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Effect of Sulfate-reducing Bacteria (SRB) under Anaerobic Conditions on the Hydrogen Sulfide Corrosion in Sanitary Sewers

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ABSTRACT

Hydrogen sulfide corrosion in sanitary sewerage environment is a result of dilute sulfuric acid dissolving the cement matrix. The acid is produced by a complex process of chemical and biochemical reactions. Hydrogen Sulfide (H2S) is produced by an action of Sulfur Reducing Bacteria (SRB) in the liquid phase, and then in time, this gas is converted by Sulfur Oxidizing Bacteria (SOB) into Sulfuric Acid (H2SO4). The last conversion occurs above the liquid level under aerobic condition. The objective of this study is to review and understand the effect of sulfate-reducing bacteria (SRB) under anaerobic conditions on the hydrogen sulfide corrosion in sanitary sewers. Published papers were reviewed that illustrated hydrogen sulfide during past years. The literature review suggests that sulfate-reducing bacteria (SRB) under anaerobic conditions in the submerged part of sewers facilitate reduction of sulfate ions and the production of various forms of sulfides. The formation of hydrogen sulfide (H2S) and its escape from the liquid sewage is an essential feed stock for the hydrogen sulfide corrosion processes in the sewer systems. Aerobic bacteria colonize on all surfaces above the water line and convert H2S gas into dilute sulfuric acid by means of a complex biochemical process.

KEYWORDS: Hydrogen sulfide corrosion, SRB, Environment, Sewerage

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INTRODUCTION

Concretes can be attacked by mobile sulfate ions. These sulfate ions can be found in hot soils and certain ground waters and seawater. They can be calcium sulfates (gypsum,) sodium sulfates (Glauber's salt) and magnesium sulfate (Epsom salt) to name a few. They harm concrete slowly over time and unlike the direct surface attack by acids, sulfates attack by penetrating the concrete and then reacting with various minerals in the hydrate system to form new powerful expansive minerals. These new minerals literally tear the concrete apart. The damage is very different appearing compared to hydrogen sulfide corrosion. Generally the increased internal stress and deterioration of the concrete matrix is caused by the large volume expansion from a complex long chained mineral known as ettringite.[1,2,3]

The sulfates react with unreacted C_3A as well as the reacted C_3A compounds in the cement hydrate system. This is a depth attack not a surface attack like acids. The problem can be reduced by using cements produced from raw materials low in alumina content like Type V Portland cement. Also reducing the permeability of the hardened concrete is effective as the mobility of the sulfate ions can be reduced. So, concretes with low water to cement ratios help as well as pozzolanic materials to bind more lime and then crystalline forming admixtures can be especially helpful. Again, it must be stressed that improving sulfate resistance has nothing to do with improving acid resistance for which there is no solution.[4]

TYPES OF CONCRETE DETERIORATION

Generally, in sanitary sewers, hydrogen sulfide corrosion is the typical cause of deterioration inside the pipe or structures. For most other concrete structures, road ways, etc. in general, deterioration is caused by:

- Freezing and thawing
- Attack of reinforcing steel by chloride ion penetration – causing expansion
- Cracking as a result of poor design
- Mechanical impacts
- Poor quality concrete and / or concrete handling / curing issues
- Carbonation
- Alkali-Silica reaction where aggregates may contain undesirable silicas

In general, these types of deterioration are not common in sanitary sewers especially underground structures. Hydrogen sulfide corrosion will attack concrete first and then ultimately find its way to the reinforcing steel but the concrete attack proceeded well in advance. Also, the above-mentioned types of deterioration visually appear very different than hydrogen sulfide corrosion. It produces a punky muck of soft material whereas these other types of attack appear to be dry and simply cracking and crumbling away. Attack of reinforcing steel often is seen as following the lines of the steel whereas the other modes just produce random patterns of deterioration.[5]

As stated above, hydrogen sulfide corrosion is the main sources of concrete deterioration in sanitary sewer structures. It is very simply the complete consumption of the binder phase in concretes by dilute sulfuric acid that is produced in a complex series of biological steps.[6]

CONDITIONS NECESSARY FOR BACTERIAL ACTIVITY IN RAW SEWAGE

Temperature conditions in sewers are moderate and almost always in a range to promote biological activity. They can exist at temperatures ranging from 32°F to 212°F with the optimum range being 75°F to 107°F. Many factors affect this activity including; design capacity versus actual flows, retention time, turbulence, organic waste levels, biological oxygen demand levels, industrial pollutants (known to impede biological activity) and Inflow and Infiltration (I and I).

Efforts to reduce industrial pollutants and I and I in many cases have increased the biological activity. Reducing I and I increase retention times as well as concentrates the organic waste levels. These efforts, while needed for many reasons, are causing increased MIC in the sewers. The first step in this complex chain of events is one where anaerobic (non-air breathing) bacteria begin to thrive in the wastewater stream and in slim layers (again under the water) attached to structures of all types. They are naturally abundant and impossible to prevent naturally.[7]

Sulfates are found in drinking water (10 to 50 ppm) and food and in turn human waste. They can be found in raw sewers up to 8,000 ppm. In a typical 1 Million Gallon per Day (MGD) sewer, a typical value could be 20 tons of sulfates flowing each day. The anaerobic bacteria consume the sulfates and produce H_2S, a gas slightly heavier than air. The solubility of H_2S in water is a function of temperature and pH but generally it is around 3,850 ppm. This is significantly higher (by around 100 times) than hydrogen or oxygen or nitrogen and about half that of Chlorine and twice that of CO_2.

With an abundant amount of H_2S gas in the moist oxygen rich atmosphere above the liquid level, the second important biological activity takes place. Here aerobic (air breathing) Thiobacillus bacteria eventually thrive. They rise from the liquid and collect on all surfaces. These bacteria consume the H_2S gas along with water vapor and oxygen via a complex process in itself, and secrete dilute sulfuric acid as their waste product. They do not need anything further to survive.[8]

In a new concrete structure, the surface alkalinity is high with a pH generally greater than 11. Over time, and again many factors can affect this timing, H_2S and carbonation along with other general atmospheric conditions reduce the alkalinity of new concrete surfaces. In the case of PVC pipe or various coatings, the bacteria can thrive much more quickly as there is no alkalinity on the surfaces. The bacteria have a neutral surface on which to begin the colonization process.

With concrete surfaces, the process is complex and involves the evolution of at least 5 strains of the sulfur consuming Gram-negative bacteria. The first strains can tolerate surface pHs as high as 9 and produce only modest amounts of very weak acid. But they are important as they work to lower the surface pH to where more prolific bacteria thrive and produce stronger acids capable of quickly destroying concrete. Some species of Thiobacillus thrive in sulfuric acid solutions as concentrated as 7 percent with a pH approaching zero. They are prolific producers of acid. Keep in mind the pH scale is logarithmic and a concentration of just 0.03% results in a pH of about 2.[9]

Much is often said of designing sewers to minimize MIC and odors. There are several computer models that attempt to predict odor and corrosion rates but they require many factors to be known. They work somewhat for understanding existing sewers but not so well for new construction. There is not much that can be done from a simple design point of view. Sewers are already very simple structures. As discussed there is a tremendous and complex biological machine involved. Also keep in mind that your sewage conditions today are not what they were nor what they will be in the future, no model can predict this.[10]

HYDROGEN SULFIDE FORMATION

The formation of hydrogen sulfide is usually believed to be the trigger to initiate MIC processes in sewer systems. Sulfate ions, largely contained but not regulated by EPA standards in wastewater, are the primary sulfur source in sewers. Sulfate-reducing bacteria (SRB) under anaerobic conditions in the submerged part of sewers facilitate the reduction of sulfate ions and the production of H_2S (gas). H_2S (aq) is released into the gas phase (H_2S (g)) with or without the aid of turbulence (turbulence increases the gas release).[11,12,13]

Typical SRB were identified as Sulfovibriodesulfuricans and Desulfovibriodesulfuricans. The equations 1 and 2 below describe the formation of hydrogen sulfide through the reduction of sulfates by SRB, in which sulfate ions are listed as the sulfur source:[14,15]

$$\overset{D.sulfricans}{CH_3COOH + Na_2SO_4\, Na_2CO_3 + H_2O} \rightarrow CO_2 + H_2S \quad (1)$$

$$CH_3CHOHCOONa + Na_2SO_4 \xrightarrow{D.sulfricans} 2CH_3COONa + 2NaHCO_3 + H_2S \quad (2)$$

Sulfides may be present in wastewater as a result of industrial processes, the formation of H_2S (aq) is most commonly attributed to the activity of anaerobic sulfate reducing bacteria (SRB). Parker in 1947 first named Sporovibriodesulfuricans as the organism responsible for the reduction of sulfates to H_2S (aq). More recent molecular surveys of biofilm communities in sewers have revealed the presence of several SRB speciespresent in wastewater; however, Desulfovibriodesulfuricans is commonly named as the primary contributor to the sulfate reduction in municipal wastewater collection systems. Desulfovibriodesulfuricans is an obligate anaerobe that relies on the availability of organic substances for food supply (electron donor) and utilizes sulfate as an oxygen source (electron acceptor).[16,17,18,19]

When DO content is low (usually < 0.1 mg/L) in sewer, the aerobic layer is limited and sulfide will be released back to sewer stream. The sulfide concentration increases and the exchange between sewerage and the pipe atmosphere occurs under certain conditions which will be explained in the following sections (EPA, 1985). Figure 1 shows the processes in sewers with sufficient oxygen to prevent sulfide from entering the sewage stream.

When H_2S begins to build up in the sewerage stream, the distribution of sulfide species in the liquid depends on the pH of the sewerage. Since sewage pH is approximately 7, two major sulfide species exist in the water as H_2S (aq) and HS^-.[21,22,23,24]

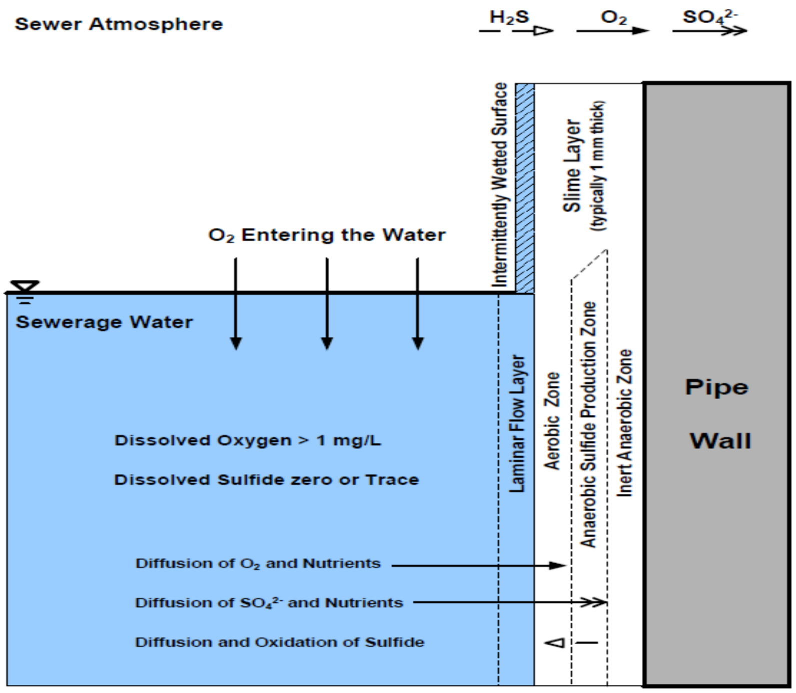

Figure 1. Processes in sewers with sufficient oxygen to prevent sulfide from entering the sewage stream[25]

The S^{2-} species is not taken into account because it exists in the liquid phase at high pH values. Figure 2 shows the processes in sewers under sulfide increasing conditions and its effect on the pipe wall.

The ionization of H_2S and HS^- is presented in the equations below in the equations 3 and 4.

$$H_2(aq) \leftrightarrow H+ + HS^{-} pKa1 \approx 7.04 \quad (3)$$

$$HS^{-} \leftrightarrow H^{+} + S^{2-} pKa2 \approx 12.92 \quad (4)$$

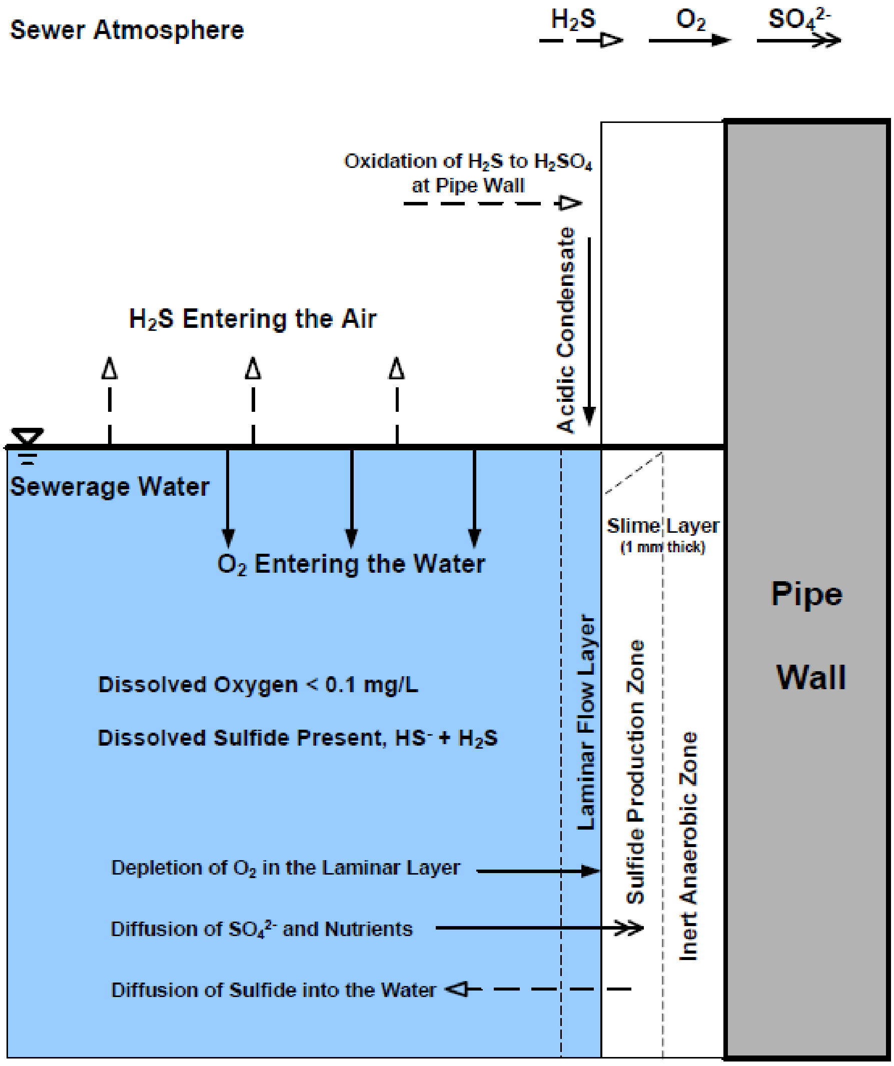

Figure 2. Processes in sewers under sulfide increasing conditions[25]

A design manual was published for odor and corrosion control in sewerage systems and treatment plants by the EPA.[26]

In other words, the two species have similar concentrations at this pH value. While on the right half of the plot, the intersection of curves of HS^- and S^{2-} lies at pH 9.5, which should be around 13 according to the pKa_2 value in the ionization equation of HS- above. Further correction of this plot, with results from basic chemistry experimental designs, should be conducted to better represent the species distribution in sewerage.

Only H_2S (aq) can be transferred across the air-water interface, giving rise to the emission of H_2S from wastewater into the gas phase (or sewer head space). Besides pH of the sewerage, temperature, hydraulic conditions of the water phase and ventilation of the air phase are also the key factors that affect the H_2S emission.[27]

$$H_2(aq) \leftrightarrow H_2S(g)\ Kc \approx 469\ (atm/molefraction) \qquad (5)$$

As to the H_2S concentration in the sewerage atmosphere, field investigations do not always record these data along with the corrosion of concrete pipes. Therefore, long term monitoring of H_2S (g) content in the headspace of sewer systems is necessary. This information could be of great help when comparing the corrosion results from different regions and further determining the complex degradation process in the field. Moreover, the daily and seasonal variation of H_2S (g) concentrations should not be ignored.[27]

A thin layer of moisture is present on the unsubmerged portions of the pipe wall exposed to the atmosphere and this is the location where the H_2S gas is dissolved into the liquid phase. The condensate layer has a high pH attributed to the alkalinity of the concrete (pH = 11-13and also serves as the driving force behind the gas dissolution. At high pH, H_2S is separated into HS^- or S^{2-} ions that attract more H_2S into the moisture layer. Table 1 shows the factors affecting sulfide content in wastewater collection networks.[27]

Table 1. Factors affecting Sulfide Content in Wastewater Collection Networks[26,27]

Factor	**Effect**
DO	Low DO encourages activity of SRB and the conversion of sulfates to sulfides
Sulfate Content	Sulfates must be present for the biological conversion to sulfide
Temperature	Increased temperatures encourage bacterial activity and lower oxygen solubility
BOD	BOD represents nutrients available for bacteria that deplete DO
Turbulence	Encourages re-aeration resulting in growth of SOM and chemical oxidation resulting in lowered potential for sulfide buildup

CONCLUSIONS

Sulfate-reducing bacteria (SRB) under anaerobic conditions in the submerged part of sewers facilitate reduction of sulfate ions and the production of various forms of sulfides. The formation of hydrogen sulfide (H_2S) and its escape from the liquid sewage is well studied and is an essential feed stock for the hydrogen sulfide corrosion processes in the sewer systems. Aerobic bacteria colonize on all surfaces above the water line and convert H_2S gas into dilute sulfuric acid by means of a complex biochemical process.

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