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Research Article

Investigation of Microbiologically Influenced Corrosion of Concrete in Sanitary Sewer Pipes and Manholes: Field Surveys and Laboratory Assessment

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Abstract

Microbiologically influenced corrosion (MIC) of concrete in sanitary sewer pipe and manholes is the result of dilute sulfuric acid (H_2SO_4) dissolving the cement matrix. The acid is produced by a complex series of chemical and biochemical reactions. The objectives of this paper are: (1) to review the basic science of the MIC process starting with the various biological processes leading to the production of dilute sulfuric acid; (2) to discuss historical attempts to fortify concrete; (3) to present methods to reduce odors and corrosion; (4) to evaluate the technology behind the use of antimicrobial admixture. The literature review and authors' on-site and laboratory investigations suggest that MIC of concrete is a complex process that involves varied surface interactions. The addition of liquid antimicrobial additive as per ASTM standard procedure shows the resistance of concrete to MIC and its direct relation with the mixing time of admixture. Many empirical inputs like corrosion areas, corrosion rates, the impact of cement, and aggregate types varying with installation and repair of sewer structures are identified. The results of this study show that with the use of antimicrobial in the concrete, there was no growth of Thiobacillus bacteria and hence no acid production. This research

facilitates both the science and long-term field experiences for the use of antimicrobial technology to provide reductions in the acid causing bacteria in sanitary manholes, pump stations and other concrete structures.

Keywords

Manholes; microbiologically influenced corrosion; pipelines; sanitary sewers; hydrogen sulfide

1. Introduction

Since the 1970s there has been ever increasing regulations on sanitary sewer collections systems. The efforts have focused on reducing Inflow and Infiltration (I and I) as well as reducing industrial chemicals and minerals [1, 2]. Combined sewers are being divided as they can. In addition, efforts have focused on reducing household flows to the system with fixtures such as low volume commodes, front loading washing machines, etc. [3-5]. While all of these things are great ideas especially when it comes to reducing the discharge from Wastewater Treatment Plants (WWTP) they are proving to have a serious detrimental effect to the collection system's concrete structures which includes concrete pipe (both gravity and pressure) access holes, pumping stations and parts of the treatment plants themselves. These concrete structures are being chemically attacked by dilute sulfuric acid produced by bacteria in a process commonly known as Microbiologically Influenced Corrosion (MIC) (Figure 1) [6].
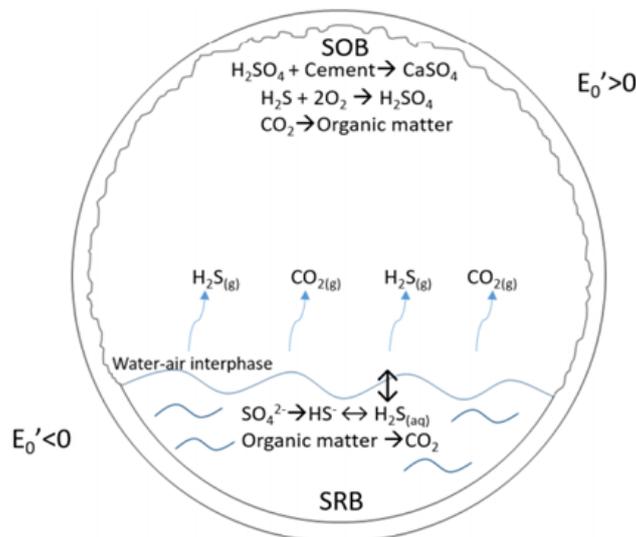

Figure 1 Schematic of MICC process on a cross-section of a concrete sewer pipe [6].

High levels of I and I improved velocities in the lines keeping the sewage fresher (less septic) by reducing its transit time. The higher flow rates also help to keep the inverts (floors) of the sewers scoured. The industrial waste often time acted as an inhibitor to certain biological reactions necessary for the complex MIC process to develop [6, 7].

Over the years many attempts have been made to fortify concretes directly against this acid attack. Methods are needed for both rehabilitation projects as well as new construction. Many types of polymer coatings and embedded plastic linings have been developed but have proven expensive and unreliable with relatively short life spans compared to the 50 to 100-year service life required by the municipal world [7]. Rather than fight the acid, the idea was to break the biological chain that produced the acid. The technology centered on treating the entire thickness of the concrete or repair mortar with a powerful antimicrobial liquid additive. It is a water-soluble additive that becomes a constitutive part of the concrete in which it is added and transfixes the membrane of acid causing Thiobacillus bacteria and reduces the corrosion before it begins [8-10].

2. Literature Review

2.1 Microbiologically Influenced Concrete Corrosion

Microbiologically influenced concrete corrosion (MICC) is a chronic issue affecting sewer systems worldwide. The continuous deterioration and degradation of the wastewater system through the effect of MICC results in a continuous loss of existing vital infrastructure, which increases the necessity for sustainable mitigation measures [1-3]. The damage caused by MICC is not only leading to substantial economic loss, but also severe environmental and health-related problems due to the accompanied generation of hazardous gases [5-10]. The corrosion rate in some severely affected concrete manholes were recorded by [11], with loss of concrete exceeding 1 cm/year, which shortened the service life of the structure to only ten years. Furthermore, the release of harmful gases such as hydrogen sulfide (H_2S), carbon dioxide (CO_2), ammonia (NH_3), methane (CH_4), and other volatile organic compounds (VOCs) represents a serious health risk for both the wastewater system operators and surrounding neighborhood residents [11]. Infrastructure maintenance costs in Germany and England were estimated to spend over \$533 & \$95 million each year, respectively [11-13]. Similarly, the United States national rehabilitation cost exceeded \$3.3 billion in 2009 and was expected to increase by more than \$390 billion over the next 20 years [13-15]. Nevertheless, to date, no viable concrete or admixture has been developed to efficiently withstand aggressive MICC conditions over its service life [11]. Therefore, proactive measures and new technologies are much needed for managing MICC in sewer systems.

Over the past 30 years, several research studies have been conducted to investigate the MICC mechanism in sewer systems. Despite these efforts, limited literature is available to develop an efficient, long-lasting mitigation methodology. The following section provides an inclusive review of the previous studies on MICC, particularly the deterioration mechanism and the mitigation factors. The discussions herein also include several previously studied mitigation technologies and testing measures to evaluate the performance of these mitigation treatments [15-18].

2.1.1 MICC Process

Proper MICC investigation requires a full understanding of the chemical and biological mechanisms responsible for the corrosion rates observed within sewer systems. Several researchers [1-18] summarized the MICC mechanism as follows. MICC is a complex interlocking process that occurs as a sequence of biogenic sulfate reduction and re-oxidation reactions. The MICC process starts when anaerobic sediment layers accumulate in manholes and slow-flowing sewer pipes due

to long retention times, exceeding 12 hours [10-15]. Subsequently, complex organic molecules (COM) are transformed to low molecule organics (LMO) during the initial fermentation processes, accompanied by CO_2 generation. Thereafter, sulfate-reducing bacteria (SRB) consume the resultant LMO during sulfate respiration, leading to the production of hydrogen sulfide (H_2S) accompanied by some other gaseous compounds [15-23].

After being liberated into the concrete pipes and manholes' confined atmosphere, these gaseous compounds accumulate and diffuse into the moist concrete pore structure [11-20]. Along the surface and inside concrete pores, colonized sulfur-oxidizing bacteria (SOB) re-oxidize the H_2S producing biogenic sulfuric acid (H_2SO_4). Acidophilic (SOB), mainly A. Thiooxidans and A. Ferrooxidans, are thought to be the key players in this process with an optimum growth occurring around pH ~ 2. The generated sulfuric acid H_2SO_4 will react with the cement compounds, mainly calcium and aluminum minerals, forming expansive minerals like ettringite and gypsum [15-25]. Eventually, the continuous H_2SO_4-production process and resultant biogenic acidic attack, lead to pH reduction and subsequent concrete deterioration [26-30].

2.1.2 Concrete Deterioration Phenomena

The fundamental deterioration processes that occur due to the aerobic progression of MICC were initially summarized by [10-30]. Starting from the strongly alkaline initial stage of concrete with a pH of ~ 13, Islander proposed the detailed corrosion model which has been adapted later by [11]. The model breaks the entire sewer corrosion process into three distinct corrosion phases as follows. The initial stage accompanies a surface pH drop from approximately 13 down to 9 due to chemical oxidation of CO_2 within the concrete and H_2S gas. This phase is controlled by the abiotic acid-base reaction, the initial stage of corrosion results in carbonation weak acids (e.g., thiosulfuric or polythionic). The microbial growth within this stage is commonly thought to be limited by the alkaline conditions typical of fresh concrete [15-25].

Limited material loss occurs during this stage. However, leaching of calcium-based hydroxides (e.g., CH, C-S-H) occurs when sulfate fluids disperse into the pores. Furthermore, concurrent precipitation of expansive sulfate salts is typically observed within the interstitial transition zone (ITZ) between the bulk cement and aggregates. This leads to an increase in pore pressure that may cause a loss of structural stability and initial formation of microcracking [30-40]. This phase is analogous to passivation of the high concrete surface pH, which typically would inhibit the growth of sulfate oxidizing bacteria. The subsequent stage begins with the colonization of neutrophilic sulfur-oxidizing bacteria (NSOB), which initiates when conducive conditions are established, primarily a surface pH ~ 9 [20-30].

Under moist conditions, SOBs oxidize distinct sulfur compounds to generate sulfuric acid (H_2SO_4) [20-30]. The continued production of biogenic H_2SO_4 depresses the pH over time from ~9 to ~4, leading to sulfate salts formation and elementary cementitious (CH) matrix degradation. No appreciable mass loss of cementitious material typically occurs during this phase [20-35]. However, the formation of secondary ettringite, observed at the gradient between the healthy (non- corroded) and severely corroded concrete, which triggers additional cracks and furthers concrete degradation [20-30].

Once the pH decreases below 4, the final corrosion stage begins. Acidophil sulfur- oxidizing bacteria (ASOB), commonly A. Thiooxidans and A. Ferooxidans, start dominating the biofilm [30-35].

Subsequently, rapid pH reduction prevails, leading to the dissolution of the calcium-silicate-hydrate (C-S-H) structure of the cement and deterioration of the concrete. A rapid loss of concrete material occurs in this final stage of MICC. For instance, significant corrosion rates of over 1 cm/year were reported [30-40].

The appearance and dominance of both NSOB and ASOB throughout the biotic phase of MICC is mainly influenced by pH, trophic (nutrient) availability, and the utilization of different sulfur compounds like H_2S, S_0, S_2O_3 [30-40]. Although SOB are more prevalent, heterotrophic bacteria and fungi were also observed in the biofilm of several deteriorated wastewater systems [11]. The existing gaps in current understanding of the biogenic and chemical corrosion need to be further investigated to produce materials durable in aggressive environments and to develop effective strategies to control MICC [10-40].

3. Objectives and Scope

The objectives of this paper are: (1) to review the basic science of the MIC process starting with the various biological processes leading to the production of dilute sulfuric acid; (2) to discuss historical attempts to fortify concretes both directly and indirectly; (3) to present methods to reduce odors and corrosion by treating the raw sewage; (4) to evaluate the technology behind the use of antimicrobial admixture using both field surveys and laboratory assessment around the Texas, USA. The literature review and authors' on-site and laboratory investigations suggest that MIC of concrete is a complex process that involves varied surface interactions. The addition of liquid antimicrobial additive as per standard ASTM D4783 procedure shows the resistance of concrete to MIC and its direct relation with the mixing time of admixture. Many empirical inputs like corrosion areas, corrosion rates, the impact of cement, and aggregate types varying with installation and repair of sewer structures are identified. The results of this study show that with the use of antimicrobial in the concrete, there was no growth of Thiobacillus bacteria and hence no acid production.

4. Method Description

To determine the resistance of treated cementitious materials, either concrete or mortars, to microbial attack by challenging the test specimen with a bacterial culture, inoculated specimen is stored at 30°C for 24 hours. If the inoculated specimen shows microbial growth on the streak plate or test surface after 72 hours, the test is discontinued, and the sample specimen is reported as not resistant to attack. whereas if the culture shows no growth, it is reported as resistant to attack and positive for the presence of the anti-microbial agent. This test method is used to demonstrate whether a cementitious material is sufficiently protected with anti-bacterial additive to resist attack by bacteria. After 24 hour of bacterial preparation, Serratia Marcescens is grown on nutrient agar at 30°C. The plates are incubated for 48 hours at 30°C. Result is positive when there is no growth of Serratia Marcescens on the agar plates within a 48 hour period and negative result is shown by the growth of red colonies of Serratia Marcescens on the agar plates which demonstrates that the antimicrobial agent was not present in the sample in sufficient concentration to kill the indicator microorganism in 48 hours. If the inoculated specimen shows microbial growth, the sample specimen is reported as not resistant to attack and negative for the presence of the anti-bacterial additive.

5. Mitigation of MICC

There are three methods that could be used to improve concrete performance in general but offer limited success in the presence of acids. These are as follows: (1) Reduce lightly bound calcium compounds; (2) Reduce permeability; and (3) Buffer the concrete with limestone/sacrificial aggregates [41-45].

5.1 Reducing Calcium Compounds

The use of pozzolans such as fly ash and colloidal silica, while producing concretes with excellent mechanical properties and low permeability, still feature an intrinsically rich calcium oxide-based hydrate system. Pozzolans work in two ways to improve basic mechanical properties. First, they are rich in amorphous silica and will react over time with the calcium hydroxide hydration by-products to form additional calcium silicate hydrates. These additional hydrates are strong, dense and offer less mobility to ions versus the watery pore space and calcium hydroxide. Secondly, they can improve the workability of concrete allowing for reduced water content [41-45].

The fine rounded fly ash particles accomplish this by a combination of their size and shape. In general, the benefit is not fully realized unless powerful dispersing admixtures (water reducer and superplasticizers) are employed. More expensive materials like fume silica (the ultra-fine *dust* collected during the production of metallic silicon) produce even higher results provided they are well dispersed [41-45].

The benefits of pozzolans in general can only be appreciated when very high-quality mix designs are used. Otherwise, cheaper but low performing concrete will result. Ground blast furnace slag is not exactly in this class as often times the chemistry/minerology is similar to Portland cement, which is rich in calcium silicates and tricalcium aluminates. Likewise, finely ground quartz silica, while beneficial over time in several ways, is not as reactive as the amorphous silica found in true pozzolans [41-45].

5.2 Reduce Permeability

5.2.1 Cement modifiers

Reducing porosity/permeability by lowering the w/c or replacing a portion of Portland cement with pozzolanic supplementary cementitious materials (SCMs) are traditional strategies to prevent the ingress of deleterious substances such as chlorides and sulfates. There has much improvement in the field of reducing permeability with additives. This included the combination of water reducing admixtures, cement substitutions with pozzolanic materials as mentioned above and cement modifiers such as latex and acrylic emulsions. These mechanisms have their applications where the acid attack is due to the penetration of the hydrate structure by the action of a mobile ion [46-49].

Various chemical reactions take place with either reinforcing steel or the hydrate system and disruptive stresses develop causing concrete degradation. Despite the reductions in permeability, the rich calcium-based cement paste remains very reactive to the *direct active surface attack* caused by dilute acids. As noted in the industry, no knowledgeable manufacturers of these products recommend them for MIC applications today [46-50].

5.2.2 Crystalline Forming Water Proofing Admixtures

These have two important functions: a) they can dramatically reduce the permeability of even mediocre concretes and b) the crystalline growth can continue so long as there is moisture and reactive mineral complexes available within the cement gel structure and space for them to grow. This last point is most important for healing cracks which inevitably form in dams, tunnels, tank structures, thin linings etc. Careful aggregate grading is essential to reduce the paste volume requirement and therefore keep the mix economical [34].

There are several types of concrete deterioration that are caused by penetrating ions such as sulfate attack from sea water and de-icing salts. The crystalline forming admixtures have real value in these situations. In recent years, there has developed some misunderstanding that these crystalline forming additives are affective against MIC. Immersion testing of the *passive* type can lead to false indications that these types of admixtures do in fact show some improved performance against acids. In fact, some manufacturers report testing in solutions of sulfates. This again is not to be confused with corrosion from dilute sulfuric acid. Sulfate attack and MIC are two completely unrelated problems. These additives cannot change the basic chemistry of the calcium oxide rich cement structure. Keep in mind the MIC chemical attack is a surface phenomenon and not a depth attack and the acid are constantly being generated [50-53].

While permeability reductions might show some ultra-short-term improvement in a concentrated clinical acidic environment, a matter of a few weeks cannot be the basis for any long-term designs in the range of 25, 50 and 100 years. As an example, liquid immersion tests are typically run for say 12 weeks. During this period, control specimens based on typical OPC mortars may lose half their weight in this period. Specimens produced with mortars fortified with a crystalline forming admixture are reported as having lost only half as much. Again, this type of performance offers no logical means for a long-term design necessary for municipal construction and repairs [54-57].

5.2.3 Buffering the Concrete with Limestone Aggregates

The concept is to use aggregates that have chemistry such that they consume some of the acid and protect the lime rich cement paste. This requires a firm understanding of many factors in a particular sewer so that an appropriate loss rate can be calculated and then the structure's wall thickness increased to compensate for the loss of concrete. In many instances, the wall thickness is not increased, and the life span incorrectly determined by using 100% of the base wall thickness. In typical concretes, these aggregates are generally limestone based and may contain dolomites as well [34].

A special case of this notion is with repair products based on calcium aluminate cement and very hard and reactive fused calcium aluminate aggregates. The benefit in the sewer application is due to both the improved resistance of the cement itself and then to the powerful buffering capacity of the entire mortar being rich in lime. Nevertheless, typical H_2S and biological availability are enough to ultimately cause deterioration. The high cost of the raw materials combined with only an improvement in life span have kept the use of these materials to a minimum. The materials are often seen to be effective in the short term of 7 to 10 years but not necessarily long enough to be judged as cost effective ultimately [54-57].

5.3 Other Means to Disrupt the MIC Chain

There are generally five general options for addressing the complex MIC process which may be summarized as follows: (1) Take no precautionary steps – wait, hope and repair; (2) Coat the concrete; (3) Embedded plastic liners; (4) Chemically treat the raw sewage; and (5) Immunize the concrete - like a vaccine [50-59].

5.3.1 Take No Precautionary Measures

MIC is intrinsic to all unprotected concrete sanitary sewer structures and it is only a matter of time that some deterioration will occur. Keep in mind that conditions are generally getting worse and not better. As evidenced by many cities which encountered only limited MIC until implementing measures that eliminated direct venting and reduced extraneous inflows and infiltration into their systems [34].

5.3.2 Placing an Impermeable Barrier between the Acid and the Concrete

This concept involves placing an acid resistant material on the concrete. The acid is still produced but the barrier protects the concrete. This sounds simple but in fact is difficult and costly to accomplish. Two common methods are reviewed below [34-48].

5.3.3 Polymeric Coatings

This is a simple sounding concept and can be very effective in a well-controlled high value-added setting. This is just not the case in sanitary sewer construction and repairs. Concrete is a moist high alkaline material (in the fresh state) and these 2 conditions are incompatible with applying a sound coating. There are many types and manufacturers of concrete coatings. The most common are epoxy and urethane based. They rely on adhesion to the concrete substrate to maintain their mechanical integrity. This adhesion is very much disrupted by high alkalinity (such as with young fresh concretes) and moisture [40-50].

This type of surface treatment is subject to delamination, pin holes/bubbles, scratching, etc. In a clean laboratory environment, it is possible to coat concrete with very good results. In a high-capacity modern precast shop or in the field, conditions for a successful coating project are diminished [40-57]. Another type of coating is a sodium silicate (water glass) spray. These are often called surface hardeners. They are sprayed on concretes after some initial curing and the silicate ions attempt to link-up with some calcium hydroxide hydrates and form a tough, less permeable surface. This has merit on industrial floors as an example. As discussed above though, MIC is a process by which dilute acids dissolve the lime rich binder matrix. No amount of surface hardening is going to help [40-62].

5.3.4 Embedded Plastic Linings

These products have been around for many decades and while the liner material itself is very corrosion resistant, the actual installation of the liner remains costly and not without risk. The installation process requires wet casting with relatively high slump concrete mixes. There is the risk of external water pressure penetrating the concrete and causing the liner to bulge and rupture [62].

5.3.5 Chemical Additions

There are three basic ways to control the build-up of hydrogen sulfide in the sewers: Prevent its formation in the first place through engineering that eliminates septicity; convert the H_2S after it has formed but while it is still in solution; and remove it from the sewer's atmosphere (both with and without odor control) [40-62].

Sulfate is a polyatomic anion with the formula SO_4^{2-}. Once the SRB have acted on the sulfate, three possible forms of sulfides can exist in the water and only one in the atmosphere. In the water, the balance is a function of pH. Hydrogen Sulfide (H_2S) can exist dissolved in water at high concentrations. In solution, it does not cause an odor or corrosion issue for concrete (metals are another issue). It will not react with water to form sulfuric acid. Hydrogen Sulfide is the only form which can escape the aqueous solution and exist as a free gas. The other two forms are Bisulfide (HS^-) and Sulfide (S^-), neither can leave the water and do not contribute to color, odor or corrosion issues. H_2S is favored at pHs below 7, HS between pHs of 7 to 12 and S at pHs greater than 12 [45-62]. In general, all of the techniques discussed below involve equipment along with varying degrees of supporting infrastructure and consumables. They appear to be used where odor is the driving concern.

Sodium Hydroxide can be used to increase the pH of the wastewater and in turn inactivate the sulfate reducing bacteria. This has no effect on the sulfides already present. Chlorine Dioxide is now readily available and when used in high dose rates it can destroy the biofilm which contains the sulfate reducing bacteria. It will also oxidize H_2S directly with enough time. Sodium Nitrate and Calcium Nitrate retards septicity and promotes the activity of denitrifying bacteria at the expense of the sulfate reducing bacteria [50, 51]. This type of activity can improve the overall operation of the wastewater treatment system. The by-products are various nitrogen containing gases and ultimately just nitrogen. Ozone injection interferes directly with the bacteria cell membranes. It is an unstable gas and must be generated on site. High capital and operational cost remain an issue. Evolving technology involves adding specially developed bacteria that compete with the SRB for available nitrogen and carbonaceous compounds essential for the SRB to thrive [52-55].

Once the H_2S has formed in solution many chemicals can be added in an attempt to oxidize H_2S. Assuming the liquid waste stream is now rich with H_2S still in solution, the idea is to oxidize it back into elemental sulfur or a complex sulfate. The candidates for chemical oxidizers range from ozone, hydrogen peroxide, potassium permanganate, chlorine dioxide, hypochlorus acid, oxygen and various forms of hypochlorite. The preference of one over the other is a complex puzzle of cost, oxidation potential and many other interactions with the complete treatment process. Additionally, various iron salts can react with sulfides to form insoluble metal sulfide. Combinations of chemicals are common [50-56].

In the third case, H_2S gas is in the atmosphere. It can be detected by the human nose in concentrations as low as 0.2 ppm. It has been measured in sewers as high as 1,500 ppm and there are many opinions as to just what level MIC will proceed. It will proceed at any concentration, but the rate of corrosion will be strongly affected by the H_2S concentrations and many other factors as discussed above. A common idea is to ensure that only aerobic conditions exist in the liquid phase. Many variations on the theme have been tried. The solubility of oxygen or air in water is very low and so the dosing would have to be very low and at frequent locations. Proper process control is difficult, and odor and corrosion problems are sometimes made worse [55-61].

6. Antimicrobial Concrete Admixture

A new approach for protecting concrete is to make it uninhabitable by the bacteria that convert the H_2S into sulfuric acid in the first place. The used antimicrobial is an EPA registered anti-bacterial additive that is added to fresh concrete as it is mixed [61-63]. The breakthrough in the 1990s was a means to stabilize the antimicrobial chemical in an aqueous solution that is readily dispersible in a high pH wet concrete mix, and then secondly stabilizes it to be compatible with fresh highly alkaline concrete until it hardens and lastly and most importantly ensure it remains active in the hardened concrete over the long term. As a thin liquid, the additive readily disburses throughout the concrete mix and ultimately bonds molecularly with all the concrete's ingredients [34, 62].

It can be used in ready mix or precast operations and in many ways for repairs to existing corroded structures by adding the admixture to a cementitious repair mortar (either directly to the mixer or in the batching water) and then applying the mortar by various means including centrifugally spinning, guniting, hand troweling, etc. The antimicrobial admixture is not a lining or coating and will not peel or chip or wear off. It is as tough as the concrete. In new construction, it is added by the concrete producer and as such no other action is needed in the field [62].

Workers install the concrete/concrete products as it they were of ordinary composition. Colorants can be added at the plant to provide visual proof of the admixture. For repair projects involving mixed onsite mortars the antimicrobial additive is simply added first to the batching water as mentioned above. A discussion on the chemistry of the antimicrobial is as follows.

6.1 Role of the Long Chain Carbon Molecules in the Antimicrobial Mechanism

Figure 2 and Figure 3 show that while it is initially a liquid chemical, it strongly bonds with every particle in hardened concrete and does not rely on a chemical reaction to kill bacteria. "The active antimicrobial ingredient in the antimicrobial is generally categorized as a complex Quaternary Ammonium Silane (QAS) antimicrobial agent. It has been modified to function within cementitious materials like concrete and repair mortars [34]." The manufacturing process is likewise a complex series of operations. When ammonium salts are reacted with certain organo- siloxanes they form an integrated system, which can then be applied to almost any surface thus forming an invisible and durable antimicrobial protection. Surface applications have a limited life span and for concrete to be protected in long term sanitary sewer applications, the antimicrobial must be mixed throughout the fresh concrete or mortar [62].

POWERFUL COMBINATION (SiQac)
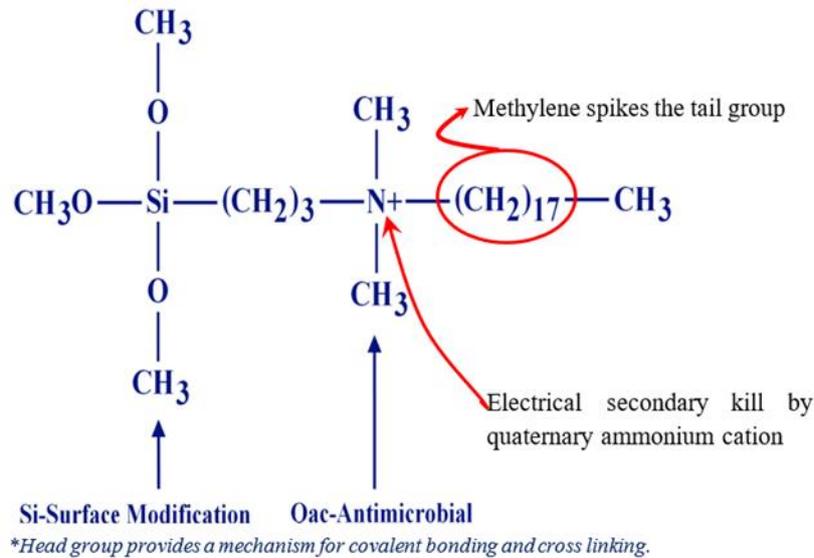
Organosilane Quaternary Amine

Figure 2 SiQac Chain [62].

Figure 3 Action of microbes against SiQac antimicrobial coating [62].

The QAS type molecule has what is considered a head group (containing the silane functional group and cationic ammonium moiety); and a tail group (hydrophobic – water shedding, carbon-chain). By virtue of these chemically distinct groups essentially a bi-functional molecule: with the head group providing a mechanism for covalent bonding and cross linking, and the cationic group and the tail group driving the interaction of the molecule with microbial membranes leading to the antimicrobial performance [34, 62].

The head group is known to react with surfaces by condensation thus forming a covalent linkage that is stable. This linking can occur both at a surface, and/or by cross linking with itself to form networks within concrete. Once the concrete is uniformly treated, it is the strongly anchored tail group that forms a rigid sharp mechanical structure that physically pierces and ruptures the cell membranes of microorganisms [34, 62].

There is a very delicate balance of hydrostatic pressure and chemistry inside the cell which is most different and not compatible with the conditions outside the cell. Once punctured, the cell becomes inactive with death of the target bacteria resulting. "With this antimicrobial distributed uniformly throughout the mix, all exposed surfaces provide a mode of antimicrobial activity. The positively charged tail group physically takes the form of long sharp mechanical spikes. There is no chemical exchange involved in the kill thus there is no chemical consumption, and the effectiveness of the antimicrobial remains unaltered [34, 62].

7. Results

To evaluate the antimicrobial technology, both field surveys and laboratory assessment around the Texas, USA were done as discussed below.

7.1 Field Surveys

Field surveys were conducted around the Texas, USA to study the use of antimicrobial additive in the protection of MICC for sanitary sewer pipes and manholes. Some of the surveys are discussed as below.

7.1.1 Low Branch Lift Station City of Mansfield, Texas, USA

A design consulting company specified antimicrobials to treat some 1,600 cubic yards of cast-in-place concrete at the Low Branch Lift station in Mansfield, Texas, USA as shown in the Figure 4.

Figure 4 Low branch lift station in the city of Mansfield.

The liquid admixture was used as an antimicrobial in the construction of the lift station and has been successful in the prevention of the MIC in the concrete as shown in the Figure 5.

Figure 5 Inside view of lift station.

7.1.2 Air Releasing Valve Box at Grand Prairie, Texas

Air release valves as shown in Figure 6 were installed on two large pressurized force mains. The valves were installed in underground concrete vaults with lids. The atmosphere inside the vault routinely features H_2S concentrations between 200 and 400 ppm and within nine years several inches of concrete had been destroyed. Figure 7 shows the walls of the valve box after pressure washing.

Figure 6 Concrete valve box after 9 years of MIC.

Figure 7 Walls of concrete valve box after pressure washing.

In this rehabilitation project, the liquid antimicrobial admixture was added to the high-performance cementitious repair mortar that was gunited in place. The structural integrity was restored and long-life protection from MIC was assured by the antimicrobial additive. It can be seen in the Figure 8.

Figure 8 Air release valve box 3 years after repair.

7.1.3 Pre-cast Antimicrobial Manholes in DFW Metroplex, Texas, USA

Around the Texas, USA, an average of 600 cubic yards of precast antimicrobial manholes containing the liquid antimicrobial as shown in the Figure 9 are installed every month. These are precast off site and transported to the job site. In this case a red pigment has been added to the fresh concrete to provide long term ease of identification.

Figure 9 Pre-cast antimicrobial manholes.

7.2 Laboratory Assessment

In addition to the field surveys, laboratory assessment to test the presence of antimicrobial in the concrete samples was done. The samples identified as R-60 and R-60-1.1 were analyzed to ASTM D4783 procedure by the addition of one of antimicrobial additive. The samples were carefully conditioned to reduce the surface pH and alkalinity and a cell suspension of Serratia Marcescens was prepared, estimated at 1x107 cfu.ml. Thereafter, the suspension was placed on the sample surface and allowed to dry. Further, the samples were incubated for 24 hours. This was followed by a cell recovery method and then the plates were re-incubated for 48 hours. After 48 hours of incubation, if the sample has light pink colonies, it indicates the absence of antimicrobial whereas if sample has no growth of colonies it indicates the presence of antimicrobial admixture [34, 62].

7.2.1 Presence of Antimicrobial Admixture

Laboratory test results in Table 1 show that with the addition of one of the antimicrobial admixtures and after 48 hours of incubation, sample 1 had light pink colonies indicating the absence of antimicrobial admixture whereas sample 2 had no growth of colonies indicating its presence [34, 62].

Table 1 Results for presence of antimicrobial admixture in concrete samples [34].

Sample	Identification	Observation	Result
1	R-60	Light pink colonies	Antimicrobial admixture absent
2	R-60-1.1	No growth of colonies	Antimicrobial admixture present

Figure 10 shows pink colonies in the sample 1 indicating growth of bacteria and absence of antimicrobial admixture whereas Figure 11 shows no growth of bacteria in the sample 2 indicating the presence of antimicrobial admixture. The antimicrobial chemical showed resistance to the growth of bacteria that produces hydrogen sulfide in the anaerobic conditions and was able to protect the concrete from microbial corrosion [34].

Figure 10 No Growth of Pink Colonies.

Figure 11 No Growth of Pink Colonies.

8. Conclusions and Recommendations for Future Research

There is a considerable biological activity in sanitary sewer collection systems which is complex and produces very corrosive sulfuric acid in municipal sewer systems everywhere irrespective of climate or geography. Due to the presence of calcium-based minerals in the binder phase, typical concretes cannot tolerate the corrosive sulfuric acid. 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 the essential feed stock for the MIC 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.

The destruction of the concrete is a surface affect. The acid causes an immediate disassociation of the calcium and associated hydroxide radicals resulting in non-structural calcium sulfate hydrate complexes and water as the by-products. The corrosion by-products are not stable and provided zero structural value. These corrosion by-products do not slow the attack or block further production of acid. The immediate surface destruction far out paces any penetration of the acid.

The antimicrobial admixture when mixed with fresh concrete is resistant to the colonization of Thiobacillus bacteria. Without the bacteria, H_2S gas will not be converted to sulfuric acid. Without the acid, there will be no deterioration of the concrete. Detailed laboratory studies show that the long carbon chains associated with the nitrogen atom mechanically penetrates and ruptures the cell

membrane completely disrupting the Bacteria's integrity. Further, the longer the chain, the greater is the antimicrobial impact.

A secondary action involves the highly charged ammonium structure which induces an ion exchange reaction between the positive charges on the surface and the cations inside the cell membrane that causes further bacterial cell disruption. The liquid antimicrobial admixture is easily added to fresh concrete and requires no other special efforts in batching the concrete or installing materials in the field. Protection from MIC with an antimicrobial admixture is completely compatible with various means to control odors.

There is a need for a reliable simple field test that can confirm the presence of the antimicrobial admixture in hardened concrete. There is a need to model H_2S production and accumulation along with corrosion rates in the sanitary sewer structures. There is a concern that acid could be generated upstream in various pipes and structures and then this acid could produce an acid rich atmosphere that could migrate downstream and attack concretes protected with the antimicrobial that are otherwise not prone to classical MIC. Study is needed on the subject.

As the deterioration of concrete is a complex process that involves varied surface interactions possibly other than classical MIC there is a need to better understand other empirical inputs as well that vary with every installation. In the future, longer H_2S exposure time and frequent re-inoculation of concrete specimens with Thiobacillus bacteria may results in more uniform corrosion across all samples. Detailed examination of the specific points where the corrosion began and the migration of the microbial community along the specimen surface are needed. Furthermore, finding better ways to continuously monitor the corrosion process would be of great help.

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Author Contributions

Both the authors listed have made a substantial, direct, and intellectual contribution to the work, and approved it for publication.

Competing Interests

The authors declare no conflict of interest.

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