

Final Report:
**Investigating and Reporting Solutions for Microbiologically
Induced Corrosion of Concrete in Sanitary
Sewer Pipe and Manholes**



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Executive Summary

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. 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. Also laundry detergent manufacturers are being pressured to reduce the phosphate contents. 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 Induced Corrosion (MIC).

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 invert (floors) of the sewers scoured. The industrial waste often times acted as an inhibitor to certain biological reactions necessary for the complex MIC process to develop.

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. In 1996, a new approach was introduced. The new technology was an additive for concrete.

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. The product, Con^{mic}Shield[®], has successfully been protecting concrete sanitary sewer structures from MIC for 21 years. 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.

This report reviews the basic science of concrete, cements, concrete deterioration in general and then the MIC process starting with the various biological processes leading to the

production of dilute sulfuric acid. A discussion is offered on some historical attempts to fortify concretes directly and then indirectly. A short review is offered on methods to reduce odors and corrosion by treating the raw sewage. A review of the technology behind Con^{mic}Shield[®] is offered and then some recent field surveys around the Dallas Fort Worth (DFW) area and lab testing verification as per the ASTM D4783 modified standard are discussed. Results show that with the use of Con^{mic}Shield[®] in the concrete, there was no growth of Thiobacillus bacteria hence no acid production; and therefore, no corrosion. Also, appendices A, B and C have been incorporated into the report which contains Laboratory test results, New Product Review (NRP) process report on Con^{mic}Shield[®] and technical presentations respectively.

The results of this study provide both the science and long term field experiences which allow the engineering community to safely rely on Con^{mic}Shield[®] antimicrobial technology to provide reductions in the acid causing bacteria in sanitary manholes, pump stations and other concrete structures.

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CHAPTER 1

INTRODUCTION

Concrete remains one of the fundamental materials of choice in sanitary collection and treatment systems. From the vast tanks needed in treatment plants to manholes, large pipes, pump stations and various tunneling techniques, it is the most cost effective, durable and adaptable construction material. However, the concrete's intrinsic lack of chemical resistance to dilute acids results in its corrosion and destruction. As a result of this type of corrosion, concrete structures have a persistent, costly, unpredictable and disruptive maintenance history often times calling for expensive difficult repairs or complete replacement.

Microbiologically Induced Corrosion (MIC) is the main source of concrete deterioration in the sanitary sewer structures. The destruction is caused by dilute sulfuric acid continuously being generated by bacteria that digest Hydrogen Sulfide gas (H_2S). This foul smelling gas is produced by Sulfur Reducing Bacteria (SRB) present under the waterline inside the sanitary sewers. The problem of MIC is not limited to certain climates or geography. It occurs in all municipal sewer systems to some degree. Over the past 70 years, attempts to fortify concrete against direct acid attack have proven fruitless.

1.1 Objectives

The primary objective of this study is to investigate and report solutions for eliminating Microbiologically Induced Corrosion (MIC) of concrete in the sanitary sewer pipe and structures which drastically increases the service life of the sewer system.

CHAPTER 2

LITERATURE SEARCH

2.1 Concrete Corrosion

Microbiologically Induced Corrosion (MIC) also known as biological sulfuric acid attack is the main source of concrete deterioration in the sanitary sewer structures. One general process describing MIC in sewer systems has been well accepted and involves a sulfur cycle in the concrete structure, starting with sulfate reduction in the submerged areas. This is followed by transport of hydrogen sulfide (H_2S) into the sewer atmosphere, and ends with sulfuric acid (H_2SO_4) production by a sulfur oxidizing bacteria (SOB) biofilm in the pipe's crown and above the waterline (Parker, 1951). Figure 2.1 shows the schematic representation of the biochemical processes contributing to MIC of a concrete sewer pipe.

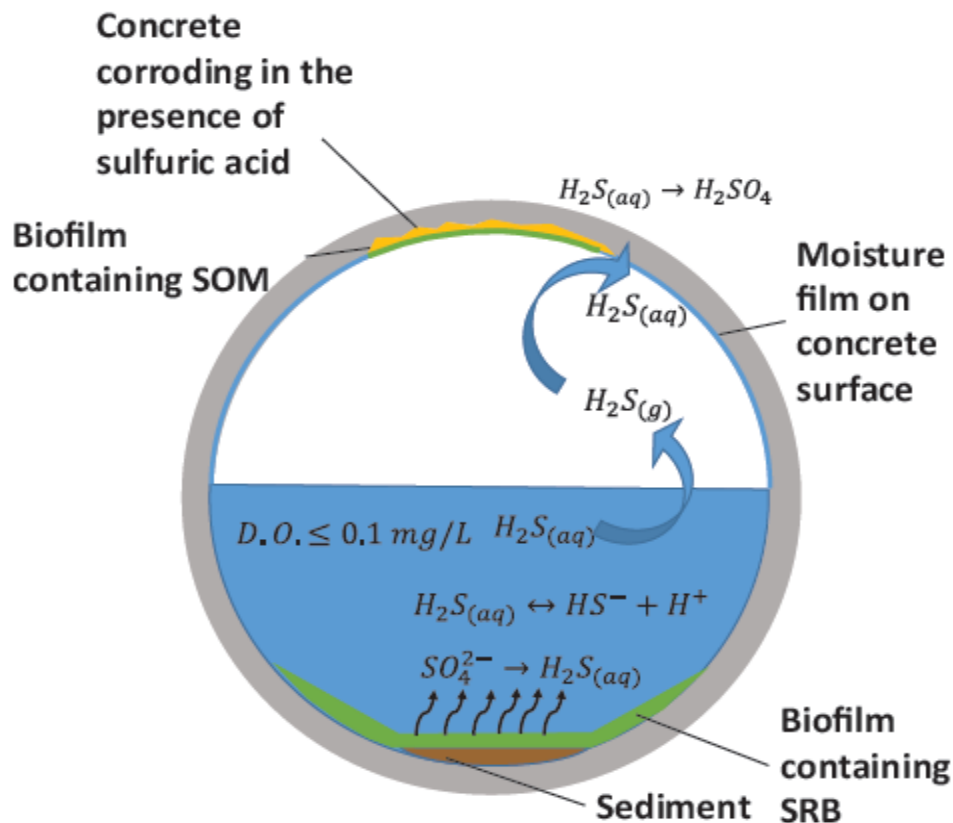


Figure 2.1 Schematic representations of the biochemical processes contributing to MIC of a concrete sewer pipe (House and Weiss, 2014)

A significant amount of research was conducted on the complex mechanisms involved with MIC (Islander et al., 1991, Jensen et al., 2009, Parker, 1951, Yamanaka et al., 2002, Zhang

et al., 2008). Based on the typical biological and physical-chemical reactions and their resulting products, MIC is usually divided into four detailed steps:

- Biological reduction of sulfates into sulfides
- Soluble sulfides are in the water but one can escape - H_2S
- Aerobic bacteria convert non-corrosive H_2S gas into dilute sulfuric acid
- This acid simply dissolves the cement binder in concretes

In subsequent sections of this chapter we will briefly discuss other types of concrete deterioration.

2.1.1 Basic Cement Chemistry

A quick review of hydraulic cements suitable for mass produced concretes shows that all are rich in calcium oxide. First, their stoichiometric chemistry at the time of production is constrained by 3 factors:

- The source of lime and silica based raw materials
- Economical production
- A limited range of chemistry that will hydrate

By far the most universal cement in the world is Ordinary Portland Cement (OPC). It is rich in calcium oxide (also known as lime - CaO or just C in cement chemistry notation). Much of the lime in OPC is contained in two minerals containing silica (silicon dioxide - SiO_2 or just S). These precise minerals form in the rotary kiln at around 2,600 to 2,800°F under sintering conditions. These minerals are:

- Alite or Ca_3SiO_5 or just C_3S - accounting for about 40 to 70% of the cement
- Belite or C_2S - accounting for about 15 to 25% of the cement

The raw materials (one rich in calcium compounds and the other rich in silica compounds) used in the production process contain impurities such as compounds of iron (Fe_2O_3 or F,) alumina (Al_2O_3 or A) and alkalies. These combine in many complex ways during the sintering process but mainly form C_3A and C_4AF . During grinding of the sintered clinker, calcium sulfate is added to control the flash setting C_3A .

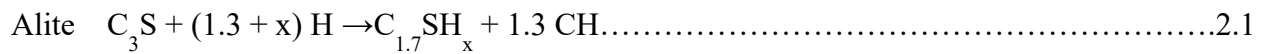
The Alite and Belite ultimately provide most of the strength development and establish the hardened cement's reactivity to various chemicals such as acids. To demonstrate the limited ways in which to manufacture cement, the three component phase diagram for Lime – Alumina

and Silica is shown in Fig. 2. The minerals in question can be seen in the small blue oval along the left most axis of the triangle.

Adding a fourth component such as iron oxides requires a three-dimensional model and adds greatly to the complexity of the system. Add still again various alkalies and the picture becomes something that cement chemists spend their entire careers studying with results often times limited to a particular plant and its available raw materials.

Just a few of the basic calcium and calcium silicate reactions are shown below in Equations 2.1 and 2.2. They dominate the Portland cements hydrate system and establish the limitations on its chemical resistance. The C-S-H hydrates do not have a set chemistry or a firm crystalline structure but are an amorphous gel with a combination of varying hydrates and watery pores.

The watery pore space is a defect in the structure but is necessary for the hydration to have space to develop. As much as half the water indicated in the equations may be in the pore space. The C and S refer to the basic lime and silicon dioxide minerals described above and the H represents water molecules.



X is in the range of 1.4 to 4 depending on time, initial water content, etc.

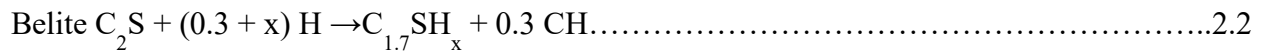


Figure 2.2 shows the Lime Alumina Silica Phase Diagram in which the arrows depict that dominate minerals found in the commercially available Portland cement are alite, belite and rankinite whereas in the calcium aluminate cements they are krotite and ferrites or grossite in high purity cements (Taylor, 1997).

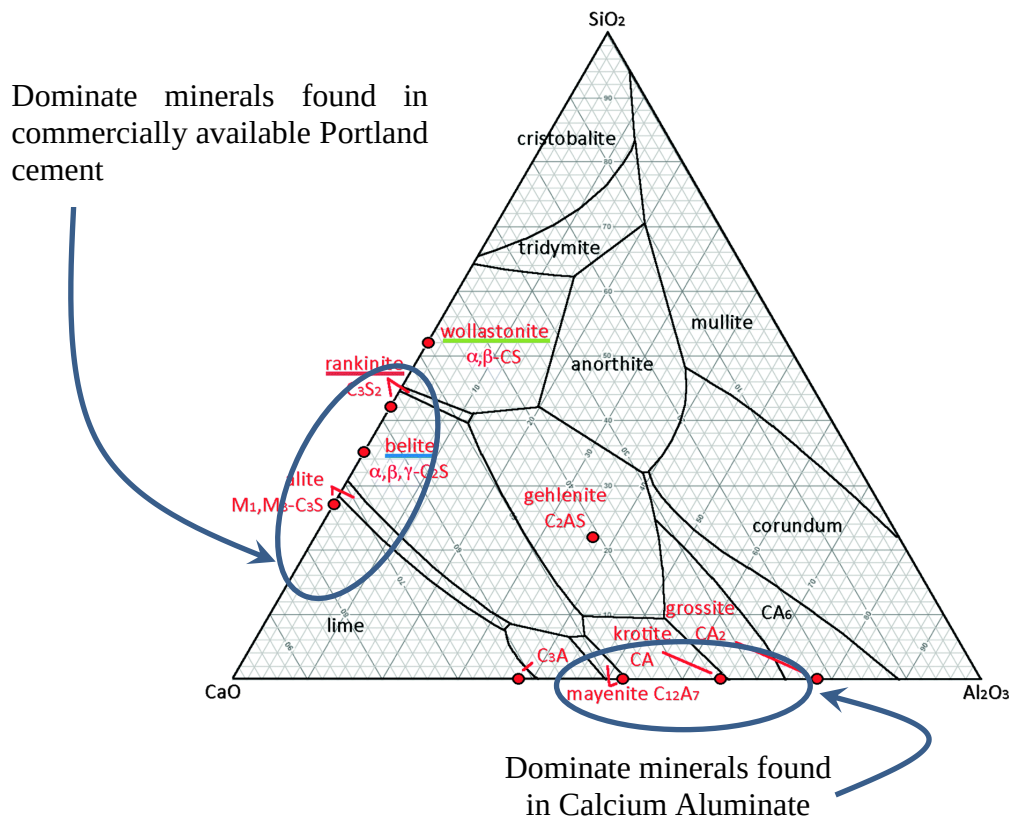


Figure 2.2 Lime Alumina Silica Phase Diagram

Source: ConShield Technologies

Hence, the confusing notion that OPC only requires about 20% water for complete hydration. Hydration would stop at some point with a water level this low. As mentioned above though, the watery pore space is a defect in the hardened structure and the best mechanical properties and resistance to penetrating ions are achieved with a compromise of water additions.

To the extreme right side of the chemical reactions in the Equations 2.1 and 2.2, are the simple calcium hydroxide (CH) hydrates. These minerals do have a pronounced crystalline structure forming early in hydration. Within the complex C-S-H gel system there can be many different imprecise combinations of atoms. The silica component in particular may be attached to anywhere from 2, 3 to 4 oxygen atoms as an example.

There may be some crystalline structures but in general the gel is amorphous. Over long periods of time, two of these crystalline minerals can be; tobermorite ($C_6S_5H_9$) and jennite ($C_9S_6H_{11}$) both allowing for the formation of even more CH as the C to S ratio drops. These minerals may become more prevalent over long periods. The single most important point to be

stressed is that the binder phase is dominated by calcium based minerals (Franke and Sisomphon, 2004).

2.1.2 The different Types of Cement

There are 5 basic types of Portland cement and all are very susceptible to attack from acids. Many confuse Portland Types II and V as being more appropriate in sanitary structures because of their sulfate resistance. See section 2.1.5 for more on this subject. The basic differences in the 5 types of Portland cement are shown in the Table 2.1 below.

Table 2.1 Basic Differences in the Five Types of Portland Cement¹

Type	Classification	Characteristics	Applications
I	General purpose	Fairly high C ₃ S content for good early strength development	General purpose
II	Moderate sulfate resistance	Low C ₃ A content (<8%)	Structures exposed to soil and/ or ground waters containing sulfate ions
III	High early strength	Usually ground finer which increases reactivity in general and may have slightly more lime content resulting in more C ₃ S	Rapid construction, cold weather concreting
IV	Low heat of hydration (slow reacting)	Low lime and alumina content resulting in less C ₃ S (<50%) and C ₃ A	Massive structures such as dams. Now rarely produced
V	High sulfate resistance	Very low alumina content resulting in low C ₃ A (<5%)	Structures exposed to high levels of sulfate ions
White	White color	reduced iron content, no C ₄ AF, low MgO	Decorative (otherwise has properties similar to Type I)

Note: The differences between cement types are rather subtle and are mainly a function of the basic chemistry of the raw materials and their proportions. All five types contain about 75 wt. % calcium silicate minerals, and the properties of mature concretes made with all five are quite similar. Thus these five types are often described by the term “Ordinary Portland Cement”, or OPC.

There are blended cements which will contain a Portland and some form of cement substitute such as blast furnace slag, limestone or fume silica. There are specialty cements that have an expansive agent interground with the Portland to offset shrinkage.

¹ Johnny Love, ConShield Technologies, Inc., Portland Cement Association and Taylor (1997)

Another class of specialty cements is Calcium Aluminate Cements (CAC). These materials were first developed in the late 1800s in order to provide resistance to sulfates found in seawater and certain soils and ground waters. They have improved resistance to many chemicals including extremely dilute acids provided the pH stays above 4. Today these cements are primarily used in high temperature applications and as a chemical component in very technical mortars such as flooring underlayment. As the name suggest they are based on lime and alumina with silica contents ranging from ~ 05 to 15% and iron from ~ 0% to 15%. Alumina contents range from ~ 38% to 80%. Lime makes up the balance and ranges from ~ 20% to 40%. For civil engineering structures the most appropriate materials are the less pure products with lime and alumina contents near 40%² (Taylor, 1997).

2.1.3 Reaction of Concretes to Dilute Acids

The reactions of various inorganic acids and lime containing concretes are all very simple. It does not matter the element for which the acid is named but simply the fact that the acid is a proton donor as shown in Table 2.2 below. The acids are all strong acids in that they completely disassociate in water with the hydrogen ions (simple protons with no electrons) being most mobile and reactive. In each case the hydrogen ions seek out the OH radicals in the lime containing hydrate structures and react to form water. At the same time, the very mobile positively charged calcium ions are reacting with the remnants of the acid, which is the chlorine or phosphate or sulfate ions. The end results are a salt and water and the complete destruction of a cementing binder phase. The salts formed are a technical curiosity but of no importance to the structure.

Table 2.2 Reaction of Concretes with Acids³

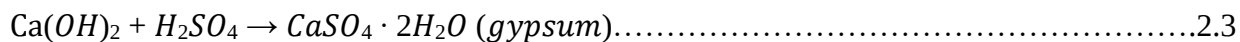
Type of Acid	Lime + Acid	Result	Salt + Water
Hydrochloric	$\text{Ca(OH)}_2 + 2\text{HCl (aq)}$	$\longrightarrow$	$\text{CaCl}_2 \text{ (aq)} + 2\text{H}_2\text{O}$
Phosphoric	$3\text{Ca(OH)}_2 + 2\text{H}_3\text{PO}_4 \text{ (aq)}$	$\longrightarrow$	$\text{Ca}_3(\text{PO}_4)_2 \text{ (s)} + 6\text{H}_2\text{O}$
Sulfuric	$\text{Ca(OH)}_2 + \text{H}_2\text{SO}_4 \text{ (aq)}$	$\longrightarrow$	$\text{CaSO}_4 + 2\text{H}_2\text{O (gypsum)}$

In the case of MIC in sanitary sewers, sulfuric acid rapidly reacts with the various hydration products of lime based cements in hardened concretes. This includes the very reactive

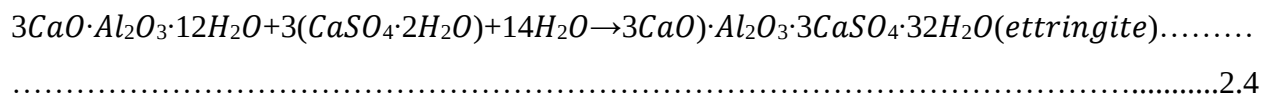
² Johnny Love, ConShield Technologies, Inc.

³ Johnny Love, ConShield Technologies, Inc.

calcium hydroxide but also many other minerals. The reaction by-products are complex and non-structural; they are a weak punky mush (House and Weiss, 2014). These by-products can include gypsum, ettringite, etc. These by-products themselves are soluble in acid and so the deterioration is ongoing. Note the cement abbreviation for calcium sulfate (CaSO_4) is $\text{C}\bar{\text{S}}$ with the $\bar{\text{S}}$ representing SO_3 . The sulfuric acid first reacts with the calcium hydroxide in the concrete to form gypsum as shown in the equation 2.3 (Monteny et al., 2000, Santhanam et al., 2001).



Gypsum could then interact with any unreacted tricalcium aluminate (C_3A) or lower forms of calcium sulphoaluminate hydrates to form ettringite, which is again a non-structural punky expansive mush as shown in the equation 2.4 (Abdelmsee et al., 2006).



Equation 2.5 below states the reaction in a different way. (Parker et al., 1997)



Today, ettringite is most typically expressed as: $\text{C}_3\text{A} \cdot 3\text{C}\bar{\text{S}} \cdot 32\text{H}$.

2.1.4 Acids - A Surface Attack

The attack occurs primarily on the surface just as with acids attacking a dense impermeable material like steel. Any intrusion of sulfates (which are formed only with the acid production) into the concrete was already proceeded by the destruction of the concrete. The acid destruction will be much more rapid than the penetration and much slower solid state reaction of the sulfate and the cement structure.

The punky mush will have gypsum and ettringite in it but they are the remnants of the concrete destruction and not the cause. However, ettringite is not stable (decomposes to gypsum) when the pH falls below 12. At this pH, limited ettringite will form in deeper sections of the concrete. Minimal ettringite in the corroding front indicates that the thermodynamics of the conversion to gypsum may be so fast that ettringite is a short-lived intermediate.

Therefore, in a sanitary sewer, MIC of concrete occurs due to the dilute sulfuric acid having pH ranging from 0 to 3, having concentration as great as 7% (7 parts acid and 93 parts water) and this acid is generated by the bacteria.

2.1.5 H₂S and Concrete

There is no direct corrosion by H₂S gas. The gas will not readily combine with oxygen and water to form an acid. There is a possibility that H₂S in water can form an acid in the presence of certain ammonia compounds under rare circumstances. H₂S can directly corrode iron based metals and other metals like lead.

Sulfuric acid (H₂SO₄) is a stable liquid and can be had in any aqueous concentration from 0 to 100%. Even very low concentrations produced liquids with very low pH and in turn cause severe corrosion to most metals and concrete. Once the sulfuric acid is present the reaction that destroys concretes and mortars is simple as shown below in the equation 2.6.

Lime (CaO) Containing Minerals + Dilute Acid (H₂SO₄ + H₂O) → Water + Various Calcium Sulfate compounds like (Gypsum CaSO₄ · 2H₂O).....2.6

The calcium sulfates are not formed well and offer no structural value. Other types of corrosion in sewers would typically be found in the areas wetted by the wastewater and not above the waterline. Industrial sewers are notorious for having complex chemical problems that may require very special attention.

Storm sewers are another special case where there can be many types of corrosion/abrasion. Corrosion in metal culverts can take place under stagnate soil deposits and classical MIC can develop where enough organic material is available such as with swampy areas. This study is limited to classical MIC issues above the water line in sanitary sewers.

2.1.6 A Short Note on Sulfate Attack – Not to be Confused with Sulfuric Acid Attack

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 MIC. 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.

The sulfates react with unreacted C₃A as well as the reacted C₃A 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 (Taylor, 1997).

2.1.7 Other Types of Concrete Deterioration

Generally, in sanitary sewers, MIC 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. MIC 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 MIC. MIC 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.

2.2 Microbiologically Induced Corrosion (MIC)

As stated above, Microbiologically Induced Corrosion (MIC) 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.

2.2.1 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.

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.

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.

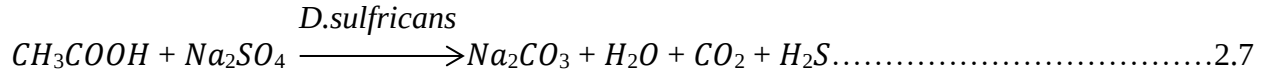
With concrete surfaces, the process is complex and involves the evolution of at least 5 strains of the sulfur consuming Gram-negative bacteria. The first strains can tolerate surface pHs as high as 9 and produce only modest amounts of very weak acid. But they are important as they work to lower the surface 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.

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 (Franke and Sisomphon, 2004).

2.2.2 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) (Taylor, 1997). H_2S (aq) is released into the gas phase (H_2S (g)) with or without the aid of turbulence (turbulence increases the gas release) (House and Weiss, 2014).

Typical SRB were identified as *Sulfovibriodesulfuricans* (Campbell et al., 1957) and *Desulfovibriodesulfuricans* (Nakatsuk and Akagi, 1969). The equations 2.7 and 2.8 below describe the formation of hydrogen sulfide through the reduction of sulfates by SRB, in which sulfate ions are listed as the sulfur source:



Note: The equations above describe as how the acetic acid and sodium lactate combine with the sodium sulfate to form the hydrogen sulfide as one of the by products through the reduction of sulfates by SRB, in which sulfate ions behave as the source of sulfur.

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 (1947) first named *Sporovibrio desulfuricans* 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 species (Santo Domingo et al., 2011) present in wastewater; however, *Desulfovibrio desulfuricans* is commonly named as the primary contributor to the sulfate reduction in municipal wastewater collection systems. *Desulfovibrio desulfuricans* 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) (House and Weiss, 2014).

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 2.6 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^- (Yang et al., 2005, Yongsiri et al., 2003).

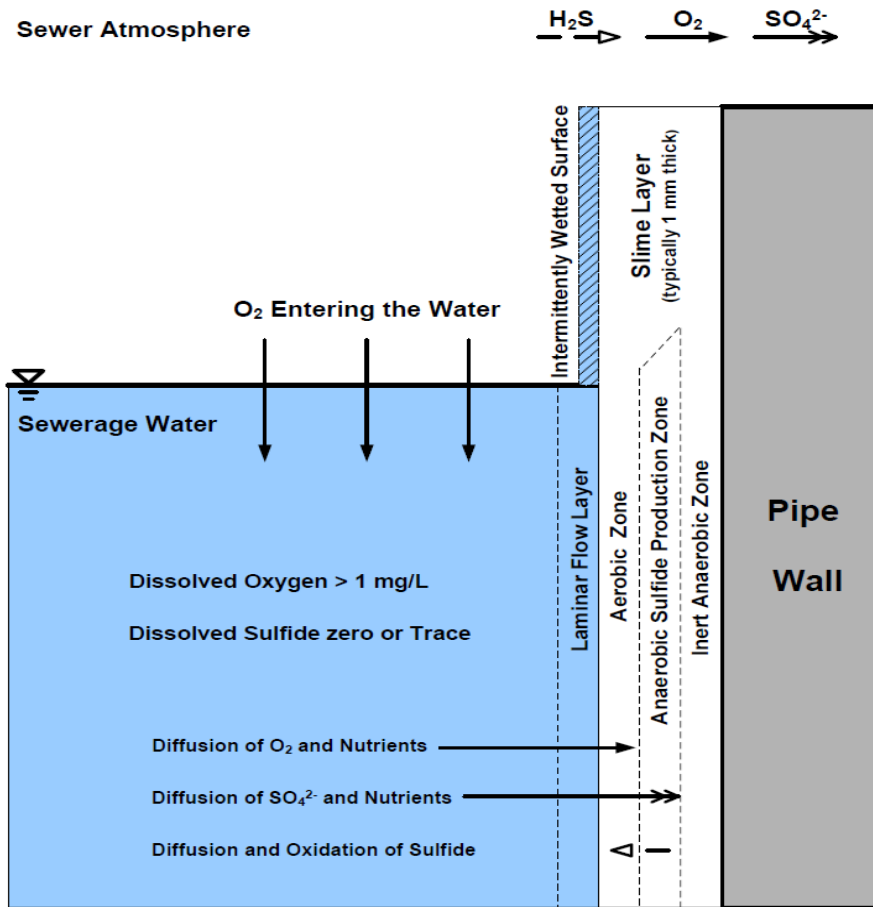
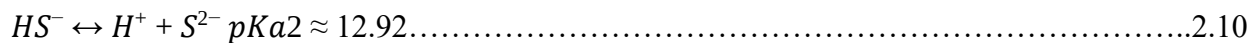
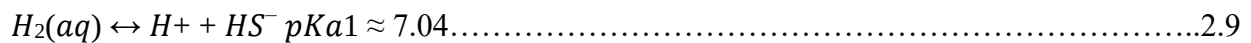


Figure 2.6 Processes in sewers with sufficient oxygen to prevent sulfide from entering the sewage stream
(Cheng, 2014)

The S^{2-} species is not taken into account because it exists in the liquid phase at high pH values. Figure 2.7 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 2.9 and 2.10.



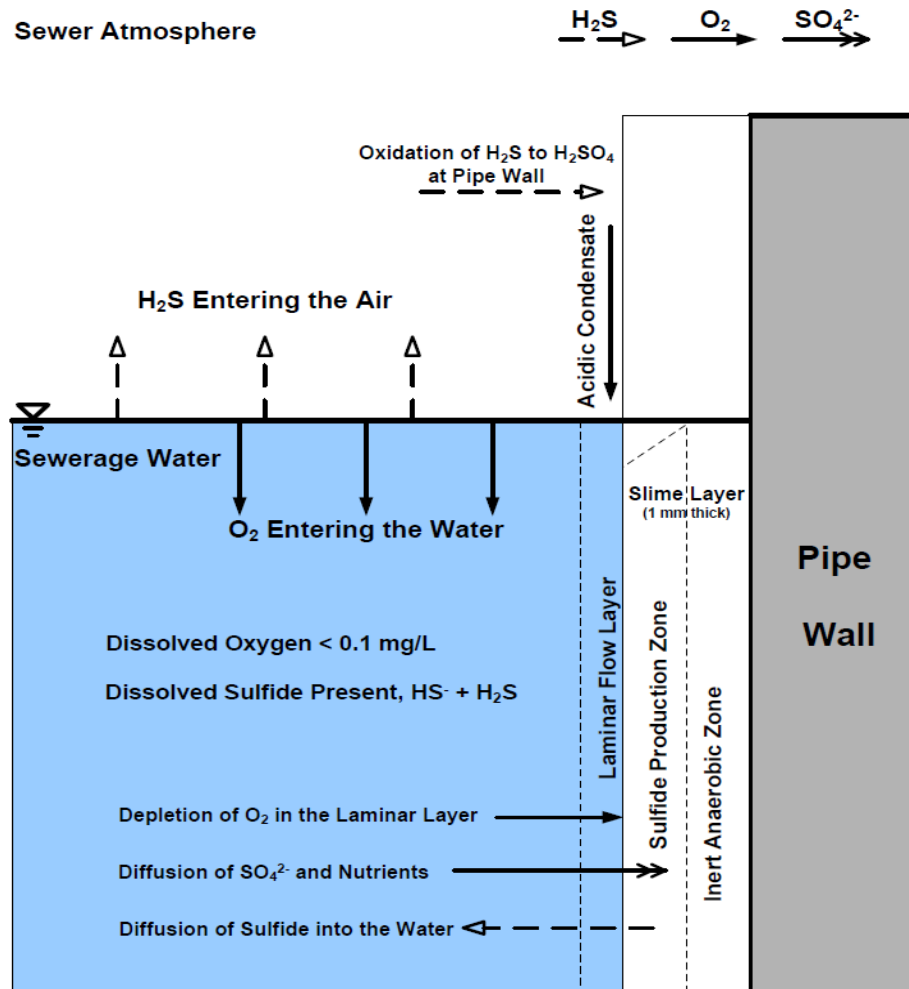


Figure 2.7 Processes in sewers under sulfide increasing conditions
(Cheng, 2014)

A design manual was published for odor and corrosion control in sewerage systems and treatment plants by the EPA (EPA, 1985). Figure 2.8 shows the effect of pH on hydrogen sulfide equilibrium in sewerage. On the left half of the plot, the curve of H_2S and the HS^- crosses around pH 7, which is consistent with the ionization $\text{pK}_{\text{a}1}$ listed above.

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 $\text{pK}_{\text{a}2}$ 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.

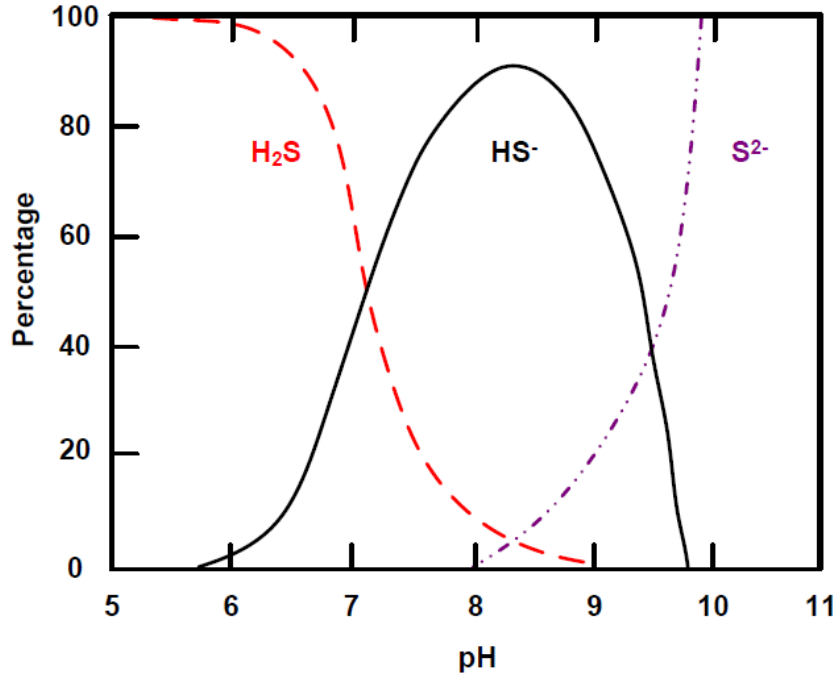


Figure 2.8 Effect of pH on hydrogen sulfide equilibrium in water
(Cheng, 2014)

Only $\text{H}_2\text{S}(\text{aq})$ 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 (Yongsiri et al., 2003, Yongsiri et al., 2004).
 $\text{H}_2(\text{aq}) \leftrightarrow \text{H}_2\text{S}(\text{g})$ $K_c \approx 469 \text{ (atm/mole fraction)}$ 2.11

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 $\text{H}_2\text{S}(\text{g})$ 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 $\text{H}_2\text{S}(\text{g})$ concentrations should not be ignored (Alexander and Fourie, 2011).

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 = 11-13) (Zhang et al., 2008) and also serves as the driving force behind the gas dissolution. At high pH,

H₂S is separated into HS⁻ or S²⁻ ions that attract more H₂S into the moisture layer. Table 2.3 shows the factors affecting sulfide content in wastewater collection networks.

Table 2.3 Factors affecting Sulfide Content in Wastewater Collection Networks (House and Weiss, 2014)

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

2.2.3 Sulfuric Acid Production

In the presence of oxygen in the sewer atmosphere, H₂S is converted to elemental sulfur or partially oxidized sulfur species and then to sulfuric acid through both chemical (abiotic) and biological (biotic) pathways. The basic reactions 2.12, 2.13, 2.14 and 2.15 are listed as follows:



However, the actual processes are much more complex involving many intermediates. H₂S is primarily chemically oxidized to thiosulfate (S₂O₃) and elemental sulfur (S). Various species of SOB present in the condensate on the concrete surface (e.g., the sewer crown) eventually oxidize the dissolved H₂S and other sulfur compounds to sulfuric acid, which corrodes the concrete (Islander et al., 1991). The creation of sulfuric acid by abiotic oxidation is

dependent on local pH. At low pH, H₂S can be oxidized directly to elemental sulfur. Oxidation to sulfate (SO₄²⁻) takes place at higher pH levels with thiosulfate (S₂O₃²⁻) as an intermediate (House and Weiss, 2014). Abiotic oxidation alone does not create the highly acidic conditions that degrade concrete during MIC.

The activity of SOM is necessary to oxidize H₂S and intermediate products to sulfuric acid. Parker (1947) was the first to name *Thiobacillus concretivorus*, later identified as *Thiobacillus thiooxidans* as the organism capable of producing sulfuric acid resulting in pH levels as low as 1.0 on concrete surfaces. Since then five species of *Thiobacillus* have been identified as contributors to MIC in concrete wastewater networks: *T. thioparus*, *T. novellus*, *T. neapolitanus*, *T. intermedius*, and *T. thiooxidans* (Islander et al., 1991). The presence of some or all of these microorganisms on corroded sewer pipes has been confirmed by multiple researchers through the use of genetic analysis (Davis, Nica, Shields and Roberts, 1998; Okabe, Odagiri, Ito, and Satoh, 2007; Santo Domingo et al., 2011; Vincke, Boon and Verstraete, 2001, House and Weiss, 2014).

Fresh concrete is highly alkaline, often exhibiting pH between 12.5 and 13.5 (Mehta and Monteiro, 1993). Abiotic lowering of the concrete surface pH is therefore necessary before colonization by *Thiobacillus* can occur. Carbonation, the process by which atmospheric carbon dioxide reacts with calcium hydroxide and water within the cement microstructure, is typically credited with the initial reduction in surface pH of the concrete. Leaching of calcium hydroxide through contact with wastewater (near the spring line) along with the growth of other microorganisms may also lead to a reduction in pH near the concrete surface. H₂S gas itself is slightly acidic (though not enough to directly attack the concrete in any reasonable amount of time) and is suspected of playing a role in lowering the high initial alkalinity of the concrete. Table 2.4 shows preferred substrates and pH ranges for SOM involved with MIC in concrete

In the sewer networks, once the concrete surface reaches a pH value of 9–10, colonization by *T. thioparus* begins. After SOM are established, abiotic lowering of the concrete pH is no longer relevant as biological production of sulfuric acid governs the surface pH (House and Weiss, 2014).

Table 2.4 Preferred Substrates and pH Ranges for SOM Involved with MIC in Concrete
Sewer Networks (House and Weiss, 2014)

Species	Preferred substrate	Preferred pH growth range
T. thioparus	H ₂ S, S ⁰ , S ₂ CO ₃ ²⁻	5–9
T. novellus	S ₂ CO ₃ ²⁻	2.5–8
T. intermedius	S ₂ CO ₃ ²⁻	2.5–8
T. neapolitanus	S ⁰ , S ₂ CO ₃ ²⁻	3–7
T. thiooxidans	H ₂ S, S ⁰	0.5–3

As many as four species may be present on sewer walls at pH values of 3.0–8.0. T. thioparus makes use of sulfides, elemental sulfur, and thiosulfate in the production of sulfuric acid. T. intermedius and T. novellus are the next species to colonize the surface, relying mainly on thiosulfate as a substrate. As pH is reduced to below 7, T. neapolitanus becomes prevalent until surface pH is reduced to around 3. Being highly acidophilic, T. thiooxidans thrives at pH values below 3 where it oxidizes both sulfides and elemental sulfur to sulfuric acid. T. Thiooxidans continues to lower the surface pH until acid production becomes self-inhibitory at pH values from 0.5 to 1.0. It is worth noting that Thiobacillus bacteria are not the only microorganisms present on corroding sewer walls. Aerobic heterotrophs, fungi, and others are commonly found in high numbers alongside Thiobacillus.

The role that these microorganisms play in the corrosion process, if any, has not been defined. The degradation mechanisms and severity of acid attack on concrete are dependent on the type of attack as well as the strength and type of acid. To properly address the acid attack found in MIC of concrete structures, a distinction must be made between what could be considered “passive” and “active” acid attack. Passive attack could be defined as exposure to a finite amount of non-flowing acid.

Examples of passive acid attack of concrete are periodic exposure to aggressive acid solutions in an industrial setting or occasional exposure to acid rain. This is also the type of attack that occurs when immersion tests (Pickle Jar) are attempted. The ability of concrete to resist this type of acid attack is related to acid neutralization capacity, composition of hydrated products, and to a mild extent porosity/permeability. Active acid attack could be defined as

sustained exposure to acid that cannot be effectively neutralized over a long period by the alkalinity found in concrete. MIC of concrete sewer infrastructure is an active degradation process where continuous biological production of acid results in sustained attack of the concrete surface.

No amount of buffering capacity or reduced permeability can prevent the destruction. Another example of active attack includes underground concrete structures exposed to flowing groundwater of acidic nature or storage of large volumes of acidic material. Evaluating concrete performance under passive conditions is useful in understanding the mechanisms of acid attack on concrete; however, it is important to understand that some mechanics will change under active conditions. The characteristics of the corrosion product layer are dependent on the solubility of the compounds and the amount of physical abrasion available for removal of the layer supporting the growth of SOM throughout its thickness. Davis et al. (1998) found high numbers of Acidophilic Sulfide-Oxidizing Microorganism (ASOM) in both the outer and inner regions of the corrosion product layer on the crown of a corroded sewer pipe.

Furthermore, Neutrophilic Sulfide-Oxidizing Microorganisms (NSOM) found in the outer region of the corrosion product layer was not present in the inner region, suggesting that conditions near the interface of the corrosion products and unaffected concrete were the most acidic. These results suggest that the corrosion product layer plays less of a role in inhibiting active acid attack by SOM compared with passive attack. The layer actually encourages the growth of SOM and the deposition of acid near the reaction zone (House and Weiss, 2014).

2.3 Corrosion Control

There are three classical means that have been attempted to improve concrete durability in general but offer limited success where acids are concerned. They are as follows:

- Reduce lightly bound calcium compounds
- Reduce permeability
- Buffer the concrete with limestone / sacrificial aggregates

2.3.1 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.

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. Many studies over the years have demonstrated that simple cement substitutions with pozzolans (and without the benefit of water reduction) only produced modest improvements.

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.

In recent years there has been much discussion of so-called geopolymer bonded concretes and mortars. By definition a true geopolymer bonding system is created by dissolving and then condensing a system of alumina silicates. There are no hydrates although water is necessary for the reaction to proceed. There are no calcium oxide minerals used. For the reactions to proceed powerful chemicals are used typically along with elevated temperature curing else the green strength development is poor. Such a binding system is clearly more corrosion resistant than Portland cement based systems.

It is expensive and has applications in high value added applications such as the iron and steel industry where heat is always available. What is actually being touted for thin linings in manholes and pump stations by several is not a true geopolymer bonded mortar but rather a hybrid. There is some alkali activation of some alumina silicates (coming from fly ash and / or Ground blast furnace slag) and then there is some classical hydration of calcium silicate hydrates. The latter reactions drive the early strength development and also the condensation reactions. Many proponents of this technology produce data showing these binders to be

approximately 6 times more corrosion resistant than Portland bonded mortars when performing short term immersion tests. Nevertheless these tests suggest concrete deterioration could reach a depth of 3 inches in just 10 years of service. The Achilles heel remains the reactive calcium minerals.

2.3.2 Reduce Permeability

- **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 (House and Weiss, 2014). There has been much work in the area of reducing permeability with additives. This has often 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 concepts have their applications especially where the attack is due to penetration of the hydrate structure by a mobile ion. Various chemical reactions take place with either reinforcing steel or the hydrate system and disruptive stresses develop causing concrete degradation. The degradation opens more pathways and the deterioration gains pace. 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.

- **Crystalline Forming Water Proofing Admixtures**

These in general are based on certain minerals that contain combinations of rare earth metal oxides. They promote a complex growth of solid crystals within the watery pore space of hardened Portland cement paste. They 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.

As explained above, 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 effective 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 is constantly being generated.

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.

2.3.3 Buffering the Concrete with Limestone Aggregates

The concept is to use aggregates (generally just the coarse fraction) 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 (which can be very difficult in new construction) 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.

In some areas of the US these aggregates are common and others they are not. In South Florida they are common, yet corrosion in sanitary concrete structures is rampant. The additional alkalinity may help slow the reduction of the surface pH and thus slow the colonization of bacteria but ultimately it is just a matter of time until the bacteria fully develop and their acid production overwhelms this buffering effect.

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 H₂S and biological availability are enough to ultimately cause deterioration. The high cost of the raw materials combined with only an improvement (difficult to forecast and sometimes not seen at all) 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.

2.3.4 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:

- Take no precautionary steps – wait, hope and repair
- Coat the concrete
- Embedded plastic liners
- Chemically treat the raw sewage
- Immunize the concrete - like a vaccine

2.3.4.1 Take No Precautionary Measures

We will not discuss this approach in any detail and assume the reader of this report is well aware of the costly and disruptive consequences of MIC in their sewers. 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

2.3.4.2 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.

2.3.4.2.1 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.

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.

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.

2.3.4.2.2 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 actually rupture.

Then there is the issue of welding all the joints and possible damage to the liner during the shipping and installation phase. Welding can only be done by specialty tradesmen which increase cost and usually lead to construction delays. The initial cost for a single custom cast in place structure like a pump station is expensive but the implications for mass produced precast shapes like manholes and round pump stations are severe.

2.3.5 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
- Remove it from the sewer's atmosphere (both with and without odor control)

In general sulfates are added to the waste water by many avenues. This 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^{2-}), 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.

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. While these concepts may be feasible at treatment plants, pump stations and other complex structures like large diameter tunnels, how to apply them to a large sprawling collection system is a huge challenge. Odor control is a bit more manageable as structures like manholes can be made somewhat air tight and then the odor issue dealt with at pump stations for example. Corrosion as a result of the increased H_2S levels would just get worse in concrete manholes and pipe.

Preventing the reduction of sulfates in the water is theoretically straight forward on a small scale but in a collection system it must be practiced everywhere in a real time fashion. 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. 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.

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, hypochlorous 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.

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. There is much conflicting data on H_2S concentrations and corrosion rates. An older common idea was to flush the H_2S just with large volumes of air. Odor quickly becomes a problem. Often times the air was introduced in the water in an attempt to purge as much of the H_2S as was possible. Odor controlling air scrubbers have been employed and they have significant issues with space, capital cost, consumables, etc. 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.

2.4 Con^{mic}Shield®: Antimicrobial Concrete Admixture

A completely different approach to protecting concrete is to render it uninhabitable by the bacteria that convert the H_2S into sulfuric acid in the first place. Con^{mic}Shield® is an EPA registered anti-bacterial additive that is added to fresh concrete as it is mixed. The product has been in use since 1996 and the concept of the basic antimicrobial dates back to the 60s and Dow Chemical.

The basic antimicrobial was developed for use on textiles and was not expected to last for more than a few months or years at the most. Initially this technology was used to treat fibers that were in turn added to fresh concrete. The fibers would not support colonization of the bacteria but could not protect the concrete in total. Today some *would-be* competitive products are based on this basic technology for treating textiles.

The breakthrough in the 90s 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 disburse throughout the concrete mix and ultimately bonds molecularly with all the concrete's ingredients.

This in turn prevents the colonization of acid producing aerobic bacteria on the concrete's exposed surfaces for the life of the concrete. It is environmentally friendly and cannot leach out nor affect the chemistry of the waste water. It is safe and easy to dose and requires no special handling or safety precautions. In the hardened concrete, the additive is nontoxic to humans and animals, but permanently inhibits the growth of single-celled organisms like *Thiobacillus*.

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 (both wet and dry processes), 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.

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 ConShield additive is simply added first to the batching water as mentioned above

A brief summary is offered as to how the Con^{mic}Shield[®] as an antimicrobial functions. Many antimicrobials kill bacteria by a chemical means. The chemical is consumed and therefore the antimicrobial is only effective for a period of time. Con^{mic}Shield[®] is based on a completely different technology.

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

Figures 2.3 and 2.4 shows 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 Con^{mic}Shield[®] is generally categorized as a complex Quaternary Ammonium Silane (QAS) antimicrobial agent. It has been modified to function

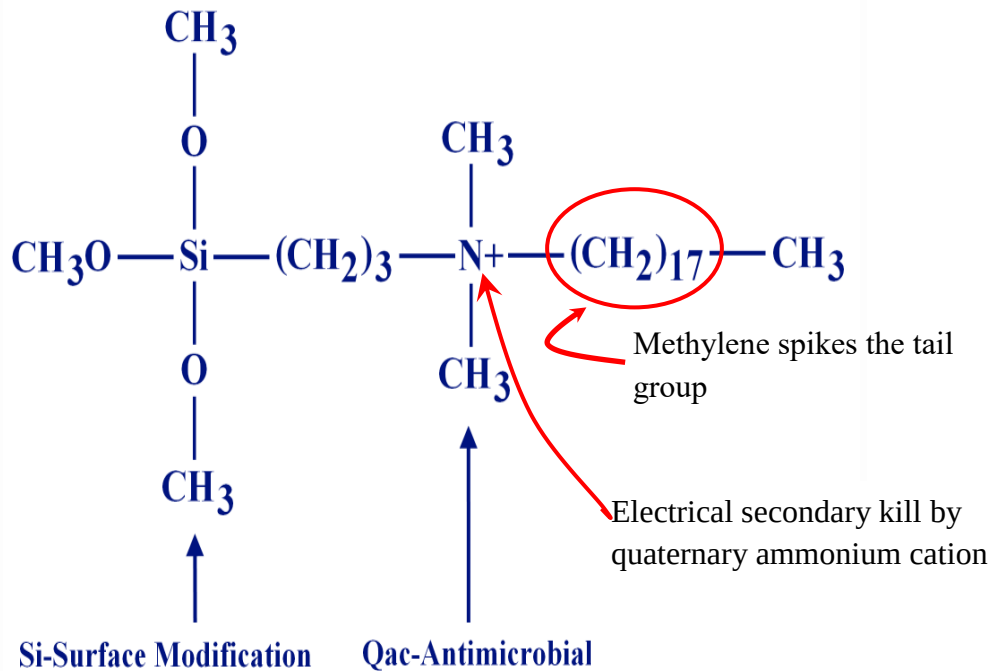
within cementitious materials like concrete and repair mortars. The manufacturing process is likewise a complex series of operations. When ammonium salts are reacted with certain organosiloxanes they form an integrated system, which can then be applied to almost any surface thus forming an invisible 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.

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.

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. The ionic association (soap bubble like thin cell membranes carry a negative charge) and lipophilic attraction, causes disruption and lysis of the microbial cell. 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 Con^{mic}Shield® 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.

POWERFUL COMBINATION (SiQac)

Organosilane Quaternary Amine



Head group provides a mechanism for covalent bonding and cross linking

Figure 2.3 SiQac Chain
Source: ConShield Technologies

There is no chemical exchange involved in the kill thus there is no chemical consumption and the effectiveness of the antimicrobial remains unaltered (Franke and Sisomphon, 2004). Fig. 2.5 shows the action of antimicrobials against the microbes.



Fig. 2.4 Action of Microbes against SiQac Antimicrobial Coating
Source: Biotech International

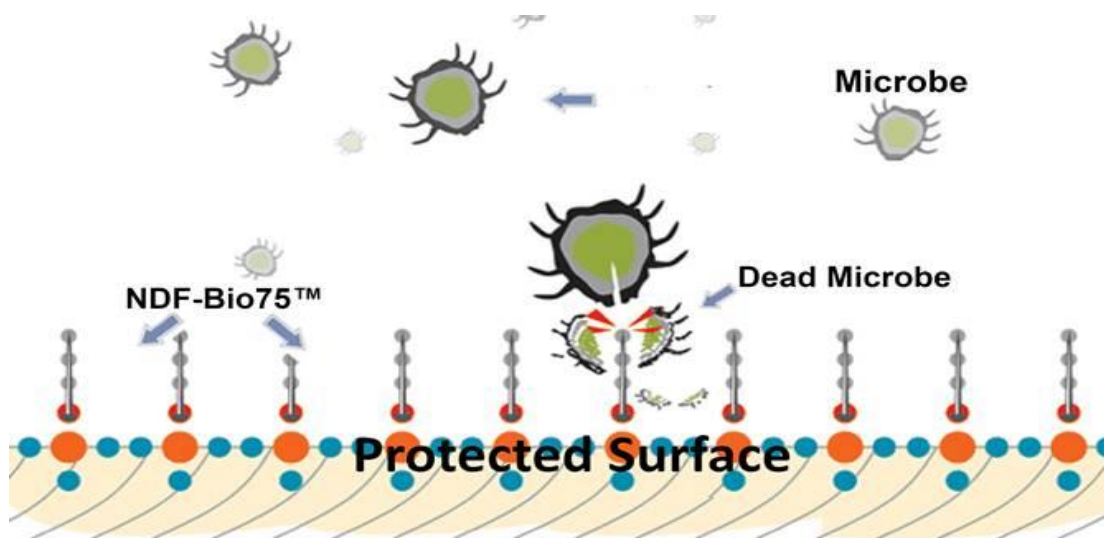


Fig. 2.5 Action of Antimicrobials Against the Microbes
Source: Biotech International

2.4.2 Role of Nitrogen Molecules in the Antimicrobial Mechanism

Two hypotheses are proposed to explain the role of the nitrogen molecule in the antimicrobial mechanism. The first theory is the long carbon chain associated with the nitrogen atom could mechanically penetrate and rupture the cell membrane completely disrupting the bacteria's integrity (Lin et al., 2003, Milovic et al., 2005, Tiller et al., 2001). The longer the chain, the greater antimicrobial impact (Ahlstrom et al., 1999, Calas et al., 1997). Another

explanation is the highly charged ammonium structure could induce an ion exchange reaction between the positive charges on the surface and the cations inside the cell membrane. The strong driving force frees these important cations from the membrane structure and causes cell disruption (Kugler et al., 2005, Murata et al., 2007).

2.4.3 Field Surveys

In this section, field surveys have been discussed which were done around the DFW area where the use of antimicrobial viz. ConShield was studied for the MIC protection in the sanitary sewer structures.

2.4.3.1 Low Branch Lift Station City of Mansfield, Texas

In 2013, Freese and Nichols Engineers specified antimicrobials to treat some 1,600 cubic yard of cast-in-place concrete at the Low Branch Lift station in Mansfield as shown in the Figure 2.6. ConShield 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 2.7.

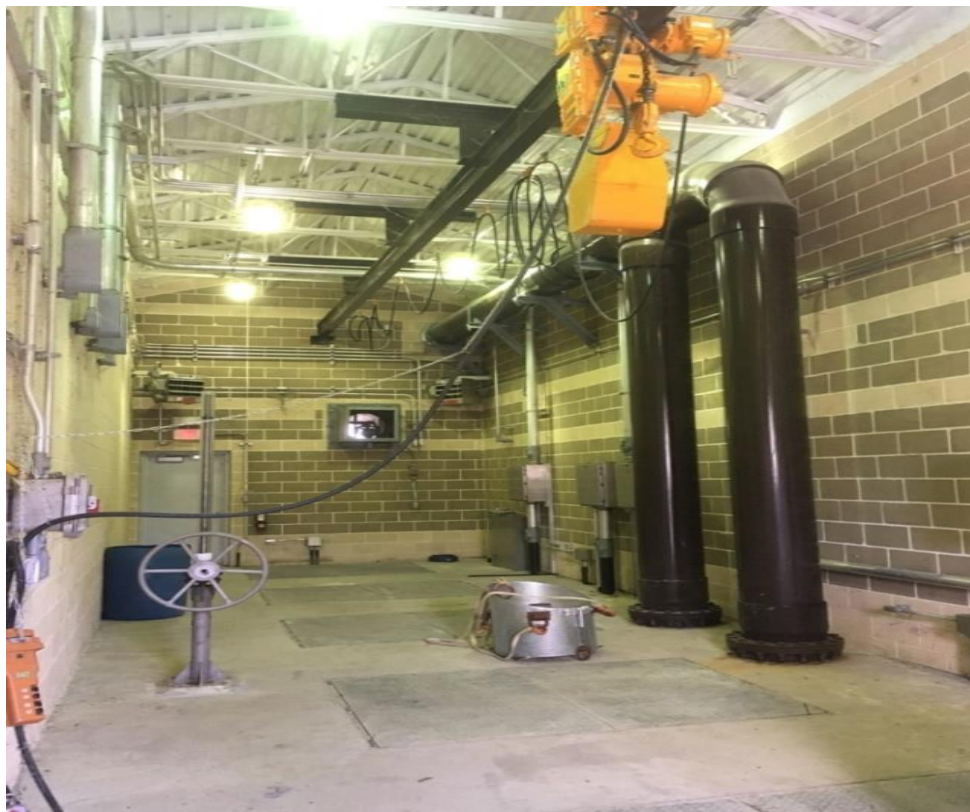


Figure 2.6 Low Branch Lift Station in the City of Mansfield



Figure 2.7 Inside View of Lift Station

2.4.3.2 Air Releasing Valve Box at Grand Prairie, Texas

Air release valves as shown in Figure 2.8 were installed in 2004 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 2.9 shows the walls of the valve box after pressure washing.

In this rehabilitation project, Con^{mic}Shield[®] 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 2.10.



Figure 2.8 Concrete Valve Box after 9 Years of MIC



Figure 2.9 Walls of Concrete Valve Box after Pressure Washing



Figure 2.10 Air Release Valve Box 3 Years After Repair

2.4.3.3 Pre-cast Antimicrobial Manholes in DFW Metroplex, Texas

In the DFW Metroplex alone, including DWU, Irving, and Ft. Worth, an average of 600 cubic yards of precast antimicrobial manholes containing ConShield as shown in the Figure 2.11 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 in order to provide long term ease of identification.



Figure 2.11 Pre-cast Antimicrobial Manholes

CHAPTER 3

METHODOLOGY

The methodology which was followed for the completion of this project has been summarized as follows.

Literature Search	• How is concrete corroded? • Conditions necessary for bacterial growth in raw sewerage and on surfaces above sewerage. • Methods used to protect concrete in sewer environments.
Field Surveys and Testing	• Around the DFW area to study the use of an antimicrobial, Con^{mic}Shield® for the MIC protection in the sanitary sewer structures.
Results	• To test the presence of ConmicShield in the concrete samples analyzed to ConShield's protocol, a modified ASTM D4783 procedure.
Discussion of Results	• To analyze the differences between the actual and modified ASTM D4783 standards used to determine the resistance of treated cementitious materials to microbial attack.
Conclusions	• Based on the study to find and validate the solutions for the MIC in the sanitary sewer pipe and manholes.

CHAPTER 4

RESULTS

To test the presence of Con^{mic}Shield[®] in the concrete samples, the samples identified as R-60 and R-60-I.1 were analyzed to Con^{mic}Shield[®] protocol, a modified ASTM D4783 procedure. First the samples are carefully conditioned to reduce the surface pH and alkalinity. A cell suspension of *Serratia Marcescens* was prepared, estimated at 1×10^7 cfu.ml. The suspension was placed on the sample surface and allowed to dry. 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.

4.1 Presence of Con^{mic}Shield[®] in the Concrete Samples

Table 4.1 below shows that after 48 hours of incubation, sample 1 had light pink colonies indicating the absence of Con^{mic}Shield[®] whereas sample 2 had no growth of colonies indicating the presence of Con^{mic}Shield[®].

Table 4.1 Results for the presence of Con^{mic}Shield[®] in the concrete samples

Sample	Identification	Observation	Result
1	R-60	Light pink colonies	Con ^{mic} Shield [®] was absent
2	R-60-I.1	No growth of colonies	Con ^{mic} Shield [®] was present



Figure 4.1 Growth of Pink Colonies



Figure 4.2 No Growth of Pink Colonies

Figure 4.1 shows pink colonies in the sample 1 indicating growth of bacteria and absence of Con^{mic}Shield[®] whereas Figure 4.2 shows no growth of bacteria in the sample 2 indicating presence of Con^{mic}Shield[®].

CHAPTER 5

DISCUSSION OF RESULTS

After 48 hours of incubation in the laboratory, sample 1 designated as R-60 had light pink colonies indicating the absence of Con^{mic}Shield[®] whereas sample 2 designated as R-60-I.1 had no growth of colonies indicating the presence of Con^{mic}Shield[®].

Table 5.1 shows the differences between the actual and modified ASTM D4783 standards that are used to determine the resistance of treated cementitious materials, either concrete or mortars, to microbial attack by challenging the test specimen with a bacterial culture.

Table 5.1 Differences Between the Actual And Modified ASTM D4783 Standards

Point of difference	Actual ASTM D4783 Standard	Modified ASTM D4783 Standard
Scope	To determine the resistance of liquid adhesive preparations to microbial attack in the container by challenging adhesive specimens with cultures of bacteria, yeast, or fungi.	To determine the resistance of treated cementitious materials, either concrete or mortars, to microbial attack by challenging the test specimen with a bacterial culture.
Summary of Test Method	Inoculated adhesive specimen is stored at 21 to 27°C (70 to 80°F) for 7 days. If the 4-h plate is positive and the 24-h plate is negative, the kill time could be narrowed down further by repeating the challenge and making streak plates at intervals of 4, 8, 12, and 24 h following the challenge.	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.
Significance and Use	Dependent upon the physiological action of living microorganisms under a reported set of conditions.	This test method is used to demonstrate whether a cementitious material is sufficiently protected with Con ^{mic} Shield [®] anti-bacterial additive to resist attack by bacteria.

Differences Between the Actual And Modified ASTM D4783 Standards (Continued)

Point of difference	Actual ASTM D4783 Standard	Modified ASTM D4783 Standard
Test Procedure	Incubated at 30±5°C (86±1°F) at the intervals of 4, 24, 48, and 72 h and at 7 days. To show the comparative degree of growth on the positive plates, qualitative gradings like light, medium, and heavy are used. Each agar plate is incubated at 30±5°C (86±1°F) for 7 days.	After 24 hour of bacterial preparation, <i>Serratia Marcescens</i> is grown on nutrient agar at 30°C. The plates are incubated for 48 hours at 30°C.
Interpretation of the Results	The highest level of biocidal protection is shown by a specimen returning to sterility by the fourth hour following the challenge, holding this sterility for 7 days, and performing in the same manner after four challenges. Returning to sterility 24 h after the challenge and holding this sterility for seven days, and showing this performance after two to four challenges is considered adequate microbial protection for some adhesives by many biological laboratories.	Result is positive when there is no growth of <i>Serratia Marcescens</i> on the agar plates within a 48 hour period and negative result is shown by the growth of red colonies of <i>Serratia Marcescens</i> 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 ConShield anti-bacterial additive.

CHAPTER 6

CONCLUSIONS AND RECOMMENDATIONS FOR FUTURE RESEARCH

6.1 Conclusions

The conclusions of this report can be summarized as follows:

1. 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.
2. Due to the presence of calcium based minerals in the binder phase, typical concretes cannot tolerate the corrosive sulfuric acid.
3. 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.
4. 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.
5. 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.
6. Despite much incorrect printed material regarding reduced permeability and its role in protecting concrete from MIC, 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.
7. The antimicrobial admixture Con^{mic}Shield[®] 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.
8. The antimicrobial admixture has now been in service since 1996 with hundreds of thousands of cubic yards of concrete products providing continuous protection against MIC.
9. 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.

10. 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.
11. 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.
12. Protection from MIC with an antimicrobial admixture is completely compatible with various means to control odors.
13. The antimicrobial admixture requires an EPA registry. Some producers of crystalline forming waterproofing admixtures suggest that MIC can be stopped by just densifying concrete. This indicates a misunderstanding of how acids attack concrete. This is a surface attack where the cement binder is dissolved by the acid. No permeability is required. Many confuse internal complex attacks from mobile ions like chlorides and sulfates with simple acidic dissolution.
14. Also care should be taken to ensure that only proven antimicrobials be used in concrete that are compatible in both the short and long term. Simple 1960 antimicrobial technology employed by the textile industry is not sufficient to protect concrete sanitary structures where classical MIC can occur. While short term testing per modified ASTM Standard D-4783 may indicate some short term effectiveness, this does not prove long term viability in the high alkalinity of concrete.
15. The findings of this study are consistent with previous research conducted at Indiana University-Purdue University at Indianapolis by Dr. D. Thomas Iseley on behalf of the City of Indianapolis in 2009; Dr. Clarence Baugh, Microbiologist at Custom Biologicals Inc. for the Miami-Dade Water and Sewer Authority in 2008; Microbac Laboratories for St. Louis Metropolitan Sewer District in 2010; and Dr. Meera Neb for Trinity River Sewer Authority in 2015. These studies were combinations of laboratory and field tests.

6.2 Recommendations for Future Research

The recommendations for future work are as follows:

1. There is a need for a reliable simple field test that can confirm the presence of the antimicrobial admixture in hardened concrete.
2. There is a need to model H₂S production and accumulation along with corrosion rates in the sanitary sewer structures.

3. 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 Con^{mic}Shield[®] that are otherwise not prone to classical MIC. Study is needed on the subject.
4. 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.
5. In the future, longer H₂S 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.
6. Furthermore, finding better ways to continuously monitor the corrosion process would be of great help.

Acknowledgements

The authors would like to express their sincere appreciation to Mr. William Shook, President, Mr. Keith Walker, Vice President, Mr. Johnny Love, National Product Manager and Mr. Van Young, Regional Manager, ConShield Technologies. Authors are also thankful to TTI Lab, Arlington and Cities of Irving and Dallas. Without their help and support, this project would not have been possible.

APPENDIX A
LABORATORY TEST RESULTS



TTI ENVIRONMENTAL LABORATORIES

800 106th Street, Arlington TX 76011. 817-861-5322

Typical ConShield Customer
Central North Carolina

Date Reported : 07/11/17
TTI Lab Number: 7064091

To Whom It May Concern:

OBJECTIVE: To test for the presence of ConShield in concrete samples.

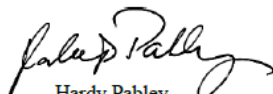
SAMPLES: Two samples were delivered by the client on June 30, 2017 and identified as follows:

1. R-60
2. R-60-I.1

TESTING: The samples were analyzed to ConShield's protocol, a modified ASTM D4783 procedure. A cell suspension of *Serratia marcescens* was prepared, estimated at 1×10^7 cfu/ml. The suspension was placed on the sample surface and allowed to dry. 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.

RESULTS: After 48 hours of incubation:
Sample 2 had no growth indicating the presence of ConShield.
Sample 1 had light pink colonies were observed indicating the absence of ConShield.

QA/QC: Control Samples [Sample 1] from the same mix design were also tested as an in-house QA/QC check for adherence to the modified ASTM D4783 protocols/procedures. After 48 hours of incubation, light pink colonies were observed indicating accurate test methods were followed.


Hardy Pabley
Operations Manager

This report applies only to the sample(s) tested or analyzed. This report may be copied only in its entirety, unless prior written consent has been granted by an authorized agent of the TTI Environmental Laboratories.



ORIGINAL KIB

5 LBS

1 OF 1

DWT:12,10,6

SHIP TO:

MEERA NEB

817-861-5322

TTI ENVIRONMENTAL LABORATORIES

800 106TH ST

ARLINGTON TX 76011-5307



TX 760 0-01



UPS 2ND DAY AIR

TRACKING #: 1Z 980 VIA 02 9920 7246

2



BILLING: P/P

Reference#1: sample - Johnny

US 19.2.05. WNYZNV30 87.0A 04/2017



APPENDIX B
NEW PRODUCT REVIEW (NRP) PROCESS REPORT ON Con^{mic}Shield[®]

Title: Indianapolis Department of Public Works (INDY-DPW) and Iupui-Purdue School of Engineering and Technology (IUPUI) INDY – DPW / IUPUI NRP (New Product Review) Process Report on Con^{mic}Shield®

Author: IUPUI, Department of Engineering Technology, School of Engineering and Technology, A Purdue University School, IN

Publication Date: April 2009

Publication Name:

Objective: Conduct a technical review of Con^{mic}Shield® for the City of Indianapolis Department of Public Works, (Indy-DPW) which involves the following:

- To review material supplied by Product Representative (PR)
- To evaluate past performance
- To compare the product to applicable industry standards and to Indianapolis' Sanitary Sewer Specifications Manual
- To review the product's manufacturing process and material characteristics
- To determine the conformity and expected service life of the product

Scope: Successful use of Con^{mic}Shield® against Microbiologically Induced Corrosion (MIC) in the construction of new and retrofit sanitary sewers.

Methodology: In August of 2008, ConShield submitted their product review application to Indy-DPW for Con^{mic}Shield®. The items submitted for review were initially evaluated by Franco Consulting Engineers, LLC. The items submitted are as follows:

- Product Data
- Technical Papers and Manufacturer Specifications
- Test Reports
- Case Studies
- References

Franco Consulting Engineers, LLC (FCE) interviewed many key users of Con^{mic}Shield® in December of 2008 which included Bull Head City, Arizona, London, Ontario, Canada, Seattle, Washington, Fairfax County, Virginia, Grand Rapids Michigan, Atlanta, Georgia, Los Angeles, California, St. Louis, Missouri, Hampton, Virginia and Miami-Dade, Florida.

A series of questions was presented to precasters that had previously used this product including:

- How much customer demand have you experienced with the product?
- How was your overall experience with the product?
- Have there been any negative reactions to the product?
- What were the costs associated with the product?

Results: The results can be summarized as follows:

Comparison to Applicable Industry Standards

STANDARD	CITY OF INDIANAPOLIS (INDOT 2008 STD. SPEC. Section 901)	PRECAST CONCRETE TREATED WITH CON ^{mic} SHIELD	Appendix
ASTM C39 Compressive Strength	R	X	C
ASTM C76-08a Standard Specification of Reinforced Concrete Culvert, Storm Drain, and Sewer Pipe	Class III, IV, or V Minimum B Wall thickness	X	D
ASTM C157 Shrinkage Testing	R	X	E
ASTM C403 Set Time	R	X	F
ASTM C457 Hardened Air Properties	R	X	G
ASTM C478 Standard Specification for Precast Reinforced Concrete Manhole Sections	R		H
ASTM C642 Absorption	R	X	I
ASTM C666 Freeze Thaw	R	X	J
ASTM C672 Scaling	R	X	K
ASTM C1202 Permeability	R	X	L
ATCC 100-1993 Colonization Test		No Colonization	
ASTM G21-96 Determining Resistance to Bacteria		X	M
ASTM G22-96 Determining Resistance to Fungus – WITHDRAWN, NO REPLACEMENT			

R = Required

X = Meet or Exceeded Standard

Courtesy of Franco Consulting Engineers

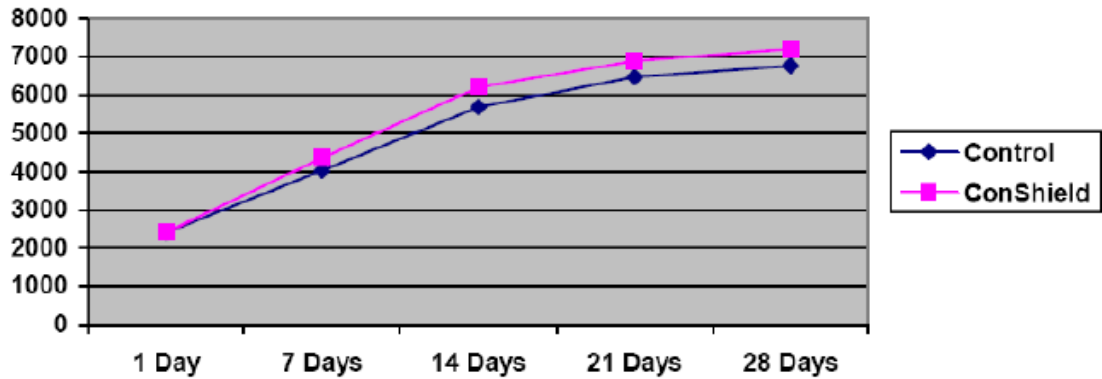
Applicable City Standards:

ConShield submitted laboratory testing reports of precast concrete samples with and without Con^{mic}Shield® for each of the above listed standards. The concrete with Con^{mic}Shield® meet or

exceeded all standards. Currently, there are no Sanitary District Standards that cover this additive.

Past Test Results

ASTM C39 Compressive Strength

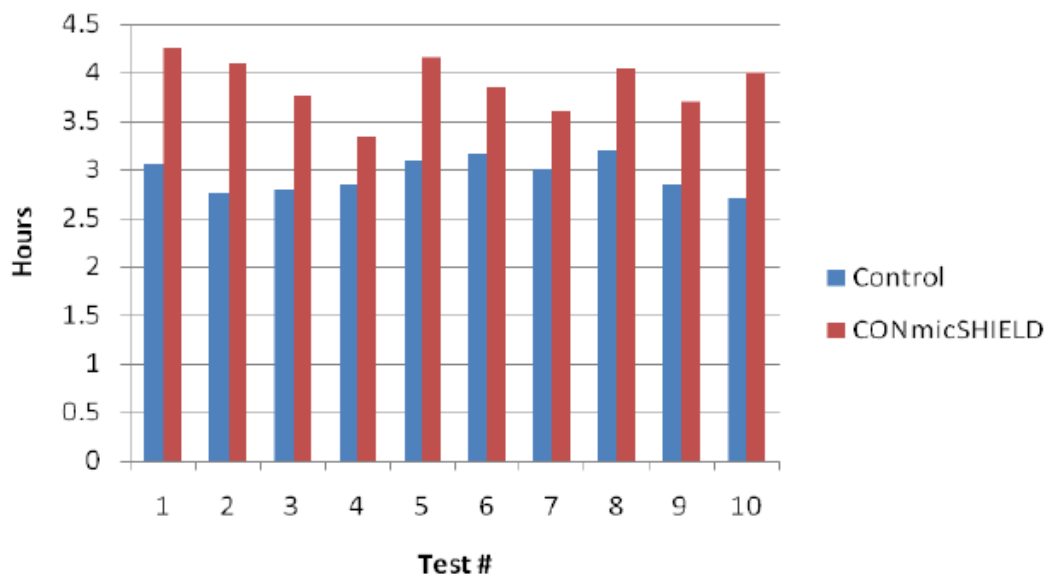


Courtesy of Rotondo / Oldcastle

ASTM C157 Shrinkage Testing

No Data Available

ASTM C403 Set Time



Courtesy of Rotondo / Oldcastle

ASTM C642 Absorption

Mix	% weight	% volume
Control	2.05	2.75
ConShield	4.62	6.44

Note: Values are an average of 10 tests each.

Courtesy of Rotondo / Oldcastle

ASTM C666 Freeze Thaw

No Data Available

ASTM C672 Scaling

No Data Available

ASTM C1202 Permeability

No Data Available

ASTM G21-96 Determining Resistance to Bacteria

Table 1 – *Thiobacillus Inoculum Test Results*

Specimen	Sample	Viable Count After 24 Hours	% Reduction
T.denitrificans	Control	1×10^7	0%
T.denitrificans	CS In	1×10^2	99.999%
T.denitrificans	CS On	1×10^2	99.999%
T.thioparus	Control	1×10^7	0%
T.thioparus	CS In	1×10^2	99.999%
T.thioparus	CS On	1×10^2	99.999%
T. thiooxidans	Control	1×10^3	0%
T. thiooxidans	CS In	0	100%
T. thiooxidans	CS On	0	100%

Courtesy of Custom Biologicals, Inc

In Situ Test Results

These successful laboratory test results were indicators of how the material will perform in the field. These tests were conducted in Atlanta, Georgia. Two cores were taken from a precast pipe, one containing Con^{mic}Shield® and one without the additive. Both were suspended three (3) feet below the manhole cover and approximately seven (7) feet above the flowline. After three (3) months of exposure to this highly corrosive environment the core without the additive had lost nearly 3.5% of its initial SSD (saturated surface dry) weight. Whereas, the treated core had lost 0.3% of its SSD weight.

Table 2 – In-situ Sewer Manhole Field Tests

CONCRETE SAMPLES	INITIAL		FINAL		WEIGHT LOSS (GRAM)
	Weight (GRAM)	pH	Weight (GRAM)	pH	
Core from concrete pipe	894.3	11	891.4	3	2.9
Core from concrete pipe without additive	890.8	11	860.2	1	30.6

Courtesy of ConShield

Recommendation:

- Based on the success of laboratory test results and the in-situ applications the IUPUI Department of Engineering Technology recommends the approval of Con^{mic}Shield[®] for tentative use for new and retrofit construction.
- Cast-in-place, precast, shotcrete, and ConShield's permaform process in accordance with ConShield's suggested specifications should be deemed an approved alternative.
- The location of Con^{mic}Shield[®] should be investigated and determined by the city, where MIC is anticipated. Preferably the additive will be utilized in a manner that would allow for objective comparisons between structures with and without Con^{mic}Shield[®].
- Third party testing was not performed when compiling this report.

APPENDIX C
TECHNICAL PRESENTATIONS ON Con^{mic}Shield®



Custom Biologicals, Inc.

1239 E. Newport Center Drive
Deerfield Beach, Florida 33442
561.998.1699

Concrete Testing for Con^{mic}Shield Additive

Miami Dade Project

9-26-08

Key Biscayne Manhole Miami-Dade Water & Sewer Authority

INSTALLED AUGUST 2001



Sample arrived in a wet condition

SEPTEMBER 11, 2008



Surface Preparation

Surface was scraped with a microscope slide to remove a large part of the slime layer and allow access to the concrete.



SAMPLE PREPARATION

Sample was dried by removing the moisture from the container.
Then, sample was cleaned using an alcohol wash and manual brush.



Sample Drying

As the sample
Dried, Debris and
Slime were easily
removed



Sample Cleaning

Alcohol wash was repeated and sample was brushed until concrete was fully exposed.



Test Area

The test area was clearly marked.



Indicator Organism Applied by Swab to the test location



Storage for Test

The test was stored in a humid, moist area.
Wet Towels are used to maintain moisture.
The container is then covered.



5 Hours After Inoculation

The RED lines are growth of the indicator organism



24 Hours after Inoculation

Samples taken by swab 24 hours after inoculation
Show NO presence of the RED indicator organism



CONCLUSIONS

1. The specimen from the Miami-Dade test manhole in service since August 2001 was delivered to our lab on September 11, 2008.
2. The surface tested at acidic levels of pH 5 as expected from natural acidic conditions on the slime layer.
3. E. Coli and similar bacteria were growing on the organic surface material on the slime layer.
4. Thiobacillus Thiooxidans bacteria were not present because this bacteria will not grow on organic material such as bio-solids.
5. The concrete exposed below the slime layer was undamaged.
6. The exposed concrete surface killed the indicator bacteria and therefore tested positive for the presence of Con^{mi}Shield additive.

By: Clarence L. Baugh, PhD.





St. Louis MSD Maline Drop Shaft Long Term Testing

1. Situation Background
2. 1999: Structural Restoration
3. 2009: Ten-year Inspection
4. Implementation into St. Louis MSD Specifications
5. 2015: Sixteen-year Inspection
6. Third-party test reports
 - a. Microbac, 3 pages, August 2010
 - b. Situ Biosciences, 3 pages, January 2011

St. Louis MSD Maline Drop Shaft Long Term Testing



Figure 1 View of the Maline Drop Shaft from the ground



Figure 2 Confined Space Entry Staging

1. Situation Background

The Maline Drop Shaft, located near the Chain of Rocks Bridge, is just like concrete sewer structures everywhere. They corrode when hydrogen sulfide gas is present. Moderately-high temperatures, long retention times, high biological oxygen demand (BOD) levels, and turbulence contribute to elevated levels of hydrogen sulfide gas which, in turn, provide the food for acid-producing bacteria. The technical name for this process is Microbiologically Induced Corrosion (MIC). This 40-year-old concrete structure was severely deteriorated from MIC. The upper portion of the walls were mushy with more than two inches of the original wall missing; in the lower half of this 50-foot-deep structure, more than five inches of the walls had corroded away.



Figure 3 Corrosion prior to repair in 1999



Figure 4 Reinforcing steel exposed after pressure washing

2. Structural Restoration

In 1999, St. Louis MSD chose Specialty Sewer Company, now ADS Environmental Services, a licensed Permacast® applicator in the St. Louis area, to provide the quickest and most cost-effective method to restore the structural integrity of this severely-corroded structure and to prevent future corrosion. Specialty Sewer Company partnered with Spray-Com, another licensed Permacast® applicator with extensive experience in deep structures, on the project. A crew of five worked for 32 days and did the following to restore the structure:

- Power washed the walls back to solid material
- Attached wire mesh to the walls for structural reinforcement of the worst areas
- Applied MS-10,000, a cementitious grout fortified with Con^{mic}Shield®, in one inch lifts
- Troweled the surface after each layer was applied to ensure a densely-compacted, uniform finish
- Troweled smooth a final one-inch layer once the entire wall was rebuilt to the plumb line

Upon completion of the job, the structural integrity of the Maline Drop Shaft was restored to a better than new condition. Thanks to the addition of Con^{mic}Shield® to the MS-10,000 repair grout, the drop shaft is permanently protected from future MIC damage. The Con^{mic}Shield® additive kills the sulfuric acid-producing bacteria; and, since it is molecularly bonded to the cementitious repair grout, it cannot wash off, chip off, delaminate, or pinhole.

Annual inspections since the restoration of the Maline Drop Shaft were completed, revealing that corrosion has stopped. After eight years, only 3/32" of the wall had been lost to abrasion or erosion. This quick and cost-efficient solution to the MIC damage in the Maline Drop Shaft has greatly extended its life in spite of the continued unstopable and highly-turbulent flows and extremely-high levels of hydrogen sulfide gas.

3. Ten-year Inspection

In 2009, MSD conducted a 10-year inspection of the pilot restoration program of the Maline Drop Shaft. The inspectors concluded the restoration project successfully protected the structure from MIC and added Con^{mic}Shield® to the approved specification for structural construction projects in the District.



Figure 5 Photo of the shaft looking down during the 2009 inspection

Core samples were taken in 2010 to verify the efficacy of Con^{mic}Shield® in the MS-10,000 lining. See figure 6 below.



Figure 6 Photo of the core sample being taken in 2010

The photo of the core sample in Figure 7 shows two pieces. The large piece was labeled Maaline 62910 large section and is a portion of the original concrete substrate. The smaller piece is MS-10,000 fortified with Con^{mic}Shield® and was labeled Maaline 62910 small section. See figure 8 below showing no bacterial growth from the MS-10,000 fortified with Con^{mic}Shield®. These samples were submitted to Microbac for testing in July of 2010. See attached Microbac test report.



Figure 7 Photo of the core sample

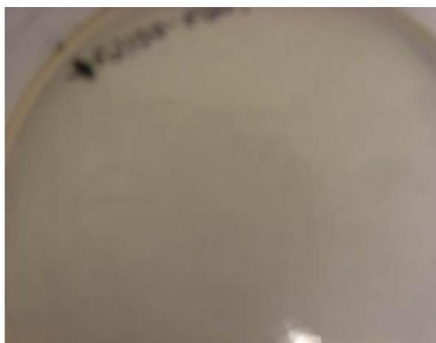


Figure 8 Photo of the agar plate showing no bacteria growth

4. Implementation into St. Louis MSD Specifications

Following the 10-year inspection, the St. Louis MSD inspectors concluded the restoration project successfully protected the structure from MIC and added Con^{mic}Shield® to the approved specification for structural construction projects in the District. St. Louis MSD subsequently began to routinely use Con^{mic}Shield® in manhole and pipe projects. MS-10,000 fortified with Con^{mic}Shield® were also added to the approved list of rehabilitation materials.

St. Louis MSD requires that concrete products containing Con^{mic}Shield® be tested prior to installation as part of their QA/QC program. The process confirms that Con^{mic}Shield® is in place and working. See attached Situ Biosciences, LLC report.

5. 2015: Sixteen-year Inspection

The shaft was again inspected, by St. Louis MSD and engineers from the City of Newburgh, IN in 2015 to further determine the viability of Con^{mic}Shield®'s effectiveness. The mortar and Con^{mic}Shield® were found to have performed above and beyond expectations.

6. Third-Party Test Reports

a. Microbac, August 2010

3 pages to follow



August 6, 2010
Page 1 of 3
Test Report: 1007-00167

TEST REPORT

CLIENT:

ConShield Technologies Inc.
541 Tenth Street NW #233
Atlanta, GA 30318-5713

Attn: Joe Cherry

OBJECTIVE:

To test for the presence of ConShield in concrete samples.

SAMPLES:

Two samples were delivered by the client on July 13, 2010 and identified as follows:

1. Maaline 62910 small section
2. Maaline 62910 large section

TESTING:

The samples were analyzed according to ConShield's protocol, a modified ASTM D4783 procedure.

The concrete samples were washed with water, dried, and then placed in a carbon dioxide chamber overnight.

A cell suspension of *Serratia marcescens* was prepared using distilled water, estimated at 1×10^7 cfu/ml. Approximately 0.2-0.3 ml of the cell suspension was placed on the sample surface and allowed to dry. The samples were then placed in a closed container with moist paper towels and incubated for 24 hours at $30 \pm 1^\circ\text{C}$.

For cell recovery, 0.2-0.3 ml of sterile water was washed over the surface of the sample, stirred with a pipette, then removed and plated on nutrient agar. Additionally, a sterile cotton swab was brushed over the surface of the sample and then used to streak another nutrient agar plate. Both plates were incubated for 48 hours at $30 \pm 1^\circ\text{C}$.

RESULTS:

After 48 hours of incubation, sample 1 had no growth indicating the presence of ConShield. Sample 2 had some pink colonies, indicating no ConShield was present.

Digital images of the samples and nutrient agar plates are presented in Figures 1 through 4 for additional information.

For any feedback concerning our services, please contact the Managing Director or James Nokes, President, at jnokes@microbac.com or Bob Morgan, Chief Operating Officer, at morgan@microbac.com. This report applies only to the sample(s) tested or analyzed. This report may be copied only in its entirety, unless prior written consent has been granted by an authorized agent of the Hauser Laboratories Division of Microbac Laboratories, Inc.

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August 6, 2010
Page 2 of 3
Test Report: 1007-00167

CLIENT:

ConShield Technologies Inc.
541 Tenth Street NW #233
Atlanta, GA 30318-5713

Attn: Joe Cherry



Small section



Nutrient agar plate from small section

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August 6, 2010
Page 3 of 3
Test Report: 1007-00167

CLIENT:

ConShield Technologies Inc.
541 Tenth Street NW #233
Atlanta, GA 30318-5713

Attn: Joe Cherry



Large Section



Nutrient agar plate from large section

**DATA REVIEWED AND
REPORT WRITTEN BY:**

REPORT REVIEWED BY:

Becky F. Kinsinger
Microbiology Manager

Angelica Tovar
Project Coordinator

For any feedback concerning our services, please contact the Managing Director or James Nokes, President, at jnokes@microbac.com or Bob Morgan, Chief Operating Officer, at morgan@microbac.com. This report applies only to the sample(s) tested or analyzed. This report may be copied only in its entirety, unless prior written consent has been granted by an authorized agent of the Hauser Laboratories Division of Microbac Laboratories, Inc.

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6. Third-Party Test Reports

b. Situ Biosciences, January 2011

3 pages to follow



Customer Report

Monday, January 17, 2011

Situ Biosciences LLC
3415 Howard St, STE 102
1-847-677-4575
Info@situbiosciences.com

Customer Report Summary

Contact	Carlos Huddleston, P.E.; Gonzalez Companies LLC
Project Title	Bacterial inhibitory performance of treated concrete
Project ID#	1110ADA0101

Overview:

Seven concrete samples treated with antimicrobial additives were submitted for microbiological testing to determine the performance of the antimicrobial product against a range of *Thiobacillus species*. For the purpose of the test, three *Thiobacillus species* were selected based on their ability to accommodate the surface of native concrete that has been aged using a rain water mist cycling protocol. The mist cycling reduced the inherent concrete pH from ~ 10.5 to a pH of 6.8 in 21 days using a solution of rain water salt solution at a pH of 5.4.

As environmentally isolated *Thiobacillus* bacteria cover a broad range of organism types that will both thrive and reduce pH to as low as pH 1, the *Thiobacillus* inoculum selected contains *Thiobacillus sp.* that can grow in a range of pH conditions from pH 6 to <pH 4.

Results: Each of the tested samples demonstrated an approximate 1.5 to 3 log reduction during the course of the testing.

Conclusion: The pH neutralized concrete samples show clear antibacterial activity against a range of *Thiobacillus* bacteria.

Don P. Satchell Ph. D.
Situ Biosciences LLC, Technology Director

This report is governed by and incorporates by reference, the conditions of testing as posted on the date of issuance and is intended for your exclusive use. Any Copying or replication of this report to or for any other person or entity, or use of our company name or Service Mark is permitted only with our prior written consent. This report sets forth our findings solely with respect to test samples identified herein. The results set forth in this report are not indicative or representative of the quality or characteristics of the lot from which a test sample was taken or any similar identical product unless specifically and expressly noted. Our report includes all tests requested and the results thereof based upon the information provided. You have 60 days from the date of issuance of this report to notify us of any material error or omission caused by our handling of the samples, provided however that such notice shall be in writing and shall specifically address the issue you wish to raise. A failure to raise such issue within the prescribed time shall constitute your unqualified acceptance of the completeness of this report, the test conducted and the correctness of the report contents.



Customer Report

Monday, January 17, 2011

3415 Howard St. STE 102
Skokie, IL 60076
1-847-677-4575
Info@situbiosciences.com

Contact Gonzalez Companies LLC Carlos Huddleston, P.E. 618-222-2221
Title Bacterial inhibitory performance of treated concrete
Project ID 1010-ADA-01-- 1 Entry Date 11/4/2010 Test Start Date 12/3/2010

Sample Result Table

Test Method ASTM D4783 - 01(2008) Adapted for determination of antibacterial resistance of concrete to thermobacillus sp.

Sample #	Inoculum	Interval	Result
1	90" w/ Stirrups w/Conshield		
<i>Mixed Thiobacillus sp.</i>			
T. intermedia; Reduction >= 99.9%		24 hr	3 Log Reduction
T. novella; Reduction = 99%		24 hr	2 Log Reduction
T. thioparus; Reduction = 99%		24 hr	2 Log Reduction
2	48" Risers w/Conshield		
<i>Mixed Thiobacillus sp.</i>			
T. intermedia; Reduction >= 99.9%		24 hr	3 Log Reduction
T. novella; Reduction >= 99.9%		24 hr	3 Log Reduction
T. thioparus; Reduction = 99%		24 hr	2 Log Reduction
3	90" CL-5 w/ Stirrups w/Conshield		
<i>Mixed Thiobacillus sp.</i>			
T. intermedia; Reduction >= 99.9%		24 hr	2 Log Reduction
T. novella; Reduction >= 99.9%		24 hr	3 Log Reduction
T. thioparus; Reduction >= 99.9%		24 hr	3 Log Reduction
4	9-29 (unlabeled)		
<i>Mixed Thiobacillus sp.</i>			
T. intermedia; Reduction >= 99.9%		24 hr	2 Log Reduction
T. novella; Reduction = 95%		24 hr	2 Log Reduction
T. thioparus; Reduction >= 99.9%		24 hr	3 Log Reduction

Situ Biosciences LLC

Result Table 1 of 2

1010-ADA-01-- 1
Monday, January 17, 2011

Sample Result Table

Sample #	10-8			
Inoculum	Interval	Result		
<i>Mixed Thiobacillus sp.</i>				
T. intermedia; Reduction >= 99.9%	24 hr	3 Log Reduction		
T. novella; Reduction = 91%	24 hr	1.2 Log Reduction		
T. thioparus; Reduction >= 99.9%	24 hr	3 Log Reduction		
Sample #	10-12			
Inoculum	Interval	Result		
<i>Mixed Thiobacillus sp.</i>				
T. intermedia; Reduction = 99%	24 hr	2 Log Reduction		
T. novella; Reduction = 95%	24 hr	1.5 Log Reduction		
T. thioparus; Reduction = 99%	24 hr	2 Log Reduction		
Sample #	10-19 (18)			
Inoculum	Interval	Result		
<i>Mixed Thiobacillus sp.</i>				
T. intermedia; Reduction >= 99.9%	24 hr	3 Log Reduction		
T. novella; Reduction >= 99.9%	24 hr	3 Log Reduction		
T. thioparus; Reduction >= 99.9%	24 hr	3 Log Reduction		

Title: Corrosion Control in Concrete Pipe and Manholes

Author: William E. Shook, Leonard W. Bell, PE

Publication Date: October, 1998

Publication Name: Technical Presentation, Water Environmental Federation, October '98
Orlando, FL

Objective: To Control Concrete Corrosion in Pipe and Manholes

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, 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 ConMICShield 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 H₂S 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.

Title: Antimicrobial Activity of Permacast MS-10,000 with Con^{mic}Shield® in Concrete Discs

Author: Dr. Clarence L. Baugh

Publication Date: April 12, 2002

Objective: To investigate the Antimicrobial Activity of Permacast MS-10,000 with Con^{mic}Shield® in Concrete Discs

Methodology: Five sample sets of concrete discs containing Permacast MS-10,000 with Con^{mic}Shield® were received in 1997. The samples were reconditioned for pH. A one milliliter aliquot of a bacterial suspension of *Thiobacillus thiooxidans* was aseptically pipetted evenly onto the surface of each disc and incubated at 25 degrees centigrade for 24 hours. The surface of each disc was then washed with 10 ml of medium ATCC medium 125 for *Thiobacillus thiooxidans*. The cell suspension was then collected into a sterile container and ten-fold serial dilutions of the bacterial suspension were made in the appropriate medium to obtain viable counts using a modified NETAC method. Four replicates were made per set. The tests were incubated for 26 days at 25 degrees centigrade.

Results:

Effect of Permacast MS-10,000 with Con^{mic}Shield® contained in concrete discs on *Thiobacillus thiooxidans*, *Thiobacillus denitrificans* and *Thiobacillus thioparus*.

reduction	Viable Count / ml (recovered from surface)			
	organism #: 1	2	3	%
Sample 0101	1000	1000	1000	99.9
Sample 8432	1000	1000	1000	99.9
Sample 1098	1000	1000	1000	99.9

organism #

1. *Thiobacillus thiooxidans*
2. *Thiobacillus denitrificans*
3. *Thiobacillus thioparus*

Inoculum = 1 X 10⁶ / ml.

Title: Mitigating the Corrosion of Concrete Pipe and Manholes

Author: Leonard W. Bell, P.E., William E. Shook, and Troy Norris

Publication Date: 1999

Publication Name: American Society for Testing and Materials

Objective: To control corrosion of concrete pipe and manholes.

Conclusion: A well operating waste water system is essential to the health and well being of any society. Because the piping system is buried in the ground, it should last forever once it is placed. Many sewer systems need upgrading because of undersize or deterioration of the piping. New technology is providing ways of doing some upgrading of existing piping, by insertion of liners, replacement by pipe bursting and shotcreting of large diameter pipe.

This paper has discussed two approaches for controlling MIC of concrete sewers.

1. New computer programs can be used to reduce the beginnings of MIC, i.e., the generation of hydrogen sulfide gas and subsequently corrosive sulfuric acid.
2. Early results with a new material, a stable quaternary ammonium salt derivative, added to concrete shows promise as a means of controlling bacterial growth on the concrete and reducing MIC.

Title: Antimicrobial Activity of Permacast MS-10,000 with Con^{mic}Shield® in Concrete Discs

Author: Dr. Clarence L. Baugh

Publication Date: December 7, 1999

Objective: To investigate the Antimicrobial Activity of Permacast MS-10,000 with Con^{mic}Shield® in Concrete Discs

Methodology: Three sample sets of concrete discs containing Permacast MS-10,000 with Con^{mic}Shield® were received in 1997. The samples were reconditioned for pH. A one milliliter aliquot of a bacterial suspension of Thiobacillus thiooxidans was aseptically pipetted evenly onto the surface of each of three discs (0101, 8432, and 1098). The same process was repeated for Thiobacillus thioparus and Thiobacillus denitrificans. All the samples were incubated at 25 degrees centigrade for 24 hours. The surface of each disc was then washed with 10 ml of ATCC medium 290. The cell suspension was then collected into a sterile container and ten-fold serial dilutions of the bacterial suspension were made in the appropriate medium to obtain viable counts using a modified NETAC method. Four replicates were made per set.

Results:

Effect of Permacast MS-10,000 with ConShield contained in concrete discs on Thiobacillus thiooxidans, thiobacillus denitrificans, Thiobacillus thioparus

	Viable count / ml. (recovered from surface)			
organism #:	1	2	3	%reduction
Sample 0101	100	100	100	99.9999%
Sample 8432	100	100	100	99.9999%
Sample 1098	100	100	100	99.9999%

organism 1= Thiobacillus thiooxidans
organism 2= Thiobacillus thioparus
organism 3= Thiobacillus denitrificans
Inoculum = 1×10^7 / ml.

Conclusion: Under the conditions of this test, all the concrete disc samples of Permacast MS-10,000 with Con^{mic}Shield[®] showed extremely high antimicrobial activity as for all practical purposes all of the test organisms were killed in 24 hours.

Title: Antimicrobial Activity of Concrete Wafers

Author: Dr. Clarence L. Baugh

Publication Date: April 24, 1997

Objective: To investigate antimicrobial activity of concrete wafers.

Methodology: Five sample sets of concrete discs containing Permacast MS-10,000 manufactured by Action Products Marketing Corporation containing Fibermesh with Con^{mic}Shield[®] were received from Stacy Kinchen, Synthetic Industries, Inc. Although the actual fiber dosages were equal, the Con^{mic}Shield[®] concentrations varied with each sample set. The samples had been adjusted for pH. A one milliliter aliquot of a bacterial suspension of *Thiobacillus thiooxidans* was aseptically pipetted evenly onto the surface of each disc and incubated at 25 degrees centigrade for 24 hours. The surface of each disc was then washed with 10 ml of medium ATCC medium 125 for *Thiobacillus thiooxidans*. The cell suspension was then collected into a sterile container and ten-fold serial dilutions of the bacterial suspension were made in the appropriate medium to obtain viable counts using a modified NETAC method. Four replicates were made per set. The tests were incubated for 26 days at 25 degrees centigrade.

Results:

Thiobacillus thiooxidans.

Sample Set		Viable count / ml. (recovered from surface)	% reduction
1.	0101	0	100%
2.	6777	0	100%
3.	8432	0	100%
4.	2706	0	100%
5.	1098	0	100%

Inoculum = 1×10^6 / ml.

Conclusion: Under the conditions of the test, all of the concrete disc samples of Fibermesh fibers with Con^{mic}Shield[®] showed extremely high antimicrobial activity as all of the test organisms were killed in 24 hours.

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