### 2.1.2 Overpressure Protection

2.1.2.1 Provide emergency relief venting for chlorine dioxide reactors, other vessels that may contain gaseous chlorine dioxide (such as dump tanks) and for atmospheric storage tanks.

The recommended vents will be adequate for most chlorine dioxide decompositions. However, if the chlorine dioxide concentration is excessive, the decomposition could proceed too rapidly for effective venting (see Appendix C, Section C4.3).

Emphasis is therefore placed upon preventing an excessive chlorine dioxide concentration with adequate process control interlocks, as discussed in Section 2.2.1, *Process Controls*.

2.1.2.2 Use low-inertia vents. Spring loaded vents are acceptable.

2.1.2.3 Size emergency relief vents on chlorine dioxide reactors and other pressure vessels that may contain gaseous chlorine dioxide (such as dump tanks) in accordance with the following equation or Figure 1 (for cases where P<sub>stat</sub> = 0.8 psig [0.05 barg]):

English Units

$$A_v = 0.758 V^{0.68} e^{-0.052 P_{stat}} P_{red}^{-0.393}$$

where:

A<sub>v</sub> = vent area, ft<sup>2</sup>

V = vessel volume, ft<sup>3</sup>

e = 2.718 (base of natural logarithm)

P<sub>red</sub> = maximum pressure developed during venting, psig (1.5 psig ≤ P<sub>red</sub> ≤ 29 psig)

P<sub>stat</sub> = vent closure release pressure, psi gauge (0.7 psig ≤ P<sub>stat</sub> ≤ P<sub>red</sub> - 0.7 psig)

Metric Units

$$A_v = 0.279 V^{0.680} e^{0.755 P_{stat}} P_{red}^{-0.393}$$

Where:

A<sub>v</sub> = vent area, m<sup>2</sup>

V = vessel volume, m<sup>3</sup>

e = 2.718 (base of natural logarithm)

P<sub>red</sub> = maximum pressure developed during venting, bar gauge (0.10 barg ≤ P<sub>red</sub> ≤ 2 barg)

P<sub>stat</sub> = vent closure release pressure, bar gauge (0.05 barg ≤ P<sub>stat</sub> ≤ P<sub>red</sub> - 0.05 barg)

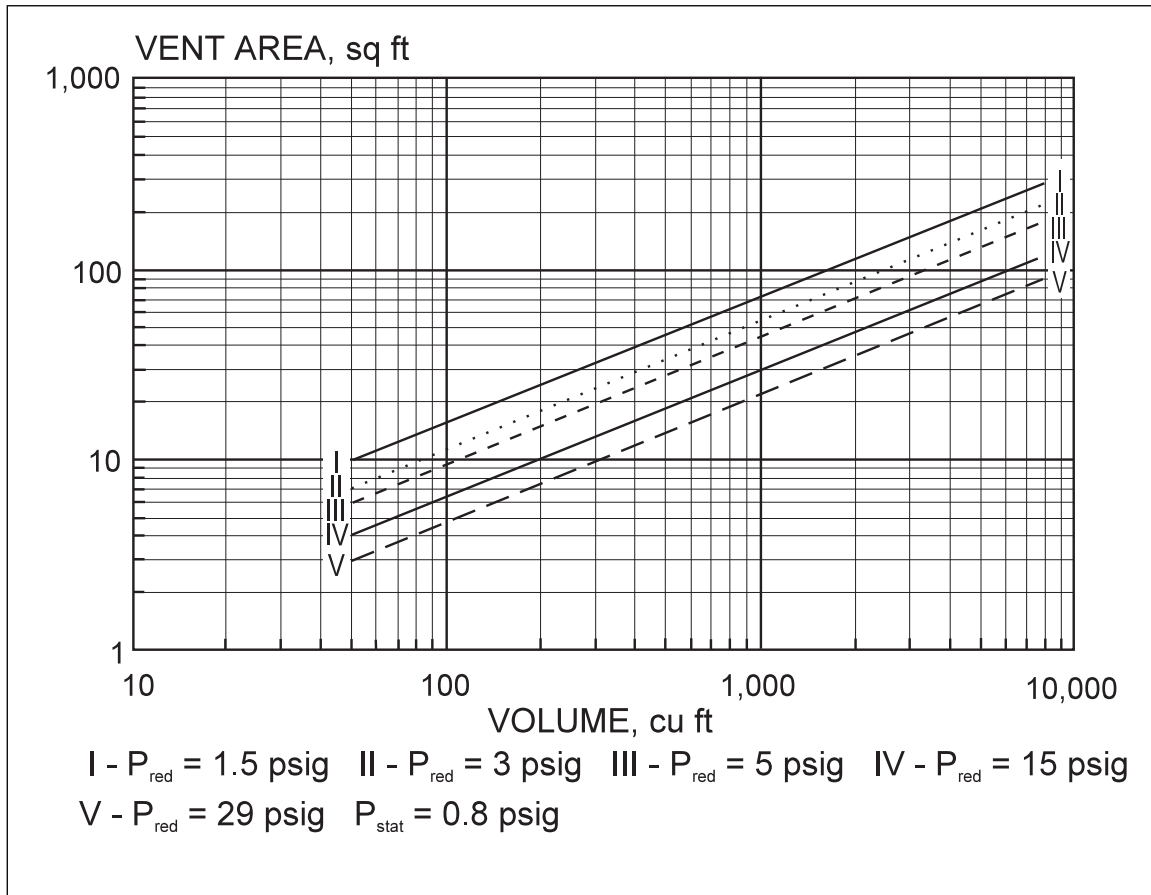


Fig. 1. Chlorine Dioxide Pressure Vessel Recommended Vent Sizes.

2.1.2.4 Provide emergency relief venting for atmospheric chlorine dioxide storage tanks designed to provide adequate relief for the worst case temperature and concentration.

## 2.2 Equipment and Processes

### 2.2.1 Process Controls

2.2.1.1 Provide an alternate power supply if a power failure could disrupt air flow to the chlorine dioxide reactor.

2.2.1.2 Interlock set points should be based upon the specific operating conditions of the process, in order to avoid excessive temperatures and/or chlorine dioxide concentrations. Interlocks should shut down raw-material feed lines and divert air flow as described in Section 2.2.2, *Start-up and Shutdown Procedures*.

2.2.1.3 Provide a reliable means of isolation for all process reactant feed lines by locating manually-operated shutoff valves in safe, accessible locations.

2.2.1.4 Test process controls associated with chlorine dioxide reactors monthly to ensure proper operation.

#### 2.2.1.5 Atmospheric Reactors

Provide the following interlocks for reactors operating at atmospheric pressure:

- a) Low reactor air flow
- b) High chlorine dioxide concentration downstream of the reactor (usually determined by analysis of liquid leaving the absorption column)
- c) High reactor temperature (above 150°F [65°C]).

### 2.2.1.6 Low Pressure Reactors

Provide the following interlocks for low-pressure reactors (4-8 psia [150-400 mm Hg]):

- Low reactor air flow
- High reactor pressure (caused by loss of vacuum)
- High reactor temperature
- High chlorine dioxide concentration downstream of the reactor
- High gas temperature downstream of the reactor.

2.2.1.7 Atmospheric chlorine dioxide storage tanks should be provided with ventilation that meets or exceeds the ventilation rate for the solution temperature shown in Figure 2. The graph may be interpolated for temperatures not shown.

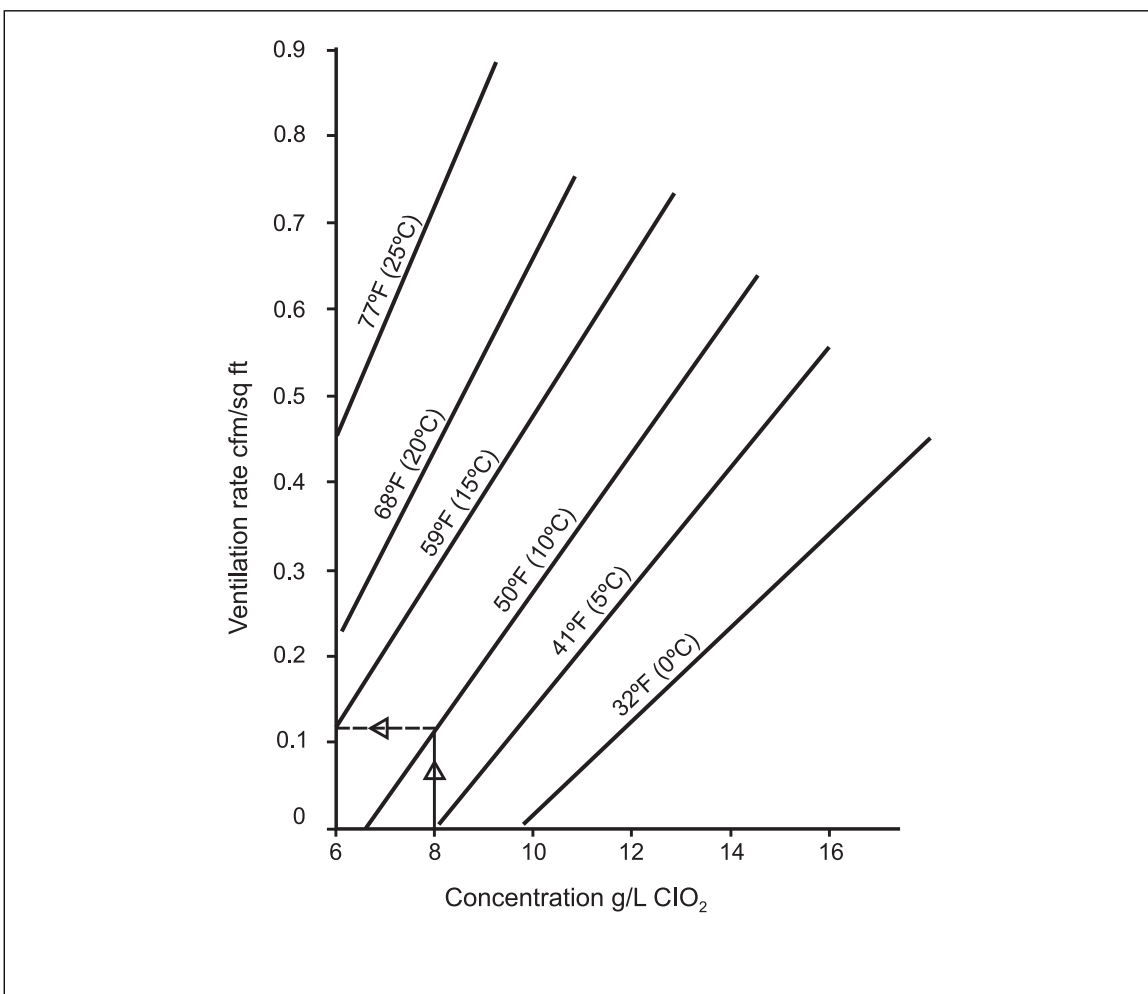


Fig. 2. Recommended ventilation rate for chlorine dioxide storage tanks versus concentration and temperature of the solution.

## 2.2.2 Startup and Shutdown Procedures

### 2.2.2.1 Startup

Prior to startup, the liquid-phase chlorine dioxide concentration should not exceed safe levels (typically 3500 ppm or 3.5 grams per liter). Dilute the liquid phase before the reactor is started if the chlorine dioxide concentration exceeds a safe concentration

After sampling the chlorine dioxide concentration in solution, purge the reactor with air prior to operation.

#### 2.2.2.2 Emergency Shutdown (due to an abnormal condition)

Safety shutoff valves should stop the feed of process reactants. Divert approximately 80% of the diluent air to the gaseous phase. Feed approximately 20% of the air through the bottom of the reactor.

#### 2.2.2.3 Normal Shutdown

Divert approximately 80% of the diluent air to the gaseous phase. Feed approximately 20% of the air through the bottom of the reactor. Leave the absorption-tower fan in operation and pass a low volume of water through the tower until the reactor is restarted.

#### 2.2.2.4 Extended Shut-down

Follow procedure for a normal shutdown until the chlorine dioxide analyzer shows a zero reading or until chlorine dioxide cannot be titrated from the absorption column's chlorine dioxide/water outlet. If the contents of the reactor are sent to a dump tank, ventilate the dump tank constantly.

### 2.3 Operation and Maintenance

2.3.1 Inspect all emergency relief vents regularly to ensure that the vents are not obstructed or frozen.

### 2.4 Training

2.4.1 Train operators to ensure that the appropriate startup and shutdown procedures are understood.

## 3.0 SUPPORT FOR RECOMMENDATIONS

### 3.1 Comments

The bleaching process may represent a major production bottleneck at a papermill. Therefore, an interruption of chlorine dioxide generation may severely impact paper production.

### 3.2 Emergency Relief Vents

Bartknecht, based on considerable testing, developed nomographs to determine the emergency relief area to adequately vent a deflagration. Although the nomographs are based on deflagrations caused by combustion reactions, it is reasonable to use the nomographs for the chlorine dioxide decomposition reaction if the proper nomograph is chosen. The proper nomograph is one where the burning velocity of the gas is similar to the decomposition velocity of chlorine dioxide.

The nomographs are based on methane, propane, coke gas and hydrogen. The burning velocities of the gases are as follows: methane- 1.3 ft/s (0.4 m/s), propane- 1.6 ft/s (0.49 m/s), coke gas 2.3 ft/s (0.7 m/s)<sup>2</sup> and hydrogen 10 ft/s (3 m/s).

"Atmospheric" chlorine dioxide reactors operate at a chlorine dioxide partial pressure of approximately 70 mm Hg. Low-pressure reactors operate at a chlorine dioxide partial pressure of 7-10 mm Hg. Process control interlocks shut down the system if the chlorine dioxide partial pressure increases beyond acceptable limits. Emergency relief venting is needed to relieve the pressure resulting from decompositions that occur during normal operation and for decompositions that may occur as a result of a process control failure.

Emergency relief venting is viable until the partial pressure reaches 300 mm Hg and the decomposition proceeds at such a rate to produce a detonation. Therefore, venting should be designed for a decomposition reaction occurring with a velocity of approximately 6 ft/s (1.8 m/s).

For low-pressure reactors, it is unlikely that the partial pressure of chlorine dioxide would exceed 130 mm Hg because the reactor operates at a total pressure of 200 mm Hg. If the reactor loses vacuum, the initial partial pressure of chlorine dioxide would be approximately 7 mm Hg. The chlorine dioxide concentration will increase if the reaction continues after loss of vacuum.

This document recommends that emergency relief venting on chlorine dioxide reactors should be designed and evaluated in accordance with the Bartknecht hydrogen nomograph for the following reasons:

1. Decompositions involving chlorine dioxide partial pressures of 150-200 mm Hg will propagate at a velocity well above the burning velocity of coke gas. Vents designed in accordance with the coke-gas model may be undersized.

2. It is not possible to vent the worst possible case - a detonation. Therefore, design is for a reasonable, credible case. This would involve an operator error and/or process control failure that allowed the chlorine dioxide partial pressure to increase. A partial pressure of 100-200 mm Hg is a reasonable and credible case.

The equations in Section 2.1.2.3 are an alternate representation of the Bartknecht hydrogen nomograph developed by Simpson.

#### 4.0 REFERENCES

##### 4.1 FM

Data Sheet 1-57, *Plastics in Construction*.

Data Sheet 7-32, *Ignitable Liquid Operations*.

Data Sheet 7-82N, *Storage of Liquid and Solid Oxidizing Materials*.

Data Sheet 7-80, *Organic Peroxides and Oxidizing Materials*.

Data Sheet 7-88, *Ignitable Liquid Storage Tanks*.

Data Sheet 7-91, *Hydrogen*.

##### 4.2 Other Sources

Bartknecht, W.; *Explosions: Course, Prevention, Protection*; Springer-Verlag; New York; 1981

Simpson, L. L.; "Equations for the VDI and Bartknecht Nomograms"; *Plant/Operation Progress*; Vol. 5, No. 1; American Institute of Chemical Engineers, New York; Jan. 1986; pp. 49-51.

#### APPENDIX A GLOSSARY OF TERMS

**Detonation:** an exothermic reaction propagating at greater than sonic velocity in the unreacted medium.

**Ignitable Liquid:** Any liquid or liquid mixture that is capable of fueling a fire, including flammable liquids, combustible liquids, inflammable liquids, or any other reference to a liquid that will burn. An ignitable liquid must have a fire point.

#### APPENDIX B DOCUMENT REVISION HISTORY

January 2012. Terminology related to ignitable liquids has been revised to provide increased clarity and consistency with regard to FM Global's loss prevention recommendations for ignitable liquid hazards.

May 2000. This document has been reorganized to provide a consistent format.

November 1989 — major revision including detail on many current production processes.

November 1981 — new document issued.

#### APPENDIX C MANUFACTURING PROCESS AND HAZARDS

This appendix discusses bleaching processes, various chlorine dioxide production processes and the hazards associated with the manufacture and storage of chlorine dioxide. Background information regarding the bleaching process is intended to highlight the importance of chlorine dioxide to paper mill operations.

##### C1.0 Bleaching Process

The purpose of bleaching is to improve pulp brightness, cleanliness and chemical purity. Bleaching involves multistage processing and reactions between chemicals and fiber components. Because each user has specific needs, a variety of bleaching processes and sequences have been developed. Some common bleaching processes and variations are described below.

A common bleaching process is the following four-stage sequential process: the pulp is treated with chlorine (Chlorination or C Stage), alkaline extraction (E Stage), hypochlorite treatment (H Stage), and chlorine

dioxide (D Stage). If used in this order, the process would be labeled a C-E-H-D bleaching sequence. Many variations exist, such as C-E-H-D-E-D, which allow for additional chlorine dioxide and extraction exposure.

In recent years, new stages have been developed. The two most favorable are hydrogen peroxide (P Stage) and oxygen (O Stage). A typical process using peroxide might be C-E-H-D-P and one using oxygen might be O-C-E-D-E-D. Many hazards and exposures exist with these various processes and chemicals. With the exception of chlorine dioxide, oxygen and hydrogen peroxide, however, the chemicals represent toxic or corrosive exposures only and are not further detailed in this document.

In larger bleach plants, extensive fiberglass-reinforced plastic (FRP) duct systems may exist in all components of the bleaching sequence.

## C2.0 Hazards

### C2.1 General Concerns

The primary concern of all chlorine dioxide processes is the exposure of high-value production equipment to fire and/or explosion hazards. Most of the older processes operate at less than 10% concentration of chlorine dioxide in air and incorporate explosion venting on the chlorine dioxide reactors. The emergency relief vents are weighted and set to relieve when internal pressure exceeds a safe range, commonly about 3 to 5 psig (1.2-1.3 bar).

In some newer processes, the reactors operate under vacuum resulting in crystallization of the sodium sulfate, evaporation of the water in the reactor and a higher concentration of chlorine dioxide. The chlorine dioxide concentration in air may be as high as 18%. The partial pressure of chlorine dioxide is maintained below 1.5 psia (0.1 bar). (Partial pressure of  $\text{ClO}_2 = \% \text{ClO}_2 \times \text{total pressure}$  [see Figure 3].)

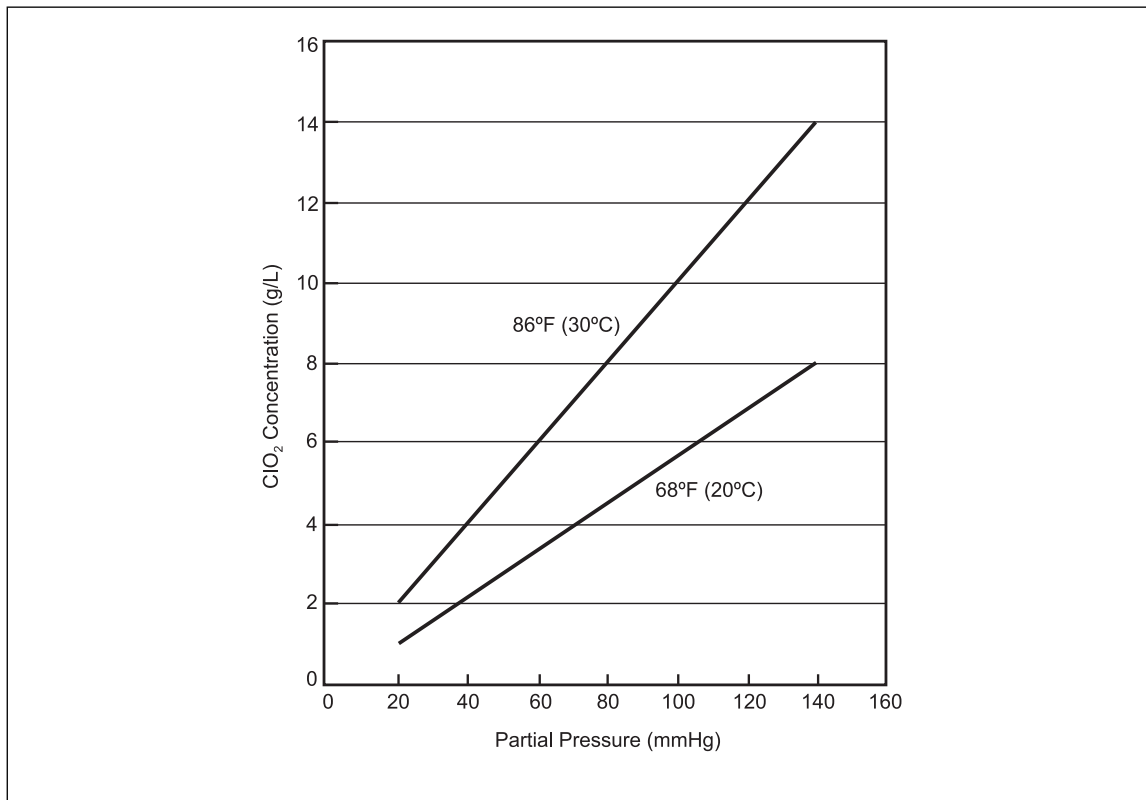


Fig. 3. Chlorine Dioxide Partial Pressure Versus Concentration.

Manufacturers of the newer processes design the equipment to withstand anticipated pressures generated from minor chlorine dioxide explosions. This is done through a combination of equipment strength and emergency relief venting. Reliance is placed on safety interlocks and operator control.



## C2.2 Decomposition Reaction

Chlorine dioxide is an explosively unstable material, therefore it is not shipped or stored but is generated at the plant and used immediately.

Chlorine dioxide decomposes according to the following exothermic reaction:  $2\text{ClO}_2 = \text{Cl}_2 + 2\text{O}_2$

Because this is not a vapor-air explosion, there is no explosive range. However, dilution of the chlorine dioxide increases the heat loss to the inert diluent, thus slowing down the reaction. In dilute water solutions, the reaction does not become explosive and in dilute air mixtures, the reaction is slow enough to vent. The reaction is even slower in an air-water vapor-chlorine dioxide atmosphere.

The auto-decomposition temperature varies with the concentration of chlorine dioxide. Under test conditions, values from 185°F (85°C) to 275°F (135°C) are reported. Impurities and other influences apparently have a catalytic effect and reduce the auto-decomposition temperature. These influences include pipe scale, traces of organic oils, pieces of rubber gasket and exposed steel surfaces due to deterioration of linings.

As the partial pressure of chlorine dioxide increases, the “flame speed” or propagation rate increases. The available data<sup>1</sup> indicates that a chlorine dioxide partial pressure of 80 mm Hg will result in a mild explosion or “puff”; a partial pressure of 130 mm Hg will result in a decomposition with a velocity of 3 ft/s (0.9 m/s); and a partial pressure of 207 mm Hg will result in a decomposition with a velocity of 6 ft/s (1.8 m/s). Partial pressures of 300 mm Hg may result in a detonation. Venting is not effective for a detonation.

## C2.3 Sodium Chlorate

Another significant hazard in newer chlorine dioxide production processes may be on-site manufacture of sodium chlorate. Sodium chlorate ( $\text{NaClO}_3$ ) is a Class 3 oxidizer. When dry or in concentrated-liquor form, this material can cause ignition and severe fires when in contact with organic materials. Normally, sodium chlorate is kept in water solution and the hazard is reduced. Sodium chlorate becomes a concern only if spills are not promptly washed down and are allowed to dry.

The newer chlorine dioxide processes may include on-site production of acid by burning hydrogen gas in the presence of chlorine gas. Primary concern is the safe handling of hydrogen, which is accomplished by using recognized fuel-burner-combustion safety controls.

## C3.0 Production Processes

### C3.1 General

For many years the three primary processes used for the production of chlorine dioxide were the Olin Mathieson process, the Solvay process and the Hooker R2 process. These are still popular and in common use.

Newer processes are now emerging, including the Hooker SVP process, the ERCO R2 - R8 processes, the Lurgi process and other processes which are similar in scope and hazard. In all of the production processes, chlorine dioxide is obtained through the reduction of sodium chlorate by an agent such as acid or alcohol.

### C3.2 Olin Mathieson

In the Olin Mathieson process (see Fig. 4), concentrated sodium chlorate is reduced by sulfur dioxide in a sulfuric acid solution. A sulfur dioxide/air mixture passes into the bottom of the reactor. The reaction between sulfur dioxide and sodium chlorate results in a chlorine dioxide/air mixture, leaving the reactor with approximately the same concentration of chlorine dioxide as that of the sulfur dioxide in the inlet system. Chlorine dioxide is recovered in an absorption tower and stored in a water solution.

Sulfur dioxide from a burner operation cannot practically exceed 15% sulfur dioxide concentration; therefore a system using a sulfur burner tends to be inherently safe. The use of purchased sulfur dioxide can increase the hazard because the concentration can be high enough to generate dangerous chlorine dioxide concentrations.

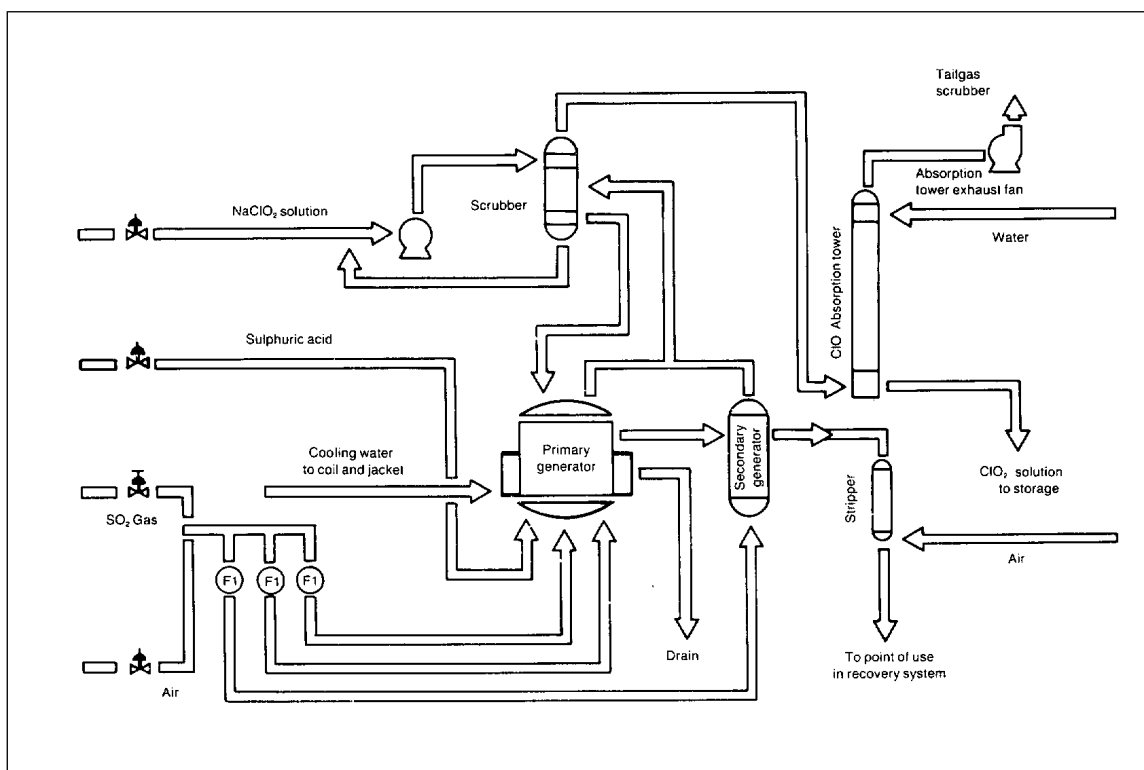


Fig. 4. Modified Mathieson process diagram.

### C3.3 Solvay

In the Solvay process (see Fig. 5), sodium chlorate is reduced by methyl alcohol in a sulfuric acid solution. This process involves two reactors in series. The products from the first reactor overflow to a second reactor where additional alcohol is added to complete the reaction. The chlorine dioxide mixes with air and passes to a water absorber. The air flow, which dilutes the gas to about 10% chlorine dioxide, is the primary safety factor. If the air flow falls below a predetermined safe level, the intensity of an explosion may be beyond the reactor's venting capacity.

### C3.4 Hooker R2 Or ERCO<sup>2</sup> R2

The R2 process (see Fig. 6) produces chlorine dioxide by the reaction of a sodium chlorate/sodium chloride solution with concentrated sulfuric acid. Air bubbles through the reactor to remove chlorine and chlorine dioxide from the reactor and to dilute the chlorine dioxide to a safe level of 10 to 12%.

### C3.5 Hooker SVP Or ERCO R3

The Hooker SVP and the ERCO R3 processes (see Fig. 7) are variations of the R2 process that operate under vacuum instead of positive pressure. The reactor operates at approximately 4-6 psia (200-300 mm Hg) and 140-160°F (60-70°C). Water in the reactor is evaporated and stabilizes the chlorine dioxide/air mixture. ERCO processes R3H-R7 are variations of the R3 process.

### C3.6 ERCO R3H-R7 Processes

Variations of the R3 process (see Fig. 8) include using hydrochloric acid in place of sulfuric acid and/or sodium chloride (ERCO 3H and R5). The ERCO R6 process combines the R5 process with a sodium chlorate plant. The ERCO R7 is also a modified R3 process. By-product chlorine reacts with sulfur dioxide to form sulfuric and hydrochloric acid, which is later used in the chlorine dioxide generator.

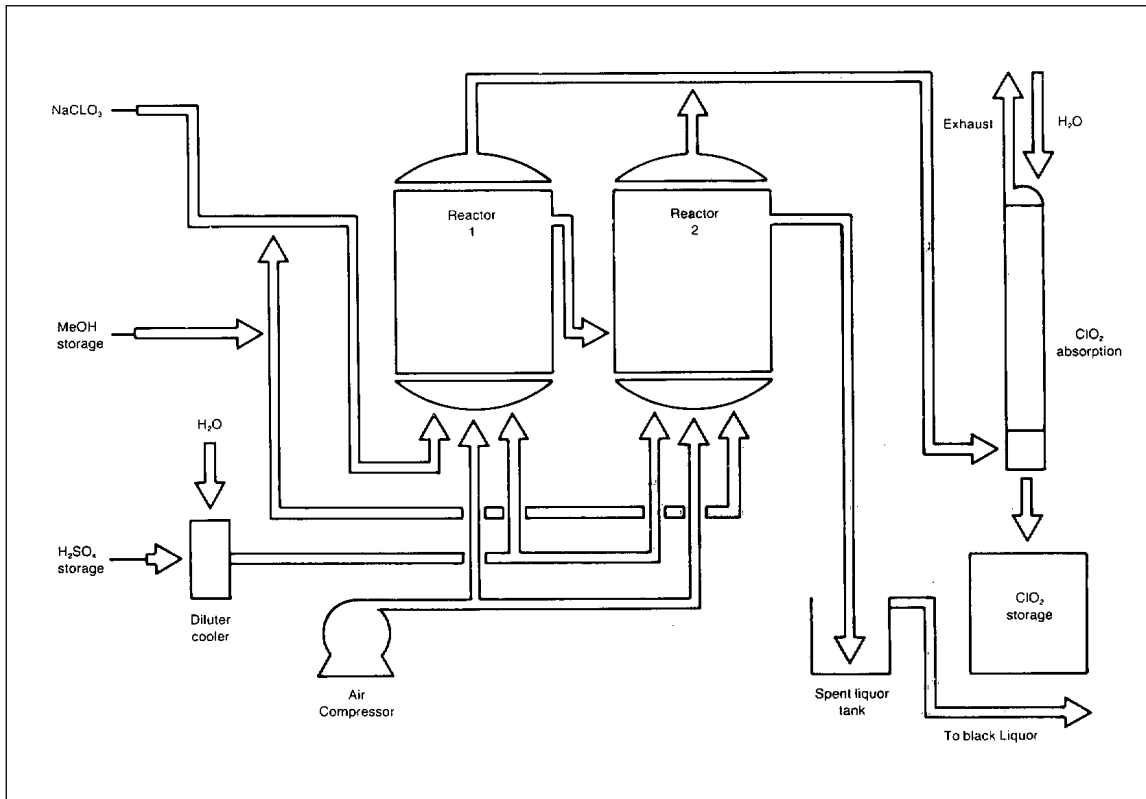


Fig. 5. Solvay process diagram.

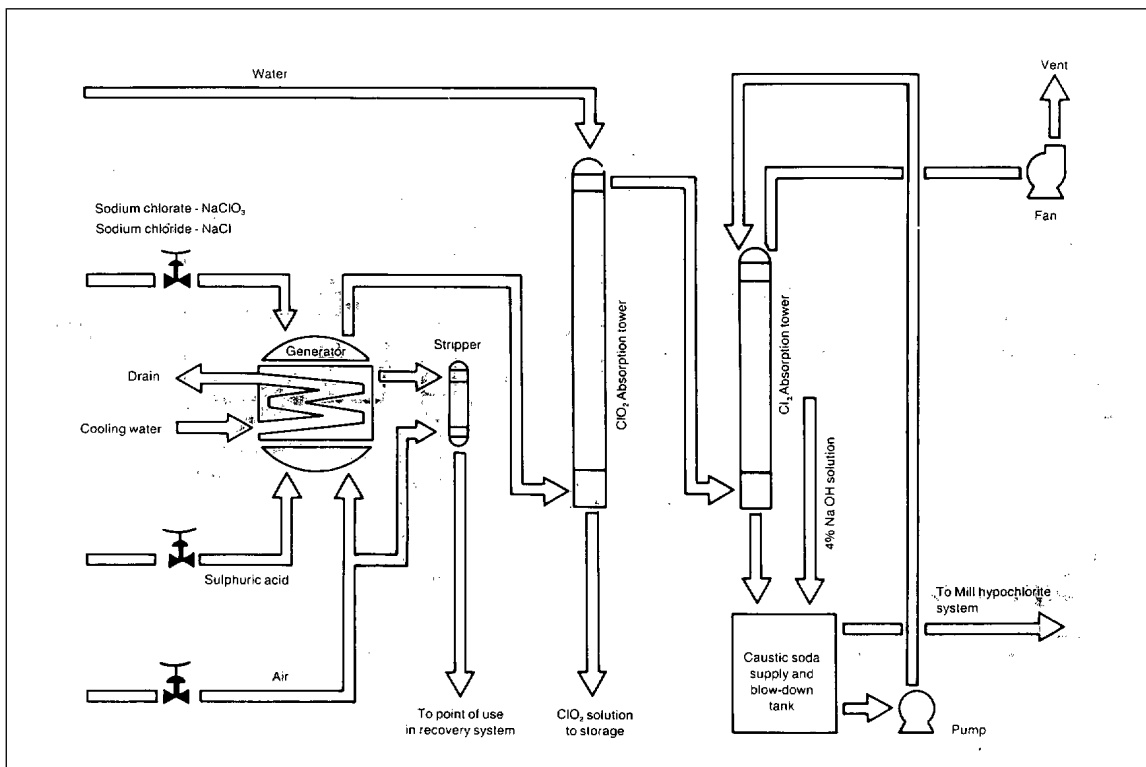


Fig. 6. R2 process diagram.

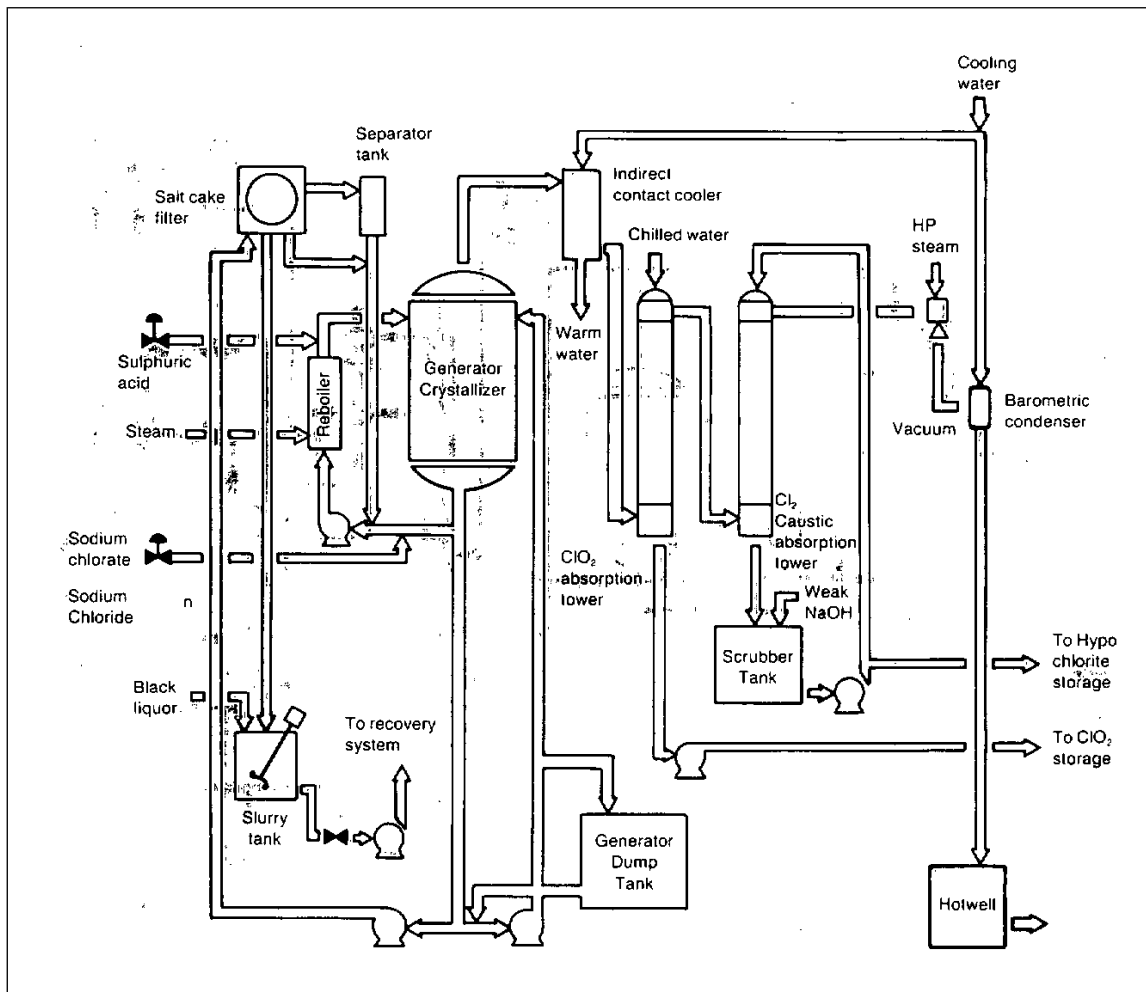


Fig. 7. R3 process diagram.

### C3.7 ERCO R8 Process

The ERCO R8 process is a modified Solvay process. Sodium chlorate is reduced by methanol in the presence of sulfuric acid at approximately 4 psia (200 mm Hg) and 150°F (65°C).

### C3.8 Lurgi Process

The Lurgi process uses hydrochloric acid to reduce sodium chlorate in a multistage reactor. Air and steam are injected into the reactor. The reactor operates at approximately 8 psia (400 mm Hg) and 100°F (38°C). The process prevents the partial pressure of chlorine dioxide from exceeding 1.5 psia (0.1 bar).

### C4.0 Storage

#### C4.1 Storage Conditions

Chlorine dioxide is stored in a water solution at various concentrations. Typical concentrations range from 8-12 g/lit. The chlorine dioxide vapor pressure results in some chlorine dioxide liberated from solution. The vapor pressure varies with the concentration and temperature of the solution, as shown in Figure 3.

#### C4.2 Ventilation

Ventilation is needed to prevent chlorine dioxide from accumulating in the tank. Normally, the ventilation is provided by exhausting the chlorine dioxide gas to the absorption tower. The amount of ventilation needed varies with the concentration and temperature of the solution, as shown in Figure 2.

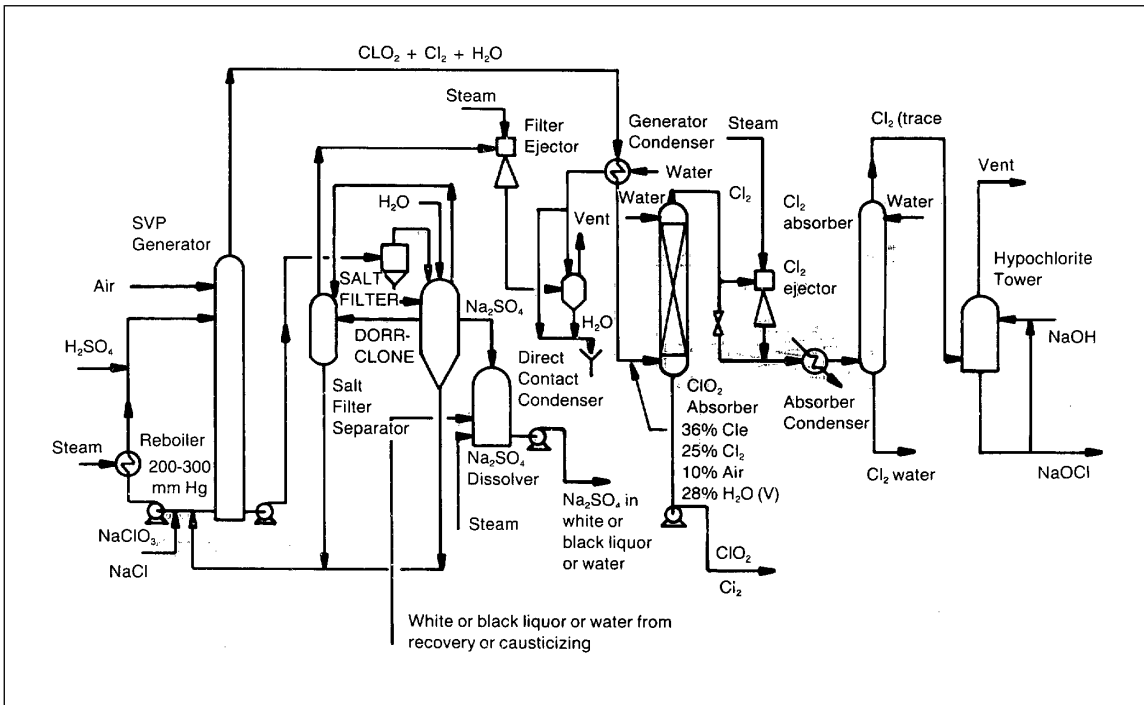


Fig. 8. SVP process diagram.

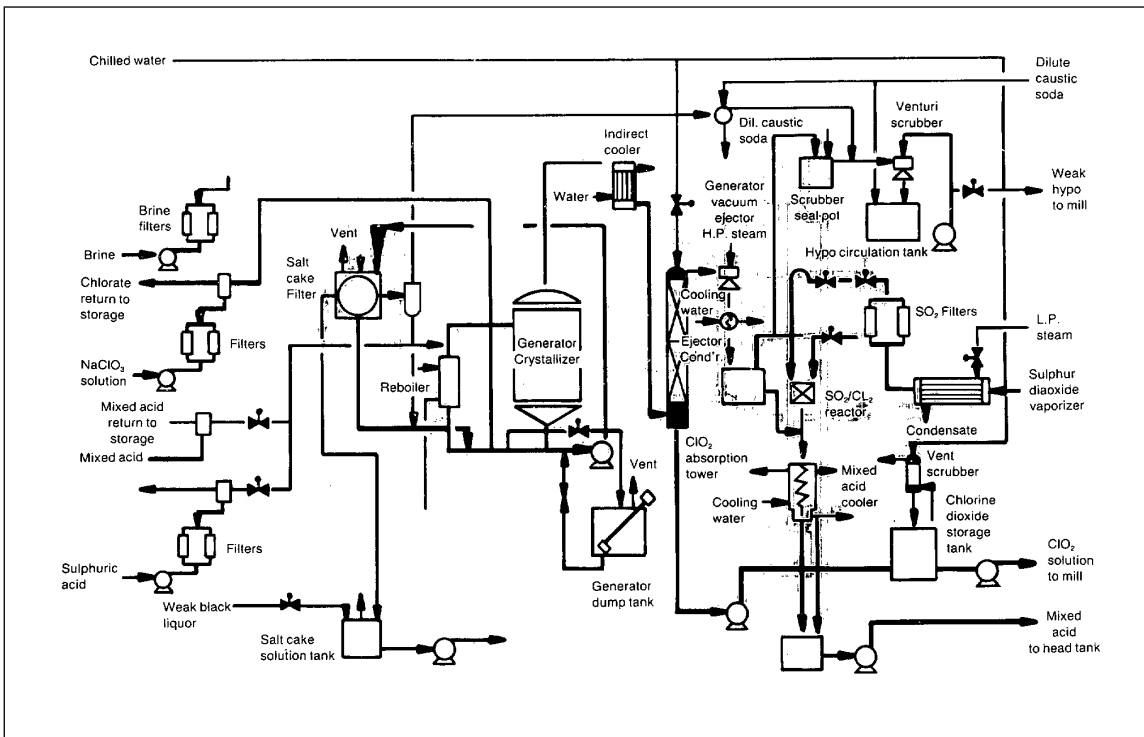


Fig. 9. R7 process diagram.

### C4.3 Emergency Relief Venting

Emergency relief venting is needed to provide overpressure relief in the event of chlorine dioxide decomposition. It is only practical to provide venting for decompositions involving approximately 15% chlorine dioxide concentrations in air. Decompositions involving larger chlorine dioxide concentrations proceed too rapidly to vent.

The vent size is determined by the concentration and temperature of the chlorine dioxide, and the size of the storage tank. The vent design should be based on the most severe credible temperature and concentration of the chlorine dioxide solution.

### APPENDIX D BIBLIOGRAPHY

- (1) TAPPI, Vol. 38, No. 4, April 1955, pp. 200.
- (2) ERCO is now Albright and Wilson Americas. The process is still often referred to as an "ERCO" process.

FM Engr. Comm. September 1989