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Chlorine dioxide (ClO₂) safe storage and handling

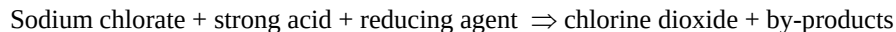
Scope

This TIP provides basic information on measures to protect personnel and equipment in the handling and storage of chlorine dioxide as a gas and as an aqueous solution. It is vitally important that any new chlorine dioxide facility design be undertaken with a supplier of chlorine dioxide technology in order to cover all of the unique design parameters and standards associated with chlorine dioxide.

Definition

Chlorine dioxide is a powerful oxidizing agent, used to produce bleached pulp. Chlorine dioxide has other applications in the mill including sterilization of drinking water and general water treatment (biocide).

Chlorine dioxide is manufactured on-site at pulp mills because it is chemically unstable and cannot be transported. Many different chemical processes are used by pulp mills to produce chlorine dioxide. The basic chemistry used is sodium chlorate based:



The acid and reducing agent can vary depending on the process selected, which are determined by the mill's operating economics and the usefulness of the by-product streams. Chlorine dioxide is made as a gas and absorbed in chilled water to produce a solution strength ranging from 8 to 13 grams of chlorine dioxide per liter of solution. Figure 1 relates the chlorine dioxide equilibrium gas partial pressure over a range of saturated aqueous chlorine dioxide solutions (3).

Properties of Chlorine Dioxide

Properties (1,2)	
Chemical name	Chlorine Dioxide
Synonyms	Chlorine Oxide, Chlorine Peroxide, "Chlo-2", Dioxide
Formula	ClO ₂
Molecular weight	67.5
Physical state	Gas
Appearance as a gas	Yellow-green to orange gas; rapidly decomposes to chlorine in sunlight to form a gray-white cloud
Physical state	Aqueous solution
Appearance as a solution	Yellow-deep green
Odor	Sharp, pungent, acrid odor present in concentrations as low as 0.1 ppm
Specific Gravity (gas):	2.4 at 11°C (air = 1)
Partial Pressure of ClO ₂ (3)	$p = C \exp[12.732 - (3102/T)]$ where C is in g/L, p is in mmHg, and T is in °K
Heat of Solution in Water	6.6 kcal/mole
Latent Heat of Evaporation	6.52 kcal/mole
Specific Heat	$C_p = 11.90 + 1.24 \times 10^{-3} T - 2.07 \times 10^{-5} T^{-2}$ (cal./mole/K)

TIP Category: Automatically Periodically Reviewed (Ten-year review)



Documents

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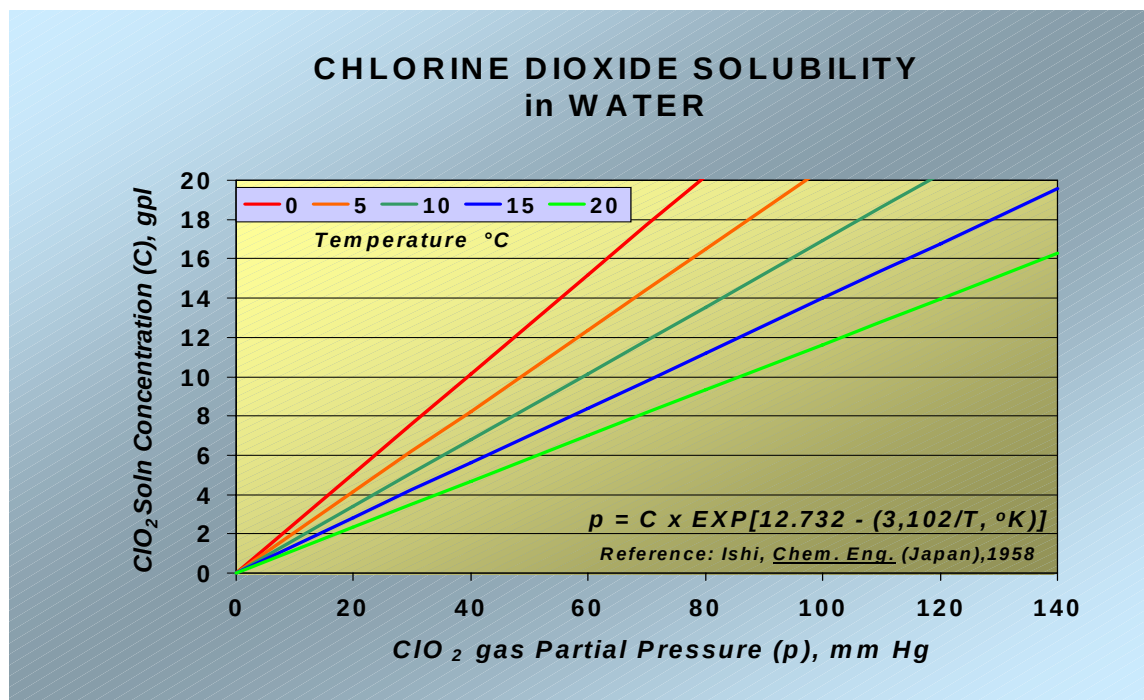


Fig. 1. Chlorine dioxide equilibrium gas partial pressure over a range of saturated aqueous chlorine dioxide solutions (3)

Safety precautions

Hazards and personnel protection

CAS Registration:	10049-04-4
DOT Number:	Cannot be transported
NIOSH RTECS Number:	F03000000

Health hazards (4)

Chlorine dioxide is toxic to all life forms. Fatalities have been reported for workers exposed to chlorine dioxide gas at 19 parts per million for an unspecified time period. At sub-lethal exposure levels, chlorine dioxide gas is a severe respiratory and eye irritant. It can also affect the body if it is swallowed.

Chlorine dioxide may cause irritation of the eyes, nose, throat, and lungs. Brief exposure to the gas may produce coughing, wheezing, and severe breathing difficulties, which may be delayed in onset. Repeated acute exposure of workers to undetermined concentrations is stated to have caused eye and throat irritation, sinus and chest congestion, nasal discharge, coughing, wheezing, bronchitis, and a phenomenon affecting peripheral vision referred to as “seeing haloes.” In worst case scenarios, repeated exposure may result in delayed onset of pulmonary edema and chronic bronchitis.

A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to chlorine dioxide.

Personal protective equipment (4, 5)

Respiratory protective equipment is required for entry into areas where airborne concentrations are or may be above 0.1 parts per million chlorine dioxide. Use only NIOSH/MSHA approved devices and the following protective measures in the event of a spill of solution or a gas leak:

Concentration (parts per million)	Minimum APF* Rating Required [19]	Minimum respiratory protection required above 0.1 parts per million
Up to 1	10	Chemical cartridge respirator or supplied air respirator.
Up to 2.5	25	Supplied air respirator operated in a continuous flow mode or powered air purifying respirator with cartridge(s)
Up to 5	50	Full face piece chemical cartridge respirator with cartridge(s); or gas mask with canister; or full face piece self contained breathing apparatus (SCBA); or full face piece supplied air respirator.
Greater than 5, or entry and escape from unknown concentrations	10,000	SCBA with a full face piece operated in pressure demand or other positive pressure mode. OR A combination Type C supplied air respirator/ auxiliary SCBA with a full face piece operated in pressure demand or other positive pressure or continuous flow mode.
Fire Fighting	10,000 rated SCBA only	SCBA with a full face piece operated in pressure demand or other positive pressure mode.

*APF = Assigned Protection Factor (more protection with a higher APF)

Cartridge type respirators should never be used for entry into an area with a suspected chlorine dioxide release. These respirators are intended for escape purposes only.

Wear neoprene or butyl rubber gloves to protect the skin. Wear a rubber suit, and neoprene-coated boots, together with chemical goggles or full face shield for a large leak.

Exposure limits

Quantitative dose-effect information on chlorine dioxide is sparse. Permissible workplace exposure limits have been set based on analogy with ozone, and by extrapolation from laboratory tests using various species of small animals exposed mostly to high concentrations of chlorine dioxide (6). The following recommended exposure limits should be followed:

- 8-hour time-weighted average (TWA): 0.1 parts per million. [OSHA 1988, (7)]
- Short-term exposure limit, 15 min. (STEL): 0.3 parts per million. [ACGIH 1991, (6)]
- Immediately dangerous to life or health (IDLH): 5 parts per million. [NIOSH 1994, (8)]

First aid (5)

Inhalation: Move to fresh air. If person is not breathing, give CPR. If breathing is difficult, give oxygen. Keep person warm and resting. Obtain medical attention immediately.

Eyes: Immediately flush with lukewarm water for 15 minutes, holding eyelids apart. Obtain medical attention immediately.

Skin: Remove contaminated clothing immediately. Wash exposed skin with soap or mild detergent and water, or flush with water for 15 minutes. Obtain medical attention.