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Understanding the Chemistry of Microbiologically Induced Corrosion (MIC) of Concrete in Sanitary Sewerage Environment: A Review Study

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ABSTRACT

Microbially Induced Corrosion (MIC) of concrete in sanitary sewers is a common problem that demands a great deal of rehabilitation investment every year. It is a result of dilute sulfuric acid dissolving the cement matrix. The acid is produced by a complex series of chemical and biochemical reactions. Hydrogen Sulfide (H_2S) is produced by an action of Sulfur Reducing Bacteria (SRB) in the liquid phase, and then in time, this gas is converted by Sulfur Oxidizing Bacteria (SOB) into Sulfuric Acid (H_2SO4). The last conversion occurs above the liquid level under aerobic condition. The objective of this study is to review and understand the chemistry behind MIC of concrete in sanitary sewerage system. Published papers were reviewed that illustrated MIC of concrete during past 40 years. The literature review suggests that concrete deterioration is not simple and involves a complex chemical process with varied surface interactions. Therefore, there is a need to better understand the chemistry behind the MIC process that varies with installation and repair of every concrete structure.

KEYWORDS: MIC, Chemistry, Environment, Sewerage

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INTRODUCTION

Microbiologically Induced Corrosion (MIC) also known as biological sulfuric acid attack is the main source of concrete deterioration in the sanitary sewer structures (Fig. 1). 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. [1,2,3,4] A significant amount of research was conducted on the complex mechanisms involved with MIC. [5,6,7,8]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

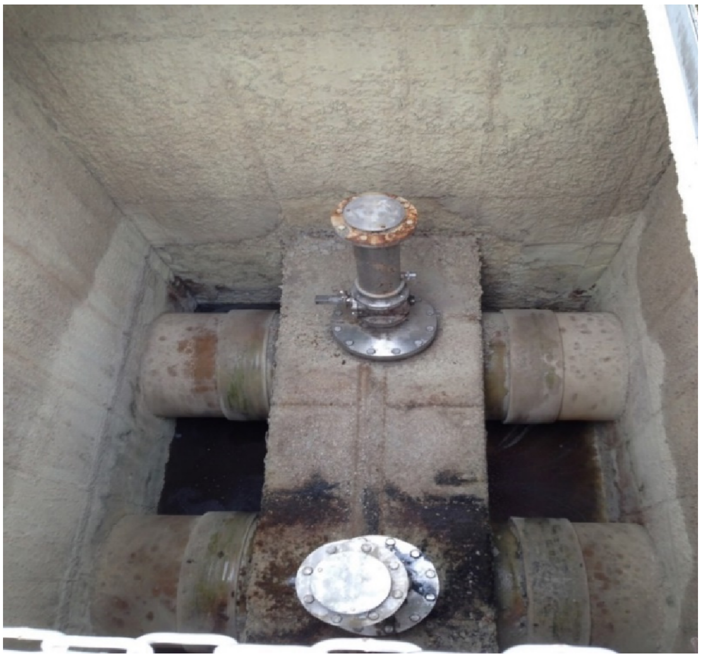

Figure 1. Concrete Deterioration in Sanitary Sewer Structures due to MIC

CHEMISTRY OF MIC

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 Ca3SiO5 orjust C3S - accounting for about 40 to 70% of the cement
- Belite or C2S - 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. 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 Equations1 and 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.

$$\text{Alite}\quad C_3S + (1.3 + x)\,H \rightarrow C_{1.7}SH_x + 1.3\,CH(1)$$

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

$$\text{Belite}\ C_2S + (0.3 + x)\,H \rightarrow C_{1.7}SH_x + 0.3\,CH(2)$$

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.[3,4]

To the extreme right side of the chemical reactions in the Equations 1 and 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.[9,10]

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. The basic differences in the 5 types of Portland cement are shown in the Table 1 below.

Table1: Basic Differences in the Five Types of Portland Cement

Type	Classification	Characteristics	Applications
I	General purpose	Fairly high C_3S content for good early strength development	General purpose
II	Moderate sulfate Resistance	Low C_3A 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_3S	Rapid construction, cold weather concreting
IV	Low heat of hydration (slow reacting)	Low lime and alumina content resulting in less C_3S (<50%) and C_3A	Massive structures such as dams. Now rarely produced
V	High sulfate resistance	Very low alumina content resulting in low C_3A (<5%)	Structures exposed to high levels of sulfate ions
White	White color	reduced iron content, no C_4AF, low MgO	Decorative (otherwise has properties similar to Type I)

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 underground with the Portland to offset shrinkage.

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.[11] 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%(Taylor, 1997).

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 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.[15]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: Reaction of Concretes with Acids

Type of Acid	Lime + Acid	Result	Salt + Water
Hydrochloric	$Ca(OH)_2 + 2HCl$ (aq)	$\longrightarrow$	$CaCl_2$ (aq) + $2H_2O$
Phosphoric	$3Ca(OH)_2 + 2H_3PO_4$ (aq)	$\longrightarrow$	$Ca_3(PO_4)_2$ (s) + $6H_2O$
Sulfuric	$Ca(OH)_2 + H_2SO_4$ (aq)	$\longrightarrow$	$CaSO_4 + 2H_2O$ (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 calcium hydroxide but also many other minerals. The reaction by-products are complex and non-structural; they are a weak punky mush. [16]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 $C\overline{S}$ with the $\overline{S}$ representing SO_3. The sulfuric acid first reacts with the calcium hydroxide in the concrete to form gypsum as shown in the equation 3.[15,16]

$$Ca(OH)_2 + H_2SO_4 \rightarrow CaSO_4 \cdot 2H_2O\ (gypsum) \quad (3)$$

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 4 (Abdelmseeh et al., 2006).

$$3CaO{\cdot}Al_2O_3{\cdot}12H_2O{+}3(CaSO_4{\cdot}2H_2O){+}14H_2O{\rightarrow}3CaO){\cdot}Al_2O_3{\cdot}3CaSO_4{\cdot}32H_2O(ettringite) \quad (4)$$

Equation 5 below states the reaction in a different way.

$$6Ca + 2Al(OH)_4 + 4OH + 3SO_4 + 26H2) \rightarrow C_6A\overline{S}_3H_{32} \quad (5)$$

Today, ettringite is most typically expressed as: $C_3A{\cdot}3C\overline{S}{\cdot}32H$.

SURFACE ATTACK BY ACIDS

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.[17]

H_2S AND CONCRETE

There is no direct corrosion by H_2S gas. The gas will not readily combine with oxygen and water to form an acid. There is a possibility that H_2S in water can form an acid in the presence of certain ammonia compounds under rare circumstances. H_2S can directly corrode iron based metals and other metals like lead.

Sulfuric acid (H_2SO_4) 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 6.

Lime (CaO) Containing Minerals + Dilute Acid ($H_2SO_4 + H_2O$) → Water + Various Calcium Sulfate compounds like (Gypsum $CaSO_4 \cdot 2H_2O$) (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.[18]

SULFURIC ACID PRODUCTION

In the presence of oxygen in the sewer atmosphere, H_2S 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 are listed in the equations 7, 8, 9, and 10 as follows:

$$2H_2S + O_2 \rightarrow 2H_2O + S \quad (7)$$

$$4H_2S + 5O_2 \rightarrow 4H_2O + 2S_2O_3 \quad (8)$$

$$2S + 3O_2 + 2H_2O \rightarrow 2H_2SO_4 \quad (9)$$

$$2S_2O_3 + 3O_2 + 4H_2O \rightarrow 4H_2SO_4 \quad (10)$$

However, the actual processes are much more complex involving many intermediates. H_2S is primarily chemically oxidized to thiosulfate (S_2O_3) 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 H_2S and other sulfur compounds to sulfuric acid, which corrodes the concrete.[18] The creation of sulfuric acid by abiotic oxidation is dependent on local pH. At low pH, H_2S can be oxidized directly to elemental sulfur. Oxidation to sulfate ($SO4^{2-}$) takes place at higher pH levels with thiosulfate ($S_2O_3^-$) 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 H_2S and intermediate products to sulfuric acid. Parker in 1947 was the first to name Thiobacillusconcretivorous, later identified as Thiobacillusthiooxidans 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. 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.[14,15,16,17]

Fresh concrete is highly alkaline, often exhibiting pH between 12.5 and 13.5.[14]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. H_2S 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 3 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 3. Preferred Substrates and pH Ranges for SOM Involved with MIC in Concrete Sewer Networks[13]

Species	Preferred substrate	Preferred pH growth range
T. thioparus	$H_2 S$, S^0 , $S_2CO_3^{2-}$	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_2S , 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.[18]

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.[19,20]

CONCLUSIONS

This paper reviewed MIC of concrete in sanitary sewer environment during past years. The literature review suggests that concrete deterioration due to MIC is not simple and involve a complex chemical process with considerable biological activity. Due to the presence of calcium-based minerals in the binder phase, typical concretes cannot tolerate the corrosive sulfuric acid.Therefore, there is a need to better understand the chemistry behind the MIC process that varies with installation and repair of every concrete structure.

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