



Sodium Chlorite Hydrogen Sulfide Control in Wastewater Collection Systems

Introduction

Hydrogen sulfide (H_2S) is a dense, colorless, strongly odorous toxic gas that corrodes infrastructures and impairs the performance of wastewater treatment operations.

Hydrogen sulfide is naturally converted to sulfuric acid, which is corrosive towards steel and concrete. Control of H_2S will result in increased life and lower maintenance cost for facilities and piping. In addition, worker safety is of concern as hydrogen sulfide is extremely toxic at levels above 500 ppm, which can be reached in confined spaces.

A number of sulfide control strategies are available depending on the system design and treatment goal.

Application Description

Sulfide exists in wastewater in three forms: hydrogen sulfide gas (H₂S), non-volatile ionic species hydrogen sulfide (HS⁻) and sulfide (S²⁻). The ratio of each of the three species H₂S, HS⁻ and S²⁻ is dependent on the pH. At pH 6, 90% of the sulfide will be present as H₂S, and the higher the H₂S concentration the greater the tendency for it to volatilize. Conversely, at pH 10, 100% of the sulfide will be present as S²⁻.

Hydrogen sulfide occurs naturally through the anaerobic decay of organic matter and recognized by its characteristic rotten egg odor. In typical domestic wastewater, microbial reduction of the sulfate ion is the dominant mechanism for sulfide formation. In the absence of dissolved oxygen (DO) 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.

SO₄²⁻ + Organic matter $\xrightarrow{\text{Microorganisms}}_{\text{(no D.O)}}$ H₂S + CO₂

Hydrogen sulfide formation in wastewater systems occurs primarily in the gelatinous slime layer 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.

Treatment Alternatives

There are two basic ways to control hydrogen sulfide:

- Prevent sulfide formation
- Remove the sulfide after its formed

Preventing Sulfide Formation

Inhibiting bacterial action or moderating the variables affecting hydrogen sulfide generation is often the basis for controlling hydrogen sulfide in wastewater treatment systems. Treatment options include the following chemicals: Chlorine dioxide and Nitrate.

Chlorine dioxide (ClO₂) is applied at or near the source of hydrogen sulfide. Chlorine dioxide, when fed at doses higher than the minimum required to destroy hydrogen sulfide will remove the biofilm layer, which contains the bacteria creating the sulfide. Chlorine dioxide



OxyChem[®]



Basic Chemicals

reacts more rapidly and completely than other available oxidizers and does not form colloidal sulfur.

Sodium nitrate (NaNO₃) is applied to retard septicity and promote bio-oxidation of organic odors in systems with a retention time greater than four hours. Sodium nitrate is a biological approach to controlling odors in wastewater, occurring providing naturally facultative anaerobic denitrifying bacteria with a source of which bound oxygen, is metabolized preferentially over other sources of oxygen like sulfate. This results in the production of nitrogen gas via intermediates like nitrite (NO₂), nitric oxide (NO), nitrous oxide (N2O) and other metabolic byproducts rather than sulfide.

 $\begin{array}{c} \text{BOD} + \text{NO}_3^- & \underbrace{\text{Anaerobic}}_{\text{(no D.O)}} \text{N}_2 + \text{CO}_2 + \text{Biomass} \end{array}$

Typical field applications require a minimum of 1.5 pounds of nitrogen-oxygen (N-O) per pound of BOD.

Removing Sulfide After its Formation

Removing the sulfide after it has been formed can be achieved using a variety of chemicals either alone or in combination. The treatment mechanism generally employed is oxidation of the hydrogen sulfide to either sulfur or the sulfate ion. In some cases, the chemical treatment program also promotes bio-oxidation of organic odors. Common treatment options include: Nitrates, Sodium chlorite, Hydrogen peroxide, and Iron Salts

Nitrate (NO₃) may also be effective for the removal of existing sulfide in the presence of bacteria that can utilize the nitrate for the oxidation of sulfide to sulfur or sulfate. Examples of such bacteria include *Thiabacillus denitrificans*, *Thiomicrospira denitrificans* and *Thiosphera pantotropha*¹. Bacteria able to utilize nitrate for the bio-oxidation of sulfide are naturally present in sewage systems.

Sodium chlorite (NaClO₂) is applied at or near the source of hydrogen sulfide. It is also applied in wastewater systems where a retention time of greater than 3 hours is encountered, such as remote sites for long duration control. Sodium chlorite selectively oxidizes sulfide and related organic odors. Unlike hypochlorite, sodium chlorite does not react with ammonia, and does not form chlorinated organics.

 $2H_2S + NaClO_2 \rightarrow 2S^0 + 2H_2O + NaCl$

Typical field applications require a minimum of 3 mg/L of sodium chlorite per 1 mg/L of sulfide.

Hydrogen peroxide (H_2O_2) is applied to the wastewater system usually where there is a retention time of less than 5 hours and at least 30 minutes prior to the point where the hydrogen sulfide is released. Hydrogen peroxide is a stronger oxidant than either chlorine or potassium permanganate. Hydrogen peroxide will oxidize the hydrogen sulfide present and promote bio-oxidation of organic odors. Hydrogen peroxide decomposes into oxygen environmentallv and water. harmless byproducts.

$$H_2S + H_2O_2 \rightarrow S^0 + 2H_2O (pH < 8.5)$$

 $H_2S + 4H_2O_2 \rightarrow SO_4^{2-} + 2H_2O (pH > 8.5)$

Typical field applications require 1 to 3 mg/L hydrogen peroxide per 1 mg/L sulfide. The reaction with sulfide is rapid with 90% of the hydrogen peroxide typically consumed within 10 to 15 minutes.

Iron Salts are applied to wastewater systems for long-duration control. Both ferrous and ferric salts react with dissolved sulfide to form metal sulfide precipitates that are removed at the treatment plant.

Ferrous Salts: $Fe^{2+} + HS^- \rightarrow FeS + H^+$ Ferric Salts: $2Fe^{3+} + 3HS^- \rightarrow Fe_2S_3 + 3H^+$



OxyChem[®] Basic Chemicals



Typical field applications require 3-5 mg/L as Fe per 1 mg/L of sulfide.

Further Information

For more information contact: OxyChemTechnical Services Department 6200 S. Ridge Rd. Wichita, KS 67215 1-800-733-1165 option #1 OxyChem_Tech_Service@oxy.com

References

 Bentzen, G., et. al., "Controlled Dosing of Nitrate For Prevention of H₂S in a Sewer Network and The Effects On The Subsequent Treatment Processes", *Wat. Sci. Tech.*, Vol. 31, No. 7, pp 293-302, (1995).

642-402 Sodium Chlorite 08/2022



Wichita Technical Service Department 6200 South Ridge Road, Wichita, KS 67215 Tel: 800-733-1165 ext. 1 OxyChem_Tech_Service@oxy.com Important: The information presented herein, while not guaranteed, was prepared by technical personnel and is true and accurate to the best of our knowledge. NO WARRANTY OF MERCHANTABILITY OR OF FITNESS FOR A PARTICULAR PURPOSE, OR WARRANTY OR GUARANTY OF ANY OTHER KIND, EXPRESS OR IMPLIED, IS MADE REGARDING PERFORMANCE, SAFETY, SUITABILITY, STABILITY OR OTHERWISE. This information is not intended to be all-inclusive as to the manner and conditions of use, handling, storage, disposal, and other factors that may involve other or additional legal, environmental, safety or performance considerations, and Occidental Chemical Corporation assumes no liability whatsoever for the use of or reliance upon this information. While our technical personnel will be happy to respond to questions, safe handling and use of the product remains the responsibility of the customer. No suggestions for use are intended as, and nothing herein shall be construed as, a recommendation to infringe any existing patents or to violate any Federal, State, local or foreign laws.