DISCLAIMER:

These guidelines were developed under contract using generally accepted secondary sources. The protocol used by the contractor for surveying these data sources was developed by the National Institute for Occupational Safety and Health (NIOSH), the Occupational Safety and Health Administration (OSHA), and the Department of Energy (DOE). The information contained in these guidelines is intended for reference purposes only. None of the agencies have conducted a comprehensive check of the information and data contained in these sources. It provides a summary of information about chemicals that workers may be exposed to in their workplaces. The secondary sources used for supplements III and IV were published before 1992 and 1993, respectively, and for the remainder of the guidelines the secondary sources used were published before September 1996. This information may be superseded by new developments in the field of industrial hygiene. Therefore readers are advised to determine whether new information is available.

Introduction

This guideline summarizes pertinent information about chlorine dioxide for workers and employers as well as for physicians, industrial hygienists, and other occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments in these fields; readers are therefore advised to regard these recommendations as general guidelines and to determine whether new information is available.

Recognition

SUBSTANCE IDENTIFICATION

* Formula
  ClO(2)

* Structure
  Data not available.

* Synonyms
  Chlorine oxide, anthium dioxide, chlorine peroxide, chlorine (IV) oxide, chloroperoxy, chloryl radical, alcide, doxcide 50
* Identifiers

1. CAS No.: 10049-04-4
2. RTECS No.: FO3000000
3. DOT NA: 9191 47 (hydrate, frozen)
4. DOT label: Oxidizer, poison (hydrate, frozen)

* Appearance and odor

Chlorine dioxide is a yellow or reddish-yellow gas at room temperature. Solid chlorine dioxide is a yellowish-red crystalline mass. Liquid chlorine dioxide is reddish-brown. Chlorine dioxide has an unpleasant chlorine-like odor and has an air odor threshold of 0.1 part per million (ppm) parts of air.

**CHEMICAL AND PHYSICAL PROPERTIES**

* Physical data

1. Molecular weight: 67.5
2. Boiling point (at 760 mm Hg): 11 degrees C (51.8 degrees F)
3. Specific gravity: 1.64 at 0 degrees C (32 degrees F) (liquid)
4. Vapor density (air=1): 2.4
5. Melting point: -59 degrees C (-74.2 degrees F)
6. Vapor pressure: Greater than 760 mm Hg at 20 degrees C (68 degrees F)
7. Solubility: Soluble in water (with decomposition), alkalies, and sulfuric acid.
8. Evaporation rate: Data not available.

* Reactivity

1. Conditions contributing to instability: Chlorine dioxide is a very unstable material even at room temperatures and will explode on impact, when exposed to sparks or sunlight, or when heated rapidly to degrees C (212 degrees F). Airborne concentrations greater than 10 percent may explode.
2. Incompatibilities: Contact with the following materials may cause fires and explosions: carbon monoxide, dust, fluoroamines, fluoride, hydrocarbons (e.g., butadiene, ethane, ethylene, methane, propane), hydrogen, mercury, non-metals (phosphorus, sulfur), phosphorus pentachloride-chlorine mixture, platinum, or potassium hydroxide. Chlorine dioxide reacts with water or steam to form toxic and corrosive fumes of hydrochloric acid.
3. Hazardous decomposition products: Toxic and corrosive gases and vapors such as chlorine gas or the oxides of chlorine may be released when chlorine dioxide decomposes.
4. Special precautions: None reported.

* Flammability

The National Fire Protection Association has not assigned a flammability rating to chlorine dioxide. Other sources rate chlorine dioxides fire and explosion hazard as extreme.
1. Flash point: Not applicable.
2. Auto-ignition temperature: Data not available.
3. Flammable limits in air (percent by volume): Lower, 10; upper, data not available
4. Extinguishant: For small fires use water only; do not use dry chemical or carbon dioxide. Flood area with water from a distance to fight large fires involving chlorine dioxide.

Fires involving chlorine dioxide should be fought upwind from the maximum distance possible. Keep unnecessary people away; isolate the hazard area and deny entry. Isolate the area for 1/2 mile in all directions if a tank, rail car, or tank truck is involved in the fire. For a massive fire in a cargo area, use unmanned hose holders or monitor nozzles; if this is impossible, withdraw from the area and let the fire burn. Emergency personnel should stay out of low areas. Chlorine dioxide may be ignited by friction, heat, or contamination. Containers of chlorine dioxide may explode in the heat of the fire and should be moved from the fire area if it is possible to do so safely. If this is not possible, cool fire exposed containers from the sides with water until well after the fire is out. Stay away from the ends of containers. Firefighters should wear a full set of protective clothing and self-contained breathing apparatus when fighting fires involving chlorine dioxide.

**EXPOSURE LIMITS**

* OSHA PEL

The current Occupational Safety and Health Administration (OSHA) permissible exposure limit (PEL) for chlorine dioxide is 0.1 ppm (0.3 milligrams per cubic meter (mg/m$^3$)) as an 8-hour time-weighted average (TWA) concentration [29 CFR 1910.1000, Table Z-1].

* NIOSH REL

The National Institute for Occupational Safety and Health (NIOSH) has established recommended exposure limits (RELs) for chlorine dioxide of ppm (0.3 mg/m$^3$) as a TWA for up to a 10-hour workday and a hour workweek and a short-term exposure limit (STEL) of 0.3 ppm (0.9 mg/m$^3$) [NIOSH 1992].

* ACGIH TLV

The American Conference of Governmental Industrial Hygienists (ACGIH) has assigned chlorine dioxide threshold limit values (TLVs) of 0.1 ppm mg/m$^3$) as a TWA for a normal 8-hour workday and a 40-hour workweek and a short-term exposure limit (STEL) of 0.3 ppm (0.83 mg/m$^3$) for periods not to exceed 15 minutes. Exposures at the STEL concentration should not be repeated more than four times a day and should be separated by intervals of at least 60 minutes [ACGIH 1994, p. 15]. Rationale for Limits

The NIOSH limit is based on the risk of severe respiratory and eye irritation [NIOSH 1992].

The ACGIH limits are based on the risk of severe irritation and by analogy to the toxicity of ozone gas [ACGIH 1991, p. 257].

**Evaluation**

**HEALTH HAZARD INFORMATION**
* Routes of Exposure

Exposure to chlorine dioxide can occur through inhalation, ingestion, and eye or skin contact [Sittig 1991, p. 379].

* Summary of toxicology

1. Effects on Animals: Chlorine dioxide is a severe respiratory and eye irritant in experimental animals. The oral LD(50) in rats is 292 mg/kg [NIOSH 1995]. Delayed deaths have occurred in animals exposed to 150 to 200 ppm for less than 1 hour. Rats exposed to 10 ppm daily died after 10 to 13 days of exposure; effects seen were nasal and ocular discharge and difficult breathing. A postmortem examination revealed purulent bronchitis [Hathaway et al. 1991]. Rats exposed to ppm of chlorine dioxide for 5 hours daily for 10 weeks did not exhibit any abnormal reactions [ACGIH 1991]. Chlorine dioxide dissolves in water to produce chlorate and chlorite ions. Chlorite has been shown to produce methemoglobin in rats and cats [Gosselin].

2. Effects on Humans: Chlorine dioxide is a severe respiratory and eye irritant in humans. Inhalation can produce coughing, wheezing, respiratory distress, and congestion in the lungs [Patnaik 1992]. Irritating effects in humans was intense at concentration levels of 5 ppm. Accidental exposure at 19 ppm of the gas inside a bleach tank resulted in the death of one worker (time of exposure is not specified) [ACGIH 1991]. Workers exposed for 5 years to average chlorine dioxide concentrations below 0.1 ppm but with excursions to higher concentrations had symptoms of eye and throat irritation, nasal discharge, cough, and wheezing; on bronchoscopy, bronchitis was observed in seven of the 12 workers [Clayton and Clayton 1982]. Concentrations of 0.25 ppm and less have been reported to worsen mild respiratory ailments [ACGIH 1991]. Two adults who ingested 250 ml of a 40 mg/l solution of chlorine dioxide experienced headache, nausea, abdominal discomfort, and lightheadedness within 5 minutes of ingestion. The symptoms disappeared within another 5 minutes [NLM].

* Signs and symptoms of exposure

Acute exposure: Acute exposure to chlorine dioxide results in irritation of the eyes, nose, and throat; cough; wheezing; shortness of breath; bronchitis; pulmonary edema; headache; and vomiting [Genium Chronic exposure: Chronic exposure to chlorine dioxide may cause chronic bronchitis and emphysema [Sittig 1991].

**EMERGENCY MEDICAL PROCEDURES**

* Emergency medical procedures: [NIOSH to supply]

Rescue: Remove an incapacitated worker from further exposure and implement appropriate emergency procedures (e.g., those listed on the Material Safety Data Sheet required by OSHA's Hazard Communication Standard [29 CFR 1910.1200]). All workers should be familiar with emergency procedures, the location and proper use of emergency equipment, and methods of protecting themselves during rescue operations.

**EXPOSURE SOURCES AND CONTROL METHODS**

The following operations may involve chlorine dioxide and lead to worker exposures to this substance:
The manufacture and transportation of chlorine dioxide
Use as bleaching agent for paper and wood pulp, textiles, cellulose, beeswax and leather; used to bleach mature flour
Use in swimming pool and municipal water treatment for purification and to remove tastes and odors by oxidation; use as a wastewater disinfecting agent; use in bleaching fats and oils; use in the cleaning and de-tanning of leather

Methods that are effective in controlling worker exposures to chlorine dioxide, depending on the feasibility of implementation, are as follows:

- Process enclosure
- Local exhaust ventilation
- General dilution ventilation
- Personal protective equipment

Workers responding to a release or potential release of a hazardous substance must be protected as required by paragraph (q) of OSHA's Hazardous Waste Operations and Emergency Response Standard [29 CFR 201.890].

Good sources of information about control methods are as follows:


MEDICAL SURVEILLANCE

OSHA is currently developing requirements for medical surveillance. When these requirements are promulgated, readers should refer to them for additional information and to determine whether employers whose employees are exposed to chlorine dioxide are required to implement medical surveillance procedures.

* Medical Screening

Workers who may be exposed to chemical hazards should be monitored in a systematic program of medical surveillance that is intended to prevent occupational injury and disease. The program should include education of employers and workers about work-related hazards, early detection of adverse health effects, and referral of workers for diagnosis and treatment. The occurrence of disease or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical surveillance program is intended to supplement, not replace, such measures. To detect and control work-related health effects, medical evaluations should be performed (1) before job placement, periodically during the term of employment, and
(3) at the time of job transfer or termination.

* Pre-placement medical evaluation

Before a worker is placed in a job with a potential for exposure to chlorine dioxide, a licensed health care professional should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the function and integrity of the eyes and respiratory system. Medical surveillance for respiratory disease should be conducted using the principles and methods recommended by the American Thoracic Society.

A pre-placement medical evaluation is recommended to assess medical conditions that may be aggravated or may result in increased risk when a worker is exposed to chlorine dioxide at or below the prescribed exposure limit. The health care professional should consider the probable frequency, intensity, and duration of exposure as well as the nature and degree of any applicable medical condition. Such conditions (which should not be regarded as absolute contraindications to job placement) include a history and other findings consistent with diseases of the eyes or respiratory system.

* Periodic medical evaluations

Occupational health interviews and physical examinations should be performed at regular intervals during the employment period, as mandated by any applicable Federal, State, or local standard. Where no standard exists and the hazard is minimal, evaluations should be conducted every 3 to 5 years or as frequently as recommended by an experienced occupational health physician. Additional examinations may be necessary if a worker develops symptoms attributable to chlorine dioxide exposure. The interviews, examinations, and medical screening tests should focus on identifying the adverse effects of chlorine dioxide on the eyes or respiratory system. Current health status should be compared with the baseline health status of the individual worker or with expected values for a suitable reference population.

* Termination medical evaluations

The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic or laboratory tests that were conducted at the time of placement should be repeated at the time of job transfer or termination to determine the worker's medical status at the end of his or her employment. Any changes in the worker's health status should be compared with those expected for a suitable reference population.

* Biological monitoring

Biological monitoring involves sampling and analyzing body tissues or fluids to provide an index of exposure to a toxic substance or metabolite. No biological monitoring test acceptable for routine use has yet been developed for chlorine dioxide.

**WORKPLACE MONITORING AND MEASUREMENT**

Determination of a worker's exposure to airborne chlorine dioxide is made using a midget fritted glass bubbler (MFGB) containing 15 milliliters of percent potassium iodide in a buffer mixture sodium carbonate and sodium
bicarbonate (1.5 mM of each). Samples are collected at a recommended flow rate of 0.5 liter/minute until a recommended collection volume of 7.5 liters for STEL samples or 120 liters for TWA samples is reached. Analysis is conducted by ion chromatography. This method (OSHAID-202) is described in the OSHA Computerized Information System and is fully validated.

Controls

PERSONAL HYGIENE PROCEDURES

If chlorine dioxide contacts the skin, workers should immediately wash the affected areas with soap and water.

Clothing contaminated with chlorine dioxide should be removed immediately, and provisions should be made for the safe removal of the chemical from the clothing. Persons laundering the clothes should be informed of the hazardous properties of chlorine dioxide, particularly its potential for causing severe irritation.

A worker who handles chlorine dioxide should thoroughly wash hands, forearms, and face with soap and water before eating, using tobacco products, using toilet facilities, applying cosmetics, or taking medication.

Workers should not eat, drink, use tobacco products, apply cosmetics, or take medication in areas where chlorine dioxide or a solution containing chlorine dioxide is handled, processed, or stored.

STORAGE

Chlorine dioxide should be stored in a cool, dry, well-ventilated area in tightly sealed containers that are labeled in accordance with OSHA's Hazard Communication Standard [29 CFR 1910.1200]. Containers of chlorine dioxide should be protected from physical damage, ignition sources, and light, and should be stored separately from carbon monoxide, dust, fluoroamines, fluoride, hydrocarbons (e.g., butadiene, ethane, ethylene, methane, propane), hydrogen, mercury, non-metals (phosphorus, sulfur), phosphorus pentachloride-chlorine mixture, platinum, potassium hydroxide, water, or steam. To avoid an explosion hazard, chlorine dioxide should be stored only in diluted forms. Solutions of more than a 10 percent concentration should not be handled. Empty containers of chlorine dioxide should be handled appropriately.

SPILLS AND LEAKS

In the event of a spill or leak involving chlorine dioxide, persons not wearing protective equipment and clothing should be restricted from contaminated areas until cleanup has been completed. The following steps should be undertaken following a spill or leak:

1. Notify safety personnel.
2. Remove all sources of heat and ignition.
3. Ventilate potentially explosive atmospheres.
4. Do not touch the spilled material; stop the leak if it is possible to do so without risk.
5. Use non-sparking tools.
6. If chlorine dioxide is in the gaseous form, stop flow of gas. If the source of the leak is in a cylinder and the leak cannot be stopped in place, remove the leaking cylinder to a safe area in the open air and repair the leak, or allow the cylinder to empty.
If chlorine dioxide is in liquid form, allow agent to evaporate while providing all available ventilation. Personnel may also use a large amount of a concentrated solution of reducing agent (bisulfites or soda ash to dilute the chlorine dioxide. After the spill has been neutralized, shovel slurry into a suitable container.

SPECIAL REQUIREMENTS

U.S. Environmental Protection Agency (EPA) requirements for emergency planning, reportable quantities of hazardous releases, community right-to-know, and hazardous waste management may change over time. Users are therefore advised to determine periodically whether new information is available.

* Emergency planning requirements

Chlorine dioxide is not subject to EPA emergency planning requirements under the Superfund Amendments and Reauthorization Act (SARA) (Title III) in 42 USC 11022.

* Reportable quantity requirements for hazardous releases

A hazardous substance release is defined by EPA as any spilling, leaking, pumping, pouring, emitting, emptying, discharging, injecting, escaping, leaching, dumping, or disposing into the environment including the abandonment or discarding of contaminated containers) of hazardous substances. In the event of a release that is above the reportable quantity for that chemical, employers are required to notify the proper Federal, State, and local authorities [40 CFR

Employers are not required by the emergency release notification provisions in 40 CFR Part 355.40 to notify the National Response Center of an accidental release of chlorine dioxide; there is no reportable quantity for this substance.

* Community right-to-know requirements

Employers who own or operate facilities in SIC codes 20 to 39 that employ 10 or more workers and that manufacture 25,000 pounds or more of chlorine dioxide per calendar year or otherwise use 10,000 pounds or more of chlorine dioxide per calendar year are required by EPA [40 CFR Part 372.30] to submit a Toxic Chemical Release Inventory form (Form R) to EPA reporting the amount of chlorine dioxide emitted or released from their facility annually.

* Hazardous waste management requirements

EPA considers a waste to be hazardous if it exhibits any of the following characteristics: ignitability, corrosivity, reactivity, or toxicity as defined in 40 CFR 261.21-261.24. Under the Resource Conservation and Recovery Act (RCRA) [40 USC 6901 et seq.], EPA has specifically listed many chemical wastes as hazardous. Although chlorine dioxide is not specifically listed as a hazardous waste under RCRA, EPA requires employers to treat waste as hazardous if it exhibits any of the characteristics discussed above.

Providing detailed information about the removal and disposal of specific chemicals is beyond the scope of this guideline. The U.S. Department of Transportation, EPA, and State and local regulations should be followed to ensure that removal, transport, and disposal of this substance are conducted in accordance with existing
regulations. To be certain that chemical waste disposal meets EPA regulatory requirements, employers should address any questions to the RCRA hotline at (703) 412-9810 (in the Washington, D.C. area) or toll-free at (800) 424-9346 (outside Washington, D.C.). In addition, relevant State and local authorities should be contacted for information on any requirements they may have for the waste removal and disposal of this substance.

**RESPIRATORY PROTECTION**

* Conditions for respirator use

Good industrial hygiene practice requires that engineering controls be used where feasible to reduce workplace concentrations of hazardous materials to the prescribed exposure limit. However, some situations may require the use of respirators to control exposure. Respirators must be worn if the ambient concentration of chlorine dioxide exceeds prescribed exposure limits. Respirators may be used (1) before engineering controls have been installed, (2) during work operations such as maintenance or repair activities that involve unknown exposures, (3) during operations that require entry into tanks or closed vessels, and (4) during emergencies. Workers should only use respirators that have been approved by NIOSH and the Mine Safety and Health Administration (MSHA).

* Respiratory protection program

Employers should institute a complete respiratory protection program that, at a minimum, complies with the requirements of OSHA's Respiratory Protection Standard [29 CFR 1910.134]. Such a program must include respirator selection, an evaluation of the worker's ability to perform the work while wearing a respirator, the regular training of personnel, respirator fit testing, periodic workplace monitoring, and regular respirator maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program (including selection of the correct respirator) requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly. For additional information on the selection and use of respirators and on the medical screening of respirator users, consult the latest edition of the NIOSH Respirator Decision Logic [NIOSH 1987b] and the NIOSH Guide to Industrial Respiratory Protection [NIOSH 1987a].

**PERSONAL PROTECTIVE EQUIPMENT**

Workers should use appropriate personal protective clothing and equipment that must be carefully selected, used, and maintained to be effective in preventing skin contact with chlorine dioxide. The selection of the appropriate personal protective equipment (PPE) (e.g., gloves, sleeves, encapsulating suits) should be based on the extent of the worker's potential exposure to chlorine dioxide. There are no published reports on the resistance of various materials to permeation by chlorine dioxide.

To evaluate the use of PPE materials with chlorine dioxide, users should consult the best available performance data and manufacturers' recommendations. Significant differences have been demonstrated in the chemical resistance of generically similar PPE materials (e.g., butyl) produced by different manufacturers. In addition, the chemical resistance of a mixture may be significantly different from that of any of its neat components.

Any chemical-resistant clothing that is used should be periodically evaluated to determine its effectiveness in preventing dermal contact. Safety showers and eye wash stations should be located close to operations that involve chlorine dioxide.
Splash-proof chemical safety goggles or face shields (20 to 30 cm long, minimum) should be worn during any operation in which a solvent, caustic, or other toxic substance may be splashed into the eyes.

In addition to the possible need for wearing protective outer apparel e.g., aprons, encapsulating suits), workers should wear work uniforms, coveralls, or similar full-body coverings that are laundered each day. Employers should provide lockers or other closed areas to store work and street clothing separately. Employers should collect work clothing at the end of each work shift and provide for its laundering. Laundry personnel should be informed about the potential hazards of handling contaminated clothing and instructed about measures to minimize their health risk.

Protective clothing should be kept free of oil and grease and should be inspected and maintained regularly to preserve its effectiveness.

Protective clothing may interfere with the body's heat dissipation, especially during hot weather or during work in hot or poorly ventilated work environments.

**References**


Occupational Safety and Health
Guideline for Chlorine Dioxide (OSHA)


