Durability considerations for mitigating corrosion caused by biogenic sulfuric acid in sewerage systems

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Abstract. In sewerage systems, the corrosion process caused by microorganisms, has been studied. This affects the structural integrity of the concrete drainage pipes and the sewage treatment plants. This article is a review of research which focuses on the study of how to reduce the production of hydrogen sulfide, how to improve the resistance of concrete through the use of additives and the implementation of antimicrobial techniques to reduce bacterial growth. This review allowed us to find a way to improve the physical simulation of exposure to the corrosive medium through chemical tests, as well as the optimization and choice of the type of zeolite that would be incorporated into the mixture with which concrete pipes are normally manufactured.

1. Introduction
Sewerage systems are essential components for the control of public health in urban centers. Many of the elements that make up these structures are built using concrete. However, this aggressive environment involving the sulfur cycle and microbiological activity causes corrosion on the surface of the concrete, which decreases the durability of such structures.

This research work has an effect not only on the technological development of new concrete mixtures aimed at increasing the durability of concrete pipes exposed to biogenic sulfuric acid, but also on the sustainable and resilient development of sewage systems. The reaction in the drainage pipes was considered a purely chemical process, in which hydrogen sulfide (H₂S) generated under anaerobic conditions is oxidized to biogenic sulfuric acid (BSA) in the presence of oxygen [1]. However, an American scientist, Parker, separated and assigned responsibility for the corrosion process to the acidophilic organisms which he called Thiobacillus concretivorus. These bacterial populations metabolize hydrogen sulfide present in the atmosphere of sewerage system pipes, producing sulfuric acid which reacts with the calcium carbonate in the concrete.

This produces expansive compounds such as the gypsum and ettringite, which changes the appearance of the surface of the pipes, with a pasty white material being observed [2]. Parker expanded the concept of chemical oxidation of sulfur species to sulfuric acid to include a mixture of chemical and biological processes [2]. The sulfur-oxidizing bacteria (SOB) which Parker isolated from concrete surfaces have the ability to grow and produce acid in wastewater [3].

These sulfur-oxidizing organisms are now known as Thiobacillus thiooxidans or Acidobacillus thiooxidans [4,5]. This type of attack has been seen in sewerage systems in several countries, including Mexico, the United States [2,6], Japan [7], Belgium [8], and China [9]. Furthermore, the restoration costs of the concrete elements affected by microbiological corrosion is a great investment in some...
countries, such as in Germany where it accounts for 40% of the US$100 billion invested, in Belgium where it accounts for 10% of the total expenditure on wastewater treatment [10], and in Los Angeles, USA where approximately US$400 million is invested [11]. It is also estimated that the United States spends around US$25 billion annuallly on the maintenance of sewerage systems [12]. In relation to the problems mentioned above, various types of tests and experimental trials have been carried out [13] to determine the characteristics of the process. In this way, different solutions can be tested to mitigate the accelerated deterioration of concrete caused by (BSA) attack. Three methods have been researched aimed at different stages of the corrosion process [10].

This review allowed us to find a way to improve the physical simulation for exposure to a corrosive medium of concrete specimens through chemical tests. It helped the optimization and choice of the type of zeolite that would be incorporated into the mixture with which concrete pipes are normally manufactured for wastewater drainage systems in Colombia, improving their durability conditions.

2. Description of the corrosion process

The attack caused by BSA in the drainage pipes is known as microbiologically influenced corrosion (MIC). This attack is carried out in four stages, which have been described by several researchers [1,14-16]. They also describe the high concentrations of $H_2S$, the presence of sulfate-reducing and sulfur-oxidizing microorganisms with the corrosion that is evidenced, involving the biogeochemical cycle of sulfur, presenting an anaerobic and an aerobic stage [17].

The corrosion mechanism essentially involves two processes, which are the production of $H_2S$ and the creation of BSA. The attack begins with the formation of hydrogen sulfide; the wastewater collected in the drainage pipes contains large concentrations of sulfate salts ($SO_4^{2-}$), as well as the anaerobic condition on the water surface and the long retention time or slow flow, the sulfate-reducing bacteria (SRB) which inhabit the biofilm of the pipes reduce the compounds to $H_2S$. However, two groups of SRB are present; the first group Desulfovibrio comprises the species whose metabolism involves the incomplete oxidation of the organic substrate to acetate, while the second group Desulfococcus includes those microorganisms capable of completely oxidizing the organic matter producing an excrement called carbon dioxide($CO_2$).

The second step is the emission of $H_2S$, in which the following conditions are combined: hydrogen sulfide gas is slightly soluble, the acidic properties of the wastewater and the decrease in the pH level when turbulence occurs; these conditions allow a disruption to the surface of the water allowing the $H_2S$ into the atmosphere above the water level in the pipes [11,12,18].

The hydrogen sulfide in the atmosphere of the pipes, together with the $CO_2$, cause the carbonation of the concrete surface, decreasing the pH to 9, in which the bacteria and fungi can start growing [2]. The production of BSA is an anaerobic process in which there is a presence of neutrophilic and acidophilic microorganisms which are capable of oxidizing sulfur into thiosulfate, which react with the hydrogen to produce sulfurous acid. However, the Thiobacillus thiooxidans bacteria that colonize when the surface pH is between 3 and 2 are truly acidophilic organisms that create the greatest impact on the deterioration caused by the BSA attack [2].

The $H_2S$ reacts first with the calcium hydroxide (CH) to form gypsum (CaSO$_4$.2H$_2$O). Later, the reaction between the gypsum and the hydrated calcium aluminate (C$_3$A) leads to the formation of ettringite 3CaO.Al$_2$O$_3$0, 3CaSO$_4$. 32H$_2$O. Both products have a greater volume in comparison to the initial compounds [19], which generates cracks, and loss of mass and concrete strength [11].

3. Methods of corrosion control

The goal of most of the research projects that have studied BSA corrosion is to seek a solution or possible mitigation of this pathology. With this in mind, researchers have tried to control the stages that occur in the process, developing techniques that increase the strength of concrete, prevent the formation of hydrogen sulfide, or act as bactericides. These methods can be classified into three types or groups:
3.1. Type I: Control of hydrogen sulfide (H₂S)

The emission and production of H₂S in sewerage systems are important stages in the corrosion process caused by BSA [20]. Severe corrosion problems have been reported in systems having a concentration equal to or greater than 2.0 mgL⁻¹ [21,22]. One of the methods of controlling sulfur production is the optimization of the hydraulic design of the system [22], using prediction models for the formation of hydrogen sulfide and for the accumulation of sulfur.

3.1.1. Decrease in the concentration of sulfates. The sulfur-reducing bacteria use the sulfates as an electron acceptor in the oxidation of organic matter, reducing it to sulfur. Therefore, different systems have been studied for the removal of sulfates such as electro dialysis, ion exchange, and reverse osmosis, among others. The addition of chemicals is expensive and not very useful [11].

3.1.2. Increase in redox potential to control the formation of sulfur. Sulfur production takes place in the biofilm of the pipes where the levels of dissolved oxygen are low [22]; therefore, the injection of air in the drainage system at levels of 0.5 mgL⁻¹ can prevent the occurrence of sulfur [22]. Injections of oxygen increase dissolved oxygen levels to between 5 mgL⁻¹ - 7 mgL⁻¹ [23]. It has been shown that the addition of 1.0 gL⁻¹ of nitrate prevents sulfide production for approximately 29 days [22].

3.1.3. Inhibition of the activity of sulfur-reducing bacteria. The effectiveness of applying NaOH to increase the pH to a range of 10.5 - 12.5, with exposure times of 0.5 to 6 hours, has shown that the rate of sulfur production in the biofilm decreases by between 70% - 90% for approximately one week [24].

3.1.4. Chemical removal of sulfur. The addition of chemicals for controlling and removing hydrogen sulfide in the liquid phase before it is released into the atmosphere of the pipes is a widely researched field. The chemicals that are commonly used are ferric or ferrous chloride and ferric nitrate. The combined use of ferric and ferrous salts generates a greater efficiency for controlling the dissolved sulfur concentrations [22].

The addition of chemicals such as chlorine, hydrogen peroxide and potassium permanganate are potential oxidants of sulfur, but can cause carcinogenic substances and heavy metals. The addition of hydrogen peroxide helps to keep the system in aerobic conditions; a concentration of 1.3 mgL⁻¹ - 4 mgL⁻¹ can eliminate between 85% - 100% of the sulfur, if it has a concentration of approximately 1 mgL⁻¹ of sulfur. With the addition of nitrous acid with hydrogen peroxide during a period of 8 to 24 hours, a decrease of 80% was measured in the production of H₂S [25].

Chlorine can reduce sulfur to sulfate, depending on the pH but it is inefficient, since the chemical reaction that occurs is slow. Another technique to control the production and emission of H₂S is the installation of catalytic iron filters with a removal efficiency of 92%. Bio filters based on the sorption capacity of the biofilm enable the sulfurs to be biochemically oxidized [11].

During the slow release of O₂ in solid phase, through the application of magnesium peroxide (MgO₂), in an environment with a high number of SRB, the (MgO₂) reacts with water, slowly releasing oxygen and producing magnesium hydroxide which inhibits the growth of SRB; an application of 0.4% (MgO₂) prevents the formation of sulfur for more than days [26-36].

3.2. Type II: Implementation of additives and coatings on concrete

The techniques used in this type of control aim to increase the durability, strength and properties of the concrete or the surface of the concrete that is exposed to sulfuric acid attack.

3.2.1. Supplementary cementitious materials. The test method used by many of these studies is the exposure of concrete samples with modifications to different chemical solutions of sulfuric acid. This does not give exact values of the behavior of these mixtures against biological attack as presented in drainage systems, but it allows the chemical reactions and yields of these new mixes to be measured.
The replacement of 15% of cement with silica fume has been found to improve the resistance in an acid solution of 1%. However, in microbiological tests, it was demonstrated that mixtures with silica fume showed a greater percentage of mass loss and a decrease in the thickness of 4.4%, and therefore has a negative influence against attack by BSA [37]. Silica fume has also been used in mixtures with pozzolanic cement, in which the expansion was lower but the mass loss increased in comparison to the samples containing no silica fume [38,39].

The concrete samples with limestone, pozzolana and blast furnace slag that were exposed to cyclical immersion in a sodium sulfate solution (50 gL⁻¹) and another sulfuric acid solution pH=2.0 presented severe damage and significant expansion compared to some mixtures that added silica fume [38]. Concrete samples with silicate hydrates were submitted to eight cycles of immersion in a microbiological environment and in chemical solutions, resulting in reduced mass loss, close to half that demonstrated by concrete specimens without modification [10]. The addition of blast furnace slag to concrete mixtures has shown a significant reduction in the incidence of the expansion caused by sulfuric acid attack [40]. In the research [41], the response of a number of mortars with different amounts and combinations of supplementary materials was tested.

The results showed that in the mixture containing 30% pozzolana and in that containing 30% ash fume the mass loss presented was minimal compared to the control mortar (composed of 95% clinker and 5% gypsum), and the sample containing 30% limestone. This is possibly due to the presence of minerals vulnerable to chemical attack that the first mortar mixes didn’t contain [41]. The addition of fly ash in different proportions to concrete mixtures from 0% to 70% showed a good performance in the samples tested against immersion for 60 days in a 5% solution of sulfuric acid, with the samples with a content of 70% showing a strength loss of 2.1% and mass loss of 1.1%, compared to the samples with a content of 0% which showed a strength loss of 58% and a mass loss of 8.3% [42].

Another material that has been studied is metakaolin which is an aluminosilicate, which influences the properties of the concrete by increasing the resistance against alkali silica reaction, the bending and compression force, and reduces the permeability of the surface improving its overall durability. In one research study, concrete cylinders with 73.5 Kgm⁻³ and 98 Kgm⁻³ of metakaolin were immersed in solutions of 3%, 5% and 7% of sulfuric acid. The analysis of mass loss shows this is decreased by 26.24%, 23.90% and 26.67% compared with the control mixture in each solution respectively. However, the use of supplementary cementitious materials does not provide an overall improvement of the resistance against deterioration caused by the combined chemical attack of sulfates and sulfuric acid H₂SO₄ [39].

3.2.2. Polymer concrete and polymer modifiers. Polymer concrete is used in non-reinforced pipes with small diameter. Some of the mechanical characteristics of these concretes are greater than those of conventional concrete; however, they are very costly. The effectiveness of the addition of styrene-acrylic ester polymer has been shown in some studies, which showed a reduction in thickness of 1.7% and weight loss of 6.5%, while the reference concrete, the mixture using portland cement, showed values of 2.7% and 7.4% respectively. These samples were subjected to 4 cycles of microbiological tests [37]. The mixtures that implement styrene-butadiene and polyvinyl chloride showed no improvement in the results, while the acrylic polymer showed better results in terms of reduction of thickness (4.1%) and weight loss (8.4%), in comparison to the aforementioned concrete.

The modified hybrid mortar with polyvinyl acetate latex, lignosulfonate, tributyl phosphate and Na₂SO₄ showed a loss of compressive strength of 29.4% and a porosity of 13.25%, after being subjected to 5 years of H₂SO₄ attack; while the reference mortar achieved values of 50.6% and 28.6% respectively. The surface of the modified mortar had fewer cracks, hence, this mortar helps mitigate chemical attack caused by acid [43,44].

3.2.3. Protective coatings. The use of coatings has shown to be greatly effective against the action of sulfuric acid; epoxy coatings and polyurea coatings show a high level of protection compared with the cement coating which shows a significant mass loss [10]. However, the use of two mortar mixtures as
coatings, prepared with a cement that has a high content of calcium aluminate (one of the CC mixtures was specifically developed to withstand corrosion attack by chemical and BSA) has demonstrated good performance in exposure to a solution of 2% sulfuric acid, showing results of a decrease in weight loss of 0.56% and loss of resistance of 34% after 150 days of exposure [45].

Polymer cement coatings (polyester) increase the lifespan of concrete elements 71 times against an attack of 3 years in a 3% sulfuric acid solution [46]. Polyurethane coatings have also been tested against the action of sulfuric acid attack, yielding results in the change in weight of between 0.44% to 0.97%, prolonging the life of the elements by between 14 to 57 times. These values depend on the physical and mechanical characteristics and the thickness of the coating layer which is applied to the concrete surface [47]. Another coating tested in this area is the epoxy coating reinforced with fiberglass, which increases the life of the elements by 70% more than the uncoated elements against exposure for 20 months in a 3% sulfuric acid solution; it also presents a probability of failure of 50% [48].

3.2.4. Fiber reinforcement. Microfibers and fibers are used to improve the toughness and impact resistance of concrete. However, the separation performance is relatively large from fiber to fiber, and it has a small specific surface area; this limits the effectiveness of the fibers and microfibers in controlling the micro-cracks that occur in the second phase of sulfuric acid attack, in other words the formation of ettringite. The weight loss and loss of thickness that was evidenced in concrete samples with different reinforcement methods showed some improvements in resistance to acid with graphite nanoplatelets (GP), synthetic microfiber and especially hybrid (GP/PVA) reinforcement [49]. Fiberglass reinforcement has proved to be a good protective system, and it also makes concrete pipes lighter, but they are only manufactured in diameters of 10 feet [39,41,50].

3.3. Type III: Antimicrobial methods

The use of antimicrobial coatings such as nanomaterials, metal oxides or additives that aim to reduce or eliminate the activity of the various microorganisms in drainage pipes is a relatively new field of research. Experiments have been carried out achieving a certain amount of suppression in microbial activity when *Thiobacillus* crops are exposed to concrete with the addition of calcium formate to the mixture [7].

The experiments have shown the efficacy of a salt in water stabilized with quaternary ammonium silicone, which was added to a concrete mixture to inhibit the growth of *Thiobacillus*. Antimicrobial coatings have been applied to concrete, using fibers treated with biocides (Fibermesh fibers containing the additive Microban B) to improve the hygienic conditions of local concrete; concrete containing these fibers is very effective in inhibiting the growth of fungi, as well as bacteria such as *Escherichia coli* and *Staphylococcus aureus*. There are no reports available on the inhibition of sulfur-oxidizing bacteria [10].

Zeolites are another component that have been researched, because they are materials with bactericial properties and metal, aluminum, silver, zinc and copper ions [10,51,52]; in the Japanese market that is available a concrete mixture whit a concentration of metal zeolite of 1% to cement weight, this is a product that prevents the bacterial growth of the *Thiobacillus*.

The efficiency of zeolites has been tested in several experiments in which the release of silver ions gives high antimicrobial properties and resistance to attack by biologically-produced sulfuric acid; additionally, the use of zeolites produces an increase in the number of micropores and a decrease in the number of macropores in the concrete, resulting in the elimination of the expansive products of corrosion by BSA within the interior of the cement paste [52-55].

4. Conclusion

The addition of chemicals to drainage systems, based on the review carried out, are not fully effective and produce significant levels of pollutants in the recipient sources of wastewater, leading to an increase in health problems. Most of the solutions of the second type that have been researched increase the life of the concrete elements exposed to different solutions of chemical acid and to different cycles of microbiological testing; however, the cost of these solutions is also much greater. Corrosion in concrete
elements caused by the action of biogenic sulfuric acid is a complex process and, despite all the research studies that have been carried out, it has not been possible to establish a mechanism that completely controls all the variables affecting the problem and mitigate it completely. Type III techniques are the most effective because they directly attack the bacteria; however, being a new field of study, the results are not completely reliable, as further studies are necessary on the increase of costs and the potential damages that they may have on the environment and human health. This review allowed us to find a way to improve the physical simulation for exposure to a corrosive medium of concrete specimens through chemical tests. It helped the optimization and choice of the type of zeolite that would be incorporated into the mixture with which concrete pipes are normally manufactured for wastewater drainage systems in Colombia, improving their durability conditions.

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