Effectiveness of Surface Treatments on Microbial Induced Concrete Corrosion in Wastewater Infrastructure

by

Ramkrishna Sapkota

Submitted in Partial Fulfillment of the Requirements

for the Degree of

Master of Science in Engineering

in the

Civil and Environmental Engineering Program

YOUNGSTOWN STATE UNIVERSITY

August 2022

Effectiveness of Surface Treatments on Microbial Induced Concrete Corrosion in Wastewater Infrastructure

Ramkrishna Sapkota

I hereby release this thesis to the public. I understand that this thesis will be made available from the OhioLINK ETD Center and the Maag Library Circulation Desk for public access. I also authorize the University or other individuals to make copies of this thesis as needed for scholarly research.

Signature:

Ramkrishna Sapkota, Student Date

Approvals:

Dr. Richard Deschenes, Thesis Advisor Date

Dr. Holly Martin., Committee Member Date

Dr. Byung-Wook Park, Committee Member Date

Dr. Salvatore A. Sanders, Dean of Graduate Studies Date

ABSTRACT

Microbially-induced concrete corrosion (MICC) is a key deterioration mechanism in wastewater infrastructure. MICC in wastewater infrastructure has caused economic loss in addition to health and environmental risks. A suitable long-term mitigation strategy would help reduce maintenance costs and related problems. Surface treatment is one such strategy that may help reduce MICC-related maintenance costs and increase service life.

In this research, the effectiveness of four treatments applied to concrete surfaces was evaluated in a laboratory experiment at YSU along with in-situ testing in a wet well located in Ellsworth Ohio. Epoxy mastic, acid-resistant coating (ARC), sodium nitrite, and a commercial biocide admixture were evaluated in this study. Among these selected treatments, the first two were selected based on the literature review, while the remaining two were recommended by manufacturers of concrete admixture and surface treatment. Laboratory and field exposure experiments were conducted to determine the efficacy of treatment strategies for mitigating MICC. The applicability of each treatment in different MICC environments was evaluated from the results of surface pH and sulfide uptake rate (SUR) tests. A Live/Dead staining test was then performed to compare the viability of bacteria in the biofilm.

Based on the test results, the epoxy coating provided the best level of protection. The biocide treatment indicated better performance than the control but was less effective than the epoxy. The ARC treatment had mixed performance and should not be used unless it is combined with an effective biocide to limit microbial growth. Similarly, a single treatment of sodium nitrite was ineffective. However, reapplication of sodium nitrite (or free nitrous acid) was effective in inactivating the sulfur-oxidizing bacteria (SOB) within the corrosion interface, which remained effective for up to six months between treatments.

ACKNOWLEDGEMENTS

I would like to express gratitude to my advisor, Dr. Richard Deschenes, for his invaluable advice and support with full encouragement and enthusiasm during this research. His supervision has been very helpful in the completion of this research and writing. Thank you, Dr. Rick, for the opportunity to collaborate with you.

I would also like to thank my thesis committee members, Dr. Holly Martin. and Dr. Byung-Wook Park, for their valuable time and consideration in advising the research and reviewing this report. I appreciate your help with measurements in the laboratory.

Additionally, I would like to express my sincere gratitude to Ohio Water Development Authority (OWDA) for sponsoring this research, and special thanks to Mahoning County Sanitary Engineers Office (MCSE) for providing all the necessary tools, instruments, and professional personnel to complete this research.

I am very thankful to all the faculty and staff members in the Department of Civil/Environmental and Chemical Engineering. I also want to thank Mostafa Nasr and Prakriti Dhungana for their support in the lab. I also want to thank all my dear friends, brothers, and sisters in Youngstown, who were around me for these two years.

Endless gratitude to my parents: my father for all his sacrifices to make my life better and my mother for her unwavering love and support. Thank you for making me who I am today and helping me move forward in my life. I would also like to thank my brother who has always been there for me in need and helped me out in every way possible. Lastly, I am extremely grateful to my wife Garima for her unconditional love and constant support to keep me motivated throughout this process. Thank you for being my best friend, life has been easier with you by my side.

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

LIST OF ABBREVIATIONS

ARC	Acid-Resistant Coating
ASOM	Acidophilic Sulfur Oxidizing Microorganisms
CAC	Calcium Aluminate Cement
FNA	Free Nitrous Acid
H_2S	Hydrogen Sulfide
H_2SO_4	Sulfuric Acid
MIC	Microbially-Induced Corrosion
MICC	Microbially-induced Concrete Corrosion
Na_2SO_4	Sodium Sulfate
$NaNO_2$	Sodium Nitrite
PBS	Phosphate Buffer Saline
PPM	Parts Per Million
RCF	Relative Centrifugal Force
RH	Relative Humidity
SOB	Sulfur Oxidizing Bacteria
SRB	Sulfur Reducing Bacteria
SUR	Sulfide Uptake Rate
YSU	Youngstown State University

1 Introduction

1.1 General overview

Microbially-induced corrosion (MIC) is a key mechanism that reduces the service life of concrete wastewater infrastructures such as main lines and utility access holes. MIC is the process by which changes in the material properties of concrete structures due to biological agents (live organisms) lead to degradation. During MIC, the cementitious material in the concrete is degraded which leads to mass loss. MIC may decrease the overall service life of sewer structures. As such, structures often require repair within a few years of construction due to MIC. If proper repair and maintenance are not completed, the life of a newly built concrete structure may be decreased by up to 90 years in the worst cases (Wu et al., 2020). Many countries, including the U.S., spend billions of dollars on sewer infrastructure maintenance each year. Maintaining the current wastewater system in the U.S. cost an estimated $390 billion between 2002 and 2022 (Wang et al., 2020). Moreover, emissions of H_2S due to MICC lead to potential health risks. In some cases, the infrastructural damage due to MIC causes injury or death. Finally, there are also regulatory fines associated with MICC(Little et al., 2020).

Several approaches have been proposed to mitigate MICC in sewer infrastructure. Based on the mechanism of action, their functioning can be summarized into three common strategies (Li et al., 2020).

1. Limit H_2S generation by application of chemical dosing agents to the wastewater stream.
2. Reduce H_2S levels in the sewer headspace by use of ventilation and treatment units.
3. Application of surface treatment to the existing sewer surfaces. The coating may be chemical, antimicrobial, or a beneficial biofilm.

Among these strategies, the research herein focuses on the third strategy—to evaluate the effectiveness of different treatments applied to concrete surfaces. Epoxy mastic, acid-resistant coating (ARC), sodium nitrite, and a commercial biocide were evaluated in this study.

1.2 Problem Statement

Though significant research efforts have been undertaken to examine various aspects of the MIC mechanism in concrete, the exact mechanism remains a debated subject (O'Connell et al., 2010; Wu et al., 2020; Zhang et al., 2008). Furthermore, several mitigation measures have been put forward with different considerations. With more than a century of research on the topic, MICC remains a significant issue worldwide. Moreover, existing cementitious materials cannot withstand the harsh conditions of MICC environments through an extended service life (Grengg et al., 2018). Nevertheless, when mitigation methods are combined, MIC can be limited to some extent. As most of the proposed methods require additional research, there is no specific solution for field applications. Some surface treatments may work well for short periods, but the long-term efficacy needs to be validated. As such, a suitable long-term treatment method would be useful in reducing maintenance costs and related problems.

1.3 Objective

The general objective of the research was to identify a possible mitigation strategy to extend the service life of wastewater infrastructure. The specific objectives of the research can be summarized as follows:

1. To investigate the effectiveness of different surface treatments for mitigating MIC.
2. To analyze the performance of surface treatments over time.
3. To evaluate the duration of effectiveness of FNA biocide applied to treated concrete.

1.4 Scope

Laboratory and field exposure experiments were conducted to determine the efficacy of surface treatments for mitigating MICC. An in-service wet well located at 11025 W Akron-Canfield Road in Ellsworth Ohio was selected as the primary field study location. The environmental conditions in the field and the progression of corrosion in the concrete were monitored for two years. A simultaneous laboratory experiment was conducted to simulate the conditions of the wet well and accelerate corrosion. The laboratory experiment in the present study was designed to simulate the effects of corrosion, which was achieved by exposing the concrete in the incubation chamber to H_2S gas and wastewater. A total of fifty concrete coupons of size 4 x 3 x 2 in, with surface treatments applied on one face, were exposed to simulated conditions. To simulate the chemical corrosion and biogenic corrosion that occurs in the wet well, 25 coupons were exposed to H_2S gas only and the remaining 25 were exposed to both wastewater and H_2S gas. The difference in MICC formation in the case of chemical corrosion and biogenic corrosion was investigated by comparing the rate of change in surface pH for the concrete coupons. The applicability of each treatment in three different MICC environments (chemical, biogenic, and field exposure) was evaluated from the results of surface pH and SUR tests.

2 Literature review

The following section provides a brief introduction to the MICC mechanism and then additional details regarding mitigation methods. Understanding the fundamental corrosion process and the key variables helped inform the development of effective mitigation methods. The mechanism of MIC in concrete differs from the microbiologically influenced corrosion of metals which has been widely researched (Soleimani, 2012). Explanations of the process of MICC in several stages vary from one to another. There are four commonly accepted phases: (1) generation of H_2S in the wastewater solution, (2) escape of H_2S from the wastewater into the headspace above the water line, (3) biogenic and chemical conversion of H_2S to sulfuric acid, and (4) biodegradation of concrete materials (Wu et al., 2020).

2.1 Mechanism of concrete corrosion

Fresh concrete is protected from biological attack due to its high alkalinity (typically, in the range of 12 to 13). This high pH is due to calcium hydroxide which is formed during the hydration of cement. When concrete comes in contact with wastewater, colonization of microbes on the concrete surface occurs (Satoh et al., 2009). Sulfur-reducing bacteria (SRB) reduce sulfates and oxidize biodegradable organic carbon, which results in hydrogen sulfide and carbon dioxide gasses (Alexander et al., 2012; Wells & Melchers, 2015).

$$\text{Organic matter} + SO_4^- \rightarrow H_2S + CO_2$$

$$CO_2 + H_2O \rightarrow H_2CO_3$$

The carbon dioxide further reacts with water on the concrete surface to produce carbonic acid (Wells et al., 2009; Zivica & Bajza, 2001). The weak acid will react with alkalis (such as calcium hydroxide) lowering the pH of the concrete surface to around 9 over time. This initial passivation of the concrete is deemed the first stage of corrosion in the three stages model proposed by

Islander et al. (1991), which was adapted by Greng et al. (2018). As the pH decreases, microorganisms such as Thiobacillus begin to grow. Once the pH decreases below 9, neutrophilic sulfur-oxidizing micro-organisms (NSOM) like *Thiobacillus sp.* colonize the concrete surface in presence of sufficient nutrients, oxygen, and moisture (Wells et al., 2009). Hydrogen sulfide gas is then oxidized to sulfuric acid by the aerobic, autotrophic *Thiobacillus sp*., which grow in a humid environment (Zhang et al., 2008). The sulfuric acid reacts with the cementitious hydration products leading to a further decrease in pH. Next, acidophilic sulfur-oxidizing microorganisms (ASOM) begin colonizing the concrete surface after the pH of the concrete drops to around 4 (second stage). The pH value is further decreased down to around ~1 or 2 (third/final stage) by the activity of the acidophilic bacteria (Wells et al., 2009). Throughout the corrosion process, biogenic acid attack degrades the cementitious material in concrete which leads to loss of strength. During the third stage of corrosion, concrete mass losses typically occur. The structural capacity of concrete also decreases, which may result in the collapse of the concrete structure (Wu et al., 2020). Different factors are responsible for the rate and extent of MICC. Environmental parameters including temperature and relative humidity (RH) affect the rate of MICC (Joseph et al., 2012). In addition, higher concentrations of H_2S and CO_2 gasses accelerate the MICC process (Grengg, 2017).

2.2 Mitigation measures

The following sections provide further details regarding the various mitigation measures identified within the literature. Mitigation of MICC starts by preventing the favorable growth conditions for the damaging microorganisms. Some common approaches to mitigate MICC include limiting sulfate sources and improving the resistance of sewer pipes to MICC. By controlling the sulfate source, hydrogen sulfide emission from sewage can be limited. This can be achieved by modifying the hydraulic design or by treating the wastewater. Moreover, pretreatment of the wastewater may help to limit the sulfates within the wastewater. Removing the bacterial biofilm and corrosive deposits by keeping the material clean (such as increased flow rates) is another way to limit MICC (Sun et al., 2016).

In addition to limiting H_2S generation, the sewer can be treated with a chemical or microbial coating to enhance its performance in a corrosive environment (Zhang et al., 2008). Additional measures like changing the composition of concrete with the addition of pozzolans can be adopted during the construction of structures to slow MICC (Wei et al., 2013). Finally, biocide treatment can be applied to the surface of the concrete to interrupt the growth conditions for the microorganisms. Biocides include chemical or antimicrobial coatings that help in the prevention and control of MICC. (Soleimani, 2012). Surface preparation, frequency of applications, or chemical pollution are some of the limitations of surface treatment identified in the literature (Jiang et al., 2013; Matthews et al., 2014; Nielsen et al., 2008).

2.2.1 Wastewater Treatment

Videla & Herrera (2005) mentioned biocide treatment as one of the most common chemical methods for controlling MICC. Biocides are oxidizing or non-oxidizing compound which kills microorganisms or inhibits growth. Biocides limit SRB respiration and the generation of H_2S gas. Chlorine, ozone, and bromine are some of the oxidizing biocides in use whereas formaldehyde, glutaraldehyde, and isothiazolinone are non-oxidizing biocides. For proper microbiological control of wastewater, different combinations of oxidizing and non-oxidizing biocides can be used (Videla & Herrera, 2005). Precautions should be taken during application as biocides may create health problems causing skin diseases and allergies (Silva et al., 2020). In addition to biocides, various chemical dosing strategies have been proposed to remove sulfates from the wastewater stream or to inhibit the reduction of sulfides (Firer et al., 2008; Ganigue et al., 2011).

A more recent development in controlling SRB is the application of intermittent free nitrous acid (FNA) and hydrogen peroxide, which effectively reduces sulfide production for a short duration after each application (Jiang et al., 2013). Field trials combining FNA with hydrogen peroxide (H_2O_2) conducted by Jiang and Yuan (2013) at a pumping station in Australia showed a significant impediment to microbial activation. The combination of FNA and H_2O_2 was successful for microbial inactivation in biofilms as well.

2.2.2 Surface Treatments

Treating the concrete surface to limit sulfate oxidation is another means of interrupting the MICC mechanism. In a study by De Muynck et al. (2009), several epoxy coatings were evaluated in addition to polyurea linings, cementitious linings, and silicate coatings. Similarly, Berndt (2011) evaluated the effectiveness of epoxy coatings over mortars mixed with admixtures. Among all the options tested, epoxy coating provided the best protection (Berndt, 2011; De Muynck et al., 2009). In new construction, CAC linings were shown to better resist MICC due to increased acid neutralization and lower porosity (Berndt, 2011; Grengg et al., 2018).

2.2.3 Surface Applied Biocides

Nitrite has been evaluated as a surface applied biocide. The application of nitrite reduces the biological oxidation of sulfide. The sulfide uptake rate after the application of free nitrous acid (FNA) on samples decreased from 84% to 92% for 15 days after spraying the nitrates. The pretreatment rate of sulfide uptake did not recover for up to 1 year after the spray. This proved the long-term- effectiveness of treatment for controlling the MICC (Sun et al., 2015). Similarly, another antimicrobial product SQA (silane quaternary ammonium chloride) mixed with cement was able to inhibit the growth of bacteria and also limit the attachment of biofilm proving its effectiveness against MICC (Erbektas et al., 2019).

2.2.4 Treatments Evaluated in the Present Study

Among the common methods of mitigation within the literature, four surface treatments were selected for evaluation, this study aimed to determine the most effective treatment. Of the treatments evaluated herein, epoxy and ARC sealants function by impeding the biofilm's progression and penetration of bacteria and acid into the concrete. The coating acts as a barrier between the concrete surface and the corrosive solution (Soleimani, 2012). The other two treatments, sodium nitrite and the biocide with mortar, function by preventing anaerobic conditions and inhibiting biological activity which limits sulfide oxidation.

2.3 Test Methods

To evaluate the efficacy of the mitigation methods, test methodologies are required to quantify MIC deterioration within the concrete. Based on the literature, three test methods were identified for quantifying the progression of MIC. The test methods include (1) surface pH, (2) sulfide uptake rate (SUR), and (3) Live/Dead staining. These methods have been used in the literature for MICC research and to quantify the performance of treatment strategies (Puthenpurayil et al., 2010; Sun et al., 2015).

Additional test methods such as ASTM C1894 and ASTM C1904 have since been developed as ASTM standards, which may prove better suited for comparing mitigation methods (Erbektas et al., 2019; ASTM C1894; ASTM C1904). However, these standardized test methodologies were not published when the present research program was established.

2.3.1 Surface pH Test

Changes in surface pH indicate the level of activity of the microbial organisms present in sewer infrastructures (Wells & Melchers, 2015). Islander et al. (1991) demonstrated that the corrosion processes occur in three distinct stages, where the three stages are differentiated by the surface pH. As such, it is important to monitor the surface pH of concrete to determine the stage of corrosion and to study the effect of treatments. Although the surface pH correlates well to the progression of MICC during the first two stages of corrosion, the surface pH tends to stabilize during the final stage when corrosion progresses deeper into the concrete. During this stage, as corrosion progresses further into the concrete, a stable biofilm may form on the surface of the concrete with a constant pH value even though the surface pH of the underlying material may be different.

To measure the surface pH of concrete, a commercial pH electrode was used by Islander et al. (1991). To provide adequate contact between the electrode and the concrete, a shallow indentation was made on the surface. Several difficulties were faced during measurement and regular cleaning and recalibration of the electrodes were necessary for accurate and repeatable pH measurements. The pH sensors provided repeatable measurements for the concrete surface conditions which were confirmed by validating with pH paper.

Sun et al. (2014) improved upon the earlier surface pH test method by using a flat surface pH electrode. To allow the glass membrane of the surface pH electrode to make sufficient contact with the concrete surface, the coupon surface (1 cm. diameter) was wetted with 0.5 mL of Milli-Q water. A series of four separate measurements were performed at distinct locations to calculate the average surface pH of each coupon. The test method was repeatable and accurate. As such, a similar procedure with minor modification was used in the present research as described in **Section 3.3.2**.

2.3.2 Sulfide Uptake Rate (SUR)

The sulfide uptake rate (SUR) is another indicator of the MIC development in concrete. The SUR test is a rapid methodology developed by Sun et al. (2014) to track the sulfide-induced corrosion mechanism on concrete by assessing the H_2S uptake rates of concrete at different stages of corrosion. The SUR is determined by monitoring changes in gaseous H_2S concentrations over time in a hermetically sealed reactor containing a concrete coupon. The temperature and humidity inside the chamber are controlled or monitored. To determine the SUR, the H_2S absorbed by the empty reactor and other components must first be determined. This value is known as the background H_2S uptake and accounts for losses in the system. After the background uptake is known, the concrete coupon, whose SUR is to be determined, is placed in the reactor and the H_2S absorbed over time (while the concrete is inside the reactor) is recorded. Next, the H_2S absorbed by the exposed surface area of concrete is obtained by subtracting the background uptake from the change in H_2S concentration with the coupon in the reactor. Finally, the SUR is reported as the mass of sulfur (mg) consumed per unit of concrete surface area (m^2) per unit of time (hour) (mg-S m^{-2} h^{-1}). The slope of the H_2S concentration with respect to time is used to determine the SUR (Nasr, 2021). The formulas used to calculate SUR are presented in **Equation 1**.

$$r_{H_2S} = -\frac{d[H_2S]}{dt} \times P_{atm.} \times \frac{MW_{sulfur}}{R\,T} \times \frac{V_{reactor}}{S_{area}} \qquad \textbf{Equation 1}$$

In **Equation 1,** r_{H2S} represents the surface-specific H_2S uptake rate (mg-S/m^2-h), $[H_2S]$ is the H_2S gas concentration (ppm), t is the test duration in hours, T is the absolute temperature in kelvin, S_{area} is the area of the exposed surface of the concrete (m^2), $V_{reactor}$ is the volume of gas in the reactor in (m^3), P_{atm} is the atmospheric pressure (101.325 KPa), MW_{sulfur} is the molecular weight of a sulfur atom (32.065 gm mol^{-1}), and finally R is the universal gas constant (8.3145 J/K-mol).

2.3.3 Live/Dead staining test

The Live/Dead staining test method is useful for quantifying the efficacy of biocides (Sun et al., 2015). During MIC, the concrete undergoes a succession of microbial ecosystems as the pH decreases from 12 down to 1 (Islander et al., 1992). The microbial growth accelerates as the pH decreases from neutral due to increased neutrophilic and acidophilic microorganisms activity, which accelerates sulfide oxidation (Jensen et al., 2011). As such, the evolution of corrosion in concrete can be studied using a combination of microscopy and microbiology approaches. (Daims et al., 2006). Sun et al. (2015) used a Live/Dead assay to quantify the change in viable bacterial cells after treatment using nitrite (FNA) treatment on concrete. The procedure described by Sun et al. (2015) was followed with modifications as per the availability of equipment at YSU for carrying out the Live/Dead staining test.

In the Live/Dead assay, sample solutions were prepared by mixing extracted scrapings of the concrete biofilm with reagents followed by centrifuging the mixture. After rinsing the sample solutions, the Live/Dead staining reagent was added to the properly rinsed bacterial cell pellet and then the mixture was resuspended and incubated for 15 minutes, while protected from light. Quantitative and qualitative analysis was conducted by placing the sample solution onto microscope slides and imaging using a fluorescent microscope. The effectiveness of surface treatment was correlated with the number of live and dead bacteria present in the samples using digital image correlation. The change in the effectiveness of the treatment over time can also be measured by conducting the Live/Dead staining test periodically.

3 Experimental Investigation

The research conducted herein is a continuation of the experimental investigation established by Nasr (2021). The experimental apparatus constructed by Nasr (2021) was used for the experiments herein. A brief introduction of the materials used, and any modifications made from the previous setup will be provided in the present thesis. Additional details regarding the experimental investigation can be found in Nasr (2021).

3.1 Lab Experiment

The experimental investigation was developed to quantify and compare the performance of concrete under accelerated MICC conditions. The performance of four surface treatments was compared to the untreated control. The performance was quantified using surface pH, SUR, and Live/Dead staining tests. An additional set of coupons were treated with FNA ($NaNO_{2\text{-}R}$) and then exposed to biogenic corrosion to determine the duration of efficacy of the FNA treatment.

The experimental setup consisted of an incubation chamber designed to simulate and accelerate the aggressive MIC conditions of a wet well. The concrete in an upper portion of the wet well in Ellsworth Ohio is exposed to the gas phase only whereas at the waterline the concrete is exposed to both wastewater and gas. This was simulated in the laboratory by dividing the incubation chambers into two regions, where the upper region is exposed to chemical corrosion (H_2S gas) and the lower region to biogenic corrosion (H_2S gas and wastewater). Additionally, the treatments were applied to a concrete wet well, and core samples were periodically collected.

Finally, to quantify MIC deterioration over time and compare the performance of treatments, the surface pH and SUR tests were periodically measured for the coupons undergoing chemical corrosion, biogenic corrosion, and field exposure.

3.1.1 Incubation chamber

Several MIC simulation chambers have been used by researchers to simulate and accelerate MICC in the laboratory. Wang et al. (2020) mentioned the reaction chamber designed by Hamburg (1984), Heidelburg (1997), and the reaction chamber developed by the researchers at Ghent university (De Belie et al., 2002) as the representative ones. Most of the reaction chambers developed more recently have been a variation or improvement on the three mentioned above. Only slight modifications have been made to the detailing by adding advanced features (Wang et al., 2020). The reaction chamber used in the present experiment was constructed following the procedures outlined by Joseph et al. (2010) and Joseph et al. (2012).

The PVC incubation chamber used in the present study consisted of two levels, as shown in **Figure 1.** The nominal dimensions of the chamber were 31 x 21 x 19 in. The chamber had an upper and lower shelf, with the upper shelf mounted at the mid-height (referred to as the upper chamber herein). The upper shelf had 25 openings (4 in x 3 in) to hold the treated coupons. The lower shelf held an additional 25 coupons, which were partially submerged in wastewater. The reaction chamber was placed inside a fume hood for safety. The front face of the chamber had a large window attached with corrosion-resistant screws, which function as a door for the chamber.

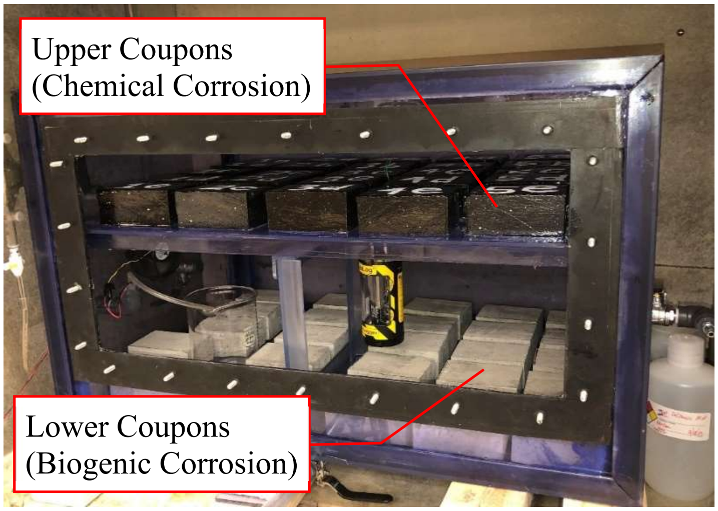

Figure 1—Incubation chamber with coupons. (Photo by Mostafa Nasr).

3.1.2 Concrete coupons

The concrete coupons used in the experiment were nominally 4 (length) x 3 (width) x 2 in. (thick). The coupons were obtained by cutting three concrete slabs that were cast in the Concrete Materials Lab at Youngstown State University. The mix design for the concrete coupon is provided in **Table 1**.

Table 1—Mixture design for concrete coupons. (Nasr, 2021).

Materials	**Weight (lbs./yd3)**	**Volume (ft3)**	**Ratio**	**S.G.**	**A.C.**	**Weight (lbs.)**
Cement	1301	6.62	1.00	3.15	-	24.10
Fine Aggregate	1952	11.50	1.50	2.72	0.01	36.14
Water	520	8.34	0.40	1.00	-	9.64
Air	-	0.54	-	-	-	-

Half the coupons (25) were prepared for chemical corrosion exposure. The coupons were coated with epoxy on all but the bottom face, which was left for treatment to be applied. The other half of the coupons (25) were left uncoated for biogenic corrosion exposure, as the sides of the coupons needed to be in contact with the wastewater.

3.1.3 Surface Treatment

The surface treatments evaluated herein included epoxy mastic, sodium nitrite, biocide (mixed with mortar), and an acid-resistant coating (ARC). The epoxy mastic and sodium nitrite were selected based on the literature review (**Section 2.2**), while biocide (mixed with mortar) and an acid-resistant coating (ARC) were used based on the manufacturer's recommendations. The concrete coupons were preconditioned by exposure to H_2S for 20 weeks before treatment application. The treatment was applied to the top face of each coupon. Each treatment was applied to 10 coupons, 5 exposed to chemical corrosion and 5 to biogenic corrosion. An additional 10 coupons remained untreated as a control, 5 of which were exposed to chemical corrosion and 5 to biogenic corrosion.

3.1.3.1 Epoxy mastic (Epoxy)

Epoxy mastic is a corrosion-resistant surface coating, which inhibits biofilm attachment and diffusion of acid and sulfur-oxidizing bacteria (SOB). It can be sprayed, brushed, or rolled on the concrete surface. Epoxy was applied to the concrete surface by mixing in equal volume with the activator as per manufacturer recommendations. In this experiment, an approximately 0.5 mm thick layer was applied to the concrete surface using a brush. A second coat was applied two hours after the first coat.

3.1.3.2 Acid resistant coating (ARC)

ARC is a proprietary mixture of sodium silicate, slag cement, and quartz flour, which is mixed with an activator to form acid insoluble hydration products limiting concrete permeability and diffusion of acid and bacteria. The ARC is essentially a geopolymer and has high acid resistance. ARC was applied to the concrete surface by mixing as per manufacturer instructions (2 parts A to 1 part B). A paint roller was used for the application of ARC. A second coat was applied 30 minutes after the first.

3.1.3.3 Biocide applied with mortar/shotcrete (Biocide)

Penetron BioMIC is a proprietary microbiostatic admixture comprised of 3-(Trimethoxysilyl) propyldimethyloctadecyl ammonium chloride, which inhibits biofilm attachment and growth. The biocide was applied to the concrete surface by mixing the manufacturer's recommended dose into Portland cement mortar. The mortar mixture was designed with a standard mixture ratio of 0.4:1:1.5 (water/cement/sand by weight) and was applied with a thickness of approximately 6 mm.

3.1.3.4 Free nitrous acid ($NaNO_2$)

An aqueous solution of ACS grade $NaNO_2$ was sprayed on the concrete to inactivate sulfide oxidizing bacteria and inhibit biofilm growth. To enhance the efficacy of FNA, hydrogen peroxide (0.6%) was sprayed before the sodium nitrite ($NaNO_2$) treatment (Sun et al., 2015). The ($NaNO_2$) was applied at a concentration of 40.9 gm/liter and a rate of 0.714 liter/m^2. A hand sprayer was used to control the rate of application of the treatment.

3.1.4 Hydrogen Sulfide (H_2S) gas

The H_2S concentration plays a significant role in determining the concrete corrosion rates when concrete is exposed to sewer conditions for a long duration (Jiang et al., 2014). In the present experiment, H_2S gas was produced by pumping 0.5 to 1.0M sodium sulfide (Na_2S) stock solution into 8M sulfuric acid (H_2SO_4) at a controlled rate. The Na_2S stock solution was prepared by mixing solid $Na_2S \cdot 9H_2O$ with deionized water. The 8M sulfuric acid was prepared by diluting 98% H_2SO_4. Hydrogen sulfide was then generated by mixing the sodium sulfide ($Na_2S_{(aq)}$) stock solution into sulfuric acid (H_2SO_4) at a controlled rate using a peristaltic pump. The hydrogen sulfide was generated based on the following chemical equation (**Equation 2**).

$$H_2SO_{4(aq)} + Na_2S_{(aq)} \rightarrow H_2S_{(g)} + Na_2SO_{4(aq)} \qquad \textbf{Equation 2}$$

To control the H_2S concentration in the incubation chamber, a beaker filled with 200 ml of sulfuric acid was placed inside the chamber and Na_2S was intermittently dripped into the beaker using a peristaltic pump and silicon tube. The beaker contained a stirrer that was operated using a magnetic stir plate (VWR® Low Profile Magnetic Stirrer) placed beneath the incubation chamber (the magnetic field was sufficient to move the stirrer through the air gap, PVC, and glass beaker). Finally, the generated H_2S gas was distributed throughout the chamber using a small (120 mm) fan that was mounted inside the chamber. Each time the beaker inside the chamber was full of Na_2SO_4 waste, it was replaced with new sulfuric acid and the stock solution of Na_2S was also refilled.

3.1.5 Wastewater

The domestic wastewater used in the laboratory experiment was collected from a wet well in Ellsworth Ohio. Eight liters of wastewater were collected during each site visit and stored in a refrigerator at the lab. Every 7 days, two liters of wastewater were removed from the chamber, and two liters of new wastewater were added.

3.1.6 Peristaltic pump

A peristaltic chemical metering pump was used to pump the Na_2S stock solution into the beaker of sulfuric acid within the chamber. The stock solution was stored in a one-liter bottle and then pumped through a silicon tube into the crystalizing basin of acid. The pump flow rate was adjusted in real-time using LabView control software designed and programmed by the research team (Nasr, 2021).

3.1.7 H_2S logger

The experimental investigation required four H_2S loggers. The AcruLog LL1000 sensors were used in the laboratory experiment while the OdaLog LL 1000 sensors were used in the wet well. The AcruLog LL1000 includes temperature and relative humidity sensors, while the OdaLog only includes a temperature sensor. The H_2S detection range for the sensors was 0-1000 PPM. The loggers require 10 days of fresh air after being exposed to H_2S gas for 30 days. Therefore, two sets of sensors were required in the field and lab for cycling between H_2S exposure and fresh air.

3.1.8 H_2S Gas Generation and Logging

The hydrogen sulfide gas was continuously generated within the chamber following the production described in **Section 3.1.4**. The concentration of H_2S was recorded using an AcruLog H_2S Gas Monitor, which can operate at up to 1000 PPM without degradation. The immediate concentration of H_2S was displayed in parts per million on the logger and recorded on the computer. The H_2S concentration in the chamber was maintained at the desired value with the help of a programmed logic controller which stopped the pump when the concentration in the chamber reaches a set value. A lower and upper limit was also set in the system so that the pump would stop if the H_2S concentration went outside the safe operating range. Such a condition would occur in the chamber if any of the components stopped functioning.

3.1.9 Laboratory Experiment

The concrete coupons were exposed to either chemical or biogenic corrosion. Chemical corrosion was simulated by exposure to H_2S gas while biogenic corrosion was simulated by exposure to H_2S gas and wastewater. The 25 coupons placed on the bottom level of the chamber were exposed directly to wastewater and H_2S gas. The bottom of the chamber was filled with domestic wastewater from the wet well in Ellsworth, Ohio (field experiment location). The water was replaced every seven days and was also poured on top of the concrete surface of the coupons on the bottom shelf. The coupons on the bottom of the chamber were placed with the treated surface facing up. The remaining 25 coupons were placed on the upper shelf with the treated side facing down and exposed only to H_2S gas.

The arrangement of the coupons replicated the wet well concrete, where the upper regions are exposed to H_2S gas but only periodically to wastewater. In contrast, the lower part of the wet well is exposed to wastewater more frequently. As such, the coupons on the upper shelf simulated the upper portion of the well (or a sewer pipe crown) whereas the coupon on the bottom simulated the waterline. This setup was desirable as the crown and waterline of sewer pipes often exhibit the most severe corrosion in wastewater infrastructure.

3.1.10 FNA ($NaNO_{2\text{-}R}$) Reapplication

In addition to the four treatments mentioned in **Section 3.1.3**, the FNA was evaluated with a repeated application as it loses efficacy over time. Free nitrous acid (FNA), the protonated form of nitrite (HNO_2), was formed on the concrete surface by applying $NaNO_{2(aq)}$ solution (Li et al., 2020). While $NaNO_2$ and FNA represent the same treatment, FNA is the preferred nomenclature in the literature (Li et al., 2020; Sun et al., 2015). In the present study, FNA was evaluated as a single application ($NaNO_2$) and with periodic reapplication ($NaNO_{2\text{-}R}$). To avoid confusion between the two treatments, the former is hereafter referred to as $NaNO_2$ and the latter is referred to as $NaNO_{2\text{-}R}$.

To determine the frequency of reapplication, coupons were first conditions by 18 months of biogenic corrosion. The ten coupons selected for evaluation (Control x 2, Epoxy x 2, ARC x 2, Biocide x 2, and $NaNO_2$ x 2) were removed from the ongoing experiment. The coupons had been stored on the bottom shelf of the incubation chamber, as described in **Section 3.1.1**. The coupons were first pressure washed with clean water and then air dried for 30 minutes before treatment with $NaNO_{2\text{-}R}$. The surface was treated with hydrogen peroxide (0.6%) to increase the effectiveness of the $NaNO_{2\text{-}R}$. $NaNO_{2\text{-}R}$ was then applied at a concentration of 40.9 gm/liter and sprayed on the surface at a rate of 0.714 liter/m². Both hydrogen peroxide and $NaNO_{2\text{-}R}$ were applied at a controlled rate using a hand sprayer. The specimens were then sealed in plastic bags for 1 hour to prevent evaporation of the $NaNO_{2\text{-}R}$ solution. Finally, the specimens were returned to the incubation chamber and exposed to biogenic corrosion for an additional 6 months. The surface pH and SUR were measured monthly.

3.2 Field Experiment

In addition to the laboratory experiment, an in-service wet well in Ellsworth Ohio was selected as the field study location. The well was located at 11025 W Akron-Canfield Road. The interior surface of the well was first divided into five sections. Leaving one section untreated as a control, the other four sections were treated with the same four surface treatments, as explained in **Section 3.1.3**. The four treatments included epoxy, sodium nitrite, biocide, and ARC sealant.

To monitor the concentration of H_2S in the well, a data logger was suspended inside the wet well at the median elevation of the treatment. The logger was replaced monthly. As the aim of the study was to evaluate the performance of the surface treatments in the field, site cores were collected from the well every two months for the first year and then quarterly for the second year. At each site visit, 10 cores were collected, two from each of the four treatments and two from the untreated control. The concrete cores were cut using a hammer drill with an attached core bit of 2.0-inch internal diameter. The cores were then taken to the lab for testing.

As drilling and collecting cores required damaging substantial portions of the wet well wall, an alternative procedure was also evaluated. Rather than collect new cores on each visit, the previously collected cores were stored in the wet well and periodically moved to the lab for surface pH and SUR testing. The cores were then returned to the wet well after conducting the laboratory tests. Between measurements, the cores were stored inside a basket and suspended in the wet well. The result from the freshly drilled concrete cores was comparable to the cores from the basket. This process was used for six months which made the fieldwork easier as no drilling was required. For the last two sets of tests, fresh cores were drilled for comparison.

In addition to collecting cores, eight liters of domestic sewage were collected every four weeks for usage in the laboratory. The older wastewater, which was replaced from the incubation chamber, was also taken to the wet well for disposal during the field visit.

3.3 Measurements

As the experiment was conducted to evaluate the effectiveness of different surface treatments, progress was monitored using two laboratory testing methods. The primary test metrics were sulfide uptake rate (SUR) and surface pH, which were conducted regularly. In addition, Live/Dead staining was conducted at the end of the experiment. Finally, visual inspection (photo documentation) was also conducted throughout the experiment for qualitative comparison.

3.3.1 H_2S gas concentration

The concentration of the H_2S gas (PPM) in the chamber and wet well were monitored in real-time using a data logger. The AcruLog LL1000 sensors were used in the laboratory whereas the OdaLog LL1000 sensors were used in the field. The logger was set to record data every five minutes. After each exposure period, the data from the logger was exported and plotted on the cumulative monitoring graph. The exported data from the OdaLog sensor consist of date, time, H_2S concentration, and temperature but the AcruLog included the relative humidity. Both the logger in the chamber and wet well were replaced monthly and stored in fresh air for at least 10 days. The logger in the lab experiment was placed in the lower chamber and the one in the wet well was suspended to a depth of around 8 to 10 ft inside the wet well. The H_2S gas concentration data are presented in the section **4.1** of the Results and Discussion.

3.3.2 Surface pH

Surface pH is a key indicator of successful mitigation of MICC in concrete. The value of surface pH should remain high if the surface treatment is limiting corrosion. Surface pH was measured for the coupons in the laboratory and cores from the field. Herein, the surface pH of concrete was measured directly using an Extech surface pH meter (pH100). The pH meter was calibrated periodically using buffer solutions of pH 4, 7, and 10.

Before testing the surface pH, the coupons were rinsed with water to remove any loose contaminants. To improve the accuracy and repeatability of surface pH measurements, the surface was first wet with 2 ml of ultrapure water, allowed to equilibrate for 30 seconds, and then the surface pH was measured (Ashok, 2014; Joseph et al., 2010). The surface pH often varied across the surface of the coupon. To improve the repeatability of measurements and limit experimental error, the surface pH was consistently measured at three points near the center of the coupon. The average surface pH of each coupon was calculated from two separate measurements performed at the three locations (N=6). The surface pH data are presented in **Section 4.2** of the Results and Discussion.

3.3.3 Sulfide Uptake Rate (SUR) Measurement

The effectiveness of the surface treatments is further indicated by a low SUR, indicating low oxidation of sulfides to acid. The SUR test was conducted for the laboratory coupons and field cores. The SUR test was conducted in a separate reaction chamber as shown in **Figure 2**. The detail of the chamber was comparable to the chamber explained in **Section 3.1.1**. To test the SUR, the H_2S was first stabilized at around 80 ppm and the surface of the coupon was then exposed to the gas environment for 1 hour. During testing, the relative humidity was 75±10%.

Generating a stable environment of 80 ppm was difficult as there were several interrelated variables involved that affected the concentration of H_2S in the test chamber (e.g., fan speed, the concentration of Na_2S or H_2SO_4, stirrer speed, etc.). To limit experimental error, these variables were maintained between measurements. Due to the small volume of the chamber, a low concentration of Na_2S was sufficient to produce the required concentration of H_2S. Na_2S of concentration 0.02M (50 times lower than that of the Na_2S used in the laboratory chamber) was used during the SUR test. The concentration of H_2SO_4 was 1.6 M (5 times less concentrated than the one used in the incubation chamber for the experiment).

Generating a stable environment of 80 ppm H_2S in the reaction chamber required a minimum of 30 minutes for each test. An additional 1 hour was required to test the coupon. As such, measuring the SUR required up to 20 hours for 10 laboratory coupons and another 10 hours for the site cores. The additional 10 coupons with $NaNO_{2\text{-}R}$ treatment added 10 hours. As such, each set of SUR measurements required up to 40 hours to collect. Therefore, it was infeasible to conduct multiple SUR tests for each coupon monthly (N=1).

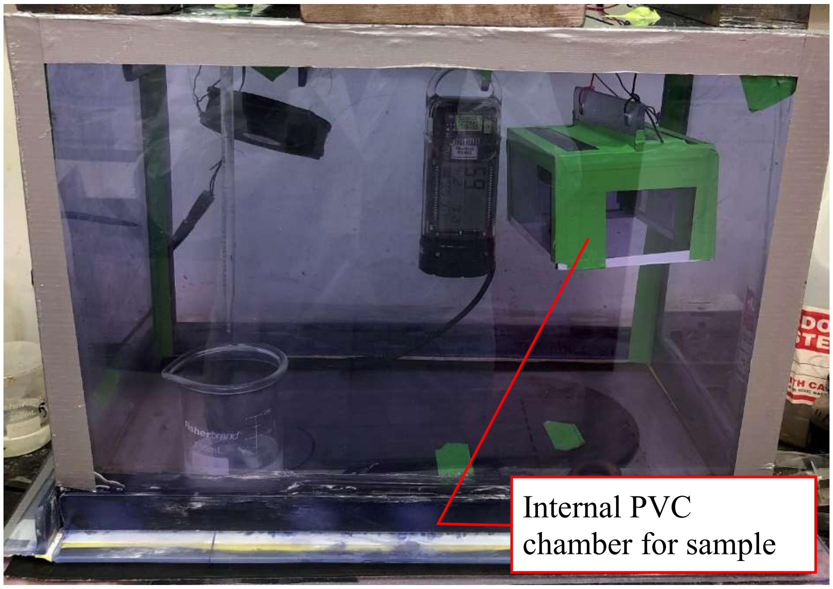

Figure 2—SUR test chamber in use. (Photo by Ramkrishna Sapkota).

To conduct the SUR test, the test chamber was first set up under the fume hood in the measurement lab. Then, 50 ml of 1.6M H_2SO_4 was placed in a small beaker within the SUR chamber. The acid mixture was continuously stirred with the help of a magnetic stirrer to avoid sharp fluctuation in the concentration of H_2S. The test apparatus was then sealed and Na_2S was added to the beaker using a pipette. Additional Na_2S was added until the H_2S logger within the reaction chamber detected approximately 80 ppm. Time was required for the gas to disperse and equilibrate within the chamber; therefore, a small fan within the chamber was necessary to circulate H_2S throughout the chamber from the beaker. After the gas concentration reached approximately 80 ppm and stabilized, gas generation ceased and the change in H_2S concentration was measured over one hour. Before measuring the SUR of any coupons, the background uptake (H_2S absorbed by the apparatus without concrete coupons) was recorded.

After measuring the background uptake, the first test coupon was placed within the chamber under the internal PVC box (see **Figure 2**). After sealing the reaction chamber, a few drops of Na_2S were added to the beaker of H_2SO_4 inside the chamber to generate more H_2S. The H_2S concentration inside the chamber was increased until it stabilized near 80 ppm H_2S gas. The internal PVC box was then lifted off the test coupon, exposing it to the H_2S gas. The coupon was exposed to the H_2S gas for one hour and the change in H_2S concentration was recorded every 30 seconds. The process was repeated for all the coupons and core samples. Finally, the corrected H_2S uptake was obtained by subtracting the background uptake from the coupon uptake, which was then used to obtain the SUR value of the coupon. The SUR data are presented in section **4.3** of the Results and Discussion.

Several variables within the SUR test have a direct impact on the SUR result, such as fan speed, background uptake, or losses due to leakage. Although there was a range of factors that potentially affected the SUR results, all the tests were conducted under similar conditions which limits experimental error while making a comparison. To reduce experimental error, the background uptake rate was remeasured periodically to account for any changes in the test apparatus. Moreover, when testing the coupons exposed to biogenic corrosion, the sides of the coupons were covered with PTFE tape, exposing only the top surface to the H_2S gas.

3.3.4 Live/Dead Staining Test

To evaluate the efficacy of biocides, Live/Dead staining was used to quantify the viability of bacteria present within the biofilm. The procedure outlined by Sun et al. (2015) was followed herein as a basis for sample collection, preparation, and measurements. The procedure was modified to fit the equipment available at YSU. This test was carried out for the control coupons exposed to biogenic corrosion and for one set of coupons treated with $NaNO_{2\text{-}R}$.

First, bacterial samples were taken from the top surface of the coupons. Next, 500 µL of the bacterial sample was placed in a microcentrifuge tube and centrifuged for 5 min at 5000 relative centrifugal force (RCF). Next, the centrifuged bacterial sample was washed with 500 µL phosphate buffer saline (PBS) twice. The washed sample was then mixed with 2µL of DMAO (green florescent nucleic acid dye staining live bacteria) and then shaken to ensure complete mixing. The mixed sample was wrapped with aluminum foil and incubated at room temperature for 15 minutes. Finally, 15µL of stained bacterial suspension was placed on a glass microscope slide and then placed in a Zeiss AxioVert A1 microscope (Jena, Germany) for fluorescent imaging. Finally, the image was then processed by ImageJ software to quantify the number of live bacteria.

3.4 Summary

The efficacy of surface treatments applied to concrete was evaluated by exposing samples to chemical corrosion, biogenic corrosion, and field conditions. The laboratory setup was designed to simulate the field condition with continuous generation of H_2S inside the incubation chamber. The concentration of H_2S was recorded both in the laboratory and in the field using a logger. Domestic wastewater was placed in the chamber and was replaced frequently. The wet well and concrete coupons in the lab were treated with one of four treatments (epoxy mastic, sodium nitrite, biocide (mixed with mortar), and ARC sealant). To quantify the effectiveness of surface treatments, three different tests were conducted periodically over the experiment duration. SUR and Surface pH were conducted every month whereas Live/Dead staining was conducted at the end of the experiment.

Surface pH was measured for both the coupons in the laboratory and cores from the field. The surface pH test was carried out to determine the stage of corrosion and study the effects of treatment. The surface pH should remain high if a treatment is successful. A continued decrease in surface pH implies that corrosion-inducing acidophilic microorganisms have developed on the concrete coupons (Jiang et al., 2014).

The effectiveness of surface treatment was further observed by measuring the SUR in a reaction chamber. During the SUR test, the surface of the coupon was exposed to H_2S gas, and the quantity of gas absorbed by the concrete was measured over a 1-hour exposure period. Generally, concrete with more severe corrosion will have higher SUR. In contrast, a lower SUR as compared to the untreated control indicates better performance of surface treatment.

The abundance of microorganisms on the coupons was measured using the Live/Dead staining method. This test was conducted for the coupons with biogenic corrosion having reapplication of FNA ($NaNO_{2-R}$). Microscopic slides were prepared by cleaning the samples and mixing them with reagents. Those slides were viewed under a fluorescent microscope for quantitative and qualitative analysis. The effectiveness of surface treatment can be correlated with the number of live and dead bacteria present in the samples after treatment and/or exposure.

4 Results and Discussion

This section includes the result obtained from data collected in the field and experimental investigation in the laboratory. The results from the surface pH and SUR test of the coupons undergoing chemical corrosion, biogenic corrosion, field exposure, and samples treated with reapplication of FNA ($NaNO_{2\text{-}R}$) are discussed below.

4.1 H_2S Concentration

Recall, that H_2S gas is a major component responsible for MICC (Li et al., 2019). Oxidation of H_2S leads to the corrosion of wastewater infrastructure. To track the H_2S exposure conditions in the laboratory experiment and field, the gas concentration in the incubation chamber and the wet well in Ellsworth Ohio were recorded using the AcruLog and OdaLog loggers, respectively.

4.1.1 H_2S Concentration in the Incubation Chamber

The H_2S gas concentration (PPM) in the chamber was logged using an AcruLog LL1000 logger. The logger was set to save the recorded data every five minutes. Each month, the data from the logger was exported and plotted on the cumulative graph in **Figure 3**. The average weekly H_2S gas concentration (PPM) inside the incubation chamber is summarized in the figure. Throughout the experimental investigation, the concentration of the solutions, stirring of sulfuric acid, and fan speed was adjusted to maintain a stable concentration of H_2S inside the chamber.

During the experiment, the concentration of H_2S in the chamber was maintained at an average of 110 ppm. However, no H_2S was generated between weeks 5 and 14 during the university shutdown due to COVID-19. Also, between weeks 73 and 76, no H_2S was generated while the loggers were sent for repair and recalibration. For the first half of the experiment, from week 15 to week 65, the average H_2S concentration was approximately 150. A higher average was necessary to accelerate the passivation of concrete and the development of SOB biofilm

(Nasr, 2021). After the coupons reached stage II of corrosion, the average H_2S concentration was reduced to 82 (week 76 to week 110). This reduction in concentration helped to decrease the frequency of replacing the acid solution in the beaker and the volume of waste generated. Moreover, fluctuation in the H_2S concentration better simulated the wet well conditions where the gas concentration fluctuates daily and seasonally.

Over the monitoring period, the average temperature was 23.5±3.5°C and the relative humidity was 95-100%. Higher average temperature and humidity as compared to the wet well conditions accelerated corrosion in the concrete coupons placed inside the chamber.

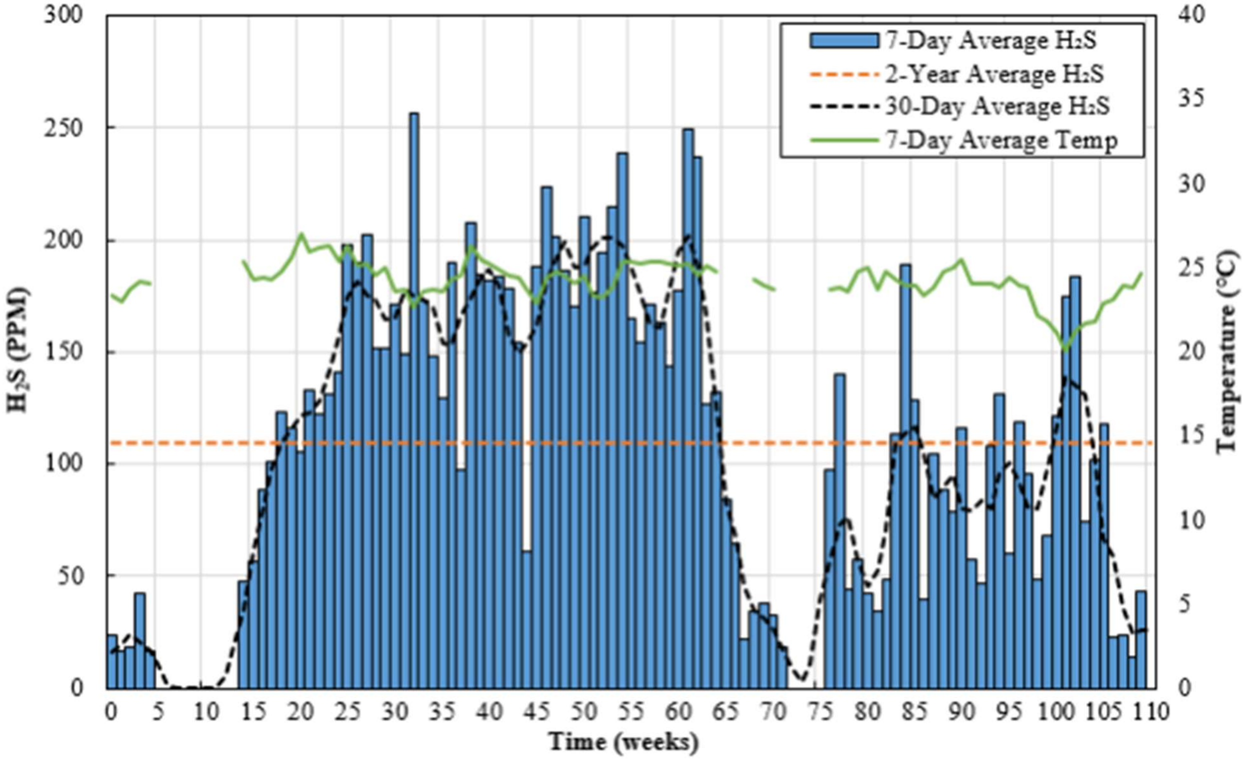

Figure 3—H_2S gas concentration in incubation chamber.

4.1.2 Gas Concentration at Ellsworth-OH Wet Well

The H_2S concentration in the wet well was also recorded for 100 weeks between March 2020 and February 2022. There were fluctuations in the concentration of H_2S with changes in the season which can be seen in **Figure 4**. The average H_2S concentration during this period was calculated to be 24.7 PPM whereas the average temperature was 11.2°C. Observing the data for the year 2021 (i.e., from week 40 to week 91) the H_2S concentration crossed the average concentration value after week 58 (the first week of May) and then decreased below the average after week 82 (the last week of October). The average H_2S concentration increased during the summer months and then decreased as the weather cooled. The decrease during winter is likely due to the less SRB respiration in the wet well when the temperature is lower (Wells & Melchers, 2015). The results followed a similar trend in 2022. The concentration reached a maximum weekly average value of 69.4 in the third week of June 2021.

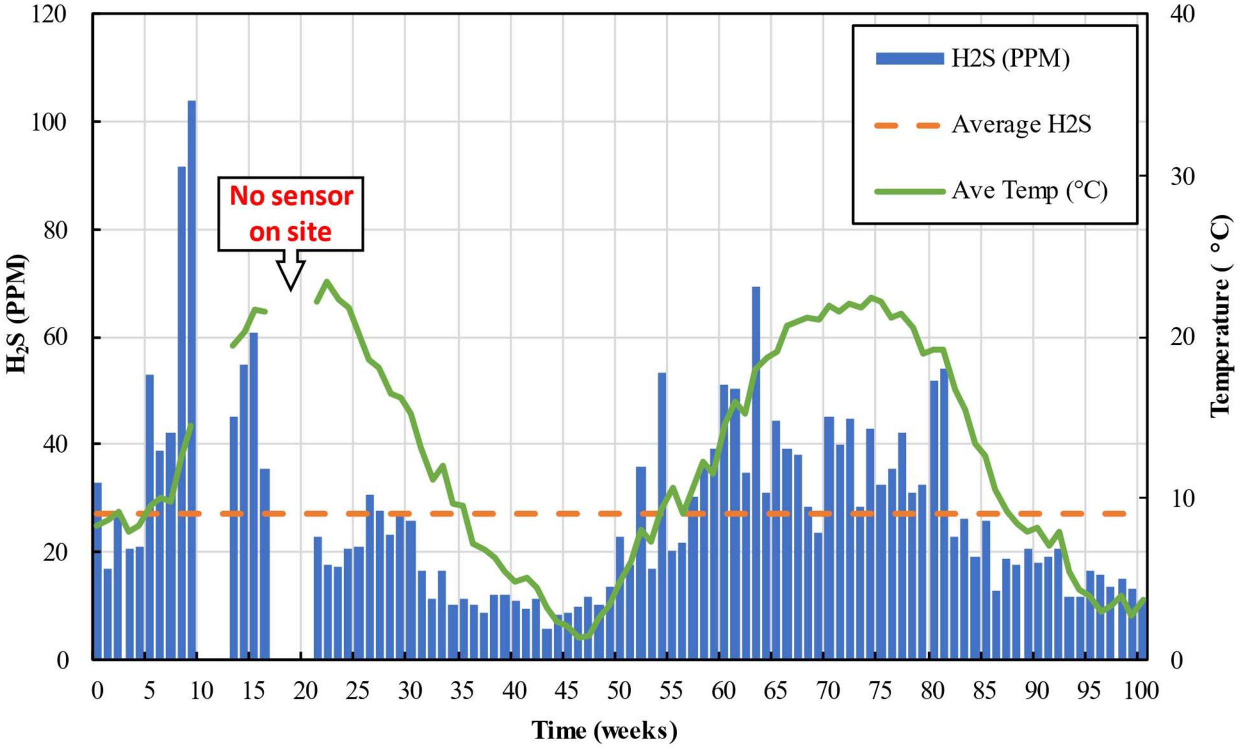

Figure 4—H_2S gas concentration in wet well.

The difference in average H_2S concentration in the laboratory experiment and the wet well was 95 PPM. The higher average H_2S concentration in the laboratory experiment helped to accelerate MICC in the concrete coupons and correlates to the result with the corroded concrete samples from the wet well.

4.2 Surface pH

Recall, surface pH indicates the progress of corrosion in the concrete. The neutralization of the alkalinity of concrete due to the reaction with H_2S is reflected by the value of surface pH. (Li et al., 2019). However, the surface pH test measures the pH of the exposed surface area but not the underlying materials. For the laboratory experiment, the surface pH test for the coupons was conducted monthly, whereas for the site cores surface pH was measured every 2 to 3 months. The site cores were tested less frequently because corrosion progressed slower in the wet well.

4.2.1 Surface pH - Chemical Corrosion

The coupons that were placed on the upper shelf of the chamber were exposed only to H_2S gas and therefore experience chemical (abiotic) corrosion. The surface pH of all the coupons trended down over time as summarized in **Figure 5** below. The surface pH data of the coupons, collected over two years, are also provided in **Table 4** in the **Appendix**.

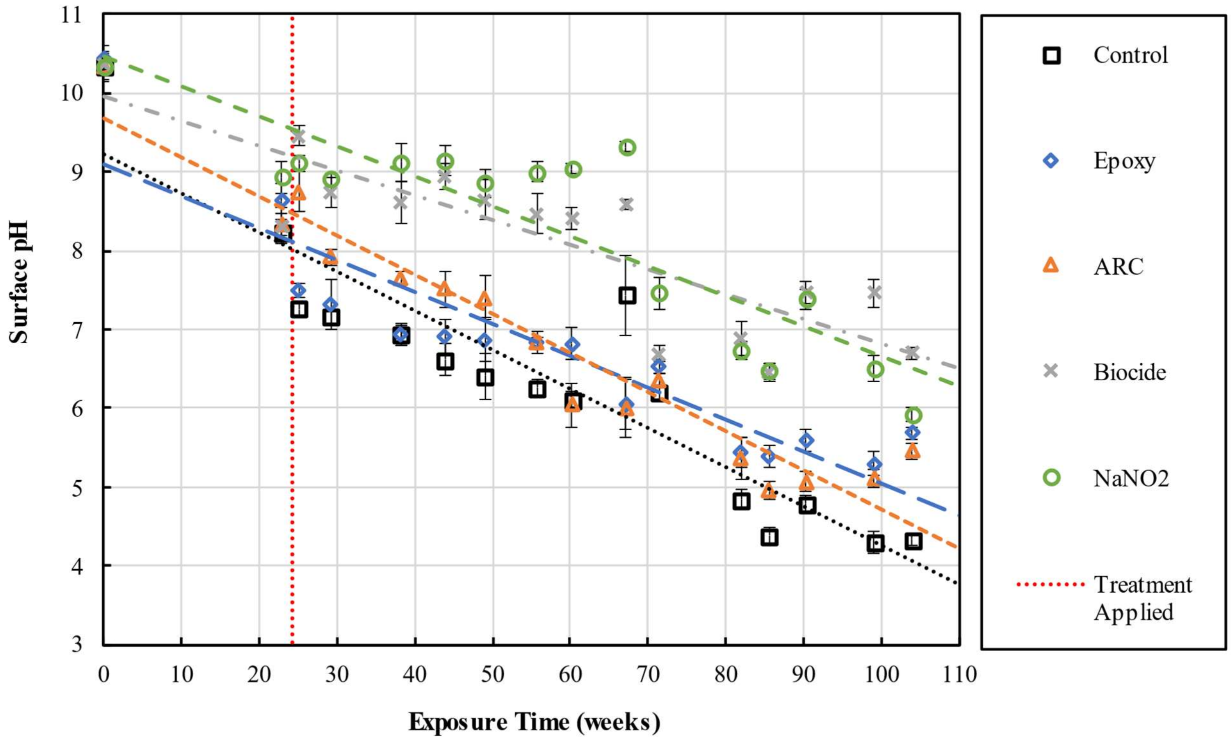

Figure 5—Trendlines showing rate of change in surface pH for coupons exposed to chemical corrosion.

The initial surface pH values of the coupons ranged from 10 to 11 before exposure to H_2S gas. The surface pH decreased to 8 or 9 after three months (week 23) of exposure, indicating the second corrosion stage has started. After the application of surface treatment (i.e., week 25), the surface pH increased for the coupons treated with biocide, sodium nitrite ($NaNO_2$), and ARC sealant whereas the surface pH decreased for the epoxy and control coupons (Nasr, 2021).

During the two-year exposure period, the surface pH decreased to a minimum of 4.3 for the control. The surface pH of control decreased by about 6 pH units from the initial value. The rate of change was 0.25/month, which was greater compared to the surface pH of other coupons with surface treatment. The surface pH of the epoxy-treated coupons decreased from 10.4 to 5.7 in two years. The surface pH of epoxy decreased continuously until week 82, after which the surface pH stabilized around 5.5 for the next 22 weeks. The surface pH of the ARC treated coupon was comparable to the epoxy treated coupons. The surface pH ranged from 10.3 to 5.5 and remained between 5 and 5.5 during the last 22 weeks. The decrease in surface pH of the biocide treated coupon was the smallest among other treatments compared to the surface pH of control. The surface pH of the biocide-treated coupons decreased from 10.4 to 6.7 by a value of 3.7. The decrease in surface pH of biocide was less than the surface pH of control during the observation period. The surface pH of $NaNO_2$ coupons, which had remained almost constant for the first year, decreased at a higher rate of 0.25/month in the second year (week 56 to 104). The decrease rate in surface pH of $NaNO_2$ treated coupons for the second year was comparable to the overall rate of decrease in surface pH of control over two years. There was an overall decrease of 4.4 in the surface pH of the $NaNO_2$ treated coupons which decreased from 10.3 to 5.92. The decrease in surface pH of $NaNO_2$ was less than that of the control. The surface pH of biocide treated coupons was the highest after 2 years, which remained at 6.7.

The surface pH trend for the ARC-treated coupon remained in line with control. When exposed to chemical corrosion, the ARC was quickly neutralized and did not maintain a high surface pH. Compared to other treatments, the coupons treated with biocide and $NaNO_2$ had a slower rate of change in surface pH with a value of 0.15 and 0.18 per month, respectively. The higher surface pH of biocide may be partly due to the admixture and mortar, which have higher pH than the underlying concrete. The mortar had an initially high pH, therefore the surface pH of biocide remained higher. Similarly, the alkalinity of $NaNO_2$ solution led to the higher surface pH of $NaNO_2$ treated coupons exposed to chemical corrosion.

4.2.2 Surface pH - Biogenic Corrosion

The coupons placed on the lower shelf of the chamber were exposed to H_2S gas as well as wastewater and therefore underwent biogenic corrosion. Biogenic corrosion is a result of biogenic oxidation of sulfides, which accelerates acid attack in the concrete. The surface pH of the coupons exposed to biogenic corrosion was observed to decrease faster than the coupons undergoing chemical corrosion. The surface pH data of the coupons exposed to biogenic corrosion over two years are tabulated in **Table 5** in the **Appendix**. A summary of the surface pH data against time is shown in **Figure 6**.

The initial decrease in surface pH value after 3 months of exposure to H_2S in wastewater was higher than the coupons exposed to H_2S gas only. After the surface treatments were applied to the coupons, the surface pH increased for all the treated coupons, whereas it continued to decrease for the control coupons with no treatment. Over the two years of exposure, the surface pH of all the coupons exposed to biogenic corrosion continued decreasing. This was due to the neutralization of the concrete because of oxidation of sulfides and acid attack. The surface pH of the control decreased from 10.4 to 2.9 in two years. The rate of change in surface pH for the control (0.53/month) during the first year was high compared to the rate for the second year (0.07/month). The explanation for the slower rate of change during the second year is the stable surface pH during the active corrosion stage (pH ≤ 4) (Li et al., 2022). As corrosion progressed, the surface pH of the control coupons decreased and then stabilized between 3.1 to 3.4 from weeks 81 and 104. This stabilization occurs because the corrosion progressed further into the concrete, while a stable biofilm layer remained on the surface. The surface pH of coupons with surface treatment also stabilized as the surface pH decreased below 4.

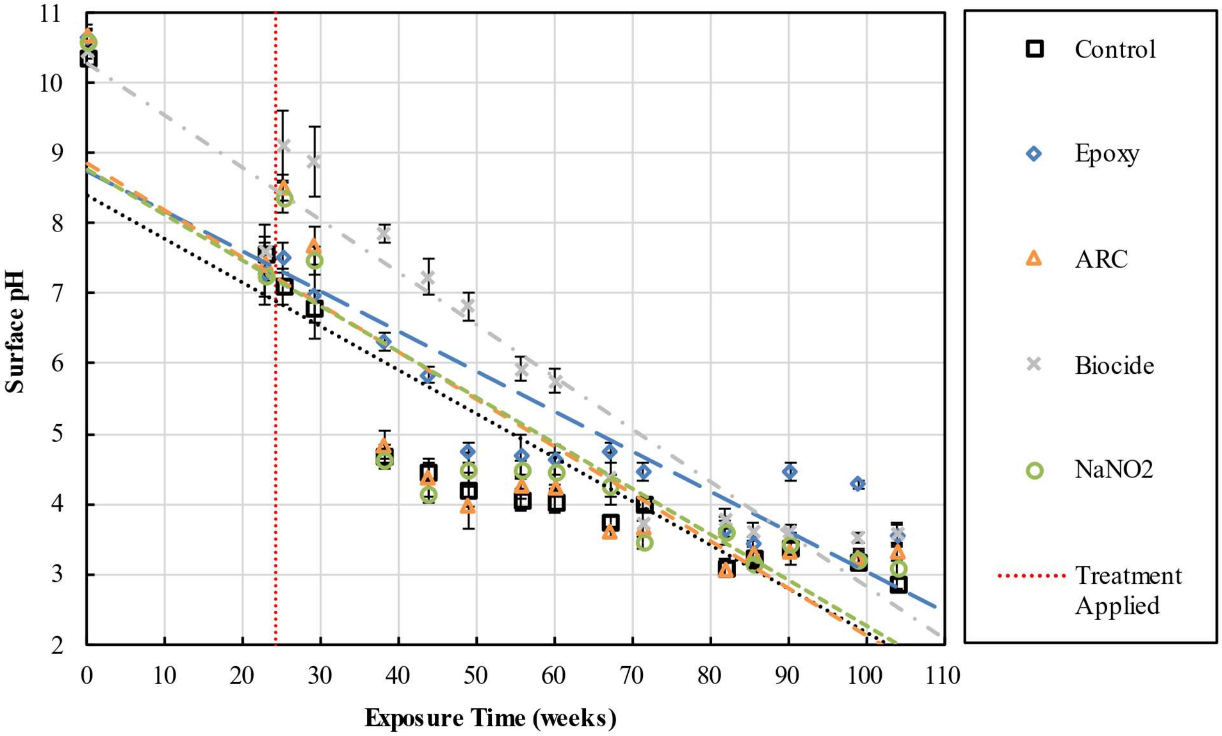

Figure 6—Trendlines showing rate of change in surface pH for coupons exposed to biogenic corrosion.

The surface pH of epoxy-treated coupons decreased from 10.6 to 3.5 over two years. The decrease in surface pH for the epoxy coupons was less than that of concrete after two years. The surface pH remained above 4.5 for most exposure duration. The epoxy treatment provided a barrier, preventing corrosion from progressing further into the concrete while maintaining a higher surface pH. The surface pH of the ARC-treated coupons dropped from 10.9 to 3.3. The value of the surface pH of ARC was also less than the surface pH of control during part of the exposure duration. The surface pH of the biocide-treated coupon remained in the range of 10.4 to 3.5 over two years which was also higher than the surface pH of control after 2 years duration. The surface pH of biocide-treated concrete stabilized between 3.5 and 4 from week 70 to 104, indicating better performance than control. However, the surface pH of the $NaNO_2$ treated coupons dropped from 10.6 to 3.1 which was just comparable to that of the control.

There was a sharp decline in surface pH after the pH initially decreased below 6.5 and then again after decreasing below 4. Between weeks 38 and 70 the surface pH stabilizes around 4 to 5 and then around 3 to 3.5 between weeks 80 and 104. The decrease in surface pH in different stages is in line with the three-stage model proposed by Islander et al. (1991) and Erbektas et al. (2019).

4.2.3 Surface pH – Field Exposure

The surface pH of site cores was measured every 2 to 3 months. The surface pH measurements were used to validate the performance of treatments in real conditions. The initial surface pH of concrete (7.79) in the wet well was lower than the surface pH of fresh concrete (typically from 12 to 13). This indicates the wet well concrete was already in the second stage of MICC at the start of monitoring. The wet well was rehabilitated with a fresh coating of mortar (0.25 to 0.4 inches thickness) approximately 5 years before the initial surface pH measurements (Nasr, 2021).

The surface pH data for the wet well cores are summarized in **Figure 7** (note the smaller range of the vertical axis as compared to **Figure 6**).

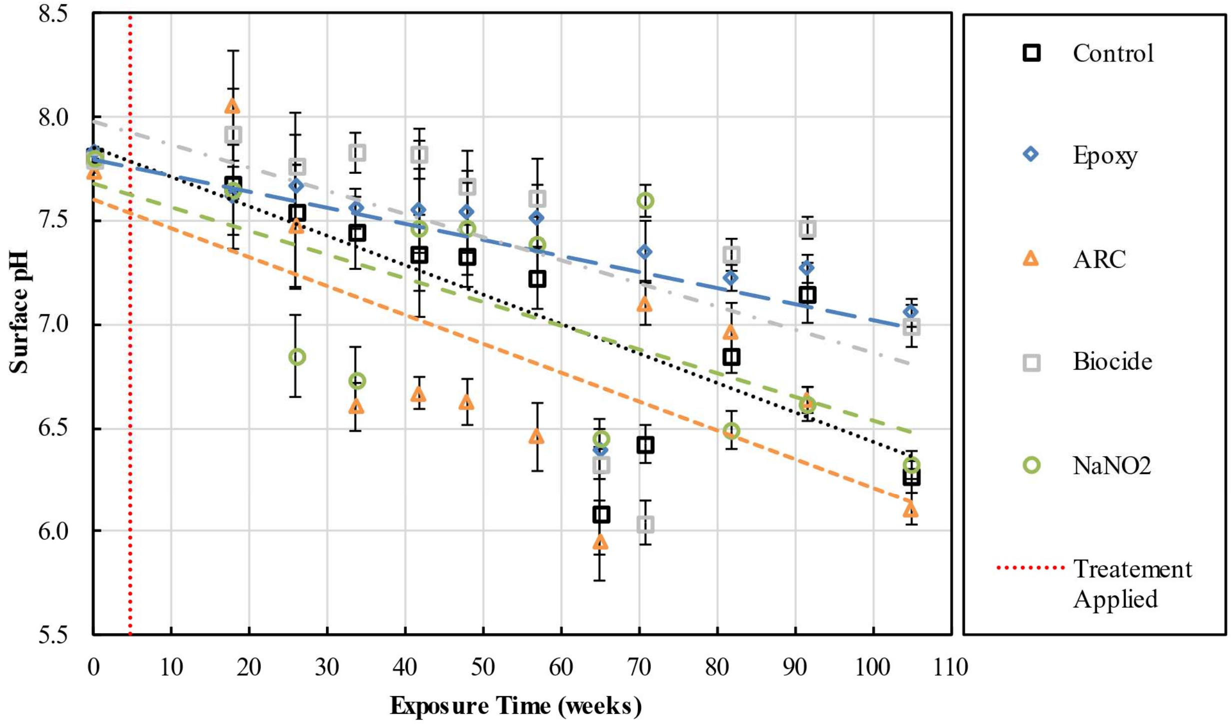

Figure 7—Trendlines showing rate of change in surface pH for core samples.

After the surface treatments were applied, the surface pH of the ARC and biocide-treated concrete was higher than the underlying concrete. In contrast, the surface pH of the control, epoxy, and $NaNO_2$ decreased after treatment showing no immediate effect of treatment. The surface pH of the $NaNO_2$ treated section continued to decrease, while the surface pH of the epoxy-treated concrete was more stable after treatment application. The surface pH data from the site cores observed over two years are tabulated in **Table 5** in the **Appendix**.

Over the monitoring period, the surface pH of the control decreased from 7.8 to 6.3, which was less compared to the surface pH for the coupons exposed to chemical corrosion. The surface pH of the site cores decreased at a slower rate compared to the concrete coupons in the chamber in the laboratory. This was due to the lower H_2S gas concentration, temperature, and relative humidity within the wet well as compared to the laboratory incubation chamber.

The rate of change in surface pH for the untreated concrete in the wet well was 0.06/month. Over two years, the decrease in the surface pH of epoxy was the lowest at a rate of 0.032 per month, which was followed by biocide at a rate of 0.033 per month. In contrast, the surface pH of $NaNO_2$ decreased at a similar rate to the control. Likewise, the ARC-treated concrete showed no improvement and the surface pH decreased more than the control concrete.

The epoxy-treated concrete cores had a more stable surface pH that ranged from 7.8 and 7.1, which was higher than the control samples. This result indicates that the epoxy again slowed the deterioration process as compared to the control. The surface pH of ARC dropped from 7.7 to 6.1 over the monitoring period. The surface pH for the ARC remained within 0.16 of control, and at times was lower than that of the control. This indicates that neutralization occurred more rapidly in the ARC-treated concrete than in the untreated control. The surface pH of biocide-treated concrete decreased from 7.8 to 7.0 whereas the surface pH of $NaNO_2$ remained in the range of 7.8 to 6.3.

4.2.4 Surface pH – FNA ($NaNO_{2-R}$) Reapplication

The surface pH was also measured for the coupons with FNA ($NaNO_{2-R}$) treatment. Recall, that the FNA treatment was applied to a set of coupons (control, epoxy treated, ARC treated, biocide treated and $NaNO_2$ treated) that were preconditioned by exposure to biogenic corrosion for 18 months. The surface pH was measured before washing the coupons, after washing the coupons, and then after treatment with FNA. The test results are summarized in **Table 7** in the **Appendix** and also in **Figure 8**. Before washing, the epoxy coupons had the highest surface pH whereas the $NaNO_2$ coupons had the lowest surface pH. There was limited change in the surface pH of the coupons after washing. However, the surface pH of the coupons increased for all the samples after the coupons were treated with FNA ($NaNO_{2-R}$). After treatment with FNA, the control coupons (no previous treatment) indicated the greatest change, as the surface pH increased from 3.9 to 5.6. The surface pH decreased with time for the other coupons, but the decrease was less compared to the surface pH of untreated coupons exposed to biogenic corrosion. After three months of exposure, the surface pH stabilized with minor fluctuations. It indicated no further deterioration in the concrete.

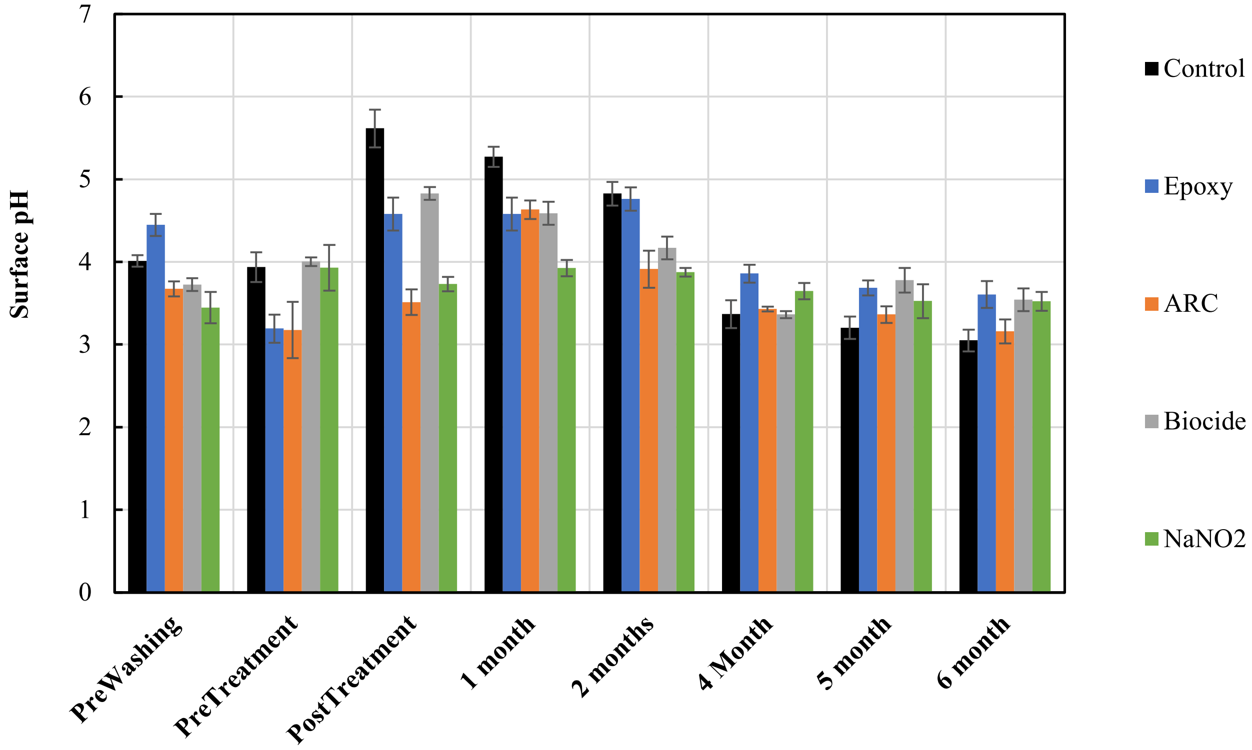

Figure 8—Average surface pH of coupons with FNA ($NaNO_{2\text{-}R}$) reapplication.

4.2.5 Surface pH - Discussion

Before exposure to H_2S gas, the surface pH of the coupons ranged from 10 to 11. Over the monitoring period, the rate of decrease in surface pH was lowest in the wet well whereas the rate of change in the concrete coupons exposed to biogenic corrosion was highest. The surface pH decreased approximately twice as fast in the coupons exposed to biogenic corrosion as compared to the coupons exposed to chemical corrosion. This indicates the corrosion rate at the waterline of sewer structures, represented by lower coupons, may be more aggressive than in the crown of sewer pipes (represented by coupons on the upper shelf).

The reason for the accelerated neutralization of the laboratory coupons as compared to the wet well was the difference in the H_2S gas concentration. The average H_2S concentration for site cores was 24.7, or 85 ppm lower than the average H_2S concentration maintained in the laboratory chamber. Moreover, H_2S gas is denser than air and will have a higher concentration around the waterline than in the upper regions of the wet well where cores were extracted.

The surface pH of control coupons exposed to biogenic corrosion decreased to approximately 3 within two years of exposure. The decrease in surface pH suggests the progress of corrosion due to the activity of the microorganisms. The regular production of acid by the bacterial movement neutralizes the concrete more rapidly (Li et al., 2020). Moreover, the surface pH was stable during the active corrosion stage (stage III) when exposed to biogenic corrosion. As such, the rate of change in surface pH during the first year was higher as compared to the second year. The stable pH occurred as a result of the stable biofilm layer developed on the surface, which remained higher as corrosion continued further into the concrete. In contrast, the surface pH of the epoxy was 0.67 greater than that of the control after two years. The epoxy treatment provided a barrier, preventing corrosion from progressing further into the concrete while maintaining a higher surface pH.

Again, the surface pH of site cores decreased at a slower rate. The surface pH of the control decreased from 7.8 to 6.3. Concrete cores coated with epoxy showed a more consistent surface pH, which was higher than the control samples and ranged between 7.8 and 7.1. With a rate of change of 0.032 per month, the epoxy-treated concrete in the wet well experienced the lowest rate of change in surface pH. This outcome suggests that the epoxy reduced the rate of deterioration as compared to the untreated control.

The coupons which had a high rate of change in surface pH before FNA ($NaNO_{2\text{-}R}$) treatment showed stable surface pH between the second and the sixth month after FNA ($NaNO_{2\text{-}R}$) treatment. In the case of the FNA ($NaNO_{2\text{-}R}$) treated concrete, the performance of the coupons which had previously been treated with FNA ($NaNO_2$) was restored.

4.3 Sulfide Uptake Rate (SUR)

The measurement of the H_2S uptake rate was carried out for the concrete coupons from the laboratory and the cores from the wet well. To measure the SUR, a data logger (AcruLog LL1000) was used in the sealed reaction chamber to measure the change in H_2S concentration due to uptake from the concrete (Nasr, 2021). The SUR of upper coupons (undergoing chemical corrosion), lower coupons (undergoing biogenic corrosion), site cores, and the coupons with FNA ($NaNO_{2\text{-}R}$) treatment were measured periodically throughout the experiment.

4.3.1 SUR – Chemical Corrosion

As reported by Nasr (2021), the initial SUR of the concrete coupons before H_2S or wastewater exposure was 52.4 mg-S/m^2-h, which was in line with the results published by Sun et al. (2014). Additional SUR measurements were conducted after the application of the surface treatments and then the SUR was measured every 1 to 2 months throughout the experiment. The SUR results for coupons exposed to chemical corrosion are summarized in **Table 8** in the **Appendix** and also in **Figure 9**.

The SUR of control decreased from 87.8 to 17.6 at a rate of -0.24/week. The epoxy-treated coupons had the lowest SUR, which decreased from 35.0 to 5.9 at a marginally slower rate of -0.22/week. The SUR of ARC treated coupons decreased from 58.4 to 11.7 at a rate of -

0.05/week. The SUR of ARC treated coupon was more stable compared to the others. The SUR of biocide treated coupons decreased from 70.1 to 11.7 at a rate of -0.26/week whereas the SUR of $NaNO_2$ decreased at a rate of -0.15/week while decreasing from 70.1 to 23.4. The SUR of the control was higher than the treated coupons, except for a few times where the SUR for the $NaNO_2$ was greater than that of the control. Specifically, on week 82, the SUR for the $NaNO_2$ was 117.3, which was marked as an outlier. Overall, the SUR decreased with time for the coupons exposed to chemical corrosion.

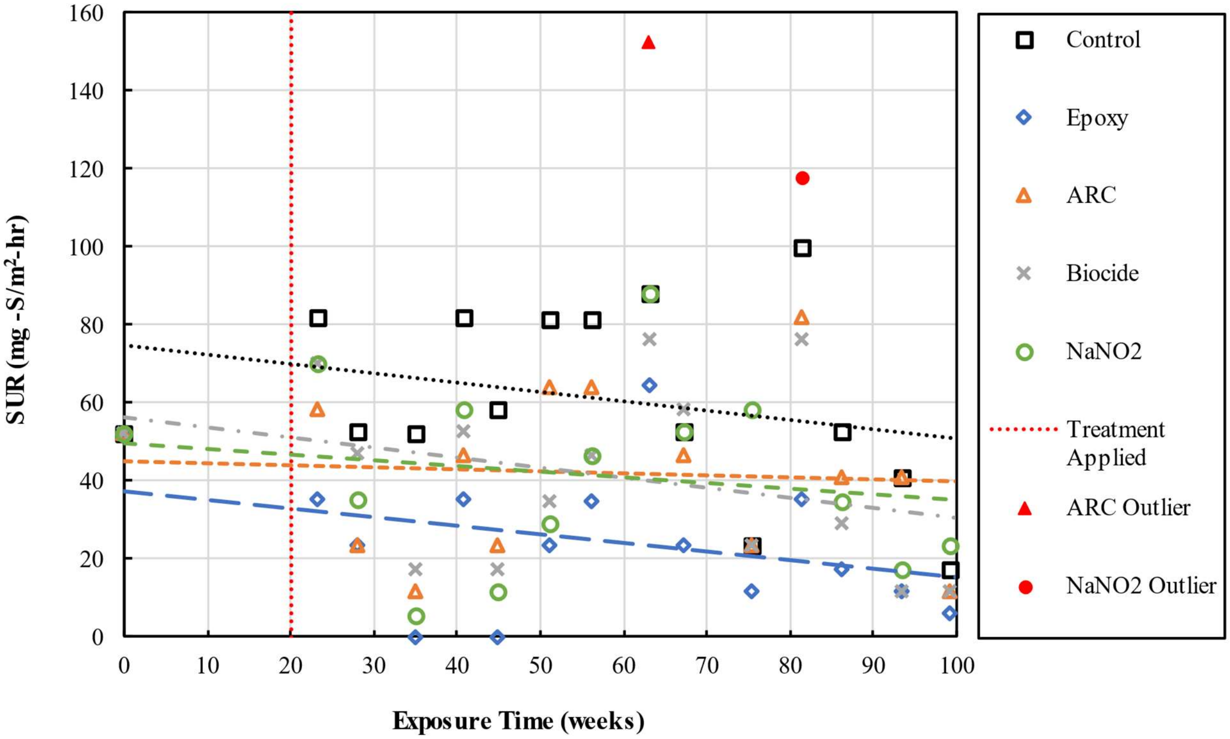

Figure 9—Trendlines showing rate of change of SUR of coupons exposed to chemical corrosion.

The SUR of epoxy ranged between 0 to 40 during the experiment period whereas over the same period the SUR ranged from 18 to 100 for the control. The epoxy performed better than the control by limiting H_2S uptake into the concrete. In contrast, the ARC functions by densifying the concrete by forming stable hydration products. However, neutralization of the ARC consumes H_2S which may increase chemical oxidation and the SUR of ARC-treated coupons.

However, the increased SUR of ARC was still lower than the SUR of the control and performed better than the control. As the ARC is neutralized, the uptake rate is expected to decrease. The SUR for the biocide-treated coupons was the second lowest and ranged from 11.7 to 76.2. Though the biocidal treatments are not intended to improve chemical corrosion, they alter the surface pH of concrete. The altered surface pH affects the rate of H_2S uptake resulting in change in SUR value. The SUR of the $NaNO_2$ treated coupons was lower for the first 50 weeks after treatment but then increased for the remaining 50 weeks.

4.3.2 SUR - Biogenic Corrosion

The SUR measurement of the coupons in the lower chamber (biogenic corrosion) was conducted in the same way as for the upper coupons (chemical corrosion). The first reading taken after the treatment of coupons showed higher uptake values compared to the upper coupons. The SUR of control increased from 52 to 100 as compared to a change of 52 to 81 for the upper coupons during the same exposure period (Nasr, 2021). Again, the results indicate the biogenic corrosion condition accelerated MIC as compared to chemical corrosion.

As SUR reflects the instantaneous oxidation rate, a higher corrosion rate is expected for coupons exposed to biogenic corrosion than those exposed to chemical corrosion. The SUR data for coupons in the lower chamber during the experimental investigation are shown in **Table 9** in the **Appendix** and the results are summarized in **Figure 10.**

The SUR of all the treated coupons was lower than the control, which increased from 100 to 152 between week 30 and 100 at a rate of 1.4/week. The lowest SUR was seen on the epoxy-treated samples, which increased to 52.8 from 47.0 at a rate of 0.96/week, over the same exposure period. The SUR values of epoxy remained stable from week 45 to 52 but started to increase after week 57, approximately one year after the treatment was applied. Despite increasing, the SUR of the epoxy-treated sample was the lowest compared to the treated samples measured on the same day. This better performance is due to the limited diffusion of sulfides and acids into the concrete. The SUR of coupons treated with ARC increased from 94.1 to 111 at a rate of 1.99/week. ARC limited the concrete permeability but did not prevent biofilm growth on the surface. The SUR of biocide treated coupons was the second lowest and increased from 76.4 to 93.8 at a rate of 0.68/week. The biocide limited the progression of SOB within the corrosion layer which caused a decrease in biogenic corrosion as compared to the control coupons. On the contrary, the $NaNO_2$ treated samples had the SUR comparable to the control and increased from 70.5 to 152 at a rate of 11.92/week. The $NaNO_2$, which performed better between weeks 30 and 56 (stage II corrosion), was ineffective between weeks 63 and 100 (stage III).

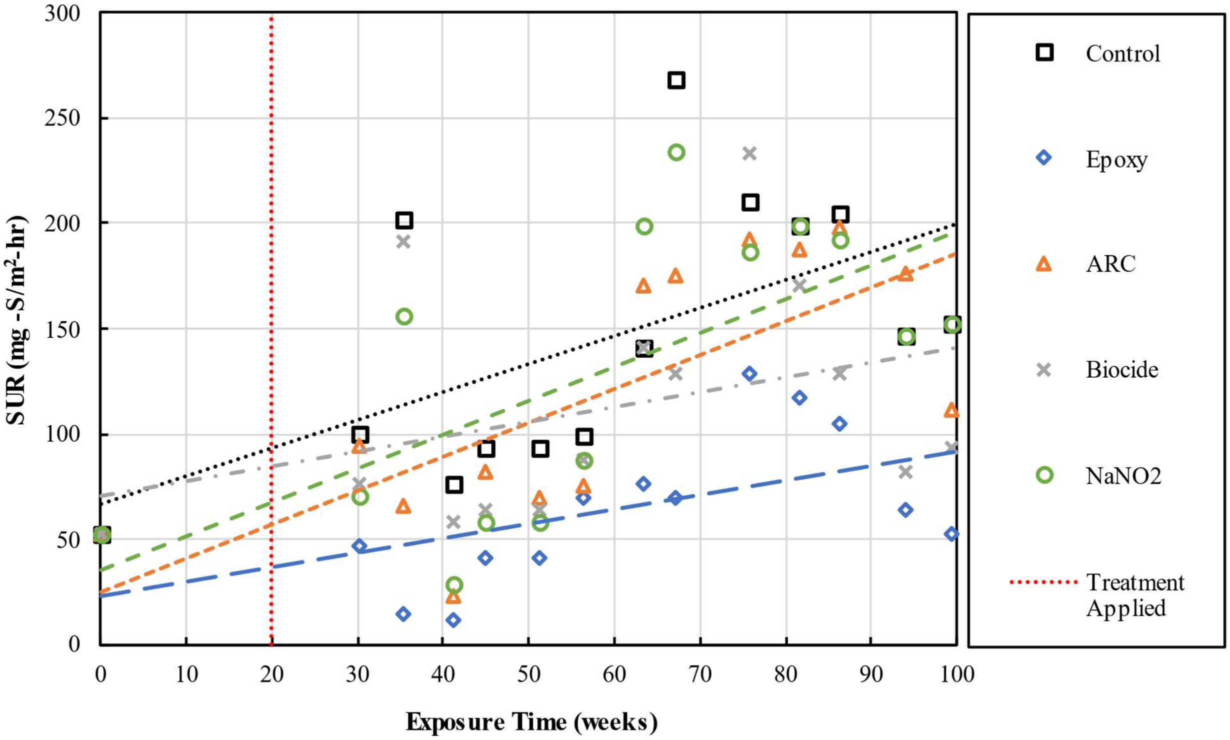

Figure 10—Trendlines showing rate of change of SUR of coupons exposed to Biogenic corrosion.

The SUR measured in the control coupons stored in the upper chamber did not exceed 100 during the two years of exposure; however, the SUR reached more than 200 during the second year for the control coupons exposed to biogenic corrosion. The higher SUR for coupons exposed to biogenic corrosion may be due to the presence of a greater number of active sulfur-oxidizing micro-organisms compared to the coupons with chemical corrosion (Sun et al., 2014).

4.3.3 SUR – Field Exposure

SUR measurement of site cores was conducted in the same way as of the coupons in the laboratory. The lower concentration of H_2S in the wet well as compared to the laboratory investigation led to slower corrosion. Therefore, the SUR was measured less frequently for the wet well. Due to COVID-19, some earlier measurements could not be taken leading to a gap during the first year. After the laboratory reopened, the SUR was measured every 2 to 3 months. This measurement trend continued for the second year as well. The data for the SUR of the site cores are summarized in **Table 10** in the **Appendix** and also in **Figure 11.**

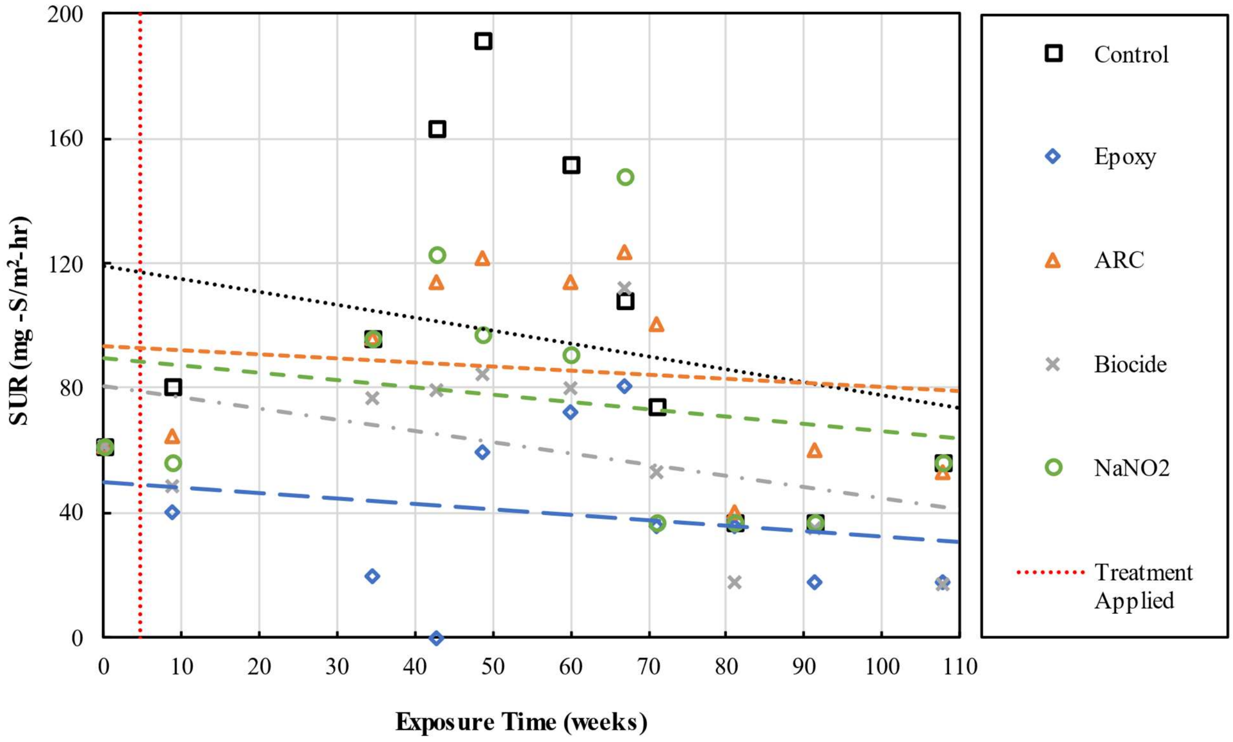

Figure 11—Trendlines showing rate of change of SUR of the site cores.

During the first year, the SUR of control increased from 61 to 191 whereas the value of epoxy-treated samples changed from 61 to 72. The SUR of the cores taken from ARC sealant and $NaNO_2$ applied surface showed marginal difference relative to control whereas the one from biocide treated surface showed marked improvement similar to the Epoxy (Nasr, 2021).

The SUR of control during the second year decreased from 191 to 56. The overall rate of change of SUR of control during the observation period was -0.41/week. The SUR of epoxy-treated cores ranged from 0 to 88.8 making it the treatment with the lowest overall SUR. The SUR of epoxy-treated cores decreased from 61 to 18.6 at a rate of -0.18/week. In contrast, the SUR of ARC-treated cores increased from 61.4 to 123 within the first 67 weeks and then decreased from 123 to 52.8 over the next 41 weeks following the trend of control. The SUR decreased from 61.4 to 17.5 at a rate of -0.36/week for cores treated with biocide. Similarly, it decreased from 61.4 to 56.2 at a rate of -0.23/week for the cores treated with $NaNO_2$. All the SUR values dropped significantly after week 71, which may be due to the lower biogenic activity in the wet well (less frequent wastewater exposure).

Epoxy performed better than the control during the observation period. The performance was better in the first half of the experiment period (till week 60) compared to the second half where it was marginally better than control. The epoxy again functioned by limiting biofilm attachment as well as inhibiting diffusion of H_2S and sulfides. The overall performance of ARC, biocide, and $NaNO_2$ was not better than the control by a statistically significant margin. However, all the treatments performed better than the control for part of the observation period. The performance of biocide and $NaNO_2$ was better than the performance of ARC. However, the ARC is designed to react with sulfuric acid which is formed by the oxidation of H_2S. As such, the uptake rate for the ARC-treated concrete may decrease when the neutralization reaction slows down.

The rate of change in SUR for the wet well cores indicates similar SUR results to the laboratory coupons exposed only to chemical corrosion. The wet well concrete is only periodically exposed to wastewater; therefore, abiotic oxidation of sulfides appears to be the primary source of corrosion, with lesser biogenic corrosion.

4.3.4 SUR – FNA ($NaNO_{2-R}$) Reapplication

The FNA ($NaNO_{2-R}$) treatment was applied to a set of 10 coupons after approximately 18 months of exposure to biogenic corrosion. The coupons had previously been treated with epoxy, ARC, biocide, or $NaNO_2$, and the FNA ($NaNO_{2-R}$) treatment was applied over the previous treatment. An untreated control sample was also treated with FNA ($NaNO_{2-R}$) for comparison. The SUR was measured for the coupons before washing, after washing, and then again on the day of treatment. The SUR before washing was the same as the coupons exposed to biogenic corrosion at week 76. The summary of the SUR data for the FNA ($NaNO_{2-R}$) treated coupons is summarized in **Table 11** in the **Appendix**.

After washing the coupons, the SUR indicated an important increase as shown in **Figure 12**. The SUR increased for all the coupons, including the control. The SUR of the control increased from 210 to 346 after washing. Likewise, SUR for the epoxy and ARC treated coupons increased by 159 (from 128 to 287) and 154 (from 192 to 346), respectively. The biocide-treated coupons had the lowest change in SUR increasing from 233 to 340 (an increase of 107) whereas the coupons treated with $NaNO_2$ had the highest increase in SUR after washing which increased from 186 to 416 (an increase of 230). While washing the concrete coupons, the corroded material on the surface of the concrete was removed which likely caused additional bacteria activity when exposing the bacteria to oxygen and sulfides. As a result, there was an increase in SUR for all the coupons. This finding can be related to the acceleration in MICC deterioration when intermittent wastewater flow removes the corroded concrete exposing the underlying bacteria to oxygen.

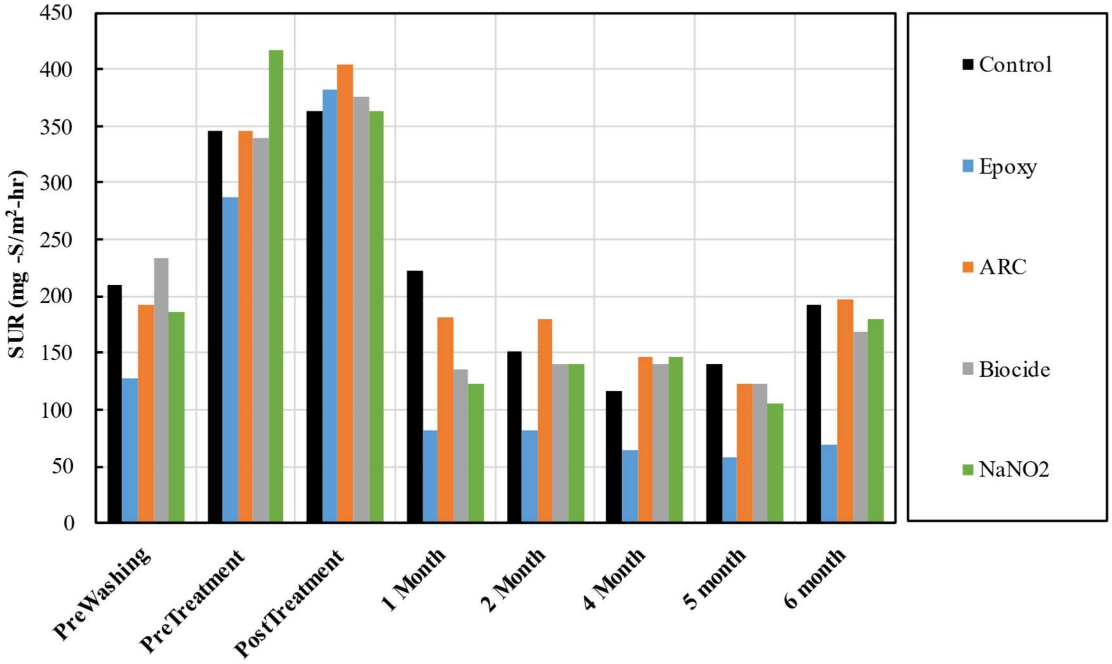

Figure 12—SUR of coupons with FNA ($NaNO_{2\text{-}R}$) reapplication.

The increased SUR continued for all the coupons after FNA ($NaNO_{2\text{-}R}$) treatment, except for the $NaNO_2$ coupons, which indicated a marginal decrease immediately after treatment. The posttreatment SUR of the coupons treated with $NaNO_2$ decreased by 53 from its pretreatment SUR value. This illustrated that the FNA reapplication began to function immediately for the coupons that had previously been treated with FNA ($NaNO_2$). Epoxy had the largest difference in pretreatment and posttreatment SUR, with an increase of 94. Since there already existed an active layer of treatment on the surface of the coupons, the FNA ($NaNO_{2\text{-}R}$) treatment increased the oxidation rate and the SUR after the reapplication of FNA over the existing treatments. The FNA solution is also basic, which temporarily increases the surface pH and chemical oxidation rate. However, when the SOB was inactivated by the treatment, the biogenic oxidation rate decreased resulting in an overall decrease in SUR.

One month after treatment, the SUR decreased below the prewashed condition for all the samples, indicating the reapplied FNA ($NaNO_{2\text{-}R}$) was effective in inactivating the SOB within the corrosion layer. The SUR of control remained below 150 for five to six months after treatment with FNA ($NaNO_{2\text{-}R}$). The Epoxy coupons indicated the lowest overall SUR after FNA ($NaNO_{2\text{-}R}$) treatment, which remained between 59 to 82 and had the highest surface pH, again indicating the best performance. The FNA ($NaNO_{2\text{-}R}$) was able to inactivate any biofilm that formed on the surface of the epoxy, restoring the performance of the epoxy. The biocide and $NaNO_2$ coupons indicated similar performance to the control coupons after the application of FNA ($NaNO_{2\text{-}R}$).

The FNA ($NaNO_{2\text{-}R}$) treatment remained effective for 5 months following treatment, and then the SUR began to increase by 6 months indicating reapplication was necessary. The $NaNO_2$ treated coupons exposed to biogenic corrosion (**Figure 10**) also indicated improved performance relative to the control for up to 50 weeks after treatment application. The results indicate the FNA ($NaNO_{2\text{-}R}$) treatment should be reapplied every 6 months for severe biogenic corrosion conditions.

4.3.5 SUR – Discussion

The SUR measurements indicated acceptable reproducibility. By visual inspection, the coupons exposed to biogenic corrosion were seen to be more severely corroded than the specimens exposed to chemical corrosion. The SUR of coupons undergoing biogenic corrosion was higher than the uptake of coupons with chemical corrosion. Moreover, the severely corroded coupon had higher SUR which was in line with the result from research published by Sun et al. (2014). The SUR of the coupons with biogenic corrosion increased gradually with exposure time as shown in **Figure 10,** which was due to higher activity of SOB. For the coupons with biogenic corrosion, the rate at which the treatment inhibited bacterial activity and MIC was less than the rate at which the bacteria multiplied due to the suitable environment and wastewater exposure. Therefore, corrosion still occurred in the treated samples, albeit less severely in some cases than in the untreated control.

The H_2S gas concentration, which is one of the main factors for corrosion rate, was lower in the field compared to the concentration in the incubation chamber. Therefore, corrosion was less severe in the field as compared to the coupons in the incubation chamber. Similarly, the upper coupons were not in direct contact with the wastewater which slowed the corrosion progress as compared to the lower coupons.

4.4 Live / Dead staining

The results obtained from Live/Dead staining are summarized in **Figure 13**. This test was only conducted for the coupons treated with FNA ($NaNO_{2\text{-}R}$). To compare the result, a control coupon (exposed to biogenic corrosion) without any treatment was also tested (**Figure 13 A**).

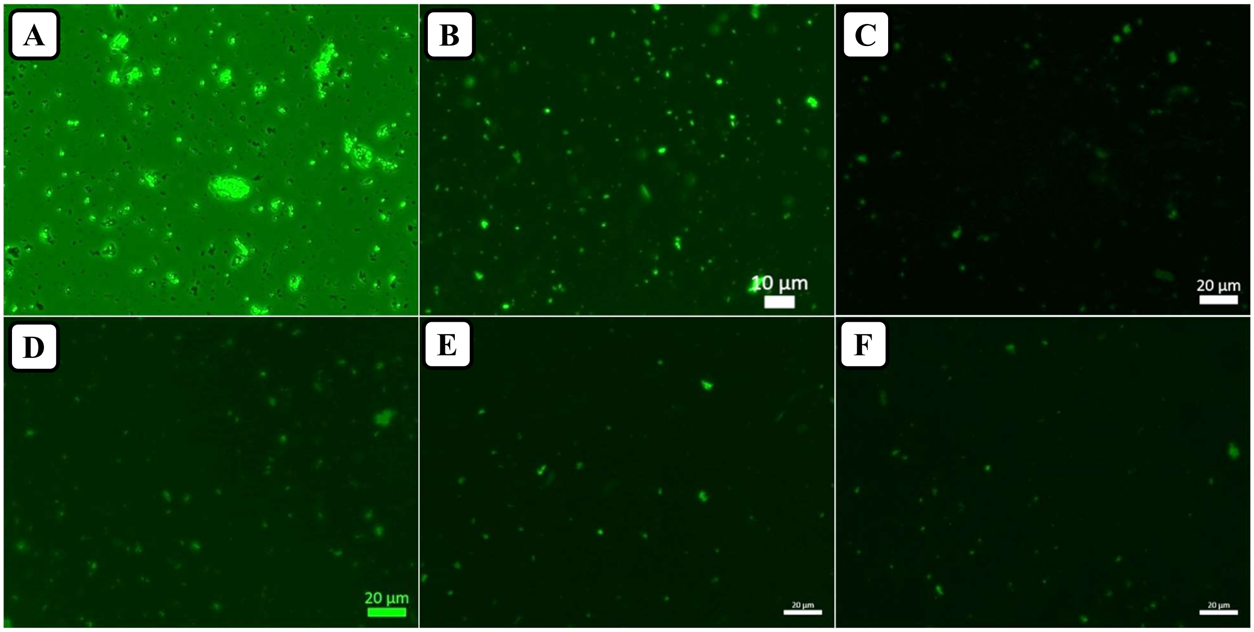

Figure 13—Live/Dead staining results for concrete treated with FNA 72 weeks after initial treatment. Samples exposed to biogenic corrosion for 6 months after FNA ($NaNO_{2\text{-}R}$) treatment. Untreated Control [A]; Control w/ $NaNO_{2\text{-}R}$ [B]; Epoxy w/ $NaNO_{2\text{-}R}$ [C]; ARC w/ $NaNO_{2\text{-}R}$ [D]; Biocide w/ $NaNO_{2\text{-}R}$ [E]; $NaNO_2$ w/ $NaNO_{2\text{-}R}$ [F]. (Photo(s) by Prakriti Dhungana).

The results indicate there were more viable bacteria in the untreated control (**Figure 13 A**) as compared to the specimens that were treated with FNA ($NaNO_{2-R}$) after 18 months of exposure to biogenic corrosion. After FNA ($NaNO_{2-R}$) treatment, the coupons were exposed to biogenic corrosion for an additional 6 months before Live/Dead staining was conducted. The FNA treatment was effective in inhibiting the growth of bacteria in the biofilm, maintaining a decreased bacteria count for 6 months.

The number of live cells in each image was obtained by processing each image using digital image analysis. The results, summarized in **Table 2,** were useful to compare the viability of bacteria in the biofilm. The number of live bacteria was more in the untreated control compared to the FNA ($NaNO_{2-R}$) treated concrete samples. The results indicate that the FNA treatment inactivated bacteria and is effective in controlling biofilm growth for up to six months. The results from surface pH, SUR, and live/ dead staining support the conclusion that FNA limits MIC if it is applied at a frequency of 6 months. This conclusion is in line with the findings from Li et al. (2022) and is supported by the findings of Sun et al. (2015) and Jiang & Yuan (2013).

Table 2—Summary of Live/Dead cell count data from image processing*

No.	**Control**	**Control w/ $NaNO_{2-R}$**	**Epoxy w/ $NaNO_{2-R}$**	**ARC w/ $NaNO_{2-R}$**	**Biocide w/ $NaNO_{2-R}$**	**$NaNO_2$ w/ $NaNO_{2-R}$**
	Count of live bacteria					
1	174	110	39	89	38	54
2	145	122	23	75	29	56
3	192	89	44	61	56	61
4	212	133	28	63	67	58
5	140	134	20	74	45	65
Ave ± SE	173±29.2	120±17.8	31±9.8	72±10.7	47±14.2	59±4.1

*All images were taken using a 63x lens. The pixel size for all images was 0.91 x 0.91 μm.

4.5 Visible Inspection

The surfaces of the concrete coupons were smooth and intact before exposure as shown in **Figure 14**. After 7 months of exposure, there was little noticeable change in the upper coupons (left columns A, C, and E). However, over the same exposure period, the lower coupons started to develop surface film from the sides of the coupons (Right column B, D, F). In the second year, the color of the surface of the coupons also started to change and corrosion products were observed at the edge of the coupons (left column G).

Figure 14—Progression of MICC deterioration in specimen over two years of exposure. 1 month of exposure [A-B]; 4 months of exposure[C-D]; 7 months of exposure [E-F]; 23 months of exposure [G-H]. Left column: specimen exposed to chemical corrosion; Right column: specimen exposed to biogenic corrosion. In each picture the specimens are arranged from left to right: Control, Epoxy, ARC, Biocide, $NaNO_2$. (Photo(s) by Mostafa Nasr & Ramkrishna Sapkota).

In addition, there was a light-yellow discoloration, and the surface material was corroded. This is comparable to the corrosion products formed when exposed to chemical-induced corrosion due to high H_2S concentration as observed by Li. et al. (2019). The thickness of the biofilm continued increasing during the second year for the lower coupons exposed to biogenic corrosion (right column H). There was also mass loss, discoloration, and delamination of the treated layer in the coupons exposed to biogenic corrosion.

4.5.1 Coupons After Washing

Samples exposed to biogenic corrosion for 18 months were pressure washed and then photographed as shown in **Figure 15.** The epoxy was the only treatment that remained fully intact with the surface (**Figure 15 B**). Parts of the biocide mixed with mortar were intact but no longer adhering to the underlying concrete surface (**Figure 15 C**). More than half of the ARC treatment was removed from the surface (**Figure 15 D**). The surface of the control and the $NaNO_2$ treated coupons both changed to white and brown color, with exposed aggregate (**Figure 15 E**). In contrast, the coupons exposed to chemical corrosion had no major physical degradation (**Figure 14 G**). However, the surface roughness increased with some minor holes and darkened regions (**Figure 14 G**).

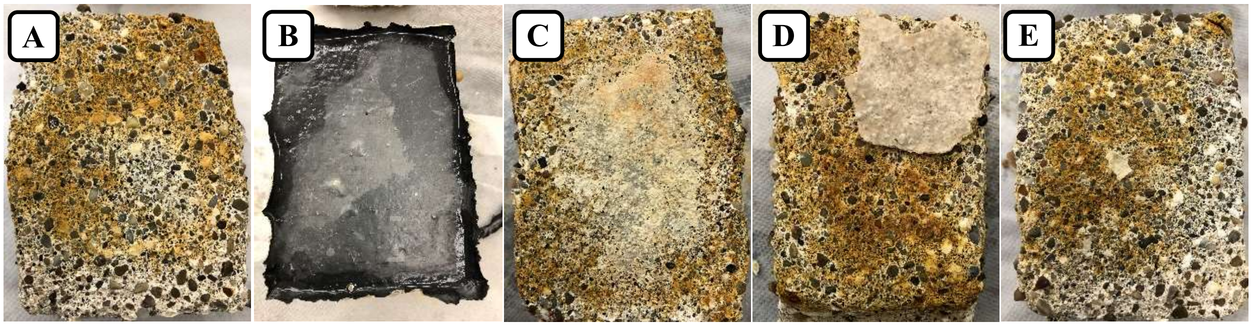

Figure 15—Condition of pressure washed coupon exposed to biogenic corrosion for 18 months (order from left: (A) Control, (B) Epoxy, (C) ARC, (D) Biocide, (E) $NaNO_2$).

4.6 Synthesis

The development of corrosion on the coupon surface was visible during the inspection, which was confirmed by changes in surface pH and SUR. The surface pH data for the control samples exposed to chemical corrosion, biogenic corrosion, and field conditions were plotted in **Figure 16** to compare the rates of corrosion. Faster neutralization was observed in the concrete exposed to biogenic corrosion as compared to concrete exposed to chemical corrosion or field conditions. During the observation period, the surface pH of the control samples exposed to chemical corrosion decreased from 10.37 to less than 4.5 in approximately 100 weeks whereas it decreased to less than 4.5 within just 50 weeks for samples exposed to biogenic corrosion. Acidification of the concrete occurred about 2 times faster when exposed to biogenic corrosion as compared to chemical corrosion.

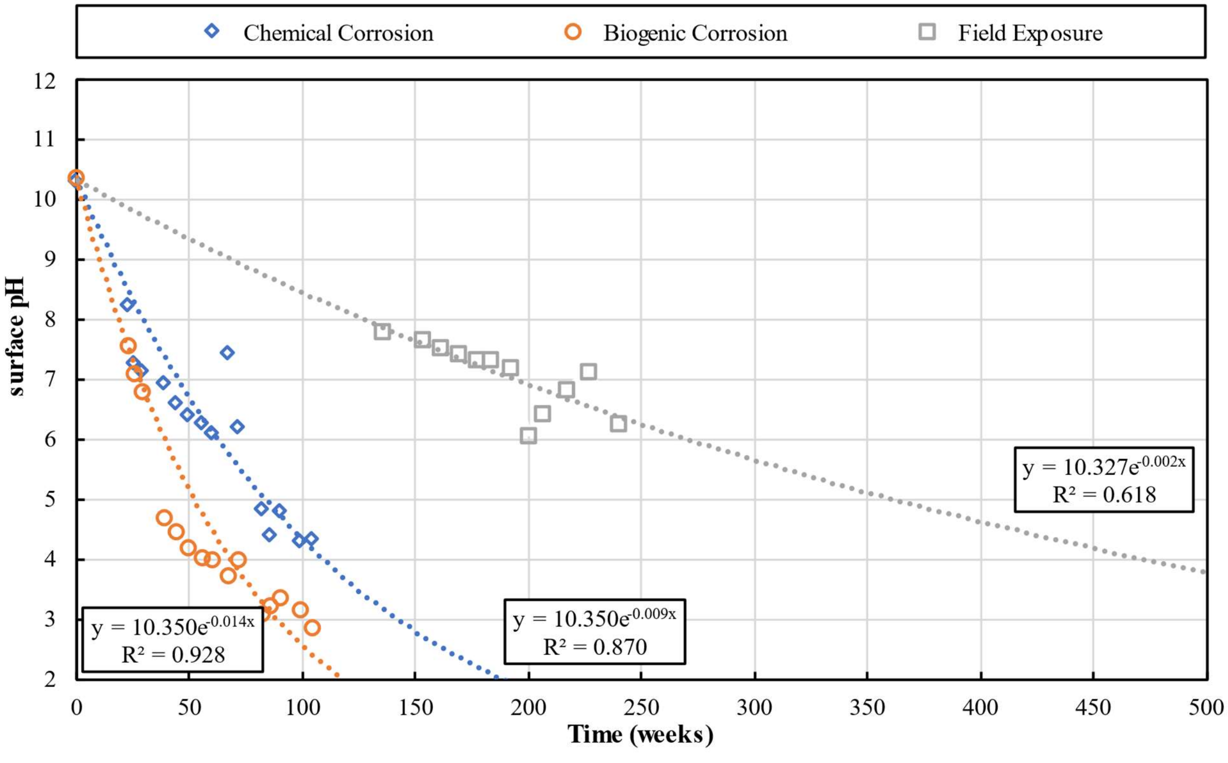

Figure 16—Comparison of surface pH results for Control samples exposed to chemical, biogenic, and field exposure conditions.

For comparison with the laboratory coupons, the trendline for the field exposure condition was projected backward to an initial surface pH of 10.35, which was estimated to occur approximately 135 weeks before the initial measurements were taken in 2020. At the current corrosion rate, the surface pH of the wet well will reach 4.5 around 450 weeks after the initial surface pH of 10.35. Therefore, the rate of neutralization of concrete exposed to biogenic corrosion occurred approximately 9 times faster as compared to field exposure conditions. At the current corrosion rate, the surface pH of the wet well is predicted to reach approximately 4 within the next 4 to 5 years resulting in Stage III corrosion and accelerated deterioration.

The SUR of the coupons exposed to biogenic corrosion increased gradually with time whereas the SUR tended to decrease over time for the site cores and the coupons with chemical corrosion. In the case of coupons with chemical corrosion and the cores from the site, the effect of treatment overcomes the corrosion activity, resulting in a decreasing trend for SUR. In all exposure conditions, epoxy treatment had the lowest overall SUR compared to the other treatments.

The SUR and surface pH results indicated different confidence levels and effect sizes. Therefore, the standard mean difference (SMD) of each testing metric for each treatment was determined. This value of SMD for the different treatments was then compared to determine the relative performance of the four treatments. A SMD greater than zero confirms the treatment performed better than the Control, and a larger SMD confirms the treatment performed better by a larger margin. Conversely, a negative SMD confirms the treatment performed worse than the Control. The rank of the treatments was determined by comparing the results of the surface pH and SUR test in three different conditions (i.e., chemical corrosion, biogenic corrosion, and field exposure conditions). The results are summarized in **Table 3**.

Table 3—Standard mean difference for surface pH and SUR as compared to the control.

Test Method	Epoxy	p<5%	ARC	p<5%	Biocide	p<5%	$NaNO_2$	p<5%
SUR Chem. Corr.	1.431	Y	0.765	Y	0.746	Y	0.651	Y
SUR Biog. Corr.	1.285	Y	0.373	N	0.504	N	0.223	N
SUR Field Exposure	1.010	Y	0.204	N	0.715	Y	0.375	N
Surface pH Chem. Corr.	0.270	N	0.283	N	1.172	Y	1.221	Y
Surface pH Biog. Corr.	0.321	N	0.077	N	0.505	N	0.099	N
Surface pH Field Exposure	0.546	N	-0.333	N	0.456	N	-0.041	N
Rank	**4.863**	**1**	**1.369**	**4**	**4.098**	**2**	**2.528**	**3**

The SMD was not used to determine the statistical significance of the result. The statistical significance of the results was determined by comparing the mean of each metric with the control using a t-test. Therefore, if $p < 0.05$ then the treatment performed better than the untreated control by a statistically significant margin.

The significance of the SUR data was more useful to make conclusions than the surface pH results. The surface pH method did not correlate well to the progression of MICC during Stage III, because the surface pH stabilized after a biofilm formed on the surface. Therefore, the SUR results proved statistically significant in more cases.

The epoxy treatment was the best performer compared to other treatments based on the results from the different tests and exposure conditions. The epoxy-treated specimens maintained a higher surface pH and lower SUR than the control specimens even in the severe biogenic corrosion condition in the laboratory. Epoxy was the only treatment that remained intact with the surface being in severe condition during the observation period. Biocide was the second-best performer and performed better than the control in most of the tests. Though the biocide tended to delaminate from the underlying concrete, it remained intact even in the severe biogenic condition during the observation period. Therefore, methods to improve the bond between the biocide-treated mortar and underlying concrete need to be investigated. The ARC treatment or a single application of $NaNO_2$ proved less effective, with the ARC indicating marginal performance. In contrast, the reapplication of FNA ($NaNO_{2\text{-}R}$) decreased the SUR for up to six months after treatment. The surface applied FNA was effective in inactivating the SOB within the corrosion interface.

5 Conclusions and Recommendations

5.1 Conclusions

This study aimed to evaluate the performance of four surface treatments on concrete in accelerated laboratory and sewer environments. The experimental investigation helped to better understand the overall corrosion process. The process was observed in three different exposure conditions (i.e., chemical corrosion (H_2S gas only), biogenic corrosion (H_2S gas and wastewater), and field exposure). The laboratory exposure conditions (chemical and biogenic corrosion) were validated using the concrete in the wet well. The simulation of accelerated biogenic corrosion was successfully conducted in the laboratory by directly exposing concrete coupons to wastewater and H_2S gas. The surface pH of concrete was reduced by the activities of bacteria inside the chamber and a biofilm was developed on the surface of the concrete. The observation and test results lead to the following conclusions:

1. The surface pH was useful to compare the neutralization and acidification rate of concrete in the laboratory and field exposure conditions. The neutralization and acidification of concrete in the laboratory were accelerated by a factor of 4.5 and 9 times for chemical and biogenic corrosion, respectively, as compared to the field exposure conditions.
2. The SUR of the coupons exposed to biogenic corrosion increased gradually with time whereas the SUR decreased over time for the site cores and the coupons with chemical corrosion. In the case of coupons with chemical corrosion and the cores from the site, the effect of treatment overcome the corrosion activity, so they had a decreasing trend for SUR.
3. The effectiveness of four different surface treatments was tested and the treatments were ranked based on the result of surface pH and SUR in three different conditions. Overall, the epoxy performed better than the other treatments. The second-best performance was

achieved by the biocide. The ARC treatment had mixed performance and should not be used unless it is combined with an effective biocide to limit microbial growth. Similarly, a single treatment of $NaNO_2$ was ineffective.

4. The epoxy coating exhibited excellent durability by remaining intact with the concrete surface even in severe biogenic conditions. There were limited textural changes and fewer biogenic corrosion products on the epoxy-coated coupons. The biocide treatment also performed well. However, in some cases, the mortar layer remained intact but was not adhering to the underlying concrete.
5. Reapplication of FNA ($NaNO_{2\text{-}R}$) was effective in mitigating the activity of corrosion-inducing microorganisms. The results from surface pH, SUR, and Live/Dead staining of FNA treated coupons indicate the FNA treatment remained effective for up to six months. Therefore, FNA can limit MICC, if it is applied at a frequency of 6 months for aggressive environmental conditions. The test results after FNA ($NaNO_{2\text{-}R}$) treatment showed performance of the coupons which had previously been treated with FNA was restored.

5.2 Recommendations

Based on the results of the experimental investigation, several recommendations are provided for future investigation:

1. As the SUR test is sensitive to the coupon surface area, the size of the concrete coupons in the laboratory should be increased to provide better test results. Also, it is recommended to cut larger core samples from the field to improve SUR test results.
2. Core samples can be used repeatedly by storing them in the wet well and periodically moving to the lab for surface pH and SUR testing.

3. Additional FNA ($NaNO_{2\text{-}R}$) testing should be conducted to determine its performance after a second six-month exposure cycle. Furthermore, Live/Dead staining should be conducted more frequently to check the progress of surface treatment with time.
4. A long-term field investigation should be conducted to determine treatment performance during advanced stages of MIC.
5. As it is difficult to apply the surface treatment on corroded surfaces, pretreatment methods should be investigated to determine the best practice.
6. In addition to SUR and surface pH, the change in thickness of the surface treatment and change in mass of the specimens should also be measured over time to draw more conclusions regarding the rate of corrosion.

6 References

Alexander, M., Bertron, A., & Belie, N. De. (2012). *Performance of Cement-based Materials in Aggressive Aqueous Environments (RILEM State-of-the-Art Reports)*. http://link.springer.com/10.1007/978-94-007-5413-3%5Cnhttp://link.springer.com/content/pdf/10.1007/978-94-007-5413-3.pdf

Ashok, M. K. (2014). Measuring Concrete Surface pH - a Proposed Test Method. *Concrete Repair Bulletin*, *April*, 16–20.

Berndt, M. L. (2011). Evaluation of coatings, mortars and mix design for protection of concrete against sulphur oxidising bacteria. *Construction and Building Materials*, *25*(10), 3893–3902. https://doi.org/10.1016/j.conbuildmat.2011.04.014

Daims, H., Lücker, S., & Wagner, M. (2006). Daime, a Novel Image Analysis Program for Microbial Ecology and Biofilm Research. *Environmental Microbiology*, *8*(2), 200–213. https://doi.org/10.1111/j.1462-2920.2005.00880.x

De Belie, N., Monteny, J., & Taerwe, L. (2002). Apparatus for accelerated degradation testing of concrete specimens. *Materials and Structures/Materiaux et Constructions*, *35*(251), 427–433. https://doi.org/10.1617/13765

De Muynck, W., De Belie, N., & Verstraete, W. (2009). Effectiveness of admixtures, surface treatments and antimicrobial compounds against biogenic sulfuric acid corrosion of concrete. *Cement and Concrete Composites*, *31*(3), 163–170. https://doi.org/10.1016/j.cemconcomp.2008.12.004

Erbektas, A. R., Isgor, O. B., & Weiss, W. J. (2019). Evaluating the efficacy of antimicrobial additives against biogenic acidification in simulated wastewater exposure solutions. *RILEM Technical Letters*, *4*, 49–56. https://doi.org/10.21809/rilemtechlett.2019.62

Firer, D., Friedler, E., & Lahav, O. (2008). Control of sulfide in sewer systems by dosage of iron salts: Comparison between theoretical and experimental results, and practical implications. *Science of the Total Environment*, *392*(1), 145–156. https://doi.org/10.1016/j.scitotenv.2007.11.008

Ganigue, R., Gutierrez, O., Rootsey, R., & Yuan, Z. (2011). Chemical dosing for sulfide control in Australia: An industry survey. *Water Research*, *45*(19), 6564–6574. https://doi.org/10.1016/j.watres.2011.09.054

Grengg, C. (2017). *Microbial induced acid corrosion in sewer environments Statutory declaration*. *December*, 93.

Grengg, C., Mittermayr, F., Ukrainczyk, N., Koraimann, G., Kienesberger, S., & Dietzel, M. (2018). Advances in concrete materials for sewer systems affected by microbial induced concrete corrosion: A review. *Water Research*, *134*, 341–352. https://doi.org/10.1016/j.watres.2018.01.043

Islander, B. R. L., Devinny, J. S., Member, A., Mansfeld, F., Postyn, A., & Shih, H. (1991). *Microbial ecology of crown corrosion in sewers*. *117*(6), 751–770.

Jensen, H. S., Lens, P. N. L., Nielsen, J. L., Bester, K., Nielsen, A. H., Hvitved-Jacobsen, T., & Vollertsen, J. (2011). Growth kinetics of hydrogen sulfide oxidizing bacteria in corroded concrete from sewers. *Journal of Hazardous Materials*, *189*(3), 685–691. https://doi.org/10.1016/j.jhazmat.2011.03.005

Jiang, G., Keating, A., Corrie, S., O'halloran, K., Nguyen, L., & Yuan, Z. (2013). Dosing free nitrous acid for sulfide control in sewers: Results of field trials in Australia. *Water Research*, *47*(13), 4331–4339. https://doi.org/10.1016/j.watres.2013.05.024

Jiang, G., Keller, J., & Bond, P. L. (2014). Determining the long-term effects of H2S concentration, relative humidity and air temperature on concrete sewer corrosion. *Water Research*, *65*, 157–169. https://doi.org/10.1016/j.watres.2014.07.026

Jiang, G., & Yuan, Z. (2013). Synergistic inactivation of anaerobic wastewater biofilm by free nitrous acid and hydrogen peroxide. *Journal of Hazardous Materials*, *250–251*, 91–98. https://doi.org/10.1016/j.jhazmat.2013.01.047

Joseph, A. P., Keller, J., Bustamante, H., & Bond, P. L. (2012). Surface neutralization and H2S oxidation at early stages of sewer corrosion: Influence of temperature, relative humidity and H2S concentration. *Water Research*, *46*(13), 4235–4245. https://doi.org/10.1016/j.watres.2012.05.011

Li, X., Bond, P. L., O'moore, L., Wilkie, S., Hanzic, L., Johnson, I., Mueller, K., Yuan, Z., & Jiang, G. (2020). Increased Resistance of Nitrite-Admixed Concrete to Microbially Induced Corrosion in Real Sewers. *Environmental Science and Technology*, *54*(4), 2323–2333. https://doi.org/10.1021/acs.est.9b06680

Li, X., Johnson, I., Mueller, K., Wilkie, S., Hanzic, L., Bond, P. L., O'Moore, L., Yuan, Z., & Jiang, G. (2022). Corrosion mitigation by nitrite spray on corroded concrete in a real sewer system. *Science of the Total Environment*, *806*, 151328. https://doi.org/10.1016/j.scitotenv.2021.151328

Li, X., O'Moore, L., Song, Y., Bond, P. L., Yuan, Z., Wilkie, S., Hanzic, L., & Jiang, G. (2019). The rapid chemically induced corrosion of concrete sewers at high H2S concentration. *Water Research*, *162*, 95–104. https://doi.org/10.1016/j.watres.2019.06.062

Little, B. J., Blackwood, D. J., Hinks, J., Lauro, F. M., Marsili, E., Okamoto, A., Rice, S. A., Wade, S. A., & Flemming, H. C. (2020). Microbially influenced corrosion—Any progress? *Corrosion Science*, *170*(April), 108641. https://doi.org/10.1016/j.corsci.2020.108641

Matthews, J. C., Selvakumar, A., Sterling, R. L., & Condit, W. (2014). Innovative rehabilitation technology demonstration and evaluation program. *Tunnelling and Underground Space Technology*, *39*, 73–81. https://doi.org/10.1016/j.tust.2012.02.003

Nasr, M. (2021). *Mitigation of Microbially Induced Concrete Corrosion in Wastewater Infrastructure using Surface Treatments*. *May*.

Nielsen, A. H., Vollertsen, J., Jensen, H. S., Wium-Andersen, T., & Hvitved-Jacobsen, T. (2008). Influence of pipe material and surfaces on sulfide related odor and corrosion in sewers. *Water Research*, *42*(15), 4206–4214. https://doi.org/10.1016/j.watres.2008.07.013

O'Connell, M., McNally, C., & Richardson, M. G. (2010). Biochemical attack on concrete in wastewater applications: A state of the art review. *Cement and Concrete Composites*, *32*(7), 479–485. https://doi.org/10.1016/j.cemconcomp.2010.05.001

Puthenpurayil, J., Bond, P., & Keller, J. (2010). Examination of concrete corrosion using a laboratory experimental set up simulating sewer conditions. *6th International Conference on Sewer Processes and Networks. Surfers Paradise, Gold Coast, Australia, 7-10 November*, *November*, 2010.

Satoh, H., Odagiri, M., Ito, T., & Okabe, S. (2009). Microbial community structures and in situ sulfate-reducing and sulfur-oxidizing activities in biofilms developed on mortar specimens in a corroded sewer system. *Water Research*, *43*(18), 4729–4739. https://doi.org/10.1016/j.watres.2009.07.035

Silva, V., Silva, C., Soares, P., Garrido, E. M., Borges, F., & Garrido, J. (2020). Isothiazolinone biocides: Chemistry, biological, and toxicity profiles. *Molecules*, *25*(4). https://doi.org/10.3390/molecules25040991

Soleimani, S. (2012). *Prevention and Control of Microbiologically Influenced Concrete*

Deterioration in Wastewater Concrete Structures Using E.coli Biofilm (Issue May).

Sun, X., Jiang, G., Bond, P. L., Keller, J., & Yuan, Z. (2015). A novel and simple treatment for control of sulfide induced sewer concrete corrosion using free nitrous acid. *Water Research*, *70*(0), 279–287. https://doi.org/10.1016/j.watres.2014.12.020

Sun, X., Jiang, G., Bond, P. L., Wells, T., & Keller, J. (2014). ScienceDirect A rapid , non-destructive methodology to monitor activity of sulfide-induced corrosion of concrete based on H 2 S uptake rate. *Water Research*, *59*(0), 229–238. https://doi.org/10.1016/j.watres.2014.04.016

Sun, X., Jiang, G., Chiu, T. H., Zhou, M., Keller, J., & Bond, P. L. (2016). Effects of surface washing on the mitigation of concrete corrosion under sewer conditions. *Cement and Concrete Composites*, *68*, 88–95. https://doi.org/10.1016/j.cemconcomp.2016.02.013

Videla, H. A., & Herrera, L. K. (2005). Microbiologically influenced corrosion: Looking to the future. *International Microbiology*, *8*(3), 169–180. https://doi.org/10.2436/im.v8i3.9523

Wang, T., Wu, K., Kan, L., & Wu, M. (2020). Current understanding on microbiologically induced corrosion of concrete in sewer structures: a review of the evaluation methods and mitigation measures. *Construction and Building Materials*, *247*(March). https://doi.org/10.1016/j.conbuildmat.2020.118539

Wei, S., Jiang, Z., Liu, H., Zhou, D., & Sanchez-Silva, M. (2013). Microbiologically induced deterioration of concrete - A review. *Brazilian Journal of Microbiology*, *44*(4), 1001–1007. https://doi.org/10.1590/S1517-83822014005000006

Wells, T., & Melchers, R. E. (2015). Modelling concrete deterioration in sewers using theory and field observations. *Cement and Concrete Research*, *77*, 82–96. https://doi.org/10.1016/j.cemconres.2015.07.003

Wells, Tomy, Melchers, R. E., & Bond, P. (2009). Factors involved in the long term corrosion of concrete sewers. *49th Annual Conference of the Australasian Corrosion Association 2009: Corrosion and Prevention 2009*, *1900*, 345–356.

Wu, M., Wang, T., Wu, K., & Kan, L. (2020). Microbiologically induced corrosion of concrete in sewer structures: A review of the mechanisms and phenomena. *Construction and Building Materials*, *239*, 117813. https://doi.org/10.1016/j.conbuildmat.2019.117813

Zhang, L., De Schryver, P., De Gusseme, B., De Muynck, W., Boon, N., & Verstraete, W. (2008). Chemical and biological technologies for hydrogen sulfide emission control in sewer systems: A review. *Water Research*, *42*(1–2), 1–12. https://doi.org/10.1016/J.WATRES.2007.07.013

Zivica, V., & Bajza, A. (2001). Acidic attack of cement based materials - A review. Part 1. Principle of acidic attack. *Construction and Building Materials*, *15*(8), 331–340. https://doi.org/10.1016/S0950-0618(01)00012-5

7 Appendix

Table 4—Average surface pH of the coupons exposed to chemical corrosion.

Date	Week	Control	Epoxy	ARC	Biocide	NaNO$_2$
2/19/2020	0	10.33±0.06	10.44±0.16	10.34±0.17	10.36±0.11	10.32±0.17
7/28/2020	23	8.23±0.13	8.62±0.22	8.33±0.15	8.31±0.22	8.93±0.19
8/13/2020	25	7.27±0.10	7.49±0.08	8.74±0.25	9.46±0.13	9.11±0.10
9/10/2020	29	7.16±0.10	7.32±0.31	7.92±0.10	8.74±0.18	8.90±0.07
11/12/2020	38	6.95±0.14	6.93±0.13	7.64±0.09	8.61±0.27	9.12±0.24
12/22/2020	44	6.62±0.20	6.92±0.22	7.51±0.24	8.95±0.16	9.15±0.19
1/27/2021	49	6.41±0.29	6.87±0.27	7.40±0.27	8.64±0.25	8.85±0.18
3/15/2021	56	6.26±0.11	6.84±0.07	6.84±0.13	8.47±0.25	9.00±0.13
4/15/2021	60	6.11±0.11	6.82±0.20	6.05±0.27	8.41±0.14	9.04±0.06
6/3/2021	67	7.44±0.50	6.06±0.31	6.01±0.37	8.59±0.06	9.31±0.07
7/3/2021	71	6.19±0.09	6.52±0.09	6.35±0.08	6.70±0.10	7.46±0.20
9/15/2021	82	4.84±0.13	5.45±0.19	5.36±0.27	6.89±0.22	6.73±0.11
10/10/2021	86	4.39±0.10	5.39±0.13	4.96±0.12	6.46±0.10	6.47±0.10
11/12/2021	90	4.79±0.11	5.60±0.14	5.07±0.13	7.48±0.15	7.39±0.12
1/12/2022	99	4.30±0.14	5.30±0.15	5.12±0.11	7.46±0.17	6.50±0.17
2/16/2022	104	4.33±0.06	5.68±0.07	5.46±0.09	6.70±0.07	5.92±0.10

Table 5—Average surface pH of the coupons exposed to biogenic corrosion.

Date	Week	Control	Epoxy	ARC	Biocide	NaNO$_2$
2/19/2020	0	10.37±0.11	10.63±0.15	10.68±0.14	10.43±0.15	10.59±0.09
7/28/2020	23	7.56±0.25	7.28±0.44	7.43±0.25	7.60±0.31	7.26±0.37
8/13/2020	25	7.10±0.25	7.51±0.21	8.52±0.18	9.10±0.22	8.36±0.49
9/10/2020	29	6.81±0.23	6.97±0.60	7.69±0.28	8.88±0.20	7.47±0.51
11/12/2020	38	4.69±0.15	6.31±0.13	4.84±0.19	7.84±0.15	4.64±0.13
12/22/2020	44	4.46±0.13	5.84±0.11	4.36±0.27	7.24±0.14	4.16±0.26
1/27/2021	49	4.20±0.25	4.74±0.15	3.97±0.32	6.82±0.25	4.50±0.19
3/15/2021	56	4.05±0.16	4.69±0.29	4.25±0.16	5.92±0.13	4.48±0.17
4/15/2021	60	4.02±0.15	4.63±0.22	4.23±0.05	5.75±0.25	4.47±0.16
6/3/2021	67	3.74±0.1	4.74±0.14	3.60±0.07	4.37±0.15	4.26±0.37
7/3/2021	71	4.01±0.07	4.45±0.13	3.67±0.09	3.73±0.08	3.45±0.19
9/15/2021	82	3.10±0.12	3.65±0.10	3.06±0.10	3.78±0.19	3.62±0.14
10/10/2021	86	3.22±0.12	3.44±0.10	3.28±0.11	3.60±0.09	3.16±0.12
11/12/2021	90	3.37±0.13	4.45±0.13	3.33±0.19	3.60±0.14	3.45±0.11
1/12/2022	99	3.18±0.14	4.28±0.06	3.25±0.09	3.52±0.15	3.22±0.08
2/16/2022	104	2.87±0.08	3.54±0.16	3.31±0.12	3.58±0.15	3.09±0.15

Table 6—Average surface pH of site cores.

Date	Week	Control	Epoxy	ARC	Biocide	$NaNO_2$
2/21/2020	0	7.81±0.02	7.83±0.03	7.74±0.01	7.79±0.04	7.80±0.02
6/25/2020	18	7.68±0.08	7.62±0.25	8.06±0.26	7.92±0.22	7.65±0.22
8/20/2020	26	7.54±0.37	7.67±0.10	7.48±0.29	7.77±0.25	6.85±0.20
10/13/2020	34	7.44±0.17	7.56±0.10	6.61±0.12	7.83±0.10	6.73±0.16
12/9/2020	42	7.34±0.18	7.55±0.20	6.67±0.08	7.82±0.12	7.46±0.42
1/21/2021	48	7.33±0.15	7.54±0.19	6.63±0.11	7.66±0.17	7.46±0.22
3/25/2021	57	7.22±0.15	7.52±0.15	6.46±0.16	7.61±0.19	7.39±0.13
5/20/2021	65	6.09±0.20	6.40±0.14	5.96±0.19	6.33±0.08	6.46±0.04
6/30/2021	71	6.43±0.09	7.35±0.15	7.10±0.11	6.04±0.10	7.60±0.08
9/15/2021	82	6.85±0.09	7.23±0.06	6.96±0.15	7.34±0.08	6.49±0.09
11/22/2021	91	7.15±0.14	7.27±0.07	6.64±0.06	7.46±0.06	6.62±0.08
2/24/2022	105	6.27±0.08	7.06±0.07	6.11±0.08	6.99±0.10	6.32±0.07

Table 7—Average surface pH of the coupons with FNA treatment.

Title	Date	Week	Control	Epoxy	ARC	Biocide	$NaNO_2$
Prewashing	8/30/2021	0	4.01±0.07	4.45±0.13	3.67±0.09	3.73±0.08	3.45±0.19
Pretreatment	8/31/2021	0	3.94±0.18	3.19±0.17	3.18±0.34	4.00±0.05	3.93±0.28
Posttreatment	8/31/2021	0	5.62±0.23	4.58±0.20	3.51±0.15	4.83±0.08	3.73±0.09
1 month	10/10/2021	6	5.27±0.12	4.58±0.2	4.63±0.11	4.59±0.14	3.93±0.10
2 months	11/12/2021	11	4.83±0.14	4.76±0.14	3.91±0.22	4.17±0.14	3.88±0.05
4 Month	1/12/2022	19	3.37±0.17	3.86±0.11	3.43±0.03	3.36±0.04	3.65±0.10
5 months	2/16/2022	24	3.20±0.14	3.69±0.09	3.36±0.10	3.78±0.15	3.53±0.21
6 months	3/20/2022	29	3.05±0.13	3.61±0.16	3.16±0.14	3.54±0.14	3.52±0.11

Table 8—SUR of the coupons exposed to chemical corrosion

Date	Week	Control	Epoxy	ARC	Biocide	$NaNO_2$
		SUR (mg-S m^{-2} hr^{-1})				
3/17/2020	0	52.39	52.39	52.39	52.39	52.39
8/27/2020	24	81.77	35.04	58.41	70.09	70.09
9/29/2020	28	52.88	23.50	23.50	47.00	35.25
11/16/2020	35	52.23	0.00	11.61	17.41	5.80
12/28/2020	41	81.89	35.10	46.80	52.64	58.49
1/25/2021	45	58.40	0.00	23.36	17.52	11.68
3/9/2021	51	81.65	23.33	64.15	34.99	29.16
4/14/2021	57	81.62	34.98	64.13	46.64	46.64
6/1/2021	63	87.82	64.40	152.22*	76.11	87.82
6/30/2021	68	52.52	23.34	46.68	58.35	52.52
8/26/2021	76	23.41	11.70	23.41	23.41	58.52
10/8/2021	82	99.68	35.18	82.09	76.23	117.27*
11/10/2021	87	52.52	17.51	40.85	29.18	35.01
12/31/2021	94	40.95	11.70	40.95	11.70	17.55
2/9/2022	100	17.58	5.86	11.72	11.72	23.44

*Outliers

Table 9—SUR of the coupons exposed to biogenic corrosion

Date	Week	Control	Epoxy	ARC	Biocide	$NaNO_2$
		SUR (mg-S m^{-2} hr^{-1})				
3/17/2020	0	52.39	52.39	52.39	52.39	52.39
10/15/2020	31	99.94	47.03	94.06	76.42	70.54
11/19/2020	36	201.47	15.11	65.48	191.40	156.14
12/31/2020	42	75.97	11.69	23.37	58.44	29.22
1/26/2021	45	93.37	40.85	81.70	64.19	58.36
3/10/2021	52	93.40	40.86	70.05	64.21	58.37
4/15/2021	57	99.02	69.90	75.72	87.37	87.37
6/3/2021	64	140.69	76.21	170.00	140.69	199.31
6/30/2021	68	268.61	70.07	175.18	128.47	233.58
8/30/2021	76	209.85	128.24	192.36	233.16	186.53
10/10/2021	82	199.33	117.25	187.60	170.01	199.33
11/11/2021	87	204.16	104.99	198.32	128.33	192.49
1/4/2022	94	146.50	64.46	175.80	82.04	146.50
2/11/2022	100	152.40	52.75	111.37	93.78	152.40

Table 10—SUR of site cores

Date	Week	Control	Epoxy	ARC	Biocide	$NaNO_2$
		SUR (mg-S m-2 hr-1)				
2/21/2020	0	61.38	61.38	61.38	61.38	61.38
4/22/2020	9	80.76	40.38	64.61	48.45	56.53
10/20/2020	35	95.67	20.09	95.67	76.53	95.67
12/17/2020	43	163.20	0.00	113.80	79.22	123.07
1/27/2021	49	191.12	59.56	121.55	84.19	97.32
4/16/2021	60	151.56	72.17	113.61	79.66	90.63
6/3/2021	67	108.01	80.77	123.50	112.28	148.09
7/2/2021	71	74.06	35.87	100.78	52.88	37.23
9/11/2021	81	37.11	35.95	40.39	17.66	37.31
11/21/2021	91	36.94	17.90	60.33	35.17	37.15
3/16/2022	108	56.24	17.59	52.82	17.49	56.20

Table 11—SUR of coupons with FNA treatment

Title	Date	Week	Control	Epoxy	ARC	Biocide	$NaNO_2$
Prewashing	9/9/2021	0	209.85	128.24	192.36	233.16	186.53
Pretreatment	9/9/2021	0	346.07	287.41	346.07	340.20	416.45
Posttreatment	9/10/2021	0	363.93	381.54	405.02	375.67	363.93
1 Month	10/11/2021	5	222.67	82.04	181.65	134.77	123.05
2 Month	11/12/2021	9	151.40	81.52	180.52	139.75	139.75
4 Month	1/6/2022	17	117.12	64.42	146.40	140.54	146.40
5 months	2/14/2022	23	140.81	58.67	123.21	123.21	105.61
6 months	3/19/2022	27	191.69	69.71	197.50	168.46	180.08