

Chapter 2

Influence of Sulfur Ions on Concrete Resistance to Microbiologically Induced Concrete Corrosion

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Abstract Concrete biodeterioration is defined as the damage that the products of microorganism metabolism, in particular sulfuric acid, do to hardened concrete. The combination of sulfur compounds and sulfur-dependent microorganisms is the origin of the process, because sulfates are found in certain groundwater, sewer and in sea water, additionally, some sulfur compounds are natural constituents of Portland cement. Along with this, the common presence and activity of microorganisms plays a very important function in the whole spectrum of degradation processes such as biodeterioration of metals and concrete. We report here the development of a possible biodeterioration resistant concrete. We assume that the elimination of sulfur compounds and acid reactive materials in the Portland cement and aggregates will prevent the formation and action of the biogenic acids that cause dissolution of calcium-containing minerals [for a narrative in Spanish see (Rendon, ¿Que es el biodeterioro del concreto? Revista Ciencia de la Academia Mexicana de Ciencias, Vol. 66 Num. 1. http://www.revistaciencia.amc.edu.mx/images/revista/66_1/PDF/Biodeterioro.pdf, 2014)]. This study was carried out on site inside a wastewater sewer drainage in Mexico City. Concrete samples whose main characteristic was being formulated without any sulfur or sulfates in its composition as well as reference concrete samples made with Ordinary Portland Cement (OPC) were used for the experiment. The weight changes and surface changes of both concrete samples were valued after 7-month exposition to the biodeterioration process. The results obtained on site suggest that both the composition of concrete and duration of aggressive environment are very important. This possible biodeterioration-resistant concrete could give a viable solution to the long known problem of microbiologically induced concrete corrosion (MICC) a typical case of biodeterioration. Furthermore, we recommend the *Portland* type cement Mexican norm (ONNCCE,

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Organismo Nacional de Normalización y Certificación de la Construcción y Edificación, S.C. (2004) Norma Mexicana (NMX – C – 414 – ONNCCE - 2004) Diario Oficial de la Federación 27 de julio de 2004, 2004) which does not take into consideration the concrete biodeterioration variable and its mechanism, to be reviewed in this aspect, or at least that a warning be issued as a key measure to mitigate biodeterioration in sewer concrete infrastructure.

Keywords Biodeterioration • Concrete • Corrosion Resistance

2.1 Introduction

Portland cement is obtained by a conventional process of sintering (solid state synthesis), from a mixture of limestone and clay to high temperature (1450 °C), where a partial melting of raw materials and formation of nodules of clinker are produced. The clinker is mixed with gypsum and grind together to make the cement. Adding sulfates and sulfur compounds are considered essential in cement and concrete composition to help with setting properties, lower the clinkering synthesis temperature, etc. Sulfur compound in cement and concrete can be broadly categorized as: Added sulfates—gypsum, hemihydrates, anhydrite, several synthetic forms of sulfates (typically by-products like flue gas desulfurization materials); Clinker sulfates—including arcanite, aphythalite, calcium langbeinite, and thenardite. Although generally reported as SO₃ (% by mass) for consistency, sulfur can be found in any combination of these forms. Elemental sulfur is almost never found in *Portland* cement, except in trace amounts, as it is generally produced in an oxidizing environment. The added sulfates (gypsum) are blended with clinker during the finish grinding of the cement in amounts needed to control early setting properties, as well as shrinkage and strength development. The amount needed varies from cement plant to cement plant, depending on the chemistry and fineness of the cement, but is typically on the order of 5% by mass. The most common form of sulfate added to *Portland* cement is calcium sulfate (CaSO₄·2H₂O), some of which is intentionally dehydrated by the heat of grinding to form hemihydrates, which is more soluble and therefore available earlier to control early hydration reactions, but sometimes may cause anomalous set as false set. Clinker sulfates form naturally during clinker production (sulfates typically are part of the raw materials as mined or fuel). These sulfates tend to volatilize at the temperatures of cement kilns (up to about 1450 °C) and tend to condense on the outer surface of clinker nodules as alkali sulfates during the last stage of clinker production (rapid cooling). Furthermore, the amount depends on the chemistry of the raw materials and kiln operating conditions, making cement somewhat unique. These alkali sulfates are usually soluble enough to help control early hydration reactions. Some clinker sulfate is also incorporated into other cement phases. Since cement is unique, chemical analyses are the best method of determining the SO₃ content of cements. Typically, the total SO₃

content is measured (or elemental sulfur is measured and converted to SO_3) through methods prescribed in ASTM C114 (or AASHTO T 105). XRF analysis is probably the most common technique. The presence and effect of sulfates and sulfur compound in cement and concrete are considered beneficial in such a degree that it has become an unbreakable paradigm, which *Portland* cement has to contain them. Consequently, every *Portland* cement is manufactured with some amount of them, therefore whatever the source of sulfates and sulfur compound in cement and concrete its presence is a fact.

2.2 Background

Most deterioration processes involve two stages. Initially, aggressive fluids (e.g., water, ionic solutions with dissolved salts, bacteria) need to penetrate or be transported through the capillary pore structure of the concrete to reaction sites (e.g., sulfates penetrating to reactive aluminate, bacteria penetrating to sulfur source gypsum) prior to the onset of the actual chemical or biochemical deterioration reactions. These fluids can be water, dissolved chemicals as sulfates, chlorides, alkalis, or acids (biogenic acids).

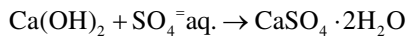
These aggressive fluids can be transported into or through the concrete pore structure by various single or combined mechanisms, some of which are:

Ionic diffusion (due to concentration gradient)

Vapor diffusion (due to humidity gradient)

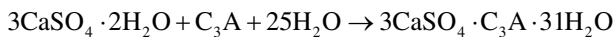
2.2.1 Sulfate Attack on Portland Cement Elements

Sulfates will attack the calcium hydroxide, tricalcium aluminate (C_3A), and hydrated aluminate phases from the Portland cement. The calcium hydroxide can convert to gypsum:



However, gypsum formation is only a precursor to the attack.

The majority of the damage occurs through subsequent growth of ettringite crystals:



In part related to the large number of attached water molecules, the ettringite crystals are large and cause a volume increase, resulting in tensile forces and cracking of the concrete. Therefore, external sulfate attack results in cracking, softening, and exfoliation.

Usually, the $\text{Ca}(\text{OH})_2$ content of the paste will be reduced through pozzolanic reaction and therefore will not be available to form gypsum or ettringite crystals as sulfate ions penetrate.

2.2.2 *Microbiologically Induced Concrete Corrosion*

There is evidence [14, 16] that sulfur compounds present in the concrete are the main reason for the dissolution of concrete by sulfate-reducing bacteria (SRB) through the microbiologically induced concrete corrosion (MICC) process. Corrosion of concrete has an enormous economic impact, especially when replacement or repair of corroded municipal sewer systems (sewer-pipe failure causes extensive damage to roads and pavements) or highway infrastructures is required.

Corrosion of concrete sewer pipes was detected as early as 1900 by Olmstead and Hamlin [7]. Hydrogen sulfide, an anaerobic decomposition product of sulfur-containing cement, was identified as one of the first corrosion perpetrator. Later, in a series of studies, Parker and coworkers established that the presence of *acidophilic thiobacilli* was correlated with concrete degradation [9–11]. Other important contributions in the microbial processes involved in concrete pipe degradation were done by Sand and Bock [20], Cho and Mori [1], Davis et al. [2], Nica et al. [6], Hernandez et al. [3], and Roberts et al. [17].

The biodeterioration of concrete sewers is the end result of a sequence of processes involving biochemical transformations of organic and inorganic sulfur compounds, by the action of anaerobic and aerobic bacteria. The submerged surface of a sewer pipe is typically coated with a film comprised of a diverse microbial community. Anaerobic conditions can develop in such films, providing a suitable environment for the growth of sulfate-reducing bacteria. Sulfate reducers oxidize organic acids and alcohol, generated as end products of many types of anaerobic fermentation, with the concomitant reduction of sulfate to sulfide [21]. Sulfide diffuses out of the film into the bulk liquid flow. At the pH of most wastewater, aqueous sulfide divides involving hydrosulfide (HS^-) and dissolved hydrogen sulfide (H_2S). Dissolved H_2S readily evolves into the sewer inner space, subsequently reaching the pipe crown. There the gas can be metabolized to sulfuric acid by sulfur-oxidizing bacteria. The sulfuric acid dissolves calcium hydroxide and calcium carbonate in the cement binder; then bacteria can reach inner cement sulfates a new source of sulfur, increasing corrosion and compromising the structural integrity of the pipe [19], see Fig. 2.1.

The microbial environment at the concrete surface is three-dimensional. Concrete is porous, and often it ends up coated by a porous layer of corrosion product (Fig. 2.3). Compounds and organisms are distributed throughout a volume that extends beneath the exposed surface. Dissolved sulfide at the surface diffuses into the concrete in both liquid and gas phases. Microbial oxidation of sulfide occurs throughout the depth of penetration. Sulfuric acid diffuses inward, dissolving and neutralizing alkaline substances as they diffuse outward from the underlying concrete, leaving an expanded residue of CaSO_4 on the surface, see Fig. 2.2.

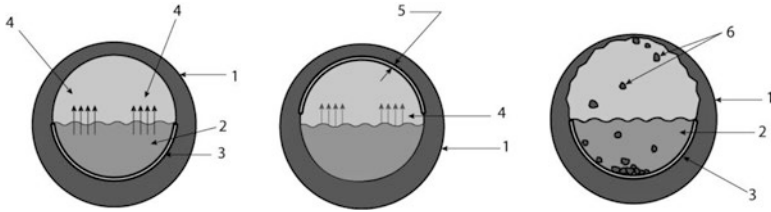


Fig. 2.1 Biodeterioration mechanism illustration: (1) concrete pipe, (2) wastewater stream, (3) anaerobic biofilm with sulfate-reducing bacteria, (4) internal atmosphere saturated with H_2S , (5) biofilm with sulfur-oxidizing bacteria (SOB), (6) concrete debris with gypsum and ettringite remains that fall to the bottom of the pipe and enrich the silt with sulfates [14]

Fig. 2.2 Expanded residue of $CaSO_4$ on the concrete surface

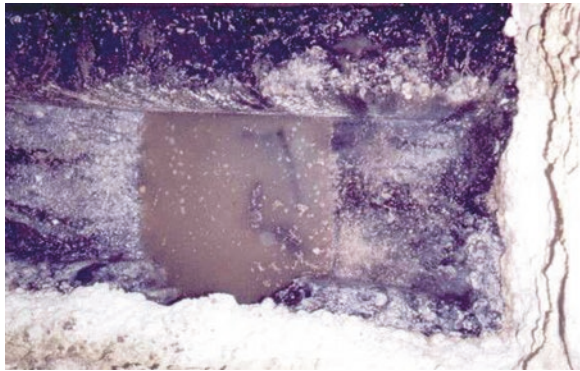


Fig. 2.3 Sulfur deposits at the visiting manholes of experimental site

New concrete has a low permeability, and only a small fraction of its pores are large enough to be penetrated by microorganisms. However, with time small interconnected cavities allow dissolved compounds to diffuse inward. Chemical gradients into the concrete are established quickly, porosity of the concrete increases as the dissolution of calcium hydroxide and calcium carbonate by acid enlarges the pores. With this puffy structure, the corrosion process is then further accelerated by the penetration of the concrete by microorganisms. Microbiologically induced concrete corrosion has been studied extensively, this concrete corrosion processes have been linked to the generation of sulfuric and nitric acids by sulfide oxidizing bacteria and nitrifying bacteria, nonetheless, the composition of concrete and presence of sulfates in it has not been implicated in the degradation of concrete. Furthermore, the objectives of this study were to evaluate the biodegradation of concrete whose composition is sulfates and sulfur compounds free in the binder cement and acid reactive compounds free in the aggregates.

2.3 Process Description

In the corrosion processes acid production is dominated by selected members of the genus *Thiobacillus thiooxidans* [4], which were recently reclassified as *Acidithiobacillus* by Kelly and Wood [5], and *Thiobacillus ferrooxidans* and the entire *Acidiphilium* genera [3, 13]. It has been known since 1945 [9] that *Acidithiobacilli* is the one that causes the rapid degradation of concrete sewer works and that corrosion occurred wherever *Acidithiobacillus* is present at an abundance of five x 10-exp. 6 cell/mg of total protein. Early work by Parker [12] as well as investigators at the Hamburg Municipal Drainage Department (Sand and Bock 1984) found *A. thiooxidans*, *A. neapolitanus*, *A. intermedius*, and *A. novellus* on sewer crowns. One approach to a better understanding of the microbial communities responsible for the production of sulfuric acid is through the analysis of their DNA. Sequence analysis of 16S rDNA and functional gene clone libraries (collections of genetic signatures) can be used to describe the phylogenetic affiliation (specific bacterial species) and function potential (what they can do) of microbial communities associated with MICC [3]. The development of comprehensive databases for bacterial communities in sewer systems within a wide range of corrosion conditions is crucial to identifying bacterial groups that could form the basis for bioassays used to develop innovative condition assessment tools for monitoring MICC.

Investigations of the causes of biogenic sulfuric acid corrosion of concrete particularly in the sewer pipes follow three criteria to diagnose MICC at the sewers: low pH measurements, the detection of neutrophilic sulfur bacteria in the pipes, and, associated with that, the observation of sulfur deposits at the visiting manholes, see Fig. 2.3. In a remarkable report, Rohwerder and Sand [18] proposed a biochemical model for elemental sulfur and sulfide oxidation in *Acidithiobacillus*. In this model, free sulfide is oxidized to elemental sulfur by a separate sulfide: Quinone oxidoreductase, and because this enzyme has only been isolated from neutrophilic

sulfur bacteria, the detection of these types of bacteria ensures that the main corrosion mechanism, MICC, is underway. In the manufacture of concrete sewer pipes, microbiologically induced concrete corrosion phenomena are rarely taken into account. Durability considerations for the pipe material are as significant as its ability to perform intended structural and hydraulic functions. The capability of the pipe to continue to perform satisfactorily for an economically acceptable period is a fundamental engineering consideration. Unfortunately, predictions of durability cannot be made with the same degree of precision as can structural and hydraulic performance, and in too many instances, durability is not accorded adequate consideration. Furthermore, at the present time, no material is known that is completely inert to chemical or biochemical action and immune to physical deterioration. Concrete is no exception, but, under what might be considered *normal* exposure conditions, it has a very long life. Concrete made by the Romans from natural cement is in excellent condition after more than 2000 years of service.

2.4 Experimental

In this study it was investigated whether eliminating any sulfur compound from the concrete can prevent microbiologically induced concrete corrosion under realistic conditions of aggressive waters, e.g., residual or sewer waters. Another approach and a more elaborated discussion on this topic to prevent acid attack on concrete can be found in Rendon [15]. Furthermore, the study of more and different concrete compositions is under way. In this study the experimented concrete mixtures were composed of Ordinary Portland Cement (OPC), Pozzolanic Portland Cement (PPC), and Grinding Clinker Cement (GCC) as cement without sulfur, all mixed with silica sand, water, talc in sample 2 and fly ash in sample 6, see Table 2.1.

Specific factors that influence concrete pipe durability are concrete compressive strength, density, absorption, cement content (composition) and type, aggregate characteristics, total alkalinity, concrete cover over the reinforce, and admixtures.

To manufacture concrete when any kind of chemical deterioration is anticipated, it is convenient to go through Mexican norm (NMX-C-414-ONNCCE-2004) basic recommendations:

1. Utilize cement (type, SR) that is resistant to sulfate attack.
2. Utilize cement with mineral additions that have pozzolanic activity. This means that the hydrated products of the cement, the portlandite $\text{Ca}(\text{OH})_2$ that would normally form, does not form because the mineral addition combines with the lime (CaO) to form a hydrated calcium silicate (C-S-H) product. This gives the characteristics of resistance, durability, and impermeability to the concrete. It avoids the formation of portlandite, which is leachable and has less resistance and durability.
3. Reduce the water/cement ratio to less than 0.45% (a fraction of 1%) maximum. This reduces the permeability of the concrete and limits the access of aggressive

Table 2.1 Concrete samples composition and data

Concrete						
	OPC 40	GCC	GCC	PPC 30	OPC 40	OPC 40
Sample composition	Sample 1	Sample 2	Sample 3	Sample 4	Sample 5	Sample 6
Cement	740 g			740 g	2775 g	600 g
Clinker		2204 g	740 g			
Fly ash						140 g
Talc		70 g				
Silica sand	2035 g	501 g	2035 g	2035 g		2035 g
Total sulfur ^a SO ₃ %	4.2%	1.0%	0.8%	4.3%	3.5%	3.7%
Water in theory	382 g	1138 g	382 g	382 g	1450 g	384 g
w/c	0.52	0.52	0.52	0.52	0.52	0.58
Slump	107	139.5	139	109.5	108	112
Water real	410.2 g	650 g	405 g	378 g	961.8 g	593.2 g
w/c real	0.55	0.29	0.55	0.51	0.35	0.89
f'c 3 days MPa	30.54	54.82	42.08	25.42	39.54	20.55
f'c 7 days MPa	35.89	64.14	45.08	31.28	77.86	26.97
f'c 28 days MPa	42.85	76.49	58.65	39.81	97.09	37.97
Initial sample weight	318.5 g	342.5 g	318.0 g	315.3 g	373.7 g	336.8 g
Final sample weight	222.9 g	332.2 g	311.6 g	223.9 g	291.4 g	252.6 g
Mass lost %	30%	3%	2%	29%	22%	25%

^aEach composition was analyzed in a Sulfur Analyzer – The LECO Corp. Model CS-225 induction furnace

fluids into the interior of the mass. The implementation of these three recommendations requires an understanding of the microstructure of the cement paste that unites stony aggregates, its density (diminished porosity), and the process of concrete manufacture including the curing process.

In addition to these recommendations our concrete samples were made with sulfur-free *Portland* cement and limestone-free aggregates (sand and coarse aggregates) or any other acid reactive mineral. So we:

- (a) Eliminate any source of sulfur from the cement and concrete.
- (b) Eliminate any acid reactive mineral from the aggregates.

See Table 2.1.

2.4.1 Concrete Composition

Concrete is a manufactured material, so the answer to its degradation problem shall focus on why concrete is being corroded? The answer to this question is concrete corrodes because it contains a significant amount of sulfur compounds. Nonetheless,

Fig. 2.4 Samples reviewed after a couple of months in experimental site



we know that correcting the composition of *Portland* cement and concrete is difficult, and complicated for two reasons: first, cement manufacturers are convinced that sulfur is beneficial for cement, and second, to remove all sulfur compounds from raw material can be difficult and costly. To mitigate biodeterioration eliminate or minimize sulfur content or look for a substitute. Nonetheless, MICC is a fact Fig. 2.4 shows the aspect of some of the different composition samples after only 2-month exposition to the biodeterioration process.

2.5 Results

Table 2.1 shows that in the concrete samples without sulfates mass lost was very low, despite the fact that all samples were settled down under the same conditions. The sulfuric acid responsible for the corrosion of concrete sewer systems is generated by a complex microbial ecosystem. Several species capable of oxidizing sulfur compounds colonize exposed concrete. When sulfates are present anaerobic microbial processes in the sewage lead to the formation of hydrogen sulfide, which is released to the atmosphere through turbulence. On the crown surface of the sewer pipe, hydrogen sulfide is chemically oxidized to sulfur under aerobic conditions; bacteria of the genus *Acidithiobacillus* oxidize sulfur to sulfuric acid (Fig. 2.1) dissolving the concrete, and losing mass while searching for more sulfates. Furthermore, if the cement of the concrete contains large amounts of calcite as filler, it will be easily dissolved by the sulfuric acid; more mass will be lost making the concrete porous, with porous layers of corrosion product coating it, Fig. 2.2.

2.6 Discussion

The expected outcomes of this research are lowered costs of operation, maintenance and replacement of aging water infrastructures, and reduced life-cycle costs of wastewater conveyance systems. Preliminary results of this experimentation using

concrete without sulfates, sulfur compounds, and limestone show that mass lost by MICC effect is lowered. In Mexico, the *Portland* type cement recommended for use with aggressive waters, e.g., residual or sewer waters are usually Pozzolanic Portland Cement (PPC) and Granulated Slag Portland Cement (GSPC) which contains calcium sulfides, besides the added calcium sulfate. And lately, there has been an emphasis to use “Blended Portland Cement” (BPC) at the same level as PPC and GSPC, see the Mexican Norm NMX-C-414 [8]. This is a poor practice because BPC contains large amounts of calcite as filler that is easily dissolved by the biogenic acids allowing a greater concrete mass loss. In conclusion regarding the composition of concrete for sewer systems, the Mexican Norm NMX-C-414 [8] does not take into consideration the concrete biodeterioration variable and its mechanism, and its recommendation that blended cement be used in situations of aggressive chemical attack neglects the hazard that results from the incorporation of a significant amount of calcite. We recommend that the norm be reviewed, or at least that a warning be issued.

2.7 Conclusion

The importance of ensuring durability of concrete has been a growing concern of engineers, and there is now considerable understanding of the mechanisms, which cause its deterioration throughout non-living environment – chlorides in seawater, carbon dioxide in the atmosphere, cyclic freezing and thawing – and means of limiting such damage through the use of appropriate materials. However, many of the deterioration mechanisms, which affect concrete, are the result of interaction with living organisms which cause damage – through both chemical and physical processes – as was previously discussed and which under the right conditions, can be severe. We must conclude that both non-living environment mechanisms as well as living organism mechanisms must be taken into consideration to expand concrete durability.

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