

1 Oxygen

1.1 Mechanism

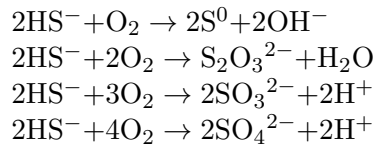
Oxygen prevents the accumulation of hydrogen sulfide in sewer by the following two mechanisms.

1.1.1 Oxidation of hydrogen sulfide

The oxidation of sulfide occurs both chemically and biologically. Chemical sulfide oxidation mainly occurs in bulk phase, while the biological sulfide oxidation takes place both in bulk water and in the aerobic portion of the sewer biofilm. However, the contribution of bulk phase is much lower than that of the biofilm due to very low biomass concentration in the bulk water.

Reaction mechanism and stoichiometry of chemical sulfide oxidation

- Chemical oxidation of sulfide is a multi step process involving a series of chemical reactions catalyzed by chemicals present in the wastewater.
- The stoichiometry of this process is a complex one because of the formation of various intermediates and products during the course of the reactions as shown below.



- Elemental sulfur (S^0), thiosulfate ($\text{S}_2\text{O}_3^{2-}$), sulfite (SO_3^{2-}) and sulfate (SO_4^{2-}) are the key intermediates and products.
- There is also a possibility of the formation of polysulfides, which originate from a reaction between elemental sulfur and hydrogen sulfide.
- Further chemical oxidation of the thiosulfate and sulfite proceeds at a significantly lower rate than that of sulfide oxidation. Depending upon the time scale considered, thiosulfate could be considered as a stable reaction product, especially when availability of oxygen is limited.
- For complete oxidation of sulfide to sulfate, each gram of sulfide (as S) requires 2 grams of oxygen, while 0.5 gram of oxygen per gram of sulfide (as S) is needed if thiosulfate is the end product.
- Kinetics of sulfide oxidation is described by the rate equation of the following form:

$$r_{\text{H}_2\text{S,oxidation}} = -\frac{d(S_T)}{dt} = k \cdot [S_T]^\alpha [DO]^\beta$$

where $[S_T]$ is the total dissolved sulfide concentration in mg S/L, $[DO]$ is dissolved oxygen concentration in mg/L, k is the reaction rate constant, α is the reaction order with respect to sulfide and β is the reaction order with respect to oxygen.

- The reaction rate constant, and the reaction order terms in the above reaction are shown to vary with type of wastewater, temperature, pH, and sulfide to oxygen ratio.
- The equation above does not adequately describe the oxidation of sulfide under high DO conditions, which is normally the case with the oxygen injection. The following kinetic expression is more appropriate under high DO conditions.

$$r_{H_2S,oxidation} = k_{bio,oxi} \times \frac{[H_2S]}{K_{H_2S} + [H_2S]} \times \frac{[DO]}{K_{O_2} + [DO]}$$

Where, r_{H_2S} , oxidation is the sulfide oxidation rate in mg S/L-h, $[H_2S]$ is the H₂S concentration in mg S/L, and $[DO]$ is the DO concentration in mg/L.

Further information can be obtained as follows:

- Reaction mechanism, kinetics and stoichiometry for low DO conditions
 - [Paper: Determination of kinetics and stoichiometry of chemical sulfide oxidation in wastewater of sewer networks by Neilsen et al. \(2003\)](#)
 - Kinetics and stoichiometry for high DO conditions
 - [Report - ARC Linkage Project on Sewer Biotransformation](#)
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Reaction mechanism and stoichiometry of biological sulfide oxidation

- Biological oxidation of sulfide is also a multi step process involving a series of biochemical reactions catalyzed by micro-organisms present in sewer biofilm.
- The reaction product of aerobic biological sulfide oxidation is normally the elemental sulfur and other intermediates such as thiosulfate under oxygen-limited conditions. The intermediate products are subsequently oxidized to sulfate, but the rate of this step is much lower than that of the first step.
- Actual oxygen consumption rate of oxygen for biological sulfide oxidation is reported to be higher than 0.5 indicating a range of oxidation products.
- Kinetics of biological sulfide oxidation at a low DO is described by the rate equation of the following form:

$$r_{H_2S,oxidation} = -\frac{d(S_T)}{dt} = k \cdot [S_T]^\alpha [DO]^\beta$$

- The equation above does not adequately describe the biological oxidation of sulfide under high DO conditions, which is normally the case with the oxygen injection. The following kinetic expression is more appropriate under high DO conditions.

$$r_{H_2S,oxidation} = k_{bio,oxi} \times \frac{[H_2S]}{K_{H_2S} + [H_2S]} \times \frac{[DO]}{K_{O_2} + [DO]}$$

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1.1.2 Maintaining aerobic condition in bulk liquid as well as a portion of biofilm

- Sulfate reducing bacteria (SRB) are obligate anaerobes and hence are greatly affected by the presence of oxygen.
- Due to low dissolved oxygen concentration in the bulk, penetration of oxygen in biofilm is generally limited, thereby giving rise to aerobic layer in the outer part and anaerobic layer in the inner part of the sewer biofilm (see figure below). Sulfide production can thus take place in anaerobic biofilm layers despite the presence of oxygen in the bulk phase.
- Sulfide produced in the anaerobic layer of the biofilm is oxidized as it diffuses out through the aerobic biofilm layer.

1.2 Actions

Dosing of oxygen results into the followings:

- Oxidation of hydrogen sulfide to intermediate products and the oxidation of the intermediate products to sulfate.
- Creation of an aerobic layer on outer surface of the biofilm preventing sulfide generation in the layer. Sulfide generated in the inner anaerobic layer will diffuse out to the aerobic layer, where it will be oxidized thereby preventing its accumulation in the bulk water despite continuous production in inner anaerobic layers.
- The presence of oxygen supports the growth of heterotrophic organisms in the anaerobic layer of the biofilm, thereby oxidizing the organic matter present in the wastewater. The oxidation of both sulfide and organic matter occurs simultaneously.

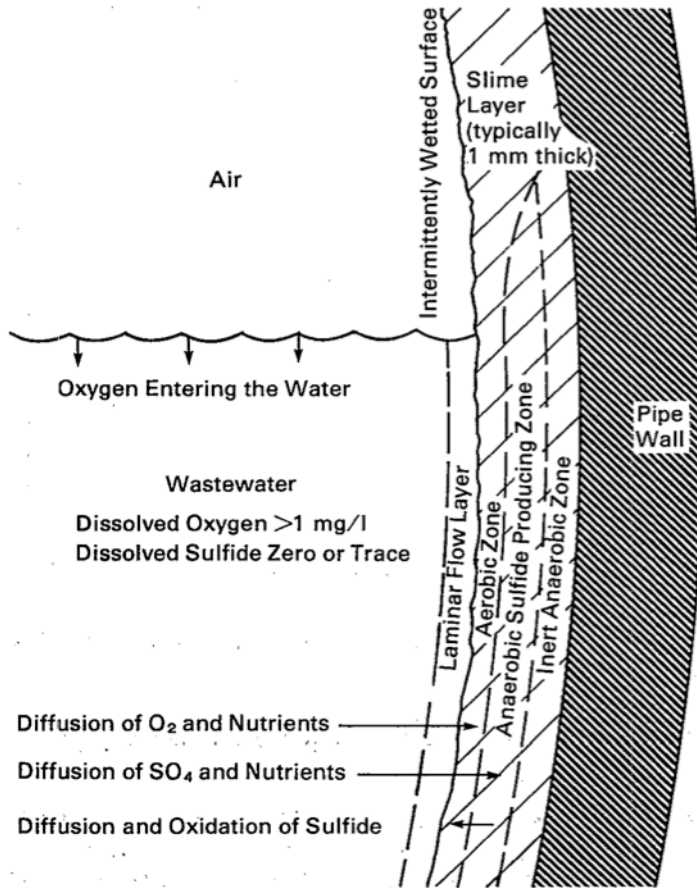


Figure 1: Processes occurring in sewers with sufficient oxygen to prevent sulfide accumulation (Adapted from USEPA, 1975)

1.3 Source of oxygen in sewers

1.3.1 Re-aeration in sewers

The gas-liquid mass exchange between flowing water and the atmosphere is one of the key processes in sewers. The transfer of oxygen to wastewater, which is commonly known as re-aeration, strongly influences the dissolved oxygen (DO) concentration of the wastewater. When re-aeration balances the microbial oxygen uptake, aerobic conditions will prevail in the sewer. On the other hand, the wastewater will become anaerobic when oxygen uptake is higher than the rate of re-aeration.

The rate of oxygen transfer (r_{O_2}) is presented by the following expression:

$$r_{O_2} = k_L a (c_l^* - c_{b,l})$$

where $k_L a$ is the mass transfer coefficient (1/h), c_l^* is the equilibrium concentration of oxygen in water, and $c_{b,l}$ is the liquid phase bulk dissolved oxygen concentration.

k_La in a sewer pipe depends upon a number of factors including hydraulic properties of the flow, pipe dimensions, slope and wastewater characteristics. A number of empirical relationships are available for the determination of the mass transfer coefficient.

Further information can be obtained as follows:

- [Paper - Empirical modeling of air-to-water oxygen transfer in gravity sewers by Jensen \(1995\)](#)
 - [Paper: Reaeration in sewers by Huisman et al. \(2004\)](#)
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1.3.2 Oxygen/air injection

Oxygen/air is normally injected into the flowing wastewater. That is, in case of the intermittent flow as in the case of rising main, oxygen/air is injected only when the pump is running. A number of oxygen injection methods are available:

- Direct injection of compressed air
- Use of Venturi aspirators
- Pressure tank air/oxygen injection
- Side stream oxygen injection

1.4 Dosing arrangement and typical dosing rates

When oxygen is dosed to sewer, it is utilized for both sulfide and COD oxidation. Oxygen dosing requirement can be estimated as follows:

Oxygen demand (g/m^3) =

$$2 \times \text{maximum sulfide level } (gS/m^3) + OUR_{biofilm}(g/m^2 \cdot h) \times HRT (h) \times A/V (m^2/m^3)$$

It is assumed that the end product of sulfide oxidation is sulfate and the oxygen uptake rate of sewer biofilm (OUR) is constant throughout the sewer length.

With the injection of pure oxygen, maximum level of DO that could be achieved is only 30-40 mg/L (depending upon the pressure) as not all the oxygen supplied gets dissolved in the wastewater. When the oxygen is dosed at the wet-well of a rising main, then the DO will be depleted in few hundred meters of the pipe, and there will be no protection against the sulfide produced in the remaining anaerobic portion of the sewer pipe. In order to avoid this, the point of injection (POI) should be “reasonably” close to the points where sulfide control is required (Point of Control - POC). An injection site should be selected such that (1) there would be an adequate hydraulic retention time (HRT) between POI and the POC to enable the full oxidation of any sulfide present at the POI before it reaches the POC, and that (2) aerobic conditions are maintained between the two points with minimum requirement of

oxygen. There should be no high points between POI and POC, as otherwise air pockets rich in oxygen and hydrogen sulfide would form at such locations causing corrosion of pipes.

Typical oxygen dosing rate: 15.9-91.5 kg O₂/ML of wastewater (exact dosing rate depends upon the pressure, type of injection and oxygen transfer efficiency).

Further information can be obtained as follows:

- Dosing arrangements
 - [Final Report - ARC Linkage Project on Sewer Biotransformation](#)
- Typical dosing rate
 - [Paper: Chemical dosing for sulfide control in Australia: An industry survey by Ganigue et al. \(2011\)](#)

1.5 Cost of oxygen injection

Oxygen injection requires storage facility for the oxygen, and proper dosing facilities depending upon the type of the dosing used. The dosing equipments can be hired.

Estimated cost of oxygen injection is \$12.8 - \$74.0/ML (the cost depends upon the oxygen dosing rate, pressure at the injection point, and oxygen transfer efficiency).

Further information can be obtained as follows:

- [Paper: Chemical dosing for sulfide control in Australia: An industry survey by Ganigue et al. \(2011\)](#)

1.6 Impacts on WWTP

The injected oxygen promotes heterotrophic activity in the wastewater and the biofilm, thereby oxidising a significant amount of organic matter in the wastewater, which results in reduced levels of volatile fatty acids (VFA) in the feed to a WWTP. This will significantly affect the biological nutrient removal in the WWTP, the extent of such impact depending upon the rate of oxygen dosing and the dosing location. The addition of a readily available carbon source (for example, methanol) may be required to improve the nutrient removal performance to the same level as in the case without oxygen injection.

Further information can be obtained as follows:

- [Paper: Integrated modelling of sewer system and wastewater treatment plant for investigating the impacts of chemical dosing in sewers by Sharma et al. \(2012\)](#)

1.7 Major limitations

- The oxygen transfer to sewage is limited due to low solubility of oxygen. As a result, it would be almost impossible to keep the entire sewer pipe aerobic, especially in the case of long pipes.
- The oxygen injection is effective in controlling sulfide production during periods when oxygen is present. In addition to preventing sulfide from formation, any sulfide present would be oxidized. However, oxygen injection has no long-lasting inhibitory or effect on the SRB activities.
- Oxygen injection enhances SRB activities in the downstream sections of sewers. This is due to the re-generation of sulfate (from sulfide) at sites where oxygen is injected so that more downstream sewer biofilms are exposed to sulfate, which enhances the growth of SRB.
- The available oxygen would be quickly consumed in sewer and during long quiescent periods, the anaerobic conditions favorable for sulfide production would be quickly established in the system, thereby negating any positive effect achieved by oxygen injection.
- High VFA consumption is another main concern as this would create a limitation of carbon source for downstream nutrient removal plant.
- Its effectiveness and efficiency are highly sensitive to the injection locations. The selection of the injection sites and the determination of the dosage profiles could be a difficult task, particularly for large, complex networks.

Further information can be obtained as follows:

- [Final Report - ARC Linkage Project on Sewer Biotransformation](#)
- [Paper: Evaluation of oxygen injection as a means of controlling sulfide production in a sewer system by Gutierrez et al. \(2008\)](#)

1.8 Case studies

[Oxygen injection in Tugun Elanora Sewer System in Gold Coast](#)

[Oxygen injection in D6 Sewer System in Gold Coast](#)