Chlorine at the Work Site

What is chlorine?

Chlorine is a greenish-yellow toxic gas with a strong, irritating odour similar to that of bleach. If the temperature of the gas is lowered, or it is pressurized, it becomes a liquid. In most cases, chlorine gas is shipped as a liquid. Because chlorine is very reactive, it does not exist as a gas in nature. However, it is often found combined with other elements. The most common chlorine compound is salt (sodium chloride) which is found naturally in seawater and rock salts. Other common chloride minerals include sylvite (potassium chloride) and carnallite.

Properties of chlorine

The odour threshold of chlorine is about 0.2 to 0.4 ppm. However, odour is not a reliable indicator for this compound since workers exposed routinely to chlorine may lose the ability to smell the chemical at lower levels.

Chlorine gas is heavier than air and will tend to collect in low-lying areas when the concentration is high enough. Although it is not flammable, it is a strong oxidizer. If chlorine comes in contact with flammable or combustible materials i.e. gasoline and petroleum products, hydrocarbons, turpentine, alcohols, hydrogen, acetylene, ammonia and sulphur, a fire or explosion can result. Some materials will burn in a chlorine atmosphere, even if there is no oxygen. Chlorine reacts with water and hydrogen sulphide to form corrosive hypochlorous acids. It reacts with carbon monoxide and sulphur to form phosgene and sulfuryl chloride.
Uses of Chlorine

Chlorine is one of the most commonly manufactured chemicals in North America. Chlorine is used to make:
- chlorinated organic chemicals such as vinyl chloride monomer, carbon tetrachloride, perchloroethylene, 1,1,1-trichloroethylene, chlorobenzenes
- organic chemicals such as propylene oxide and glycols
- chlorinated inorganic chemicals such as sodium hypochlorite, hydrochloric acid, hypochlorous acid, sulphur chlorides, phosphorous chlorides, titanium chlorides and aluminum chloride.

It is also widely used:
- as a bleaching agent in the manufacture of pulp and paper and textiles
- to make pesticides, herbicides, refrigerants, propellants, household and commercial bleaches, detergents for dishwashers, antifreeze, antiknock compounds, plastics, synthetic rubbers, adhesives and pharmaceuticals
- for drinking and swimming water purification
- for sanitation of industrial wastes and sewage
- in the degassing of aluminum metal.

Health effects

Chlorine gas is a severe irritant to the eyes and respiratory system because it reacts with body moisture to form acids. Chlorine gas or liquid can also burn the skin. People who are exposed to chlorine can develop some tolerance to its odour and irritating properties. Most of the inorganic chlorine compounds have similar health effects to chlorine, but in varying degrees of severity.

Workers are exposed most often to chlorine from inhalation or skin contact with the gas or liquid. Direct contact with liquid chlorine with the skin can cause frostbite as well as severe burns.

Poisonous gases can be released when chlorine compounds such as bleach are mixed with other cleaners (ammonia, acids, oven cleaner, hydrogen peroxide, some insecticides). Mixing chlorine compounds with acids will release chlorine gas. When chlorine compounds are mixed with ammonia or other nitrogen compounds, chloramines are released. For example, when chlorine or chlorine compounds are
added to swimming pools, monochloramine, dichloramine and trichloramine (nitrogen trichloride) can form due to the reaction of the chlorine with ammonia and amino-compounds from sweat and urine of swimmers. Chloramines are also highly irritating and toxic gases.

**Acute health effects**

Table 1 summarizes the acute (short-term) health effects from exposure to chlorine.

Table 1: Acute Health Effects from Chlorine Exposure

<table>
<thead>
<tr>
<th>Chlorine Concentration (parts per million)</th>
<th>Health Effect</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.03 – 0.4</td>
<td>Range of odour threshold</td>
</tr>
<tr>
<td>1 – 3</td>
<td>Mild irritation of the eyes, nose and throat</td>
</tr>
<tr>
<td>3 – 5</td>
<td>Stinging or burning in the eyes, nose and throat, headache, watering eyes, sneezing, coughing, breathing difficulty, bloody nose</td>
</tr>
<tr>
<td>5 – 10</td>
<td>Severe irritation of the eyes, nose and respiratory tract</td>
</tr>
<tr>
<td>10</td>
<td>Immediately dangerous to life and health (IDLH) concentration</td>
</tr>
<tr>
<td>10 – 25</td>
<td>May be fatal after 30 minutes of exposure</td>
</tr>
<tr>
<td>&gt;25</td>
<td>Immediate breathing difficulty, build-up of fluid in the lungs (pulmonary edema) possibly causing suffocation and death. Pulmonary edema may be immediate or delayed</td>
</tr>
<tr>
<td>&gt;1000</td>
<td>Fatal after a few breaths</td>
</tr>
</tbody>
</table>

Workers who have pre-existing lung disorders, for example asthma or allergies, tend to be more sensitive to the irritating effects of chlorine.

**Chronic health effects**

Chronic exposure to low levels of chlorine gas can cause dermatitis, tooth enamel corrosion, coughing, chest pain and sore throat. Workers who have had one or more exposures to chlorine that caused acute health effects may have long-term damage to the lungs.
Cancer

Chlorine itself is generally not considered to be a carcinogen, but it has not been evaluated by the International Agency for Research on Cancer (IARC). Chloramines, chlorinated drinking water and hypochlorite salts have been evaluated by IARC and all fall into Group 3, not classifiable as to their carcinogenicity to humans due to lack of scientific evidence.

Preventative measures

Preventing exposure to chlorine is the best way to protect health. Options that should be considered include the following (listed in order of preference):
- use of less hazardous substitutes
- use of engineering controls
- changes in work practices to reduce exposure (administrative controls)
- use of personal protective equipment.

Substitution

One option to control exposure to chlorine is to use other chemicals when practicable.

For cases where chlorine is added to water for sanitation or treatment, there are a number of options. Some examples include:

- Use of chlorine compounds such as sodium hypochlorite instead of chlorine gas.

- Ionization – copper or silver electrodes are used to introduce the dissolved metals into the water. Copper is used to control algae, while silver will control bacteria. However, due to its toxicity, silver cannot be used in Canada as a sanitizer in water treatment. Also, copper tends to precipitate out and discolour surfaces with a grey or black stain.

- Ozone – ozone is a very powerful oxidizing agent, but is also very unstable.
Ultraviolet (UV) devices – UV generators can be used for sterilization and water treatment. UV treatment is often used for small scale drinking water treatment.

In the pulp and paper industry, the use of chlorine for bleaching pulp creates dioxin (2,3,7,8-TCDD) as a by-product in mill wastewater. The use of chlorine dioxide or ozone as a substitute for chlorine does not produce this by-product.

There are also a number of chlorine-free alternatives for cleaners and disinfectants.

**Engineering Controls**

Engineering controls are processes used to eliminate exposure to a substance. Engineering controls remove the substance from the air or provide a barrier between the worker and the substance. Examples of engineering controls that can be used to prevent exposure to chlorine include:

- installation of local ventilation hoods
- use of general ventilation
- enclosures around work processes i.e. fume hoods, glove boxes
- use of automatic systems to transfer chlorine gas from storage containers to process containers
- good design of buildings where chlorine is used or stored to control/prevent exposure.

Where ventilation systems are used at the work site, they must be properly designed and not vent back into the work area.

If engineering controls are working properly, they will eliminate or greatly reduce the potential hazard. They only need to be installed once and do not place a physical burden on workers. However, an initial investment is required and the systems must be properly operated and maintained once installed.
Administrative Controls

Work practices that can be used in the workplace to reduce exposure to chlorine include:

- Educating workers about the hazards of chlorine. Workers should be encouraged to participate in training and monitoring programs in the workplace.

- Using good hygiene practices. Workers must not eat, drink or use tobacco products in areas where chlorine or products containing chlorine are used or stored. The hands and face should be washed before eating, drinking or smoking.

- Using and maintaining engineering controls and other equipment used to reduce exposure properly.

- Installation and use of an alarm system to warn of chlorine leaks.

- Storing chlorine properly.

- Ensuring that unprotected workers are not in areas where products containing chlorine are used.

- Clean up spills quickly and properly done using appropriate protective equipment and clothing.

- Keeping product containers tightly sealed when they are not in use.

Implementing work practices to reduce exposure are often less expensive than other control measures, but workers must be properly trained and use the safe work practices. The employer must monitor this in the workplace.

Work procedures

If chlorine is used in the workplace, it is important that the employer develop written work procedures to cover normal operations and emergencies. These procedures should include details on the proper operation and maintenance of workplace controls and alarms as well as protective equipment to be used by workers.
In general:

- The storage room for chlorine should have a sign warning that chlorine is present, respiratory protection is required and that access is restricted to authorized personnel. The door should be locked when no one is in the room.

- Chlorine cylinder changes should be done, if possible, when there are no workers or members of the public in the building.

- The ventilation system in the chlorine storage room should be on and functional when workers are in the room.

- A chlorine alarm system should be installed, with an indicator located outside the room.

- Workers must wear appropriate protective clothing and respirators when changing cylinders or handling chlorine compounds.

- Emergency procedures for dealing with leaks and spills must be developed.

- Nothing but chlorine cylinders should be stored in a chlorine storage room. Compounds containing chlorine should not be stored with other chemicals (e.g. store in a separate cabinet).

- Care must be taken when mixing chlorine or other compounds containing chlorine (such as hypochlorites) with other materials. Follow the manufacturer instructions and instructions on the material safety data sheet for the product.

For more information

Guidance document developed by the Workers’ Compensation Board of British Columbia, Chorine Safe Work Practices
Workplace Air Monitoring

When chlorine or a product containing chlorine is used in the workplace, air monitoring should be done periodically to ensure that the Occupational Exposure Limit (OEL) is not exceeded. Air samples must be collected and analyzed using a National Institute of Occupational Safety and Health (NIOSH) method or a method approved by a Director of Occupational Hygiene. NIOSH has one method that can be used for chlorine (Method 6011). The NIOSH Manual of Analytical Methods is available online at http://www.cdc.gov/niosh/nmam/.

There are a number of direct reading instruments available that can be used to monitor or screen for chlorine in the workplace. These devices come in two types; electrochemical sensor or solid state. They can be used for a number of toxic gases, depending on the sensors installed. These devices are often used as part of an alarm system for chlorine.

Personal Protective Equipment

If it is not practicable or feasible to use substitutes, engineering controls or administrative controls to reduce the potential for exposure, or they are not sufficient, the employer must provide workers with appropriate protective equipment.

Both air-purifying and air supplying respirators may be used for chlorine. The type of respirator chosen will be determined by the concentration of chlorine in the air. For emergencies (such as leaks or spills), entry into unknown concentrations or IDLH conditions, a positive pressure self-contained breathing apparatus is required.

For more information, Alberta Human Resources and Employment has the following publications available on respiratory protective equipment:

Guidelines for the Development of a Code of Practice for Respiratory Protective Equipment - PPE004
Employers should also refer to the CSA Standard Z94.4-02, Selection, Use and Care of Respirators.

Since chlorine and chlorine compounds can damage the skin and eyes and contact with liquid chlorine can cause frostbite, appropriate gloves and other protective clothing are needed for workers who handle the chemicals or may be exposed to airborne levels. Workers who may be exposed to chlorine should wear protective clothing that covers and protects the arms and legs. Airtight goggles or full-face respirator masks should be worn to protect the eyes from irritation or splashes. Where skin contact occurs, the area should be thoroughly washed immediately.

Although the use of personal protective equipment may initially seem less costly, workers need to be trained to use, care for and maintain the protective equipment they use. Employers need to monitor use and ensure that the protective equipment is properly maintained. In some cases, personal protective equipment can create a hazard to workers (heat stress, limited vision, allergic reactions to the equipment material). These issues need to be evaluated when personal protective equipment is selected.

**Regulatory requirements**

The health and safety legislation has general and specific requirements related to chlorine. OELs are provided for chlorine and many common chlorine compounds. These limits apply to workers directly involved with tasks using chlorine or products containing chlorine, and also to other workers in the workplace who may be exposed to indirectly from these operations. It is important to note that OELs represent standards for the protection of most healthy workers. Steps must be taken to keep airborne levels as low as reasonably practicable.
The employer must also:

- Train workers on the health hazards from exposure to chlorine and the safe work procedures developed by the employer.

- Establish an emergency response plan for responding to leaks and spills of chlorine at the work site.

- Comply with requirements for handling and storage of hazardous materials.

- Ensure that the need for ventilation is properly assessed and systems that are installed are properly designed and maintained. Workers also need to be trained on the proper operation and maintenance of these systems.

- Provide appropriate protective equipment, including respirators, where concentrations of chlorine or chlorine compounds cannot be controlled below the OELs. Workers must use the required protective equipment and must be trained on its proper use and care.
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