EVOQUA
WATER TECHNOLOGIES

SULFIDE ODOR CONTROL WITH CHLORINE DIOXIDE

Chlorine dioxide (ClO_2) 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 sulfide without the formation of colloidal sulfur, which can plug up equipment.

APPLICATION DESCRIPTION

Sulfide exists in wastewater in three forms; hydrogen sulfide gas (H_2S), non-volatile ionic species hydrogen sulfide (HS^-) and sulfide (S^{2-}). The ratio of each of the three species H_2S, HS^- and S^{2-} is dependent on the pH. At pH 6, 90% of the sulfide will be present as H_2S, and the higher the H_2S concentration the greater the tendency for it to volatilize. Conversely at pH 10, 100% of the sulfide will be present as S^{2-}.

Sulfides are produced by both biological and chemical action. They are produced biologically by anaerobic bacteria, and chemically by many industries including the chemical, petroleum, paper, and textile industries.

H_2S occurs naturally through the anaerobic decay of organic matter and is easily recognized by its characteristic rotten egg odor. In the absence of dissolved oxygen and in the presence of soluble Biological Oxygen Demand (BOD), Desulfovibrio desulfuricans (SRB) and other sulfate-reducing bacteria (SRB's) convert the sulfate ion to sulfide.

$$SO_4^{2-} + \text{Organic matter} \blacktriangleright H_2S + CO_2$$

Many systems provide an environment that promotes the growth of a healthy biological community. H_2S formation in wastewater systems occurs primarily in the gelatinous slime layer (biofilm) that accumulates on pipe walls and in the sludge blankets of clarifiers and other solids processing units. The rate of sulfide production is dependent upon the concentrations of sulfate ions, organic matter, and dissolved oxygen, as well as other factors such as pH, temperature, retention time, stream velocity, and surface area.

Many industrial processes produce sulfide-containing gases and waste products. These are generated, for example, during petroleum refining, coal coking, black liquor evaporation in kraft pulping, viscose rayon manufacture and natural gas purification. In addition to their disagreeable "rotten egg" odor, sulfides are corrosive to concrete and are extremely toxic. These gases and wastes are frequently scrubbed with alkaline solutions and require treatment before discharge.

TREATMENT ALTERNATIVES

Sulfide can be removed from a system by precipitation with iron, or by oxidization. Various oxidizers including chlorine, hydrogen peroxide, and potassium permanganate are commonly used for oxidation of sulfide. Different treatment strategies are required depending on the application.

CHLORINE DIOXIDE

Chlorine dioxide is effective where alternative oxidants don't work, such as when rapid destruction of sulfide is important or the formation of halogenated byproducts prevents treatment with chlorine.

Chlorine dioxide reacts very rapidly with hydrogen sulfide gas or the sulfide ion. Between pH 5-9, minimum 3.36 mg/L of chlorine dioxide should be used to instantly oxidize 1 mg/L of sulfide to sulfate.

$$5H_2S + 8ClO_2 + 4H_2O \rightarrow 5SO_4^{2-} + 8Cl^- + 18H^+$$

In wastewater systems where the odor causing sulfides are produced from colonies of bacteria metabolizing sulfate, chlorine dioxide is an effective control strategy. Chlorine dioxide, when fed at somewhat higher dosages than those required to destroy the sulfide, will remove the biofilm that contains the bacteria creating the sulfide.

ADVANTAGES OF CHLORINE DIOXIDE

- Chlorine dioxide reacts more rapidly and completely than other available oxidizers.
- Only chlorine dioxide does not form colloidal sulfur[1]. Hydrogen peroxide, potassium permanganate and chlorine all require excess oxidizer and a basic pH to avoid colloidal sulfur formation[2].
- Chlorine dioxide does not form chlorinated organic byproducts. While chlorine is the least expensive oxidizer available, it cannot be used when organic compounds are present due to the formation of chlorinated organic by-products. When chlorine can't be used, hydrogen peroxide has the lowest chemical cost.
- Chlorine dioxide forms soluble byproducts. Potassium permanganate and catalyzed hydrogen peroxide (Fentons chemistry) result in high solids loading and significant disposal costs.

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 Evoqua 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.

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 spectrophotometri-cally, 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[3].

4500-ClO_2 B	Iodometric Method
4500-ClO_2 D	DPD-Glycine Method
4500-ClO_2 E	Amperometric Method II

REFERENCES

1. Synan, J.F., Malley, H.A., "Chlorine dioxide as an alternative for Disinfection in Water Systems", Engineering Panel of the Campden Foold Preservation Research Assoc., Chipping Campden, Glos., England, Oct 21, (1975)
2. Bowker et. Al., "Odor and corrosion control in Sanitary Sewerage systems and treatment plants", Design Manual, EPA-625/1-85-018, US EPA Washington, D.C.
3. Standard Methods for the Examination of Water and Wastewater, APHA, AWWA and WEF, Washington, D.C. (20th Ed. l998).

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