Understanding Biogenic Sulfide Corrosion

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Biogenic sulfide, which develops from the formation of hydrogen sulfide (H_2S) and sulfuric acid (H_2SO_4) in sewage, causes extensive deterioration of concrete. This article describes the chemistry involved and recommends protective measures.

It is widely understood that wastewater collection and treatment systems are a source of malodorous odors. The most prevalent odorous gas is hydrogen sulfide (H_2S), a toxic and corrosive gas with a characteristic rotten egg odor. What may often be overlooked, however, is that H_2S is also a precursor to the formation of sulfuric acid (H_2SO_4), which causes the destruction of metal and concrete substrates and appurtenances within wastewater collection and treatment facilities. The bacterially mediated process of forming H_2S gas and the subsequent conversion to H_2SO_4 causes what is called biogenic sulfide corrosion. Also referred to as microbiologically influenced corrosion, biogenic sulfide corrosion is of increasing concern among engineers and practitioners, as it contributes to the considerable cost of renovation of deteriorated facilities.

Fresh domestic sewage entering a wastewater collection system contains an abundance of sulfates ($SO_4^{=}$). In the absence of dissolved oxygen (DO) and nitrates, these sulfates are reduced by sulfate-reducing bacteria (SRB), identified primarily from the obligate anaerobic species *Desulfovibrio,* to form H_2S (via an esoteric reaction). Conditions favorable for producing sulfide within wastewater conveyance/treatment processes have been identified as:

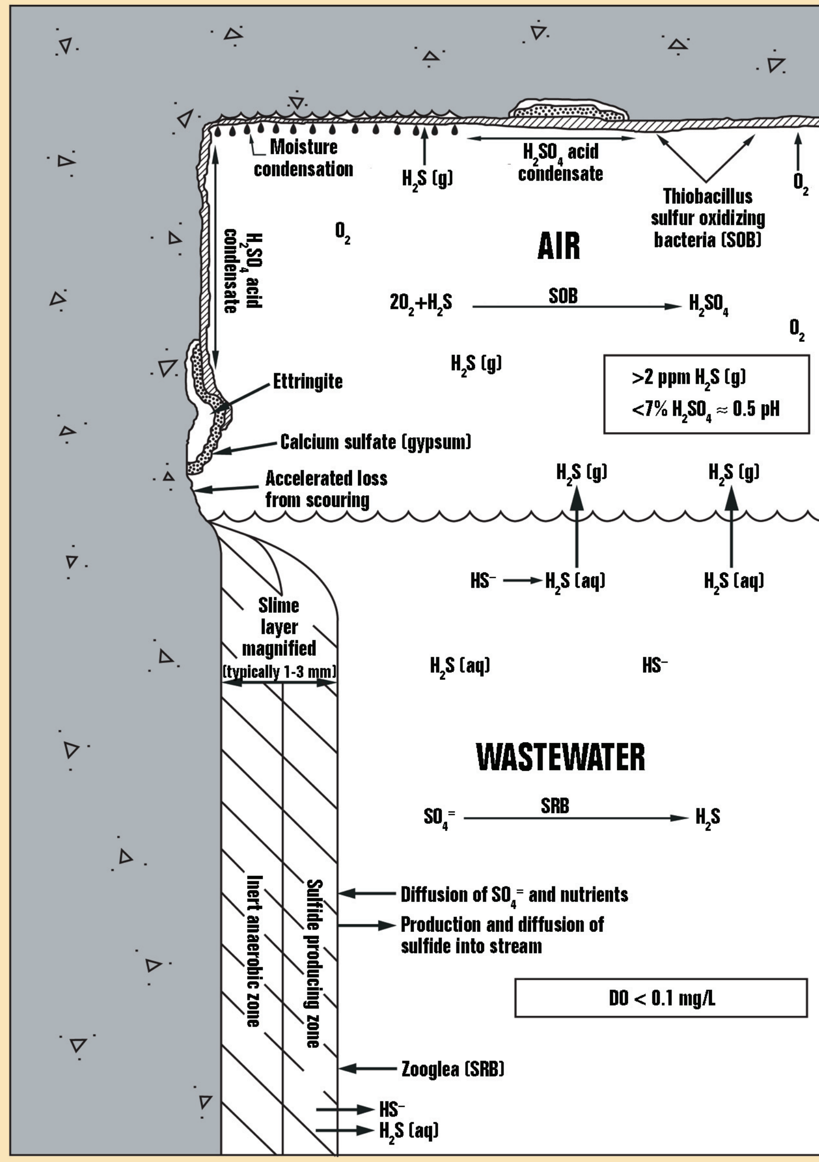
- Low DO content.
- High-strength waste water (in terms of elevated biochemical oxygen demand).
- Low flow velocity and long detention times.
- Turbulence/extensive pumping.
- Elevated wastewater temperatures.

Hydrogen Sulfide Generation

Sulfide generation is a bacterially mediated process occurring in the submerged portion of sanitary sewage systems. This process begins with the establishment of a slime layer below the water level. The slime layer is composed of bacteria and other inert solids, held together by a biologically secreted protein "glue," or biofilm, called zooglea. When this biofilm becomes thick enough to prevent the diffusion of DO, an anoxic zone develops under the surface. It has been estimated that it takes approximately two weeks to establish a fully productive biofilm layer, complete with anaerobic zone, in a typical wastewater collection system.

SRB located within the anaerobic zone use the ubiquitous sulfate ion, $SO_4^{=}$—a common anion component of waste water—as an oxygen source for the assimilation of organic matter. As $SO_4^{=}$ is consumed for oxygen, the $S^{=}$ by-product is released back into the waste water, where it establishes a chemical equilibrium under normal wastewater conditions as 50/50 bisulfide ion (HS^-) and dissolved hydrogen sulfide [$H_2S_{(aq)}$]. Upon turbulence or aeration, waste water will release the dissolved gas as free H_2S gas, and more bisulfide ion is converted to the dissolved gas form to replace that lost to the atmosphere. The rate at which H_2S leaves the aqueous phase is governed by Henry's Law coefficient for that gas.

FIGURE 1



Formation of biogenic sulfide corrosion from oxidation of H_2S to H_2SO_4.

Sulfuric Acid Production

Once the H_2S gas diffuses into the headspace above the waste water, a sulfur-oxidizing bacteria (SOB), primarily genus *Thiobacillus* aerobic bacteria, which colonize on surfaces above the waterline in wastewater pipes and structures, metabolize the H_2S gas and oxidize it to H_2SO_4 (Figure 1). This oxidizing process can take place where there is an adequate supply of H_2S gas (>2 ppm), high relative humidity, and high atmospheric oxygen content. These conditions are thought to exist in the majority of wastewater systems for at least some portion of the year. Up until the late 1970s, however, H_2S levels were generally <10 ppm. Shortly thereafter, it was not uncommon to see H_2S levels spike to well above 50 ppm. Many concrete surfaces experiencing severe biogenic sulfide corrosion were measured and found to have a pH of 0.5, which indicates a ~7% H_2SO_4 solution.

Concrete Corrosion

The effect of biogenic sulfide corrosion and formation of H_2SO_4 up to 7% on concrete surfaces exposed to a sewer environment can be devastating. Entire pump stations and manholes, as well as large sections of collection interceptors, have been known to collapse due to loss of structural integrity from biogenic sulfide corrosion.

H_2SO_4 attacks the matrix of the concrete, which is commonly composed of calcium silicate hydrate (CSH) gel, calcium carbonate ($CaCO_3$), and unreacted calcium hydroxide [$Ca(OH)_2$]. The primary product of concrete decomposition from biogenic corrosion is calcium sulfate ($CaSO_4$), more commonly known by its

FIGURE 2

The effects of biogenic sulfide corrosion of concrete, identified by the whitish decomposition products $CaSO_4$ and ettringite.

FIGURE 3

Severe concrete attack from biogenic sulfide corrosion in the headspace of a grit chamber.

mineral name, gypsum. It is usually present in sewers and structures as a pasty white mass on concrete surfaces above the waterline. Another damaging effect of biogenic corrosion is the formation of the mineral ettringite, chemically known as calcium sulfoaluminate hydrate (Figure 2). When $CaSO_4$ or ettringite form, these expansive products can lead to increased internal pressure that causes small cracks, especially in protective liners. The corroded materials can be removed by the flow of sewage, accelerating the corrosion. The resultant erosion can be particularly evident at the high waterline, where diurnal or other high flows intermittently scour the walls above the waterline. Figure 3 shows an example of severe biogenic sulfide corrosion.

One of the common methods to prevent biogenic sulfide corrosion of concrete within wastewater conveyance/treatment structures is the use of a 100% solids, high-performance epoxy lining. Since the overall performance is formulation-specific, it is important that 100% solids epoxies be designed for severe wastewater exposures. Specifically, the epoxy formulations must have low permeation properties to resist H_2S and other gases, as well as H_2SO_4.

There are several types of epoxy coatings: mortars, trowel-applied between 125 to 250 mils (3 to 6 mm); spray-applied high-build liners at 60 to 80 mils (1.5 to 2 mm); and spray-applied fiberglass-reinforced high-build liners at 80 to 125 mils. Epoxy system selection depends on the level of H_2S gas, impact and abrasive forces, and thermal changes within the structure. Each system has specific merits. A reputable coatings manufacturer or consultant can assist with product selection for particular structures and exposure conditions.

Summary

The protection against biogenic sulfide corrosion of concrete structures in wastewater collection and treatment systems is vitally important. Such measures include the use of high-performance lining systems that can resist the permeation of H_2S gas and the chemical attack of H_2SO_4.

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