Chlorine Dioxide
Health & Safety

Introduction
Chlorine dioxide (ClO₂) is an effective disinfectant and an oxidant that is widely used in water treatment. At ambient temperatures, chlorine dioxide is a reactive gas that is potentially explosively unstable at concentrations above 10% by volume in air. It is normally generated on site and used as a dilute aqueous solution.

Chlorine Dioxide Gas
Chlorine dioxide is a yellow to reddish-yellow gas with a pungent, sharp odor similar to that of chlorine and ozone. It has an odor threshold concentration of 0.1-0.3 ppm and will become irritating at concentrations above 0.5 ppm. The density of chlorine dioxide gas is about 2.4 times that of air, allowing it to collect in low-lying areas.

Health Hazards
Chlorine dioxide is a severe respiratory and eye irritant in humans. It is harmful if swallowed or inhaled.

Inhalation may cause irritation of the mucous membranes and respiratory tract. Symptoms may include coughing, wheezing, and severe breathing difficulties which may be delayed in onset. Pulmonary edema is common following severe exposure.

<table>
<thead>
<tr>
<th>Chlorine Dioxide Exposure Limits</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>8 Hour Time-Weighted Average (TWA)</strong></td>
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<tr>
<td>ACGIH – TLV</td>
</tr>
<tr>
<td>OSHA – PEL</td>
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<tr>
<td><strong>Short-term Exposure Limits (STEL)</strong></td>
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<tr>
<td>ACGIH - STEL (15 min)</td>
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<tr>
<td><strong>Immediately Dangerous to life or health</strong></td>
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<td>IDLH</td>
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</tbody>
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Direct eye contact may cause severe irritation and possibly burns. Symptoms may include tearing, redness and in severe cases, eye damage due to burns.

All users should read the appropriate Chemical Fact Sheet or Safety Data Sheet (SDS) before handling chlorine dioxide in any form.

Reactivity
Chlorine dioxide gas is normally stable at concentrations up to 10% (v/v) in air but contact with oxidizable materials can cause decomposition at lower concentrations.

Chlorine dioxide gas is explosive at concentrations above 10% (v/v) in air and can be ignited by almost any form of energy such as sunlight, heat or sparks. The reaction is as follows:

\[ \text{ClO}_2 \rightarrow \frac{1}{2}\text{Cl}_2 + \text{O}_2 \]
At concentrations between 10% and 14% the reaction is categorized as a low order explosion, because the flame propagation is only 1 meter/second. This decomposition is often referred to as a “puff” (Figure 1). At concentrations of chlorine dioxide in air above 14% (v/v) there is the potential for sustained decomposition and a violent reaction.

**Chlorine Dioxide Dilute Solutions**

Chlorine dioxide gas does not react with water. Chlorine dioxide is soluble in water but remains as a dissolved gas, which can be removed from dilute aqueous solutions by aeration or by heat. Its solubility is a function of both temperature and pressure following a linear relationship. See Figure 2 at end of document.

The stability of chlorine dioxide solutions is also dependent on the pH of the solution and the presence of UV light. Chlorine dioxide decomposes in the presence of UV light. Decomposition is a function of time and intensity of the UV light source.

\[
10\text{ClO}_2 + 5\text{H}_2\text{O} + h\nu \rightarrow 6\text{ClO}_3^- + 4\text{Cl}^- + 10\text{H}^+ + 3.5\text{O}_2
\]

Normally chlorine dioxide solutions are generated and used immediately. However, acidified aqueous solutions of chlorine dioxide (below pH 7) retain their strength for several months when stored in a cool, well-ventilated place away from heat, extreme cold, ignition sources, light and or direct sunlight. Chlorine dioxide will decompose in basic solutions (pH >8) hydrolyzing to form chlorate and chlorite ions.

\[
2\text{ClO}_2^- + 2\text{OH}^- \rightarrow \text{ClO}_3^- + \text{ClO}_2^- + \text{H}_2\text{O}
\]

Chlorine dioxide may be safely handled in dilute aqueous solutions providing:
- The solution is maintained at a concentration and temperature that the partial pressure of the gas is always below 50 mmHg. This equates to 6-7% (v/v) of chlorine dioxide gas in the vapor phase (Figure 2).
- The maximum solution concentration at 25°C (77°F) is below 3.0 g/L (0.3% by weight, 3000 ppm).

Chlorine dioxide solutions should be applied to the processing system at a point, and in a manner, which permits adequate mixing and uniform distribution. The feed point should be well below the water level to prevent volatilization of the chlorine dioxide.

For specific information regarding the suitability or dosage requirements for your application consult the sodium chlorite product label or contact OxyChem Technical Services.

**Storage and Handling Precautions**

Water should always be readily accessible whenever chlorine dioxide is used. Safety showers and eye wash stations should be close by and clearly marked. Portable or temporary systems are available and may be used where permanent installations are not available. Every precaution should be taken to ensure that a suitable system is in place and operational before generating chlorine dioxide. Only trained personnel should be allowed to enter areas where chlorine dioxide is generated.
The following precautions should be followed when handling chlorine dioxide solutions:

- **DO NOT** store chlorine dioxide solutions at temperatures above 100 °F (38 °C).
- **DO NOT** expose chlorine dioxide solutions to ultra-violet light, as this will reduce product strength.
- Chlorine dioxide gas and concentrated solutions will attack some forms of plastic, rubber and coatings. Store chlorine dioxide ONLY in containers that are approved for chlorine dioxide use.
- **DO NOT** allow chlorine dioxide gas to come into contact with dust and other combustible materials such as organic matter and sulfur as this may cause fires and explosions.
- Chlorine dioxide gas is incompatible with mercury, carbon monoxide, hydrocarbons, fluoramines, potassium hydroxide, phosphorous and sulfur.
- **DO NOT** allow chlorine dioxide gas to build up in any enclosed space. Ventilation is required for all handling operations.
- **DO NOT** breathe chlorine dioxide vapors. Toxic gases and vapors (such as chlorine gas) may be released when chlorine dioxide decomposes.
- **DO NOT** enter confined spaces such as tanks or pits without following proper entry procedures. Entry into these spaces must be in accordance with 29CFR§1910.146. Before entering tanks or opening pipelines that have contained chlorine dioxide solutions, they should be drained or pumped out and thoroughly flushed with water. Contact with the liquid draining from the equipment should be avoided.
- Avoid breathing vapors. After handling, always wash hands thoroughly with soap and water.

Good housekeeping practices are important where chlorine dioxide is used. All spills should be contained or flushed with water into a chemical sewer or segregated holding tank or pond, which is provided for the specific purpose of neutralization. Chlorine dioxide solutions must NEVER be flushed to a sanitary sewer or other outlet, which connects to waterways or uncontrolled runoff streams. Contact local and federal authorities for applicable regulations.

**Personal Protective Equipment**

Personnel working with chlorine dioxide should always wear the proper protective equipment. OxyChem recommends that employees be provided with and required to use personal protective equipment and clothing necessary to prevent any possibility of skin or eye contact with chlorine dioxide. Remember the use of personnel protective equipment is not a substitute for safe handling practices.

Avoid breathing vapors. After handling, always wash hands thoroughly with soap and water.

Where vapor concentration of chlorine dioxide exceeds or is likely to exceed 0.1 ppm, a NIOSH approved full-face acid gas respirator is acceptable. A NIOSH approved self-contained breathing apparatus, with full-face piece, is required for vapor concentrations above 5 ppm and for leaks and/or emergencies. Follow any applicable respirator use standards and regulations.

**First Aid**

Due to the toxic characteristics of chlorine dioxide, if someone receives accidental exposure it is extremely important to seek first aid immediately.

**If in eyes:**
- Hold eye open and rinse slowly and gently with water for 15-20 minutes.
- Remove contact lenses, if present, after the first 5 minutes, then continue rinsing eye.
- Call a poison control center or doctor immediately for treatment advice.

**If on skin or clothing:**
Basic Chemicals

- Take of contaminated clothing.
- Rinse skin immediately with plenty of water for 15-20 minutes.
- Call a poison control center or doctor for treatment advice if burning or irritation of the skin persists.

If swallowed:
- Have person drink a glass of water immediately if able to swallow.
- Call a poison control center or doctor immediately for treatment advice.
- Do not induce vomiting unless told to do so by the poison control center or doctor.
- Do not give anything by mouth to an unconscious person.

If inhaled:
- Move person to fresh air and monitor for respiratory distress.
- If cough or difficulty in breathing develops, consult a physician immediately.
- If person is not breathing, call 911 or an ambulance, then give artificial respiration.
- Call a poison control center or doctor for further treatment advice.

Notes to Physician: If chlorine dioxide vapors are inhaled, monitor patient closely for delayed development of pulmonary edema, which may occur up to 48-72 hours post-inhalation. Following ingestion, neutralization and use of activated charcoal is not indicated.

Further Information
More detailed information on sodium chlorite is available on request through the OxyChem Technical Service Department. Call or write:

OxyChem Technical Service Department
6200 S. Ridge Rd.
Wichita, Kansas 67215
800-733-1165 option #1
OxyChem_Tech_Service@oxy.com
Figure 2: Partial Pressures in Solution