Corrosion In Wastewater Systems: More Than One Bug

Already susceptible to old age, wastewater infrastructure systems are also threatened by corrosive bacteria — but they needn't be.

by Heather Ramsey, John Davis, and Gary Hall

The role of various bacteria in the destruction of concrete in wastewater systems has been recognized since 1945. Parker[1] described the role of an acid producing bacterium that he called *Thiobacillus concretivorous*, which he had isolated from corroded concrete from a Melbourne, Australia sewage system. *Th. concretivorous* was described as a sulfate reducing bacterium (SRB) which converts hydrogen sulfide (H_2S) and uses thionates, polythionates, and elemental sulfur as sources of energy, and in the process secretes sulfuric acid as a metabolic byproduct. This class of bacteria are collectively referred to as SRBs. The acids they secrete are often referred to as biogenic, as they were produced by a biological process. *Th. concretivorous* was later re-classified as *Th. Thiooxidans*. In 2000, *Bergey's Manual of Systematic Bacteriology*[2] reclassified this species as *Acidithiobacillus Thiooxidans*. Several other microbes that are thought to be involved in the microbiologically influenced corrosion (MIC) processes were reclassified at the same time. Severe corrosion of concrete in sewage systems has been reported in Australia, Iraq, Israel, Ireland, the United States, the UK, Lebanon, Germany, and Mexico, among others. In many instances, the corrosion rate has been catastrophic, often resulting in total collapse of a concrete appurtenance, pipe line, or other structure. Concrete corrosion rates as great as 10-inches (25.4-cm) in less than 4-years have been described. With declining federal budgets and tightening local funding, municipalities and sewage authorities are faced with the necessity of protecting its expensive, difficult to replace infrastructure.

The crown section of this 14'tunnel experience severe degradation

In order to determine the most effective means of protecting these critical assets, it is beneficial to understand the corrosion process, a process called microbiologically Influenced Corrosion. Recent studies have found that the processes involved in MIC in wastewater collection and treatment systems, are more complex and the organisms involved more diverse than originally thought. Further, it has been determined that the microbial species involved require the establishment of synergistic/mutualistic communities, in addition to certain non-biological chemical reactions, in order for the process to proceed. Studies have also confirmed that in addition to bacteria certain fungi are also implicated in the processes.

MIC Processes

Ubiquitous in the wastewater system are microbes, consisting of bacteria and fungi, molds, and yeasts. Some of these bacteria produce acidic metabolic byproducts that are secreted as waste products onto the surfaces upon which these microbes form their communities. The fungi digest their food externally and secrete enzymes in order to do so. These enzymes are amino acids and can cause corrosion on susceptible substrates. Additionally, fungi, molds and yeasts secrete short chain fatty acids (SCFA). It is now recognized that the establishment of these synergistic communities is critical to the overall corrosion process. Most articles published on the subject of MIC in wastewater collection and treatment systems have focused upon the role of certain bacteria, notably the *Acidithiobacillus thiooxidans*. These bacteria cannot cause the observed corrosion without contributions from other species and some inorganic chemistry.

Decaying solid waste in sewage gives off H_2S gas which is poorly soluble in water. Sulfate reducing anaerobic bacteria, such as *Desulfovibrio* convert sulfates in the solid waste into sulfides, including hydrogen sulfide. The H_2S escapes easily from the sewage with turbulence caused by flow through the sewer system. Points of increased turbulence increase the amount of H_2S evolved. The H_2S then dissolves in a thin layer of water that condenses on the crown of the structure. This condensate layer will have a high pH due to the pH of the virgin concrete on which it is condensed, which is 12 to 13. Tests have shown that distilled water will obtain a pH of 12.5 within

4-days of exposure to the concrete. At high pH levels, H_2S forms HS^- or S^{2-} ions. These serve to allow more H_2S to enter the condensed water layer. As the pH of the concrete decreases, the H_2S concentration increases. In the presence of oxygen, the H_2S reacts to form elemental sulfur and partially oxidized sulfur species. Refer to the equation below. CO_2, which is also ubiquitous in the sewage system, also dissolves in the water vapor condensate that accumulates above the sewage to form carbonic acid (H_2CO_3). These acids combine to reduce the pH of virgin concrete to ~8 to 9. It is felt by most cement technologists that the primary acidification reaction is due more to the carbonate formation.

$$2H_2S + O_2 \rightarrow 2S^0 + 2H_2O$$

Oxidation of H_2S to S by autotrophic bacteria

At this pH level, certain fungi and bacteria can begin to proliferate. Fungi grow best where there is an abundant supply of decaying preformed organic matter and plenty of moisture, although they are desiccant resistant and will grow at humidity levels as low as 65%. Most fungi are saprobic, meaning they obtain their nutrients from dead organic matter. They are described as being chemoheterotrophic, or more specifically chemo organotrophic, i.e. they obtain their energy from oxidation of organic matter. Fungi secrete specific enzymes onto their nutrient source. Enzymes are designed to facilitate one very specific chemical reaction. The enzymes breakdown the nutrients into smaller molecules and the fungi absorbs the digested meal. Most fungi grow at a pH of 5 to 6. Most fungi species grow best at a temperature of 25°C (77°F), except pathogens which grow best at body temperature, 37°C (98.6°F). Various fungi also secrete several short chain fatty acids (SCFA) such as acetic acid, citric acid, formic acid, butyric acid, glutaric acid, propionic acid, oxalic acid, and lactic acid. These organic acids will attack alkaline substrates such as concrete as well as susceptible metallic components. It appears that the enzymes, even though acidic, do not participate much in the corrosion process, as they are very specific reaction facilitators.

Concrete in wet-well deteriorated to reinforcement

The overall corrosion process of concrete in a wastewater environment must take into account the presence of these fungi and their acidic secretions. As noted earlier, the reaction of water, hydrogen sulfide, and carbonic acid will reduce the pH of virgin concrete. Raw, i.e. untreated, sewage has a near neutral pH of 6 to 8.5, which is considerably more acidic than the concrete. Exposure to raw sewage will further serve to decrease the pH through direct neutralization of the free lime in concrete and through demineralization of alkaline chemical species within the concrete by the sewage. Fungi will grow in a pH range of ~4.5 to 8.3. As the pH drops below 8.3, fungi of many genera and species begin to grow. See Table 1 below for a partial listing of fungi found in sewage. As these organisms proliferate, the SCFAs and enzymes secreted will attack concrete (and susceptible metallic alloys) further decreasing the surface pH.

Table 1. Partial listing of fungi associated with municipal sewage.

Alternaria
Aspergillus
Aureobasidium
Absidia
Botrytus
Candida
Cephalosporium
Chaetomium
Cladosporium
Coniothyrium
Cryptococcus
Epicoccum
Epidermophyton
Fusarium
Geotrichum
Gliocladium
Gliomastix
Monialiales
Mucor
Paecilomyces
Penicillium
Phialophora
Phycomyces
Phoma
Prototheca
Pyrenochaeta
Rhiocladiella
Rhizopus
Rhodotorula
Sepedonium
Septoria
Torulopsis
Trichoderma
Tricophyton
Tricosporon
Verticillium

As the substrate pH decreases, conditions become more favorable for acidophilic and acid secreting bacteria. The formation of the biofilm begins with the initial approach and attachment of the bacteria in a random pattern. The second phase is consolidation and is indicated by the appearance of microbial communities. The final stage is maturation which is characterized by cells embedded in a matrix of expolymers where the distribution of the microorganisms is well established and biodiversity increases significantly over earlier stages. The expolymers, comprised primarily of polysaccharides, serve to anchor the biofilm and to stratify the biofilm community. These stratified communities serve to control component concentration (O_2, P, S, etc), density, absorption, diffusion, and the biomass activity.

It is at this point, where acidophilic and acid secreting bacteria, such as *Acidithiobacillus thiooxidans*, begin to dominate. Sulfur oxidizing bacteria, such as *Desulfovibrio*, oxidize elemental sulfur and sulfides to a sulfate. See the equations below. Sulfate reducing bacteria (SRB), such as *Acidithiobacillus thiooxidans*, then convert sulfates to sulfuric acid (H_2SO_4). It is common in microbial communities to find such mutualism, where the changes produced in the local environment by one microbe's metabolism serve to facilitate the growth of another species, which returns the favor. Mutualism has been observed in microbial communities comprising more than 100 species.

Other bacteria will oxidize elemental sulfur to a sulfate, which then reduced to form sulfuric acid:

$$2S^0 + 3\ O_2 + 2H_2) \rightarrow 2(S_2)^{-2} + 4H^+$$

Elemental sulfur oxidized to sulfate by SRB

Sulfide oxidizing bacteria (SOB) will convert hydrogen sulfide (H_2S) to a sulfate:

$$H_2S + 2O_2 \rightarrow (SO_4)^{-2} + 2H$$

With the following intermediate chemical species:

$$SH^- \rightarrow S^0 \rightarrow (S_2O_3)^{-2} \rightarrow (S_4O_6)^{-2} \rightarrow (SO_4)^{-2}$$

Researchers have found that the corrosion of both alloys and concrete in biological systems is many times greater than in the acids themselves. This is not a surprising finding when one considers the complex chemistry that is occurring within these microbial communities. That means that it is not sufficient to test a proposed material of sewer construction or protection in sulfuric acid, for instance, when the exposure is biogenic sulfuric acid secreted within a microbial community with a complex chemistry that includes oxidizing conditions, reducing conditions, redox conditions, organic chemistry and inorganic chemistry. This fact points to the futility of laboratory simulations designed to duplicate the corrosive potential found in domestic sewer systems. If one were to try to culture in a laboratory all the microorganisms found within a sewer, one would quickly discover that only a fraction of the microbes can be successively cultured. That means that the environment found within a sewer cannot be, at least presently, duplicated in a lab experiment. That means that the only meaningful exposure tests are those that are carried out within an active sewage collection and/or treatment system.

Consider The Concrete

An additional consideration for prolonging the life of a sewer system is the type of cement used to make the infrastructure. For many years, municipalities and their design-engineering firms specified the use of ASTM Type V portland cement for their pipelines and manholes. This was done based upon the belief that Type V would resist sulfuric acid better than Type I. Type V is a so-called “sulfate resistant” cement. It is more resistant to alkaline sulfate salts, such as sodium sulfate, magnesium sulfate, calcium sulfate, or potassium sulfate. These are the types of salts often found in groundwater and can cause degradation of Types I and III portland cement. It must be noted that these are alkaline salts. While Type V portland is more resistant to these alkaline salts, it is actually less resistant to sulfuric acid and other acid species, such as the SCFA previously described, than either Type I or Type III.

Some researchers have carried out laboratory simulations showing that some cements are more resistant to the biogenic sulfuric acid than other types. For example, calcium aluminate cements have fared well in these tests, as well as in actual installations. Some manufacturers have done studies that purport to prove that a calcium aluminate cement (CAC) binder blended with a fused calcium aluminate aggregate gives superior resistance to biogenic sulfuric acid as compared to portland concretes and to calcium aluminate cement bonded siliceous aggregates. Field exposures do not reflect the laboratory results. In the field, there is no difference in the performance of CAC with calcium aluminate aggregate and silica aggregate. The same laboratory tests were reported to prove that biofilms were more difficult to establish on CAC concretes. Again, results from the field do not bear this claim out. Biofilms in a wastewater system are prevalent throughout, regardless of the base concrete.

Conclusion

The corrosion mechanisms at play within an active sewer system are complex and involve many different microorganisms including bacteria, molds, yeasts, and fungi. Other microorganisms such as rotifers and worms may also play a role, especially within the sewage sludge. Fungi, molds, and yeasts do not secrete mineral acids such as sulfuric acid. They do however secrete amino acids and SCFAs. These are also active in the corrosion processes occurring within the mutualistic microbial communities common to sewage systems. It has been found that some types of protective coatings can be attacked by fungi, whereas they resist sulfuric acid. The composition of the microbial population will vary somewhat from sewage system to sewage system, but the primary corrodents will remain fairly constant. The role of fungi and bacteria must be considered when evaluating microbiologically influenced corrosion within a sewer system.

Based upon the likelihood of concrete corroding in a wastewater collection and treatment system, it becomes imperative to apply appropriate corrosion control methodologies such as protective linings in order to extend the service life of concrete in MIC environments. ■

References:

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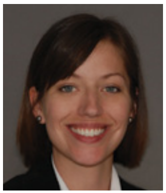
2. Bergey's Manual of Systematic Bacteriology. Second Edition. Volume Two Part A, Appendix 1, p. 188 and pgs.60-61, Springer, NY 2001



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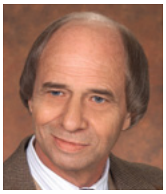

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