

Inhibition of Microbial Induced Corrosion of Concrete using Admixture and Surface Applied Corrosion Inhibitors

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ABSTRACT

Microbiologically Induced Corrosion (MIC) is a complex problem facing global concrete sewer structures. Despite the substantial efforts made, MIC of concrete sewers remains a significant challenge. Concrete is susceptible to corrosion induced by microbial species which convert the main binding agent $\text{Ca}(\text{OH})_2$ to CaSO_4 , leading to the disintegration of concrete, loss of strength and structure failure short of its predicted life. Concrete specimens were prepared with corrosion inhibitors and immersed in sodium sulfide and sulfuric acid solutions for more than 400 days. The concrete samples without inhibitor or admixtures showed more than 33% loss of compressive strength, roughly 6.2 mm layer of sulfate attack and concrete disintegration. The concrete samples treated with admixture and surface applied corrosion inhibitors demonstrated no loss of compressive strength and less than 0.12 mm layer of the sulfate-- attack after 400 days immersion in the aggressive solutions. A combination of admixture and highly hydrophobic surface applied corrosion inhibitor is recommended for aggressive waste water systems such as manholes, channels and pipes to assure a satisfactory performance for these concrete structures.

Key words: Chemical admixture; Migration Corrosion Inhibitors; Microbial Induced Corrosion, sulfate attacks, concrete

INTRODUCTION

The life-cycle of concrete structures used in waste water systems should consider all factors that might cause a structural system to perform unacceptably at any point during its lifetime. This includes the progressive and sustained loss of load capacity caused by operational or environmental factors. In general terms, deterioration can be defined as a loss of structural load capacity with time as a result of the action of external agents causing chemical attacks or material weakening due to these environmental interactions. Concrete is the most extensively utilized building material in structures designed to collect, store, transport and treat municipal and industrial wastewater because of its ease of use, availability, structural capabilities, and cost effectiveness. However, at highly acidic conditions ($\text{pH} < 3.0$), the physical and chemical qualities of concrete formed with hydrated Portland cement make it susceptible to deterioration and breakdown. As a result, a considerable portion of the concrete wastewater infrastructure may be vulnerable to microbially induced corrosion (MIC), a complex multistage deteriorating process. Biodeterioration is caused by organisms that grow on concrete surfaces with dissolved oxygen, high sulphate concentration, low pH, high COD (chemical oxygen demand) and BOD (biological oxygen demand). These organisms can induce corrosion in various places like fire sprinkler pipes, chiller pipes, sewer systems, potable water, oil and gas pipes [1]. Conducive environments include elevated relative humidity around 60% to 98%, long cycles of humidification and drying, freezing and defrosting, high carbon dioxide concentrations, high concentrations of chloride ions, high concentrations of sulfates and small amounts of acids [2]. Increased temperature and sulphate containing detergents are also considered to be contributors for MIC [3].

Mechanism of MIC

The mechanism of MIC which includes its initiation and propagation has 4 major steps, as shown in Figure 1. Formation of hydrogen sulfide begins when sulfates in the waste stream are converted to $\text{H}_2\text{S}_{(\text{aq})}$ with the biological activity of anaerobic sulfate reducing bacteria (SRB) in the biofilm below the waterline. Secondly, the gas phase escapes to the sewer spaces above the waterline with or without the help of turbulence in the waste stream. In the third step, $\text{H}_2\text{S}_{(\text{g})}$ migrates into the moisture layer present on concrete surfaces above the waterline and is converted to sulfuric acid by aerobic sulfur oxidizing bacteria (SOB).

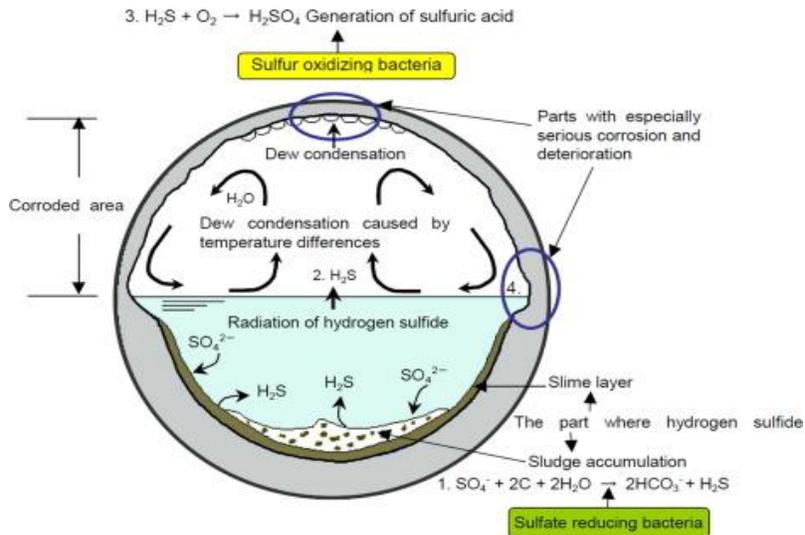
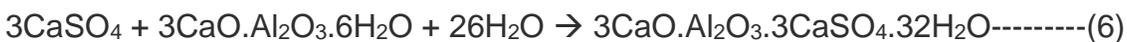
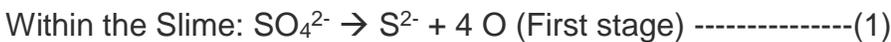


Figure 1: Mechanism of MIC in Concrete [2]

Deterioration of the Concrete

The generated sulfuric acid (including other possible biogenic acids) reacts with the concrete matrix, leading to progressive disintegration of the concrete. The generated H_2SO_4 reacts with cement and leads to the dissolution of calcium hydroxide $(Ca(OH)_2)$ and carbonate compounds, as shown in reactions 4 and 5. These reactions result in the formation of gypsum and subsequently, the gypsum may react with the aluminate phases to form ettringite, as seen in reaction 6.



Research Significance

The use of admixtures, migrating corrosion inhibitors and surface applied corrosion inhibitors to inhibit MIC were studied in this investigation. There are various methods described in literature that address MIC [4]. Development of new concrete materials like geo polymer concrete [5, 12], and application of coatings like polyurea and epoxy coatings on the surface of the concrete [6-8]. However, the goal in this investigation was to incorporate chemical inhibitors to combat MIC and protect the concrete structural integrity [11-13]. It is believed that there is very less research done using inhibitors and admixtures to maintain the concrete chemistry and improve the life-cycle of concrete structures. In this investigation, the effectiveness of corrosion inhibitors was assessed in very aggressive chemical solutions simulating wastewater environments.

EXPERIMENTAL PROCEDURE

A concrete mixture (4 Aggregate: 2 Sand: 1 Portland Cement type II with moderate sulphate resistant hydraulic cement) was used to make the concrete (0.5 water to cement ratio). The premixed concrete was used to cast 5x10 cm (2 inch x 4 inch) cylinders. Curing and compression tests were done per ASTM C31[9] and ASTM C39 [10] standards. The specimens were cured for four weeks. Compression tests were conducted on the specimens to determine compressive strength and assure proper concrete quality for this investigation. A Universal testing machine was used to perform the compressive tests. The cylindrical specimens were loaded at the rate of 0.2 inch/min and the compressive strength was on average 5,400 psi after four weeks of curing.

Four types of samples were prepared: 1) samples surface coated with migrating corrosion inhibitor; 2) samples made with admixtures; 3) samples made with 5% admixtures and coated with surface applied migrating corrosion inhibitors; and 4) control samples (no admixtures, no corrosion inhibitor coatings). The corrosion inhibitors and admixtures used are listed in Table 1. Concrete samples were prepared from pre-mixed concrete mixture without admixture as control samples, while concrete admixture was added to concrete mix. Three layers of the surface applied migrating corrosion inhibitor (SACI-A and SACI-B) were applied to the cylindrical samples after curing and prior to the immersion corrosion tests. Two and concentration of admixture/inhibitor (commercially available migrating corrosion inhibitor, Admix-A, 5% admixture additions).

Table 1: List of inhibitors and admixtures used

Sample Identification	Migration corrosion Inhibitor	Admixture	Combination
1	SACI-A	Admix-A	Admix-A + SACI-B
2	SACI-B		

Surface applied corrosion inhibitor = SACI, Admix-A = admixture corrosion inhibitor. Data for the Admix-B was not included in this paper.

All samples were immersed in sulfuric acid and 300 ppm sodium sulfide solution with pH ~ 2.0, for a period of 400 days. The immersion test solution was to simulate the effects of sulfate reducing bacteria (SRB). The test solution is a common solution of pH 2.0 (adjusted with H₂SO₄ with tap water) + 300 ppm S⁼ (sodium sulfide) that is used to simulate the SRB and SOB attacks. The solution temperature was ~ 25-30 °C. Laboratory simulation experiments proceeded for ~ 400 day (~14 months). Solution pH and temperature was monitored daily to maintain a relatively constant chemistry during testing. Compression tests were conducted on concrete specimens after 90 days of continuous exposure. The weight changes and loss in compression strength were calculated; the depth of sulfate attack was also monitored. During the corrosion tests, samples were sectioned to measure sulfate attack. Phenolphthalein etching indicates the pH level of concrete, the pink color indicates good concrete with proper >pH ~12. A light brown color indicates the loss of Ca(OH)₂, a concrete binding agent, thereby reducing the concrete pH and strength. The test solutions were replaced every month.

RESULTS

The changes in compressive strength for the concrete samples are shown in Figure 2. The concrete control samples showed a loss of more than 45% of their compressive strength after ~400 days of immersion. The depth of sulfate attack layer exceeded 12.20 mm around its outermost diameter with severe loss of strength mainly due chemical etching and concrete disintegration (Figures 3-4). Figure 5 shows the severe concrete disintegration due to sulfate attack of the concrete control sample. The overall diameter changes due to chemical attacks was more than 44.5% for the control. The sulfate attack layer thickness after 200 days for the exposed control sample is shown in Figure 6. The surface treated concrete with SACI-A showed a loss of more than 28% compressive strength after ~400 days of immersion. The depth of sulfate attack exceeded 3.62 mm; this left the concrete without appropriate strength due to loss of outer coating. SACI-A showed some improvement and protection in the short term (~ 90 days, Figure 6), however, due to its low surface adhesion, eventually the concrete samples suffered loss of strength due to sulfate attacks.

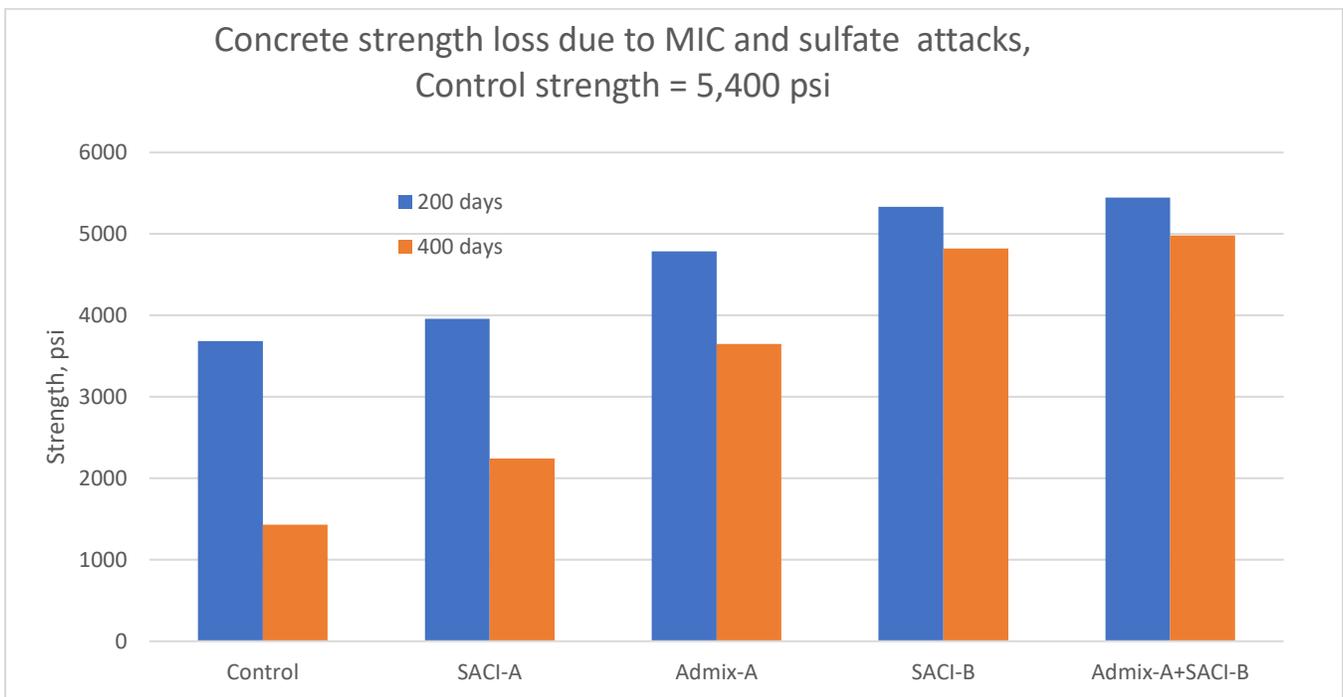


Figure 2: Comparison of compressive behavior for concrete samples after 400 days of immersion tests. The combination of Admix-A +SACI-B had the best performance in highly acidic solution.

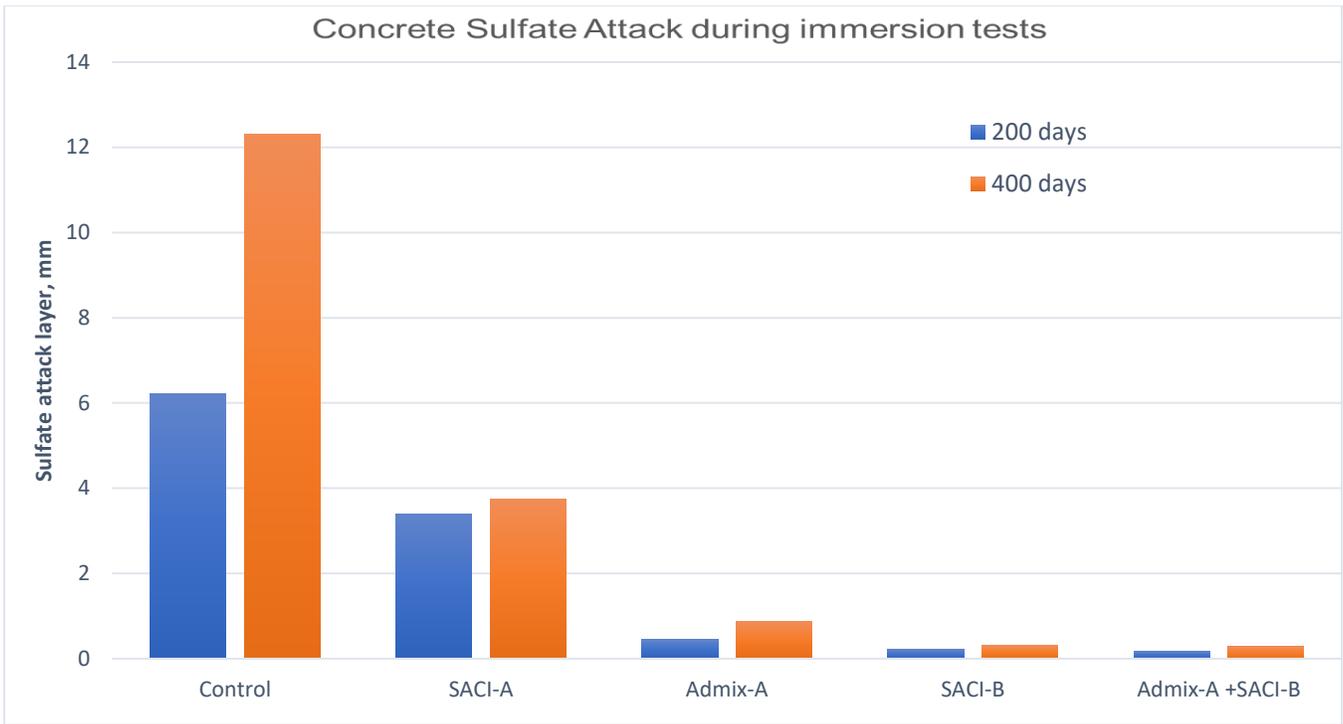


Figure 3: Comparison of sulfate attacks for 200 and 400 days exposure to highly acidic solution. SACI-B and Admix-A have the lowest sulfate attack reactions.

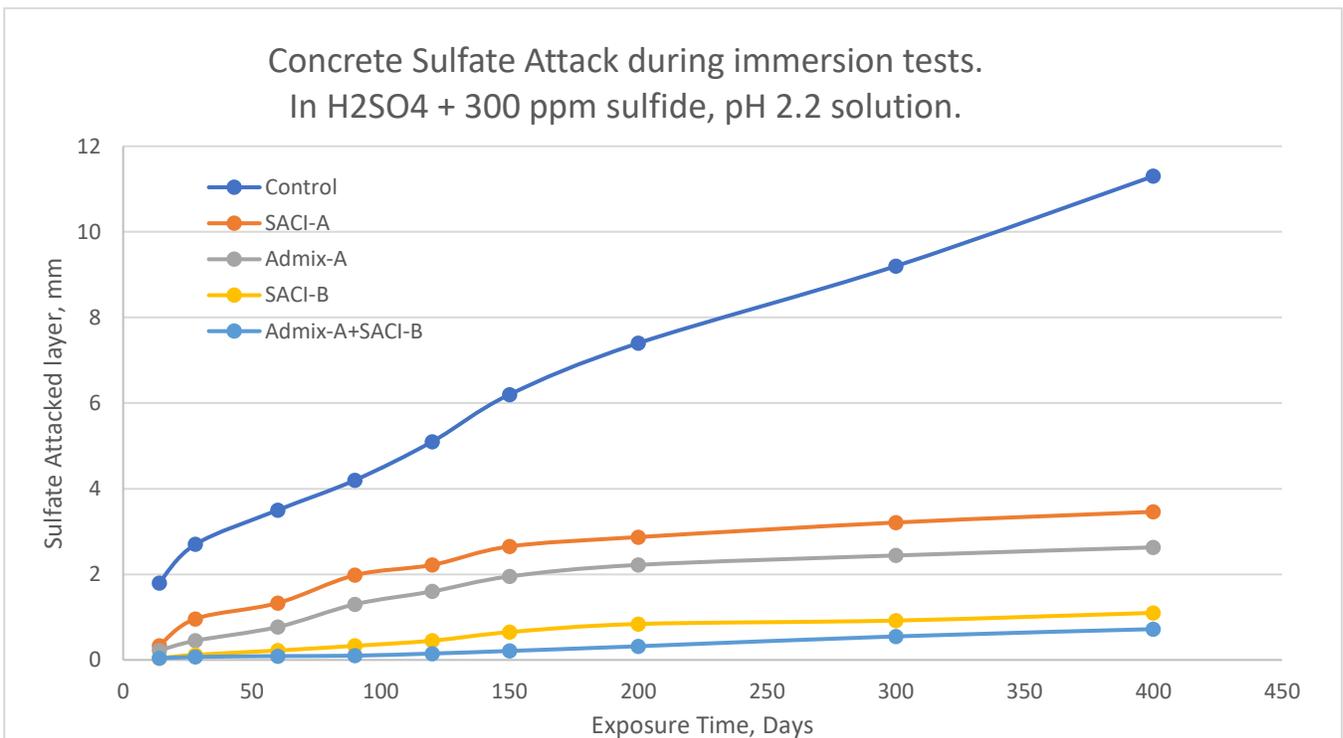


Figure 4: Sulfate attack layer thickness after 400 days exposure to highly acidic solution shows that Admix-A+SACI-B have the lowest sulfate reactions.



Figure 5: The exposed surface conditions for concrete samples after 400 days of immersion. Control and Concrete + 5.0%Admix-A + SACI-B in pH 2.2 solution+300 ppm sulfide. The control concrete sample showed severe sulfate attacks while combination of Admix-A+SACI-B showed no sign of any surface corrosion attacks.

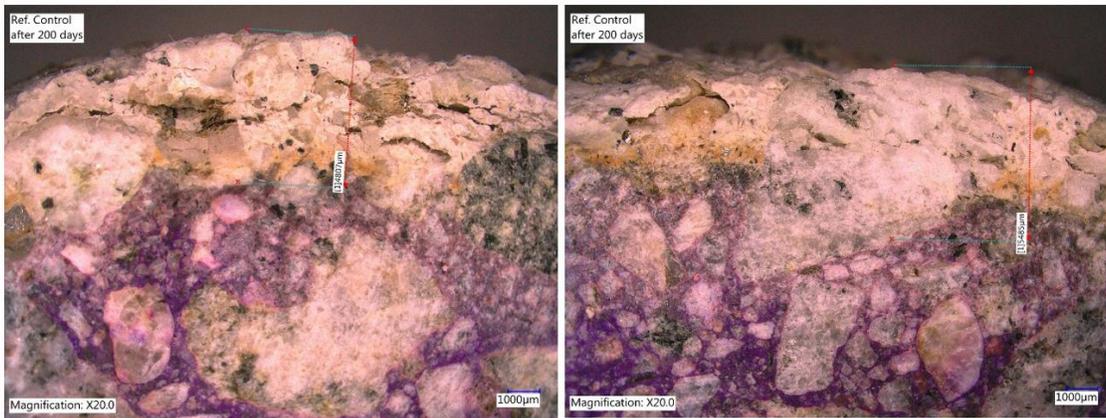


Figure 6: Optical etched micrographs of the concrete control samples after immersion for 200 days, shows severe sulfate attacks and cracking of the concrete due to severe chemical MIC attacks.

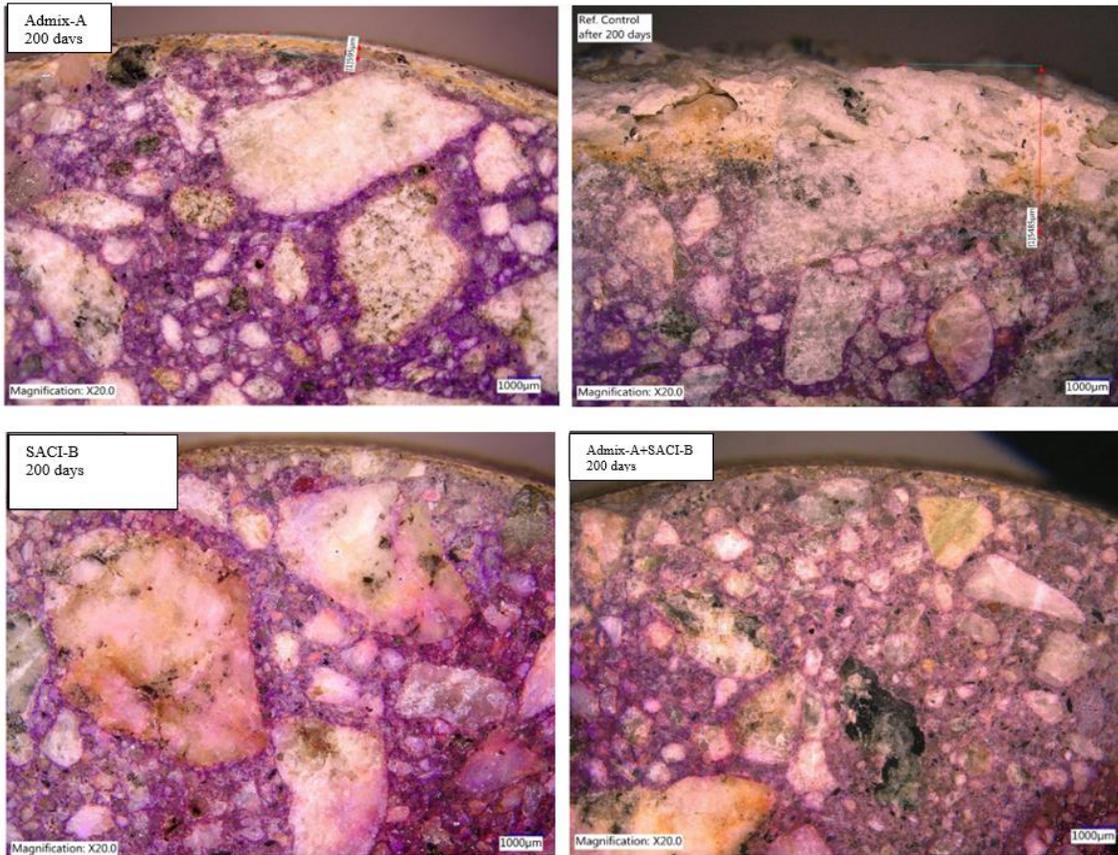


Figure 7: Comparison of concrete sections used to measure the sulfate attack layer thickness after 200 days. As can be seen, both Admix-A and SACI-B are very effective resisting sulfate attack. The control sample showed more than 24.5% thickness loss due to severe sulfate reaction, (samples are etched with Phenolphthalein).

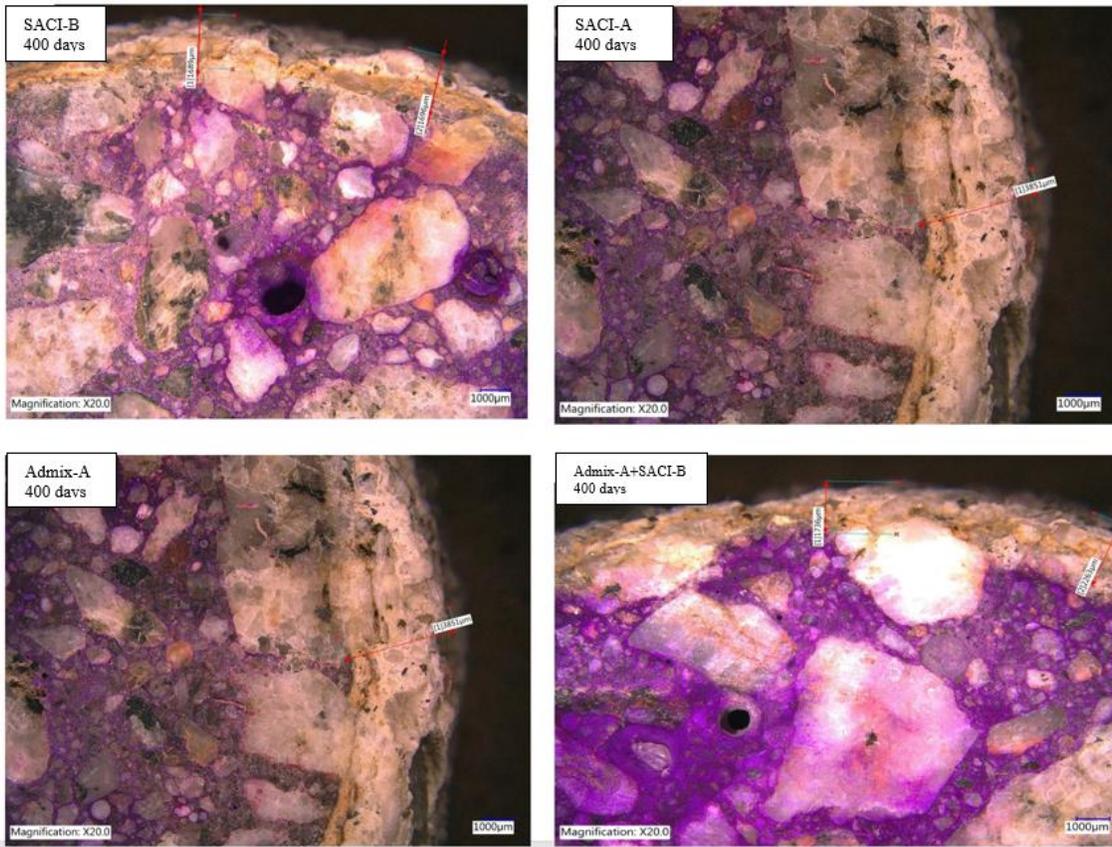


Figure 8: Comparison of Concrete sections used to measure the sulfate attack layer thickness after 400 days. Both Admix-A and SACI-B significantly improve resistance to sulfate attacks. The control sample showed a severe thickness loss due to sulfate attacks (Figure 5). The samples protected with admixture and surface applied corrosion inhibitors showed less than 1.7% thickness loss.

The concrete samples with 5.0% Admixture-A demonstrated better performance; compressive strength loss was ~8-10% after roughly 400 days of immersion and thickness of concrete sulfate attack was less than 3.1 mm after 400 days. The surface treated concrete with SACI-B showed a minor loss of compressive strength (less than 3.0%) after ~200 days of immersion, and less than 8% loss after 400 days. The depth of sulfate attack layer was very small (less than 0.8 mm) and had no impact on the concrete strength (Figures 7-8). The SACI-B is a very active hydrophobic coating that does not allow surface wetting, therefore, its presence on concrete surfaces is very effective in retarding chemical degradation. The concrete samples made with 5.0% Admixture-A and then coated with SACI-B showed the best performance with very negligible compressive strength loss (less than 1.0%) after ~400 days of immersion (Figures 7-8). The sulfate attack layer was ~0.5 mm without any concrete degradation. The best demonstration of effectiveness for these corrosion inhibitors can be seen in Figures 5 and 8. The concrete control sample showed severe sulfate attacks with more than 44.5% thickness loss while Admixture-A, SACI-B and combination of Admixture-A/SACI-B showed no sign of surface corrosion attack after 400 days exposure to the aggressive sulfate rich acid solution.

CONCLUSIONS

Microbiologically influenced corrosion of concrete was investigated in a highly acidic solution +300 sulfide (similar to SRB and SOB attacks) for more than 400 day. The concrete control samples suffered severe corrosion attack, presenting with a very thick sulfate layer, surface etching, disintegration of concrete (more than 12.0 mm) and significant loss of compressive strength, more than 78% after 400 days exposure.

Admixture-A and surface applied SACI-B, a super hydrophobic corrosion inhibitor, showed excellent protection for the concrete samples without any loss of strength and a very thin layer of sulfate attack (~0.1-0.5 mm) for 200 day immersion tests. After 400 day immersion tests the strength loss for these samples was less than 8%.

SACI-A showed some improvement and protection in the short term, however, due to its low surface adhesion, ultimately, the concrete samples showed some strength loss due to the sulfate attack after 150 days of exposure tests.

In summary, to assure a satisfactory performance for concrete structures (such as manhole, channels and pipes) in aggressive (sulfate rich) waste water systems, a combination of admixture-A and surface applied (highly hydrophobic) SACI-B is recommended.

REFERENCES

1. D. Wagner, A.H.L. Chamberlain, "Microbiologically influenced copper corrosion in potable water with emphasis on practical relevance", *Biodegradation*, Vol. 8, 1997, pp.177–187.
2. Vincke, Elke, et al. "Recent Developments in Research on Biogenic Sulfuric Acid Attack of Concrete." *Environmental Technologies to Treat Sulfur Pollution: Principles and Engineering*, edited by PNL Lens and L Hulshoff Pol, IWA Publishing, 2000, pp. 515–41.
3. Tesfaalem Haile and George Nakhla, "Inhibition of microbial concrete corrosion by *Acidithiobacillus thiooxidans* with functionalized zeolite-A coating", Vol. 25, No. 1, *Biofouling*, 2009, pp.1–12.
4. Georgios Fytianos, Vasilis Baltikas, Dimitrios Loukovitis, Dimitra Banti, Athanasios Sfikas, Efthimios Papastergiadis, and Petros Samaras, "Biocorrosion of Concrete Sewers in Greece: Current Practices and Challenges", *Sustainability*, 2020, pp.1-16
5. Parviz Soroushian, Habibur Chowdhury, and Tewodros Ghebrab, "Evaluation of Water-Repelling Additives for Use in Concrete-Based Sanitary Sewer Infrastructure", *Journal of Infrastructure Systems*, V.15, No.2, 2009, pp.106-110.
6. N. De Beliea, J. Montenya, A. Beeldensb, E. Vinckec, D. Van Gemertb, W. Verstraetec, "Experimental research and prediction of the effect of chemical and biogenic sulfuric acid on different types of commercially produced concrete sewer pipes", *Cement and Concrete Research*, V. 34, 2004, pp.2223 – 2236.
7. Ling Ding, W. Jason Weiss, Ernest R. Blatchley, "Effects of Concrete Composition on Resistance to Microbially Induced Corrosion", *Journal of Environmental Engineering*, V.143, No.6, 2017, pp.1-9.
8. H. S. Jensen, A. H. Nielsen, T. Hvitved-Jacobsen and J. Vollertsen, "Survival of hydrogen sulfide oxidizing bacteria on corroded concrete surfaces of sewer systems", *Water Science & Technology*, V.57, No.11, 2005, pp.1721-1726.

9. ASTM C31 Standard Practice for Making and Curing Concrete Test Specimens in the Field, Annual Book of ASTM Standards, Vol. 04.02, 2012.
10. ASTM C39, Standard Test Method for Compressive Strength of Cylindrical Concrete Specimens, Annual Book of ASTM Standards, Vol. 04.02, 2012.
11. B. Bavarian and L. Reiner, Migrating Corrosion Inhibitor Protection of Steel Rebar in Concrete, Materials Performance, 2003.
12. Muhammad Wasim, Tuan Duc Ngo, David Law, "A State-of-the-art review on the durability of geopolymer concrete for sustainable structures and infrastructure", Construction and Building Materials, V.291, 2021, pp.1-21.
13. Cyrill Grengg, Florian Mittermayr, Neven Ukrainczyk, Günther Koraimann, Sabine Kienesberger, Martin Dietzel, "Advances in concrete materials for sewer systems affected by microbial induced concrete corrosion: A review", Water Research, V.134, No.1, 2018, pp. 341-352.