Hydrogen Sulfide (H2S) - The Relationship of Bacteria to its Formation, Prevention, and Elimination

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Background

Wastewater is commonly known for its potential to create odor nuisances from a variety of sources, including odors escaping from sewer manholes, wastewater treatment facilities, and animal factory lagoons.

Hydrogen sulfide (H2S), a gas detectable in very low concentrations and notable for both its toxicity and its ability to corrode various materials used in sewer and treatment plant construction, is a major source of odor in wastewater treatment systems.

Traditional sanitary sewer design practice has not fully acknowledged the importance of corrosion and odor control, as evidenced by widespread occurrence of sulfide and odor control problems throughout the United States for sanitary sewers, serving both small and large tributary areas.

The EPA Needs Survey estimates the aggregate cost of major sewer rehabilitation to be US$3.2 billion. This doesn't include the cost for correcting infiltration/inflow problems, which involve major infrastructural repair or replacement of sanitary sewers, a significant part of which may be attributed to sulfide-induced deterioration. The same survey further estimates the construction costs for new collectors and interceptors through the year 2000 to be US$38.8 billion. These cost estimates reflect the importance of adequately considering sulfide control in the design of new sanitary sewer systems.

Animal farmers have tried a variety of solutions to lagoon odor and continue to offer grants to universities to research solutions.

Theory, Prediction and Measurement of Odor and Corrosion

Evaluation of existing or potential odor or corrosion problems requires knowledge of the type of compounds likely to cause such problems and the mechanisms of their formation in wastewater systems. Hydrogen sulfide generation is inversely related to flow rate, so that waste streams with low flow rates are more likely to possess high levels of hydrogen sulfide.

Where odor and/or corrosion problems exist, a monitoring program should be developed to characterize the severity of the problem. Such a program should involve careful evaluation of the data obtained from sample collection and analysis. Because collection of samples or inspection can be hazardous, plant operators and sewer workers must be familiar with the potential dangers of confined spaces in contact with wastewater, and must strictly observe appropriate safety practices, outlined later in this brochure.
Sulfur Compounds Causing Odor and Corrosion

Odor-producing substances found in domestic wastewater and sludge are small, relatively volatile molecules having molecular weights between 30 and 150 g/mole. Most of these substances result from anaerobic decomposition of organic matter containing sulfur and nitrogen. Inorganic gases produced from domestic wastewater decomposition commonly include hydrogen sulfide, ammonia, carbon dioxide, and methane.

Of these gases, only hydrogen sulfide and ammonia are malodorous. Often, odor-producing substances include organic vapors such as indoles, skatoles, mercaptans and nitrogen-bearing organics.

Hydrogen sulfide is the most commonly known and prevalent odorous gas associated with domestic wastewater collection and treatment systems. It has a characteristic rotten egg odor, is extremely toxic, and is corrosive to metals such as iron, zinc, copper, lead and cadmium. Hydrogen sulfide is also a precursor to sulfuric acid formation, which corrodes lead-based paint, concrete, metals and other materials.

The conditions leading to H2S formation generally favor production of other malodorous organic compounds. Thus, solving H2S odor problems can often solve other odor problems as well. Many of the odors detected in wastewater collection and treatment systems result from sulfur-bearing compounds being present. For example:

**Substance Molecular Weight**

- Allyl Mercaptan 74.15
- Amyl Mercaptan 104.22
- Benzyl Mercaptan 124.21
- Crotyl Mercaptan 90.19
- Dimethyl Sulfide 62.13

**Sources of Sulfur in Domestic Wastewater**

Sulfur is present in human and livestock excreta and sulfates are found in most water supplies. Sufficient sulfur is normally available in domestic wastewater in the form of organic sulfides such as mercaptans, and disulfides for the production of odorous gases by anaerobic and facultative bacteria.

The sulfate ion (SO42-) is one of the most universal anions occurring in rainfall, especially in air masses that have encountered metropolitan areas. Sulfate concentrations in wastewater can vary from only a few milligrams per liter (mg/L) to hundreds of milligrams per liter. Generally, for domestic wastewater, the main source of sulfide is sulfate.
Physical and Chemical Properties of Hydrogen Sulfide

Hydrogen sulfide is a colorless gas that has a foul odor (rotten egg smell) and is slightly heavier than air. Human exposure to small amounts of hydrogen sulfide in air can cause headaches, nausea, and eye irritation.

Higher concentrations can cause respiratory system paralysis, resulting in fainting and possible death.

Hydrogen sulfide is moderately soluble in water, possible maximum concentrations ranging between 3,000 and 4,000 mg/L at the normal temperatures found in wastewater. Hydrogen sulfide solubility decreases with increasing temperature.

See Hydrogen Sulfide Hazards in Municipal & Industrial Accounts and the Toxicity Chart, page 8

Sulfide Production Rate

The rate at which sulfide is produced by a slime layer on collection pipes depends on the following environmental conditions:

- Concentrations of organic matter and nutrients
- Sulfate concentration
- Dissolved Oxygen (DO)
- pH
- Temperature
- Stream Velocity
- Surface area
- Retention time
Desulfovibrio

*Desulfovibrio desulfuricans*, found in the digestive tract of both man and animals, is the most common bacteria which produce H2S under anaerobic conditions. These obligate anaerobes use sulfate as their oxygen source, ammonia as their sole source of nitrogen, and various forms of organic matter as a food supply including amino acids, carbohydrates, organic acids, etc., when in an oxygen limited environment. These reactions often take place in the slime layer on collection pipes and in the sludge of lagoons, etc.

These bacteria cannot compete well with the facultative anaerobic strains in *Alken Clear-Flo®* formulas, which use nitrate as a hydrogen acceptor and reproduce more quickly than the sulfur-reducing pure anaerobes.

Sulfur-reducing bacteria also attack the protective sulfate coatings on metal and concrete, leaving them vulnerable to corrosion by sulfuric acid (H2SO4), resulting from oxidation of H2S. Other bacteria attack the asphaltic coatings which are normally resistant to chemical attack. Minimizing retention time will minimize the action of this bacteria. Oxidation Reduction Potential (ORP) between -50mV to -300mV favor sulfate reducing bacteria. -100mV to -200mV are favored by other anaerobes.

Reductions Which Create Hydrogen Sulfide:

The serious odor and corrosion problems associated with the collection, handling and treatment of domestic wastewater are primarily the result of sulfate reduction to hydrogen sulfide under anaerobic conditions, as shown by the following reactions:

1)  

\[
\text{Sulfite ion + organic matter + water } \xrightarrow{\text{d.d. bacteria}} \text{bicarbonate ion + hydrogen sulfide gas} \\
\text{SO}_4^{2-} + \text{C} + \text{H}_2\text{O} \xrightarrow{\text{d.d. bacteria}} 2\text{HCO}_3^- + \text{H}_2\text{S}
\]

2)
In the biochemical oxidation of organic matter, bacteria remove hydrogen atoms from the organic molecule and, in the process, gain energy. Through a series of biochemical reactions, the hydrogen atoms are transferred to a hydrogen acceptor. The hydrogen acceptor may be an inorganic or organic substance. Under aerobic conditions, free oxygen is the final acceptor for hydrogen, the oxygen being reduced to water. In the absence of free oxygen, combined oxygen may be used as a final acceptor of hydrogen.

**Other Reductions Which Lead to Odor**

1) 

$$\text{Sulfate ion} + \text{organic matter} \xrightarrow{\text{d. d. bacteria}} \text{elemental sulfur} + \text{water} + \text{carbon dioxide}$$

$$\text{SO}_4^{2-} + \text{CH}_4 \xrightarrow{\text{d. d. bacteria}} \text{S} + 2\text{H}_2\text{O} + \text{CO}_2$$

2) 

$$\text{Thio compounds} + \text{hydrogen ions} \xrightarrow{\text{d. d. bacteria}} \text{mercaptans}$$

$$R=S + H^+ \xrightarrow{\text{d. d. bacteria}} RSH$$

**Other Reductions which do NOT produce significant odor:**

1) 

$$\text{Nitrate ion} + \text{hydrogen ions} \xrightarrow{\text{bacteria}} \text{nitrogen gas} + \text{water}$$

$$2\text{NO}_3^- + 12H^+ \xrightarrow{\text{bacteria}} \text{N}_2 + 6\text{H}_2\text{O}$$
2) Carbon dioxide + hydrogen ion \( \xrightarrow{\text{bacteria}} \) methane + water
\[ \text{CO}_2 + 8\text{H}^+ \xrightarrow{\text{bacteria}} \text{CH}_4 + 2\text{H}_2\text{O} \]
Solving the Hydrogen Sulfide Odor Problem

Adding Oxygen

Oxygenation assists aerobic and facultative anaerobic bacteria to reproduce faster than anaerobes, thus out-competing them for nutrients.

\[
\text{oxygen} + \text{ionized hydrogen sulfide} \xrightarrow{\text{bacteria}} \text{thiosulfate ion} + \text{water} \\
2\text{O}_2 + 2\text{HS}^+ \xrightarrow{\text{bacteria}} \text{S}_2\text{O}_3^{2-} + \text{H}_2\text{O} \\
\ast \text{anaerobic or facultative anaerobic bacteria}
\]

Chemicals Which Have Been Tried to Control Hydrogen Sulfide

Hydrogen Peroxide

Hydrogen peroxide has been injected, upstream of the headworks or primary clarifiers, to react with hydrogen sulfide forming sulfur and water. Excess hydrogen peroxide decomposes to release oxygen and water, thereby increasing the dissolved oxygen in the stream. Generally 90% of the reaction between hydrogen peroxide and hydrogen sulfide takes place within 10 to 15 minutes, with the balance reacting in an additional 20 to 30 minutes.

Disadvantages: For small installations, 500 lb. drums are purchased. Larger installations buy in tank-trucks or tank-cars. Special safety handling including protective clothing, face shields must be worn during bulk storage loading, and repair and maintenance of the facility. Spontaneous combustion is another possible problem.

\[
\text{hydrogen peroxide} + \text{hydrogen sulfide} \rightarrow \text{elemental sulfur} + \text{water} \\
pH < 8.5 \quad \text{H}_2\text{O} + \text{H}_2\text{S} \rightarrow \text{S} + 2\text{H}_2\text{O}
\]

\[
\text{hydrogen peroxide} + \text{sulfide ion} \rightarrow \text{sulfite ion} + \text{water} \\
pH > 8.5 \quad 2\text{H}_2\text{O}_2 + \text{S}^{2-} \rightarrow \text{SO}_2^{2-} + 2\text{H}_2\text{O}
\]

Chlorine
Chlorine has been applied to wastewater in a dose that is at least three to nine times the concentration of sulfide to be oxidized. Chlorine combines with water to form hypochlorous and hydrochloric acids.

**Disadvantages:** Chlorine kills the natural (and Clear-Flo®) waste-degrading bacteria. Chlorine combines with the urine in the waste stream to form chloramines, which are difficult to remove. Toxic or carcinogenic chlorinated hydrocarbons may form during treatment. Chlorine is a hazardous material, requiring special safety precautions.

**Metal Salts**

By reacting certain metal salts, such as ferrous sulfate, with hydrogen sulfide, an insoluble metallic sulfide will be formed. The dose is 4.5 grams of ferrous sulfate for each gram of sulfide to be oxidized. This is less expensive than peroxide or chlorine.

**Disadvantages:** These products may contain a high free acid content which causes detrimental changes in the pH and alkalinity of the stream, which can interfere with biodegradation of the waste.

**Potassium Permanganate**

Potassium permanganate is a strong oxidizing agent that can react with hydrogen sulfide in a variety of ways, depending on whether the stream is acidic or alkaline. In **acidic conditions**, the following reaction takes place:

\[
3 \text{H}_2\text{S} + 2\text{KMnO}_4 \rightarrow 3\text{S} + 2\text{H}_2\text{O} + 2\text{KOH} + 2\text{MnO}_2
\]

Under alkaline conditions the following takes place:

\[
3 \text{H}_2\text{S} + 8\text{KMnO}_4 \rightarrow 3\text{K}_2\text{SO}_4 + 8\text{MnO}_2 + 2\text{KOH} + 2\text{H}_2\text{O}
\]

Under conditions that are in between acidic and alkaline pHs, a variety of reactions occur, yielding elemental sulfur, sulfate, thionates, dithionates and manganese sulfide.
end products. Potassium permanganate has been fairly effective when added to the sludge dewatering operation, where it is added to the suction side of the sludge pumps feeding the dewatering unit.

**Disadvantages:** Dosages are difficult to predict and control in most liquid applications. The high cost and high dose, 6 or 7 parts of potassium permanganate are needed for each part of hydrogen sulfide, are discouraging. Safety precautions are required for handling and storage.
Bacteria which consume H2S by Oxidation include:

*Thiobacillus denitrificans* and *Paracoccus pantotrophus* (formerly *Paracoccus denitrificans* and *Thiromicrospira pantotrophus*) can function aerobically or anaerobically using nitrate as a source of oxygen. Our recently reformulated powdered product, **Alken Enz-Odor 6** contains both of these species along with the obligately aerobic sulfide and mercaptan oxidizer, *Starkeya novella* (formerly *Thiobacillus novellus*) which does not produce acid during oxidation and is facultatively able to degrade general BOD and a wide assortment of fatty acids.

Alken-Murray sells *Starkeya novella* alone, under the name **Alken Enz-Odor 14**, and also includes it in a variety of other products.

Most recently of all, Alken-Murray's Valerie Anne Edwards isolated a new species of heterotrophic, facultatively anaerobic, sulfide oxidizing *Bacillus*. Dr. Frederick Cohan of Wesleyan University has done the DNA probe work on this new species and we will be proposing the name *Bacillus sulfidophilus* for it. For now, the strains are listed with the name of their closest relative, *Bacillus mojavensis*. Three strains of this new species are currently included, singly or together, in the following Alken-Murray formulas: **Alken Clear-Flo 1003, Alken Clear-Flo 1005, Alken Clear-Flo 1008, Alken Clear-Flo 1400-50x, Alken Clear-Flo 7114, Alken Clear-Flo 7139, Alken Enz-Odor 2, Alken Enz-Odor 4, Alken Enz-Odor 5, Alken Enz-Odor 6, Alken Enz-Odor 8, Alken Enz-Odor 9, Alken Enz-Odor 10, Alken Enz-Odor 12, Alken Nu-Bind, Alken Nu-Bind 2, Alken Nu-Bind 3, and Alken Treat-A-Loo 2**.

The following bacteria are autotrophic aerobes, requiring a sulfur source (hydrogen sulfide, elemental sulfur or thiosulfate) for energy:

- *Ancalochloris beggiatoa*
- *Beggiatoa alba*
- *Sulfbacillus*
- *Thiohalocapsa halophila*
- *Thiomargarita*
- *Thioploca*
The following bacteria are autotrophic anaerobes, requiring a sulfur source (hydrogen sulfide, elemental sulfur or thiosulfate) for energy:

- *Chromatium warmingii*
- *Thiobacillus*
- *Ectothiorhodospira mobilis*
- *Halochromatium glycolicum*
- *Marichromatium purpuratum*

### How Adding Sodium Nitrate and Alken Clear-Flo® to an Anaerobic System Assists Odor Reduction

With the addition of 10 to 100 ppm of sodium nitrate (or a specialty nitrated blend like *Alken 896, Alken Enz-Odor 9* or *Alken Enz-Odor 10*) to the prescribed dosages of *Alken Enz-Odor 8* or *Alken Clear-Flo 7020* (see dosage chart, linked from product bulletin for correct dosage), the following reactions will occur. Bacteria prefer hydrogen receptors in the following order: oxygen, nitrate ion, and sulfate.

Theoretically, in the absence of oxygen, no sulfide will be generated until all of the nitrate has been reduced to nitrogen gas.

1)  

\[
\text{sodium + mercaptan nitrate} \xrightarrow{\text{Alken Clear-Flo}^0} \text{sodium + oxygen + nitrogen + organic matter}
\]

\[2\text{NaNO}_3 + \text{RSH} \xrightarrow{\text{Alken Clear-Flo}^0} \text{Na}_2\text{SO}_4 + \text{O}_2 + \text{N}_2 + \text{RH}\]

2)  

\[
\text{sodium + elemental sulfur} \xrightarrow{\text{Alken Clear-Flo}^0} \text{sodium + oxygen + nitrogen}
\]

\[4\text{NaNO}_3 + \text{S}_2 \xrightarrow{\text{Alken Clear-Flo}^0} 2\text{Na}_2\text{SO}_4 + 2\text{O}_2 + 2\text{N}_2\]

3)  

\[
\text{sodium + hydrogen sulfide} \xrightarrow{\text{Alken Clear-Flo}^0} \text{sodium + oxygen + nitrogen + water}
\]

\[4\text{NaNO}_3 + 2\text{H}_2\text{S} \xrightarrow{\text{Alken Clear-Flo}^0} 2\text{Na}_2\text{SO}_4 + \text{O}_2 + 2\text{N}_2 + 2\text{H}_2\text{O}\]

### Oxidation of hydrogen sulfide by different strains of Thiobacillus:

If pH is below 5, *Thiobacillus concretivorus* will perform the following reactions, in the presence of up to 7 percent sulfuric acid concentrations. They draw a carbon source from carbon dioxide. A pH above 10 will kill this strain.

1) Elemental sulfur, hydrogen sulfide, thiosulfate and polythionates can be degraded by *T. concretivorus* to sulfuric acid, which lowers the pH to around 2.
2) In a pH range of 5 to 7, *Thiobacillus thioparus* will establish itself and degrade hydrogen sulfide to thiosulfuric and polythionic acids.

\[
\text{sulfur + oxygen + water} \xrightarrow{\text{Thiobacillus concretovus}} \text{sulfuric acid}
\]
\[
2S + 3O_2 + 2H_2O \xrightarrow{\text{Thiobacillus concretovus}} 2H_2SO_4
\]

\[
\text{hydrogen sulfide + oxygen} \xrightarrow{\text{Thiobacillus concretovus}} \text{sulfuric acid}
\]
\[
H_2S + 2O_2 \xrightarrow{\text{Thiobacillus concretovus}} 2H_2SO_4
\]

\[
\text{water + thiosulfate + oxygen} \xrightarrow{\text{Thiobacillus concretovus}} \text{sulfuric acid}
\]
\[
12H_2O + 6S_2O_3^{2-} + 9O_2 \xrightarrow{\text{Thiobacillus concretovus}} 12H_2SO_4
\]

*Controlling H2S by Combining Bonding and Degradation*

Another safe option for eliminating the odor from hydrogen sulfide is the application of high molecular-weight humified peat moss combined with appropriate bacteria to bind the hydrogen sulfide and degrade the source of odor. Be sure that the product you select is a humified peat moss, not leonardite and that it is not a low molecular weight product, as is commonly marketed to agriculture to enhance plant growth. A high molecular weight humified peat moss, such as that found in *Alken Nu-Bind*, binds hydrogen sulfide and ammonia, while increasing bacterial cell wall permeability, catalyzing higher performance and increasing activity levels from the bacteria in the product. *Alken Nu-Bind* is popular for solving municipal waste treatment, industrial applications, and animal farming odors.

Other alternatives for binding hydrogen sulfide and mercaptans are certain natural polymers, which also work co-operatively with bacteria. *Alken Nu-Bind 2* is an example of such a product, binding mercaptans that the original product cannot, while its hydrogen sulfide binding is second only to the original *Nu-Bind*. For garbage cans, dumpsters, etc, there is no better product.

The client's budget, regulatory demands, and composition of the waste, temperature, pH etc. will dictate the appropriate solution, whether it is bacteria alone, bacteria with nitrate, or bacteria with a binding agent.
Diagram of the Sulfur Cycle

by Kenneth J. Edwards Jr. - VP Alken-Murray Corp.

The Sulfur Cycle

Hydrogen Sulfide Hazards

in Municipal & Industrial Accounts

Alken-Murray personnel working in areas where hydrogen sulfide is present are to diligently study this section of the website.

Hydrogen sulfide has the characteristic odor of rotten eggs. However, it rapidly deadens the sense of smell. Therefore, odor cannot be depended upon as a means of detection of this gas. After working for a short time in an area with a small amount of hydrogen sulfide, a person can no longer detect this gas and will not identify larger lethal concentrations.

Hydrogen sulfide is a highly toxic gas which, when inhaled in higher concentrations has no odor and can rapidly cause death, perhaps in 2-3 minutes. It is also highly flammable and certain concentrations (4.3-46%) in air can explode upon ignition.

Even at low concentrations, hydrogen sulfide acts as an irritant to the eyes and respiratory tract. Moderate concentrations cause headaches, dizziness, nausea and vomiting in that order. The greatest danger, however, is from its acute effects. Massive dosage, that is contact with high concentrations (1000 ppm or more) can cause immediate loss of consciousness (in 1-2 seconds) which is rapidly followed by respiratory failure and death (2-3 minutes).

(See toxicity chart in front of this article).

Most industrial and municipal waste water treatment plants have information concerning the amount of hydrogen sulfide present in the gas produced on their properties. Always obtain this information before visiting a plant. Your safety depends on your knowledge of the hazards, and the application of adequate safety procedures including the intelligent use of appropriate personal protective equipment such as:

1. A respirator with canisters suitable for use with hydrogen sulfide up to 2% concentration (20,000 part per million).
2. A hydrogen sulfide detection unit for monitoring amounts of hydrogen sulfide present.
3. A self-contained air breathing apparatus.

This equipment should be available at the waste water treatment plant. OSHA regulations require that they measure the amount of hydrogen sulfide in their plant and that they provide you with these data.
Regulation Section 1910.134 (e)(1) of the Occupational Safety & Health Act says "In areas where an individual using a respirator could be overcome by a toxic or oxygen deficient atmosphere due to the failure of the respirator, at least one additional man shall be present. Communication, (visual, voice, or signal line) shall be maintained between both or all individuals present. Planning shall be such that one individual will be unaffected by any likely incident and have the proper rescue equipment to be able to assist the other(s) in case of emergency."

Alken-Murray Corporation insists that its representatives follow the above regulation. If the area is contaminated by a hazardous or noxious gas (over 300 ppm hydrogen sulfide) and another individual is not present, do not enter the area or do any work in the contaminated area.

Procedure to be used based on detection tests

- If the concentration is equal to or less than 10 parts per million, a respirator (gas mask) is not required.
- If the concentration is more than 10 ppm, but less than 50 ppm, exposure without a respirator is permissible, but only ONCE and for less than 10 minutes. Beyond this time, a respirator is to be used.
- When the concentration is higher than 50 parts per million, a respirator is to be used at all times.
- One hour of exposure to concentrations of hydrogen sulfide between 50 and 100 ppm will cause the average individual to exhibit sub-acute poisoning symptoms such as mild conjunctivitis and respiratory tract irritations.
- Concentrations between 200 and 500 ppm produce marked poisoning symptoms.
- Hydrogen sulfide at a concentration of 600 ppm can be fatal in 30 minutes, and only 1,000 ppm, that is 0.1% hydrogen sulfide, can be fatal in only 2 to 3 minutes. You cannot detect when concentration increases from 100 to 1000 ppm by smell. There is no warning odor at higher concentrations!
Chart corrected 1/12/2002, due to e-mail from a victim of H2S poisoning

0.03 ppm  Can smell. Safe for 8 hours exposure

4 ppm  May cause eye irritation. Mask must be used as it damages metabolism.

10 ppm  Maximum exposure 10 minutes. Kills smell in 3 to 15 minutes. Causes GAS EYE and throat injury. Reacts violently with dental mercury amalgam fillings.

20 ppm  Exposure for more than 1 minute causes severe injury to eye nerves.

30 ppm  Loss of smell, injury to blood brain barrier through olfactory nerves

100 ppm  Respiratory paralysis in 30 to 45 minutes. Needs prompt artificial resuscitation. Will become unconscious quickly (15 minutes maximum)

200 ppm  Serious eye injury and permanent damage to eye nerves. Stings eye and throat.

300 ppm  Loses sense of reasoning and balance. Respiratory paralysis in 30 to 45 minutes

Asphyxia! Needs prompt artificial resuscitation. Will become unconscious in 3 to 5 minutes. Immediate artificial resuscitation is required.

500 ppm  Breathing will stop and death will result if not rescued promptly, immediate unconsciousness. Permanent brain damage may result unless rescued promptly.

700 ppm  E-MAIL
Hydrogen Sulfide Treatise References

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