biotech armor for concrete

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Corrosion Control in Concrete Pipe and Manholes

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Abstract

Of the 19,500-wastewater systems in the United States of America, approximately 40% consist of concrete pipes, manholes, pump stations, interceptors and wet wells. The structural integrity of these concrete components is severely compromised by corrosion. This erosion of the infrastructure by corrosion is causing a nationwide premature replacement of failed structures.

The primary cause for this corrosion is Microbial Induced Corrosion (M.I.C.). This is a process by which sulfuric acid is produced in sewer systems by the interaction of hydrogen sulfide gas and Thiobacillus bacteria.

This paper details the use of a newly developed antibacterial admixture that makes the concrete an unfriendly environment for bacteria growth. This concrete admixture stifles the corrosion generated by hydrogen sulfide gas, a common problem for concrete pipe, manholes, and similar structures in municipal sewer systems. As an additive, it permeates the concrete or repair mortar during the mixing phase and molecularly bonds to the cement particles to become an integral component of the hardened concrete product and to create an environment incompatible to Thiobacillus growth.

It cannot wash off, deteriorate, or lose its effectiveness from wear. Abrasion or erosion of the concrete surface only serves to expose additional material to the surface, which would otherwise foster bacterial growth. As bacterial growth is neutralized, hydrogen sulfide gases released from the raw sewerage cannot be metabolized and converted to sulfuric acid in concentrations and amounts sufficient to damage the treated concrete or mortar. Thus, the structural integrity of the concrete-sewer components is maintained and the life of sewer systems is extended.

KEYWORDS: Corrosion, bacteria, hydrogen sulfide, sulfuric acid.

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INTRODUCTION

The work of C. D. Parker, reported in 1945 in the *Australian Journal of Experimental Biology and Medical Science*, identified Thiobacillus genus bacteria as the source of Microbial Induced Corrosion (M.I.C.) in sewers. Sulfuric acid produced by these bacteria collects on the surfaces above the flow line.

The effect of sulfuric acid on concrete surfaces exposed to the sewer environment can be devastating. Sections of collection interceptors and entire pump stations have been known to collapse due to loss of structural stability from corrosion. We have all seen the news photographs of cars being swallowed by streets opened by the loss of a section of large diameter pipe. The process of concrete corrosion, however, is a step-wise process, which can sometimes give misleading impressions. The following briefly describes the general process of concrete corrosion in the presence of a sewer atmosphere.

Freshly placed concrete has a pH of approximately 11 or 12, depending upon the mix design. This high pH is the result of the formation of calcium hydroxide [$Ca(OH)_2$] as a by-product of the hydration of cement. Calcium hydroxide is a very caustic crystalline compound, which can occupy as much as 25% of the volume of concrete. A surface pH of 11 or 12 will not allow the growth of any bacteria, however, the pH of the concrete is slowly lowered over time by the effect of carbon dioxide (CO_2) and hydrogen sulfide gas (H_2S). These gases are both known as "acid" gases because they form relatively weak acid solutions when dissolved in water. CO_2 produces carbonic acid and H_2S produces thiosulfuric and polythionic acid. These gases dissolve into the water on the moist surfaces above the sewage flow and react with the calcium hydroxide to reduce the pH of the surface. Eventually the surface pH is reduced to a level, which can support the growth of bacteria (pH 9 to 9.5).

The time it takes to reduce the pH is a function of the concentration of carbon dioxide and hydrogen sulfide in the sewer atmosphere. It can sometimes take years to lower the pH of concrete from 12 to 9, however in some severe situations it can be accomplished in a few months.

Once the pH of the concrete is reduced to around pH 9, biological colonization can occur. Over 60 different species of bacteria are known to regularly colonize wastewater pipelines and structures above the water line. Most species of bacteria in the genus Thiobacillus have the unique ability to convert hydrogen sulfide gas to sulfuric acid in the presence of oxygen. Because each species of bacteria can only survive under a specific set of environmental conditions, the particular species inhabiting the colonies change with time. Since the production of sulfuric acid from hydrogen sulfide is an aerobic- biological process, it can only occur on surfaces exposed to atmospheric oxygen.

As a simplified example, one species of Thiobacillus only grows well on surfaces with a pH between 9 and 6.5. However, when the sulfuric acid waste product they excrete decreases the pH of the surface below 6.5, they die off and another species, which can withstand lower pH ranges, takes up residence.

The succeeding species grow well on surfaces with a pH between 6.5 and 4. A new species takes over when the acid drops the pH below 4. The process of successive colonization continues until species, which can survive in extremely low pH conditions, take over. One such specie is Thiobacillus thiooxidans, which is sometimes known by its common name, Thiobacillus concretivorous, which is Latin for "eats concrete." This organism has been known to grow well in the laboratory while exposed to a 7% solution of sulfuric acid. This is equivalent to a pH of approximately 0.5.

Sulfuric acid attacks the matrix of the concrete, which is commonly composed of calcium silicate hydrate gel (CSHG), calcium carbonate from aggregates (when present) and un-reacted calcium hydroxide. Although the reaction products are complex and result in the formation of many different compounds, the process can be generally illustrated (see Table I "*Sulfuric Acid Reactions with Limestone Concrete*").

The primary product of concrete decomposition by sulfuric acid is calcium sulfate ($CaSO_4$), more commonly known by its mineral name, gypsum. From our experience with this material in its more common form of drywall board, we know that it does not provide much structural support, especially when wet. $CaSO_4$ is usually present in sewers and structures as a pasty white mass on concrete surfaces above the water line. In areas where high flows intermittently scour the walls above the water line, concrete structural deterioration can be particularly fast. It is generally believed by most investigators that the surface coating of gypsum paste somewhat protects underlying sound concrete by providing a buffer zone through which freshly produced sulfuric acid must penetrate. Because Thiobacillus bacteria are aerobic, they require free atmospheric oxygen to survive. Therefore, they can only live on the thin outer covering of any surface. This means that acid produced on the surface must migrate through any existing gypsum paste to reach sound concrete. By washing off the "protective" coating of gypsum with high flows or wet weather flows, fresh surfaces are therefore exposed to acid attack, which accelerates the process. Sewer cleaning practices and equipment should be checked to determine the degree of gypsum layer loss during cleaning and the effects of such cleaning on the ultimate pipe life.

The color of corroded concrete surfaces can also be various shades of yellow caused by the direct oxidation of hydrogen sulfide to elemental sulfur. This only occurs where a continuous high concentration supply of atmospheric oxygen or other oxidants is available. The upper portions of manholes and junction boxes exposed to high hydrogen sulfide concentrations are often yellow because of the higher oxygen content there.

Traditionally, efforts to control corrosion of concrete sewers have been directed at two links in the corrosion chain. The first link is <u>protection</u> of the concrete with a corrosion resistant barrier such as a coating. Experience shows that coatings delaminate from the old substrate over time because of 1) improper preparation of the old surface; or 2) inadequate or improper application in the field. The second link targets <u>reduction</u> <u>of</u> <u>harmful</u> <u>gases</u> by continuous and regular dosage of chemicals such a potassium permanganate, chlorine, oxygen injection, etc. directly in to the raw sewerage. Both of these treatments for these links in the chain of corrosion are costly and ineffective.

The third and previously untried link is a direct attack on the corrosion causing bacteria. Reducing the growth of Thiobacillus bacteria reduces production of sulfuric acid; and thereby, prevents its subsequent corrosion of concrete. We have chosen this approach, as it is effective, economical, and long lasting.

After years of research and many attempts of experimenting with different products, one product has been discovered that meets the above criteria, and is also safe for humans to handle (nontoxic to humans) and is water-soluble. This means that it can be mixed into the wet concrete where it becomes an integral part of the concrete.
No longer do concrete pipes and structures need to be coated - a method that is not effective. Thiobacillus bacteria can penetrate coatings and live happily on the concrete surface beneath the coating, and destroy the bond of the coating to the concrete. Instead, the concrete becomes an unfriendly environment to the bacteria, and they can no longer live in the minute pores and crevices of the concrete surface, secreting acid and destroying its host living quarters - the concrete.

It is interesting to note, even though it has been known since 1945 that the source of sulfuric acid in crown corrosion of concrete sewer pipes was Thiobacillus bacteria, all attempts to combat the corrosion was by lining or coating the inside of the concrete pipe. No attempt, which we know of, was ever made to stop or reduce the bacteria growth; and thus, the formation of sulfuric acid.

Our approach to reducing sewer corrosion or the elimination of it was to find a way to affect the acid-producing bacteria. One way would be to eliminate the H_2S gas. H_2S is formed beneath the liquid level within the slime layers on sewer piping, pump stations, and manholes. The slime layers are a barrier to dissolved oxygen and become host to anaerobic sulfide reducing bacteria (SRB). SRB use oxygen from sulfate ions (SO_4^{2}) found in wastewater to metabolize organic species in the wastewater. The metabolic process creates a sulfide ion by-product that is returned to the wastewater where it combines with hydrogen to form hydrosulfide. These ions further react to form aqueous hydrogen sulfide (H_2S). The dissolved H_2S is subsequently released into the airspaces of manholes, piping, and pump stations as the result of surge-flow turbulence. This results in the odors associated with sewer collection and treatment processes.

Numerous methods are available to control the generation of anaerobic sulfide in wastewater. Methods affect the oxygen balance in sewage, oxidize generated sulfide, react chemically with dissolved sulfide to form insoluble sulfide, or affect the sulfide generation capability of the sulfate or organic sulfur reducing organisms.

The methods include:

- oxygen injection in force mains, inverted siphons, U-tubes, hydraulic falls, and side streams
- chlorination
- hydrogen peroxide
- iron and zinc salts
- shock dosing with sodium hydroxide
- potassium permanganate
- sodium nitrate
- ozone
- bacterial cultures and enzymes.

All of the foregoing are repetitive measures which are not a lasting solution and over time can be very expensive.

The ideal method of reducing this type of corrosion (M.I.C.) would be to permanently affect the bacterial-cell growth or the pH of the concrete such that the bacteria no longer could grow and convert H_2S gas to H_2SO_4.

In 1993 an anti-microbial material, which affected cell growth by physically penetrating the thin-cell wall of bacteria, was introduced into the concrete market. This material was non-toxic to humans and other animals. It could be integrated into a polypropylene fiber, which in turn could be introduced into concrete, thus making the concrete an anti-microbial material. However, the anti-microbial affect was only on the fiber surface and not in the entire mass of the concrete. Later testing at a laboratory specifically adept in growing Thiobacillus bacteria, proved that this agent was not capable of affecting Thiobacillus cell growth. Not wanting to give up on this theory of stopping sewer corrosion, a search was made for a water-soluble agent, which would be non-toxic to humans, but would affect Thiobacillus bacteria. In June 1996 such a material was found and laboratory testing was initialized. Wafers of concrete mortar were prepared using this new material, Con$^{(MIC)}$Shield ™, in the mix water and also as brush-applied to untreated samples. All samples, including control samples, were treated with carbon-dioxide gas to lower the pH of the concrete surface to pH 9. Most bacteria, including Thiobacillus, do not grow at pH above 9. In the laboratory, there was 100% reduction in growth (see Table 2: *Thiobacillus Inoculum Test Results*).

The next step was to prepare samples for testing in a municipal sewer system. The test protocol called for weighing the samples in a saturated-surface dry condition, and reading the initial sample surface pH. A sewer manhole was selected, which had obvious corrosion taking place and an obviously high H_2S reading. The indicator needle went off the scale when the manhole was tested. The samples were suspended three (3) feet below the manhole cover and left there for three (3) months. At the end of three (3) months, weight and pH readings were taken. See Table 3 "*In-Situ Sewer Manhole Field Tests*" for results.

Discussion

Other methods of sewer-corrosion prevention or protection are expensive, require repetitive operations, need replacement, and are not 100% effective. History has proven this. The best way to stop the corrosion is to eliminate the sulfuric acid. The next best is to reduce the amount of sulfuric acid generated and thereby increase the longevity of the concrete. When added to this, a cement which resists the acid corrosion, the ultimate solution is achieved. This means that concrete that lasts perhaps only ten (10) years can be made to last indefinitely. In a non-acid condition, the concrete of the Roman Empire has lasted for over 2000 years. The anti-microbial agent Con^{MIC}Shield^{TM} can make everlasting concrete for use in new structures and for rehabilitating existing structures. The City of Atlanta has been using this anti-microbial material in new sewer construction since January 1997. Manholes using this material have been rehabilitated in Columbus, OH, Oskaloosa Co., FL, Mt. Prospect, IL, Miami, FL, and Corsica, TX In the USA alone billion$ are being spent annually to repair corroded concrete because of M.I.C. With these new materials, that spending does not have to continue.

Conclusion

The problem of H_2S generation can be partially solved with the injection of oxygen or other chemicals into the sewage flow. These are very high-cost maintenance solutions. To protect concrete pipe and structures from corrosion, coatings and liners have been used with some success. Only those instances where they were effective was the cost worth the expense. Where liners and coatings failed, it was very costly. With today's technology and the products available to stop M.I.C. in sewer systems, new construction as well as rehabilitation work can benefit greatly by adding ConShield TM for long lasting corrosion protection.

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TABLE 1
SULFURIC ACID REACTIONS WITH LIMESTONE CONCRETE

H_2SO_4 +	Ca,Si ⇒	$CaSO_4$ +	Si +	$2H^+$
H_2SO_4 +	$CaCO_3$ ⇒	$CaSO_4$ +	H_2CO_3	
H_2SO_4 +	$Ca(OH)_2$ ⇒	$CaSO_4$ +	$2H_2O$	

TABLE 2
THIOBACILLUS INOCULUM TEST RESULTS

SAMPLE	VIABLE COUNT	TIME	% REDUCTION
Control	1×10^7	24 hrs	0
Treated	0	24 hrs	100%

A bacterial suspension of Thiobacillus thiooxidans, Thiobacillus thioparus, and Thiobacillus denitrificans were aseptically pippetted evenly onto the surface of concrete wafers and incubated at 25^{O} C for 24 hours. Viable counts were then obtained using a modified NETAC method. Four test replicates were made per set and incubated at 25 ^{O} C for 26 days. The test material killed all of the organisms with a complete 100% kill in 24 hours. In addition to the viable counts, a pH change did not occur and no growth was detected microscopically.

TABLE 3
IN-SITU SEWER MANHOLE FIELD TESTS

Concrete Samples	INITIAL		FINAL		WEIGHT DIFFERENCE (GRAM)
	WEIGHT (GR)	pH	WEIGHT (GR)	pH	
Core from Concrete Pipe	894.3	11	891.4	3	2.9
Core from concrete pipe without ConShield	890.8	11	860.2	1	30.6