

# Organic Odor Control with Chlorine Dioxide

Chlorine dioxide (ClO<sub>2</sub>) is effective as both a disinfectant and an oxidant in water and wastewater treatment. Its selective reactivity makes chlorine dioxide a powerful non-chlorinating oxidizing agent useful in many water treating applications for which chlorine and other oxidizing agents are unsuitable. Unlike most oxidants, chlorine dioxide may be used over a broad pH range to oxidize industrial odor causing compounds.

## Application Description

A variety of odors are created or liberated in waste treatment applications. Odor causing compounds include inorganic gases and organic gases and vapors generated as a result of biological activity. Organic vapors may also originate from the direct discharge of industrial chemical wastes. Industrial odors can be caused by a variety of compounds, including inorganic and organic sulfides, organic sulfur compounds including mercaptans (the sulfur analog of alcohols (RSH)), organic disulfides (RSSR), (intermediate oxidation products of mercaptans), various amines, aldehydes, ketones, fatty acids, phenols and ammonia.

Reduced sulfur compounds and nitrogen-bearing amines tend to be the most odorous compounds because of their relatively low threshold concentrations (Figure 1).

The major sources of odorous substances such as mercaptans and substituted amines include the chemical and petroleum industries, coking and sanitary processes, animal feedlots and rendering plants.

## Treatment Alternatives

A variety of technologies has been used for the control of odors. Three of the more effective technologies include carbon adsorption, chemical addition (including oxidants), and wet chemical scrubbing.

The effective approach to controlling odor requires a good understanding of the characteristics of the waste stream, the types of chemicals causing the odors and facility constraints.

Figure 1<sup>1</sup>

Substance	Formula	Odor Threshold (mg/L)
Allyl mercaptan	CH <sub>2</sub> :CHCH <sub>2</sub> SH	0.0001
Ammonia	NH <sub>3</sub>	17
Amyl mercaptan	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>4</sub> SH	0.0003
Benzyl mercaptan	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> SH	0.0002
Crotyl mercaptan	CH <sub>3</sub> (CH) <sub>2</sub> CH <sub>2</sub> SH	0.00003
Diphenyl sulfide	(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> S	0.0001
Ethyl mercaptan	C <sub>2</sub> H <sub>5</sub> SH	0.0003
Hydrogen sulfide	H <sub>2</sub> S	0.0005
Indole	C <sub>6</sub> H <sub>4</sub> (CH <sub>2</sub> )NH	0.0001
Methyl mercaptan	CH <sub>3</sub> SH	0.0005
Phenyl mercaptan	C <sub>6</sub> H <sub>5</sub> SH	0.0003
Propyl mercaptan	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>2</sub> SH	0.0005
Skatole	C <sub>9</sub> H <sub>9</sub> N	0.001
Thiocresol	CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> SH	0.0001
tert-butyl mercaptan	(CH <sub>3</sub> ) <sub>3</sub> CSH	0.00008
Trimethylamine	(CH <sub>3</sub> ) <sub>3</sub> N	0.0004

The pH of a waste stream has a major effect on both the generation of odors and the necessary treatment protocol required. Some odor causing compounds are substantially more soluble in acidic media while others are more soluble in alkaline media (Figure 2). Thus, by the proper choice of pH of operation, and oxidant, many odors can be minimized or eliminated.

Chemical oxidation is best suited to moderate volume waste streams containing moderate to high strength pollutants and wastewater's with noxious odors, toxic compounds, and compounds which survive primary treatment processes.

## Application Note

To use oxidants, the odor must be dissolved, or be contained in a solid (sludge). In complex wastewater streams the odor causing compound may be absorbed in acidic or basic scrubbing solutions first which are then treated by chemical oxidation.

Alkaline scrubbing solutions

are effective for sulfides mercaptans, aldehydes/ ketones. Acidic scrubbing solutions are effective for ammonia and amines.

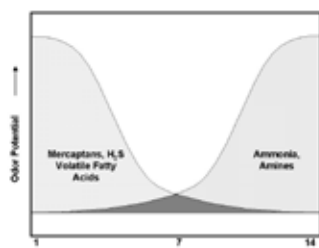


Figure 2 - Effect of pH on Odor Generation

## Chemical Oxidation with Chlorine Dioxide

Chlorine dioxide is a powerful oxidant effective for the control of reduced sulfur compounds and secondary and tertiary amines.

Between pH 5 and 9, 4.5 mg/L of chlorine dioxide instantaneously oxidizes 1 mg/L of a mercaptan (expressed as sulfur) to the respective sulfonic acid ( $\text{RSO}_3\text{H}$ )/sulfonate compound, destroying the mercaptan odor. Similarly, chlorine dioxide reacts with organic sulfides and disulfides, destroying the original odor. Organic disulfides are split at the sulfur atoms and oxidized to sulfonic acid.

The oxidation of amines with chlorine dioxide depends on the pH of the reaction mixture and the degree of substitution of the amine. Between pH 5 and 9, an average of 10 mg/L of chlorine dioxide oxidizes 1 mg/L of a tertiary aliphatic amine (expressed as nitrogen), destroying the amine odor. At pH above 7, an average of 5 mg/L of chlorine dioxide oxidizes 1 mg/L of a secondary aliphatic amine (expressed as nitrogen), removing all traces of amine odor. The higher the pH of the reaction mixture (chlorine dioxide and tertiary and/or secondary aliphatic amines), the more rapidly oxidation proceeds.

## Alternatives Oxidants

**Hydrogen Peroxide** does not destroy mercaptans and phenols unless catalyzed by ferrous sulfate. Hydrogen peroxide-ferrous sulfate, which requires acidic pH's, has the lowest chemical cost, but results in high solids loading and increased disposal costs.

**Chlorine** is the only oxidant that reacts with ammonia, however, halogenated by-products restrict use.

**Potassium Permanganate** is a strong oxidant, which yields insoluble  $\text{MnO}_2$  as a byproduct. This results in high solids loading and significant disposal costs.

## Advantages of Chlorine Dioxide

- Chlorine dioxide reacts more rapidly and completely than other available oxidizers.
- Chlorine dioxide does not require pH adjustment and does not increase solids loading.
- Chlorine dioxide does not form THMs.

## Feed Requirements

For industrial applications dosages will vary depending on the application. Dose rates may be determined by completing a chlorine dioxide demand study. For once-through systems, or systems where treated water may enter a U.S. waterway, the concentration of residual chlorite ion should be monitored such that it does not exceed the requirements of the NPDES permit and is in compliance with local, state and federal regulations.

For more information on dosage requirements specific to your application, contact your Siemens representative.

## Method of Feed

Chlorine dioxide is a gas produced by activating sodium chlorite with an oxidizing agent or an acid source. Sodium chlorite is converted to chlorine dioxide through a chlorine dioxide generator and applied as a dilute solution. 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. The feed point should be well below the water level to prevent volatilization of the chlorine dioxide.

## Chlorine Dioxide Analysis

Residual chlorine dioxide concentrations should be determined by substantiated methods, which are specific for chlorine dioxide. Chlorine dioxide solutions can be analyzed by iodometric and amperometric titrations, and spectrophotometrically, with the standard DPD (N,N-diethyl-p-phenylenediamine) method. These methods are described in detail in *Standard Methods for the Examination of Water and Wastewater*<sup>2</sup>.

4500- $\text{ClO}_2$ B	Iodometric Method
4500- $\text{ClO}_2$ D	DPD-Glycine Method
4500- $\text{ClO}_2$ E	Amperometric Method II

## References

- Odor Control in Wastewater Treatment Plants*, WEF, Manual of Practice No 22, ASCE Manuals of Reports on Engineering Practice No 82., Page 8, (1995)
- Standard Methods for the Examination of Water and Wastewater*, APHA, AWWA and WEF, Washington, D.C. (20th Ed. 1998).

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Literature No.: WT.085.272.016.IE.AN.0409  
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