GASEOUS CHLORINE AWARENESS AND EXPOSURE PROGRAM

PURPOSE / SCOPE

The purpose of this procedure is to advise employees in areas where gaseous chlorine is being used and to supply on an awareness level basis about the properties and hazards of gaseous chlorine, general guidelines and training requirements.

WHAT IS GASEOUS CHLORINE?

Chlorine is a powerful disinfectant and bleaching agent. In both gas and liquid forms, chlorine is a toxic substance that presents a number of hazards. Gaseous chlorine refers to chlorine purchased in its elemental form, occurring in the gaseous or-liquid state. It is supplied commercially in pressurized containers sized to contain either 100 pounds, 150 pounds or 2,000 pounds of chlorine. In addition, chlorine can be purchased in single unit and multi-unit railroad tank cars, as well as tank trucks.

Chlorine has a characteristic penetrating and irritating, pungent odor. The gas is greenish yellow in color and the liquid is clear amber. Gaseous chlorine is 2.5x heavier than air and will initially remain in low-lying areas unless wind or other conditions provide air movement.

CHEMISTRY

- Chlorine can be used as a gas or as a liquid. Calcium hypochlorite is the dry form of chlorine which can be mixed to prepare a liquid chlorine solution.
- Vapor pressure increases with temperature; however, it is not impacted by volume. In other words, the 1 pound of chlorine and 100 pounds of chlorine have the same vapor pressure.
- When added to pure water, chlorine forms hypochlorous (HOCL) and hydrochloric (HCL) acids.
- HOCL is a stronger oxidant and disinfectant than OCL-, which is why disinfection is more effective at a lower pH.
- The effectiveness of chlorine increases as temperature increases. Conversely, longer contact times are required to disinfect water at lower temperatures.
- In addition to disinfecting water, chlorine can also be used to oxidize materials such as iron, manganese, cyanide, sulfide, and organic matter.

HOW IS GASEOUS CHLORINE USED?

Chlorine has a variety of uses. It is used to disinfect water and is part of the sanitation process for sewage and industrial waste. During the production of paper and cloth, chlorine is used as a bleaching agent. It is also used in cleaning products, including household bleach which is chlorine dissolved in water. Chlorine is used in the preparation of chlorides, chlorinated solvents, pesticides, polymers, synthetic rubbers, and refrigerants.

DANGERS OF GASEOUS CHLORINE EXPOSURE

Chlorine is a respiratory irritant, and under conditions of sufficient concentration and exposure, can cause vomiting and death by suffocation. Chlorine, especially when combined with even small amounts of water, is highly corrosive, and can cause severe frostbite burns when brought into contact with skin and eyes.

Chlorine reacts with many organic compounds to form chlorinated derivatives. Some reactions can be extremely violent, especially those with hydrocarbons, alcohols and ethers. Proper methods must be followed, whether in laboratory or plant, when organic materials are reacted with chlorine.

Chlorine is only slightly soluble in water (0.3% to 0.7%) depending on the water temperature. However, the resulting water phase is extremely corrosive. The reaction rate of dry chlorine with most metals increases rapidly above a temperature which is characteristic for the metal. Two of the more common metals are titanium and steel. In the presence of dry chlorine, titanium is flammable. Care should be taken to make sure titanium materials are not used in dry chlorine service. Steel is the most common material used in dry chlorine service.

At temperatures above 300°F (149°C) a chlorine/steel fire can result. It is important to make sure steel in chlorine service does not go above this temperature either through internal/external heating or mechanical abrasion. Moist chlorine, primarily because of the hydrochloric and hypochlorous acids formed through hydrolysis, is very corrosive to most common metals. Platinum, silver, tantalum and titanium are resistant. Consult CI Pamphlet 6 (11.1) for detailed information on reactivity with metals.

Chlorine is neither explosive nor flammable. Chlorine will support combustion under certain conditions. Many materials that burn in oxygen (air) atmospheres will also burn in chlorine atmospheres. Many organic chemicals react readily with chlorine, sometimes violently. An important specific compound of concern is hydrogen. Chlorine reacts explosively with hydrogen in a range of 4% to 93% hydrogen. The reaction is initiated very easily much the same way as hydrogen and oxygen. See Pamphlet 121 for more information.

WHAT IS CHLORINE'S MECHANISM OF ACTION?

When chlorine enters the body as a result of breathing, swallowing, or skin contact, it reacts with water to produce acids. The acids are corrosive and damage cells in the body on contact. Chlorine burns the eyes, nose, and throat--eventually causing bronchial inflammation, respiratory tract damage, and death.

RULE OF EXPOSURE

Toxic effects of chlorine	
Chlorine concentration (parts per million)	
0.03–0.1 ppm	Range of odor threshold
1–3 ppm	May cause mild irritation of the eyes, nose, and throat
3–5 ppm	Stinging or burning in eyes, nose, and throat; may cause headache, watering eyes, sneezing, coughing, breathing difficulty, bloody nose, and blood-tinged sputum
5–15 ppm	Severe irritation of the eyes, nose, and respiratory tract
10 ppm	Immediately Dangerous to Life or Health (IDLH)

30–60 ppm	Immediate breathing difficulty resulting in pulmonary edema (fluid buildup in lungs), possibly causing suffocation and death
430 ppm	Lethal after 30 minutes
1000 ppm or more	Fatal after a few breaths
Note: Chlorine gas is not visible as a greenish-yellow cloud at concentrations below 1000 ppm.	

HOW CAN PEOPLE BE EXPOSED TO GASEOUS CHLORINE?

Chlorine is found in many industrial processes, including those used to make plastics, vinyl, and nylon, as well as pharmaceuticals and the food/beverage industry, too. The electronics industry relies on chlorine in the production of microprocessors and computers. Chlorine supports the manufacture of gasoline additives, brake fluid, and antifreeze, as well as popular metals such as titanium, magnesium, and aluminum.

Because of its widespread use in industrial and commercial locations, exposure to chlorine could occur from an accidental spill or release, or from a deliberate terrorist attack. The most harmful route of exposure is from breathing chlorine gas. Exposure may also result from skin contact or eye contact with chlorine gas or by swallowing chlorine-contaminated food or water.

OIL REFINERIES

Oil refineries inject chlorine directly into stacks to reduce sulfur emissions (H2S, for example) and require monitoring. The sulfur monochloride compound that forms in the stack is a solid and can drop out of the air flow in the stack and coat the inside of the stack itself or drop down to the bottom of the stack, where it can be collected. Portable and fixed toxic gas detectors also can be used to monitor potential chlorine leakage around the bulk storage tanks.

CLEAN WATER TREATMENT

Chlorine is added to treat drinking water to destroy bacteria and other harmful micro-organisms. It also controls algae or slime and helps improve the taste and smell of fresh water. Chlorinating basins and well sites have small buildings enclosing chlorine storage tanks with mixing systems. Fans provide a ventilation system, with gas detectors installed for monitoring and alarm purposes in case of a system leak. Portable gas detectors often are carried into these confined space areas.

SEWAGE WASTEWATER

For neutralization of effluent, a complete (Cl2) chlorination system is often used at waste treatment facilities. Toxic gas detectors are used to detect chlorine gas at these locations: the chlorine tanks, the chlorine dosing pump, the chlorine mixer, and the sampling area. In open settling pond areas, portable gas detectors are carried to warn workers of excessively high concentrations of gas.

PHARMACEUTICALS PRODUCTION

Most prescription and over-the-counter pharmaceuticals contain or are manufactured with chlorine. Some of the more common medications that are made using chlorine include pain relievers, decongestants, antihistamines,

and antibiotics. Toxic gas detectors are utilized both within the areas where pharmaceuticals are processed and in storage tank areas.

PULP/PAPER BLEACHING

Bleaching of pulp is a series of chemical reactions conducted in stages. These reactions are carefully controlled to bleach the pulp without destroying the strength of the fiber. Chlorine gas and water are added to the eductor prior to the mixing stage. Toxic gas detectors can be used to monitor for chlorine gas leakage during the bleaching process.

AGRICULTURAL PESTICIDES

With world hunger continuing to be a pressing problem, chlorine is used in the manufacturing process for crop protection chemicals. Such chemicals help crops resist disease, insects, and weeds. In large pesticide manufacturing operations, toxic gas detectors are found in the mixing and blending areas, as well as in storage tank areas for both raw materials and finished products.

FOOD & BEVERAGE

From meat to produce to beverages, chlorine is applied as a disinfectant and antimicrobial agent. Chlorine is used as a sanitizer in cleansing employees' hands and footwear, in the washing of beef carcasses, in fruit/vegetable spray washing or flume systems, and in the processing of eggs, seafood, and much more. Wherever chlorine is stored in tanks or dispensed with injection systems in heavy concentrations, portable and fixed toxic gas detectors can protect people and equipment.

EMERGENCY AID OF CHLORINE EXPOSURE

If you have been exposed to a release of chlorine, take the following steps:

- Quickly move away from the area where you think you were exposed. If the release was indoors, go outdoors.
- If you are near a release of chlorine, emergency coordinators may tell you to either evacuate the area or to "shelter in place." To "shelter in place" means to remain indoors to avoid being exposed to the chemical.
- While indoors, shut and lock all doors and windows, turn off air conditioners, fans and heaters, and close fireplace dampers.
- Quickly remove any clothing that may have chlorine on it. If possible, clothing that is normally removed over the head (like t-shirts and sweaters) should be cut off the body to prevent additional contact with the agent.
- Place your clothing inside a plastic bag and seal the bag tightly.
- Do not handle the plastic bag, and wait for instructions on proper disposal.
- Disposing of your clothing in a sealed bag helps protect you and other people from additional exposure.
- Store the bagged clothing in a secure location away from people, especially children.
- Quickly wash any chlorine from your skin with large amounts of soap and water, and flush your eyes with large amounts of water.
- Remove and dispose of contact lenses.
- Wash eyeglasses with soap and water before wearing.
- If needed, seek medical attention right away.

There is no antidote for chlorine poisoning, but chlorine's effects are treatable, and most people recover. People who experience serious health effects (such as severe eye or airway irritation, severe coughing, difficulty breathing, pulmonary edema) may need hospital care.

WORKING SAFELY WITH CHLORINE

Every year, workers are injured needlessly in plant accidents caused by leaking toxic gases. These gases include chlorine and others such as ammonia, carbon monoxide, hydrogen sulfide, and more. Most of these accidents are preventable with personal safety or plant gas monitoring equipment. Employees should be aware of owners' site specific contingency/emergency plans and provisions. Employees must be informed where chlorine is used in the host facility and aware of additional plant safety rules. Wear personal protective equipment. Employees will be provided with and required to use impervious clothing, gloves, face shields and other appropriate protective clothing necessary to prevent any possibility of skin contact with gaseous chlorine.

In the workplace, both portable gas detectors and fixed gas detection systems are employed to help protect workers from chlorine. Depending on the type of workplace hazard, one or both types of gas detectors may be in use. The use of chlorine is prevalent in so many industries that it is helpful to have a broader understanding of its applications before developing a chlorine gas safety program and determining the requirements for portable and/or fixed gas detectors in any plant.

Knowing when to utilize portable gas detectors versus fixed gas detection systems is important. Portable and/or fixed-point gas detectors are essential to protect workers and equipment from chlorine gas, as well as an OSHA and EPA requirement. Portable detectors rely on electrochemical cell (EC) sensors, and they are utilized in confined spaces or large areas where fixed systems are impractical or cost prohibitive.

In confined spaces, the access is often infrequent and the danger may be more from oxygen deficiency than from a toxic gas such as chlorine or a combustible gas requiring continuous fixed monitoring. When portable detectors sense a toxic or combustible gas, they immediately warn the technician through visual, audible, and vibrating alarms.

DESIGN OF GASEOUS CHLORINE FACILITIES

1. If gas chlorination equipment and chlorine cylinders are to be installed or stored in a building used for other purposes, a gas-tight partition should separate the chlorination room from any other portion of the building. Doors to this room should open only to the outside of the building; and should be equipped with panic hardware. Such rooms should be at ground level, and should permit easy access to all equipment; the chlorine storage area(s) should be separated from the chlorine feed area(s).
2. A clear glass, gas-tight window should be installed in an exterior door or interior wall of the chlorination room to permit the chlorinator(s) to be viewed without entering the room.
3. Chlorination rooms should be equipped with heating and ventilating equipment designed to maintain the room(s) containing the chlorine containers at approximately 18-21°C (65-70°F) and the room(s) containing the chlorinator feed equipment at a temperature of 5-10°F higher.
4. Containers (except insulated rail or cargo tanks) should be shielded from direct sunlight or from overheating above 60°C (140°F) any source, either while in storage or in use. Pairs of level rails or properly designed cradles should be provided for storing one ton cylinders.
5. Forced mechanical ventilation should be included that will provide a complete air change at least every 1-4 minutes. Because chlorine gas is heavier than air, location of air inlets and outlets should be carefully considered to ensure that the entire room will be thoroughly ventilated. For example, in the exhaust ventilation system, the exhaust outlet should be located near the floor, with the discharge being positioned outside of the building at a point where it will not contaminate the air inlet to any buildings or inhabited areas. The fresh air inlet should be located at the opposite end of the room from the exhaust outlet, to facilitate complete air replacement.
6. Exhaust equipment should be automatically activated by external light switches. That is, an operator should be able to turn the lights on outside of the chlorination room and thereby activate the ventilation

system prior to entering the enclosed area. Other automatic systems, including door-activated mechanisms,' should also be considered.

7. Emergency showers and eye baths should be located near, but external to, the chlorination facilities.
8. For facilities having a design hydraulic capacity of five million gallons per day or more, an automatic chlorine detection system should be included as part of the chlorination facility., The detection system should sound alarms and activate flashing lights that are audible and visible within the POTW. Connection of the alarm system to the local police station, POTW operator's area, or both, is also recommended where practical. Consideration of such detection and alarm systems should also be given in the case of smaller facilities, where the potential benefits are sufficient to warrant the additional cost and associated increase in operational complexity.

Chlorine Handling and Storage

- Chlorine has health and environmental hazards. Specifically, it is severely corrosive to the skin, eyes and mucous membranes. First-aid measures to remove chlorine from skin or eyes include showering with large quantities of water for at least 15 minutes.
- A Safety Data Sheet (SDS) formerly known as an MSDS contains an assessment of chemical characteristics, hazard, personal protection equipment and other information relative to health, safety and the environment.
- The self-contained breathing apparatus (SCBA) is required when entering a room with chlorine concentrations great than 1% or when a longer exposure time is required. The SCBA should be located near the door outside of the chlorinator room for easy access. If a chlorine leak is large, contact the local fire company and local emergency management agency for assistance.
- Forced air ventilation (or exhaust fans) are required in chlorine storage and feed rooms. Fans should be located near the floor, since chlorine is 2.5 times heavier than air.
- First aid, chlorine leak response, emergency measures, and risk management plans should be reviewed with all employees.
- Rooms for chlorine storage and feed should be separate from other operating areas.
- Chlorine leaks may occur around valve stems, leaded gaskets at the discharge valve outlet, cylinder valves or fusible plugs. Repairs may be as simple as tightening the packing gland nut, replacing the leaded gasket or more complex repairs that require emergency repair kits for leaks at fusible plugs and cylinder valves.
- The quantity of chlorine that escapes from a leak is significantly less as a gas than as a liquid. Consequently, if a leak occurs in a cylinder, you should turn it so that the leaking side is on top, if possible, so that gas escapes rather than liquid.
- Do not immerse a leaking container in water because the hydrochloric acid formed will increase corrosion at the leak location and make the leak worse and gas will be released at the water surface.
- Position and store 100 and 150 lb. cylinders vertically and secure them with chains. When using ton containers of chlorine, align the valves vertically to feed chlorine gas and install locking devices to prevent containers from rolling.
- A fusible plug is designed to soften or melt at 158° F to 165° F to prevent buildup of excessive pressures and the possibility of rupture due to a fire or high surrounding temperatures. Cylinders and ton container are equipped with fusible plugs.
- The chlorine feed room temperature should be kept between 60° F and 120° F to vaporize liquid chlorine. Below 60° F, chlorine gas forms chlorine hydrate, also known as “green ice,” when it comes in contact with water. This green ice can clog the ejector (injector) and gas piping, creating a serious maintenance problem.

Changing Chlorine Cylinders

This work procedure should specify that only competent workers can change cylinders and how many of these workers should be present. The following example of a safe work procedure for changing cylinders is for a non-

emergency situation, when the alarm has not been activated. (If the alarm has been activated, workers would follow the emergency procedures posted in the workplace.)

1. Turn on the light and visually ensure that the room is safe to enter (there may be visible signs of damage).
2. Put on appropriate personal protective equipment (be specific about the type of equipment). This procedure requires a respirator other than an escape respirator.
3. Turn on the exhaust ventilation before entering the room.
4. Close the main chlorine container valve.
5. Allow the system to purge itself of chlorine. Ensure that the float drops to the bottom of the feed-rate indicator (rotameter). Verify that there is a high vacuum and that the weigh scale reads zero.
6. Loosen the chlorinator (auxiliary valve or vacuum regulator) and remove it from the empty cylinder.
7. Replace the cylinder cap on the empty chlorine cylinder and remove the cylinder to secured storage.
8. Secure the new cylinder into place.
9. Remove the protective hood from the new cylinder.
10. Ensure that there is no chlorine leaking from the packing gland. Use ammonia vapor from the ammonia test bottle, which contains a strong ammonia solution (25% or 26° Baumé).
11. Ensure that the cylinder valve is closed. Do not open the valve yet.
12. Remove the cylinder outlet cap and check that the cylinder outlet face is clean and smooth. 13. Using a new washer, connect the vacuum regulator or the yoke assembly (be specific for the system in use) to the valve outlet using the supplied wrench only. Note: Never use oil-based material or water to clean the mating surfaces.
13. Crack open the chlorine cylinder valve and then quickly close it again. This will let enough chlorine into the lines to charge them. The valve should open with no more than a sharp rap from the heel of your hand. Never use a “helper” wrench or a larger wrench than the one supplied. If the valve will not open, carefully loosen the packing gland slightly.
14. Check all the connections you have made to ensure there are no leaks. Use the vapor from the ammonia test bottle (see step 10). If a leak is indicated, activate the leak control procedure (see example two below).
15. When no leaks are indicated, open the chlorine cylinder valve no more than half a turn and leave the cylinder wrench on the valve.
16. Open any additional system valves (be specific for your facility) and test for leaks as each stage is charged with chlorine.
17. Check for leaks again with the ammonia test bottle to be sure that everything is in order.
18. Ensure that the alarm system is functioning.
19. Turn off the exhaust ventilation and lights and close the door when you leave.
20. Remove your respirator and other personal protective equipment.

Leak Detection And Control

This example includes two components: what to do if a leak is indicated after a cylinder change and what to do if the chlorine alarm is activated during routine operation of the system.

If the ammonia test indicates a leak after a cylinder change, follow these steps. Note that the worker will already be wearing a respirator:

- Immediately close the main cylinder valve.
- As long as the monitor reads less than 10 ppm, the cylinder hookup procedure may be repeated.
- Open (and close) the main cylinder valve and repeat the ammonia test.
- If a leak is still indicated, make a third and final attempt to get a good seal using a new lead washer.
- If the leak cannot be corrected after three attempts, remove the cylinder from service and contact the supplier. Ensure that there is no leak from this cylinder with the main valve closed. A different cylinder must be connected to the chlorination system.

- Leave the chlorine room and remain nearby to restrict access to the room or provide other assistance, as directed, until the chlorine alarm has automatically shut off.

If the chlorine alarm has been activated during routine operation of the system, at least two people must respond. Follow these steps:

- Approach the location cautiously.
- If chlorine gas can be smelled in the open, immediately leave the area and activate full emergency procedures. Do not attempt to turn on the exhaust ventilation.
- If there is no smell of chlorine gas outside the room, put on respiratory and check the monitor readout.
- If the chlorine concentration is less than 10 ppm: Put on the appropriate personal protective equipment. Enter the room and close the main cylinder valve. Turn on the ventilation system and leave the area until the alarm stops. While still wearing the respirator, enter the room after the alarm has stopped, isolate the leak, and perform necessary repairs. Remember that all chlorine lines must be free of oil, grease, and moisture before re-opening the chlorine cylinder.
- If the continuous monitor indicates a chlorine concentration greater than 10 ppm, immediately leave the area and activate full emergency procedures. Do not turn on the ventilation system and do not wait downwind of the building for help to arrive.

Note: Never apply water to a chlorine leak. Moist chlorine is more corrosive than dry chlorine and the leak will worsen rapidly if water is applied to it. Remember also that a chlorine leak never gets better — it always gets worse.

WHERE TO GET MORE INFORMATION

- Centers for Disease Control and Prevention Public Response Hotline: 888-246-2675
- Agency for Toxic Substances and Disease Registry: 888-422-8737
- Regional Poison Control Center: 800-222-1222

TRAINING

All Winger Companies employees that perform work activities, where the potential of exposure to gaseous chlorine may be apparent, will be provided awareness training in this program in order to be familiar with the potential hazards and proper safe work procedures to follow. This training will include an overview of gaseous chlorine, and provide explanations of how exposure may occur and what can be done to treat exposure.

Training records shall be kept at the Winger corporate office at 918 Hayne Street, Ottumwa, Iowa.

SOURCE CREDITS:

Chlorine Institute, Chlorine Chemical Properties,
https://www.chlorineinstitute.org/stewardship/about-chlorine/chemical-properties.cfm
Chlorine Safe Work Practices, WorkSafeBC,
http://www.worksafebc.com/publications/health_and_safety/by_topic/assets/pdf/chlorine.pdf
Drinking Water Operator Certification Training Module #24, Gas Chlorination, Revised January 2015, Pennsylvania Department of Environmental Protection, (Pa. DEP) in cooperation with the following contractors, subcontractors, or grantees: The Pennsylvania State Association of Township Supervisors (PSATS), Gannett Fleming, Inc. Dering Consulting Group, Penn State Harrisburg Environmental Training Center
New York State Department of Health, The Facts About Chlorine,
https://www.health.ny.gov/environmental/emergency/chemical_terrorism/chlorine_general.htm
Occupational Health & Safety, Preventing Chlorine Gas Accidents, May 2005,
https://ohsonline.com/Articles/2005/05/Preventing-Chlorine-Gas-Accidents.aspx
United States Environmental Protection Agency, Oct 23, 1978 Construction Grants Program Requirements Memorandum, PR No. 79-1, Subject: Safety Requirements for the Design and Operation of Chlorination Facilities Using Gaseous Chlorine

DOCUMENT CONTROL:

Initial Program November 30, 2015
Revised October 19, 2016
Revised September 13, 2017
Revised September 26, 2018