

Laboratory Investigation of Biocide Treated Waters to Inhibit Biofilm Growth and Reduce the Potential for MIC

Susmitha Purnima Kotu, Christopher Kagarise,
Richard B. Eckert
DNV GL
5777 Frantz Road
Dublin, Ohio, 43017
USA

Torben Lund Skovhus
VIA University College, Research Center for
Built Environment, Energy, Water and Climate
Chr. M. Østergaards Vej 4, DK 8700 Horsens,
Denmark

ABSTRACT

Introducing water into pipelines for various applications, such as hydrotesting, long term layup, hydraulic fracturing, water injection, and other production related activities poses the threat of microbiologically influenced corrosion (MIC) when conditions are favorable. The focus of this paper is to outline a test method to evaluate the potential for MIC with untreated waters and subsequently assess the effectiveness of biocides to inhibit biofilm growth and mitigate MIC. The changes in the microbial activity, abundance, and diversity in the biofilm along with pitting and general corrosion rates on the carbon steel are used as evaluation techniques in this laboratory test method. The results of this work demonstrate the importance of using biofilms for biocide evaluations and could be used to support new industry standards for evaluating the effectiveness of biocides for MIC control, rather than basing performance on planktonic kill studies.

Key words: Microbiologically influenced corrosion (MIC), biofilms, biocides, hydrotest, hydraulic fracturing, layup

INTRODUCTION

Introduction to MIC

Microbiologically influenced corrosion (MIC) is a significant corrosion problem caused by microbial metabolism and microbial activity, assisting other abiotic processes and not just by the mere presence of microorganisms.¹ Metabolic reactions of microorganisms in biofilms coupled with metal oxidation reactions are characteristic to MIC. It is therefore important to focus on the characteristics of the microbial community and corrosion when investigating the threat of MIC.²

Water is commonly introduced into pipelines and tanks for various applications such as hydrotesting, long term layup, hydraulic fracturing, water injection, and production related activities. In addition to the presence of microorganisms, water provides nutrients necessary for biofilm growth and corrosion and hence, the presence of water even in minimal amounts increases the likelihood of MIC. If left

uncontrolled, MIC can ultimately result in leaks and ruptures of pipelines and tanks.^{3,4} Therefore, it is of utmost importance to monitor the threat of MIC and design appropriate mitigation methods to reduce the potential for MIC.

The threat of MIC in assets is commonly identified by using culture-based tests such as serial dilution bottles, to detect the presence of sulfate reducing bacteria (SRB), acid producing bacteria (APB), and general heterotrophic bacteria (GHB).⁵ Although MIC is caused by sessile communities of microorganisms or biofilms, these serial dilution tests are frequently conducted using liquid samples. Despite frequent false positives and false negatives,⁶ these tests continue to be employed for the identification of SRB, APB, and GHB and eventually MIC. Furthermore, these tests only detect the presence or abundance of a few commonly known microbial groups capable of causing MIC, but not whether these microorganisms are causing the observed corrosion.

To address these drawbacks in MIC threat identification with culture-based tests, in this paper, a laboratory test method to evaluate the potential for MIC and subsequently assess the effectiveness of biocides to inhibit biofilm growth and mitigate MIC is presented and discussed. In addition, a case study is provided that demonstrates a methodology for performing laboratory experiments using process waters to determine if MIC is a viable threat and evaluate the effectiveness of proposed mitigation.

MIC threat assessment and monitoring of mitigation

Because MIC is characterized by microbial community, the chemical and physical environment, and corrosion products, it is important to use multiple lines of evidence to assess the threat of MIC.⁷ When investigating the extent of corrosion, it is important to also examine pit rates in addition to general corrosion rates as MIC is most typically characterized by localized corrosion. It is well known that systems with low rates of general corrosion can have high rates of pitting. If only general corrosion rates are monitored, information about pit rates and pit density is not accounted for, resulting in an incorrect MIC threat assessment and inaccurate monitoring of mitigation effectiveness. As MIC is mediated by biofilms, it is essential to monitor biofilm populations in addition to planktonic populations as significant differences between microbial abundance, microbial activity, and microbial diversity can exist between biofilms and the planktonic microbial populations.^{8,9} It is also important to analyze the water chemistry to identify compounds that support microbial metabolism and growth (such as sulfate, acetate, lactate, and organic compounds) as well as species that can result in abiotic corrosion (such as dissolved sulfides, dissolved oxygen, chlorides).¹⁰ Monitoring for changes in the water chemistry reveals the flux of various chemical species enabling further understanding of the corrosion mechanism. Evidence supporting abiotic corrosion mechanisms should be weighed against evidence supporting MIC to identify the threat of MIC and further evaluate the effectiveness of mitigation methods for MIC.

A reliable method for MIC threat assessment and monitoring the effectiveness of mitigation requires examining the impact on biofilm growth and corrosion either by the direct assessment of the corrosive environment in the field or by using process fluids to simulate the corrosive environment in the laboratory. In this paper, we focus on describing a test method for assessing the threat of MIC and monitoring the effectiveness of mitigation methods in the laboratory by mimicking field conditions using actual process fluids.

Differentiation between abiotic and biotic corrosion can be accomplished by preparing two sets of experiments: one using the process fluids and the other using process fluids that have been sterilized (either through autoclaving, UV, or other appropriate methods). The changes to the biofilms and planktonic microbial populations (abundance, diversity, and activity), corrosion/pitting rates, and corrosion products should be monitored throughout the duration of the testing. Comparison and

integration of evidence from these parameters between the process fluids and the sterilized fluids can reveal the cause of corrosion.

For monitoring the effectiveness of mitigation, an untreated control should be used to compare the effectiveness of mitigation (chemical and/or concentration) on microorganisms, the chemical and physical environment, and the corrosion products that form. Based on the situation, the impact of the chemical addition can be determined, either on biofilm and MIC prevention or biofilm and MIC mitigation. For investigating biofilm and MIC prevention, chemically treated and untreated fluids should be incubated with metal coupons and the changes to the biofilms and planktonic microbial populations (abundance, diversity, and activity), corrosion/pitting rates, and corrosion products should be monitored throughout the duration of testing. For investigating biofilm and MIC mitigation, process fluids should be first incubated with metal coupons and after an appropriate incubation time, the fluids should be treated with the chemical and the changes to the biofilms and planktonic microbial populations, corrosion/pitting rates, and corrosion products between the untreated and treated experiments should be monitored. Comparing the differences between these parameters of the treated and untreated experiments reveals the effectiveness of the mitigation.

In this paper, a detailed laboratory test method for evaluating the potential for MIC and the effectiveness of mitigation is described using a case study. The potential for abiotic corrosion and MIC to assets from untreated and treated process water was evaluated. Additionally, two different concentrations of biocide were assessed for their effectiveness in mitigating MIC.

EXPERIMENTAL PROCEDURE

Water sources and chemicals

A water sample from an asset of interest with integrity issues (suspected to be MIC) was used as the water source for the laboratory tests. Water samples were collected in large, sterile plastic containers and filled to the top to minimize oxygen ingress. After collection, the water sample was shipped on ice overnight to the laboratory. The water sample was stored in the refrigerator until the start of the experiment.

One-third of the water sample was left untreated (W1) and a protective film-forming, diamine-based biocide was used to treat one-third of the water sample at a lower concentration, 100 ppm (W1B1), and the remaining one-third of the water was treated at a higher concentration, 1,000 ppm (W1B2). The experimental design is depicted in Figure 1. Biocide was added to the waters while they were held in their respective reservoirs. After four hours, the reactors containing the carbon steel coupons were filled from their respective reservoirs. Pre-treatment of the waters with biocide before introducing to the test setup was done to replicate the biocide treatment approach used for the asset of interest. The test results are hence applicable to this specific biocide application method.

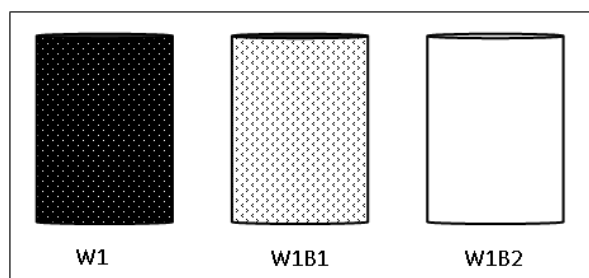


Figure 1: Experimental design consisting of untreated water (W1), water treated with 100 ppm of biocide (W1B1), and water treated with 1000 ppm of biocide (W1B2).

Test setup

Two liters each of the untreated and biocide treated waters were filled in their respective reservoirs and a peristaltic pump was used to continuously circulate water from the reservoirs to the bioreactors (Figure 2). The bioreactors can hold a liquid volume of 350 mL and the excess liquid is discharged back to the reservoir. Both the reservoirs and bioreactors were continuously stirred and kept on hot plates to maintain a constant temperature of 30°C (selected based on the operating range of the asset). Carbon steel coupons were immersed in each of the bioreactors and fluids were circulated slowly through the reactor for a time period of four weeks to monitor biofilm growth and corrosion. The reactors and reservoirs were kept anaerobic by continuously sparging with ultra-pure nitrogen.

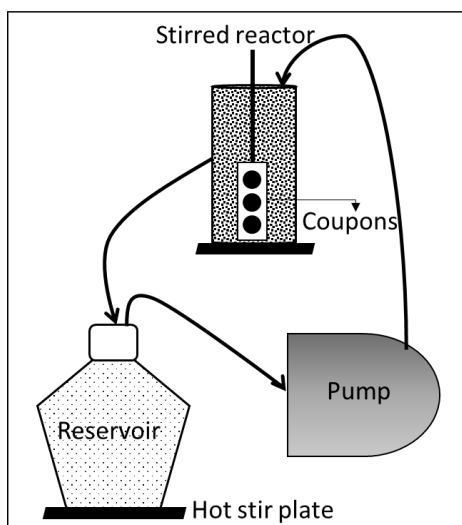


Figure 2: Schematic of the experimental setup.

Analysis

Coupons collected from the reactor were used for corrosion rate measurements, optical profilometry, scanning electron microscopy (SEM), adenosine triphosphate (ATP) assay, and quantitative polymerase chain reaction (qPCR).

Corrosion rate

Some of the metal coupons exposed to the untreated and biocide treated waters were periodically removed from the bioreactors, cleaned with inhibited acid, and dried to measure their weight loss during exposure to the respective waters. The measured weight loss was then used to calculate the general corrosion rate of the coupons. Weight loss measurements were done in duplicate.

Optical profilometry analysis

After weighing, the acid cleaned coupons were examined using a Keyence VR-3200 3D macroscope[†] in a high magnification mode at 40X to quantify the corrosion features present on the coupon surface. Pits deeper than 5 μm with respect to the reference plane and with a minimum cross-sectional area of 650 μm^2 were recorded by the macroscope. Pit depth, pit volume, and surface roughness measurements were done over the entire coupon surface. The maximum pit depth measured on a coupon was reported and was used to calculate the pitting rate of the coupon. Optical profilometry analyses were performed in duplicate.

[†] Trade name

SEM of biofilms and coupon surface

High magnification images of the biofilms and acid cleaned coupon surfaces were obtained using SEM to monitor the biofilm structure and pit initiation mechanisms respectively.

ATP assay

Microbial activity of the planktonic and sessile samples was measured using the concentration of ATP. Planktonic ATP assays were conducted on liquid samples collected from the reactors periodically, while sessile ATP assays were conducted on the deposits and biofilms formed on the metal coupons. Sessile ATP assays were performed in duplicate. ATP concentration was converted to microbial equivalents (ME) or number of cells as per industry accepted guidelines, 1 pg=1000 ME.

qPCR

qPCR was used to measure the abundance of total bacteria, total archaea, and several functional groups such as SRB, APB, methanogens and others implicated in microbial communities associated with MIC. A list of microorganisms and their gene targets used for qPCR assay is provided in Appendix A. qPCR was performed on a sample of the untreated water collected immediately before testing was initiated. qPCR of the coupon surfaces was performed on the coupons pulled from the reactors after one week and after four weeks exposure.

Other analysis

In addition to the analyses mentioned above, pH, dissolved hydrogen sulfide concentration, sulfate concentration, lactate concentration, and acetate concentration are commonly measured parameters. These parameters support the understanding of the changes in the chemical environment over time and facilitate the interpretation of the underlying corrosion mechanisms. However, these analyses were not performed in this case study.

RESULTS

Chemical composition of the as-received water

Table 1: Chemical composition of the as-received water.

Parameter	Value	Parameter	Value
Alkalinity, Bicarbonate (ppm)	925	Nitrate (ppm)	ND
Alkalinity, Carbonate (ppm)	ND	Nitrite (ppm)	ND
Alkalinity, Total (ppm)	925	Phosphorus (ppm)	0.15
Aluminum (ppm)	ND	pH	8.0
Barium (ppm)	ND	Potassium (ppm)	28
Bromide (ppm)	8.4	Silicon (ppm)	51.1
Calcium (ppm)	ND	Sodium (ppm)	1360
Chloride (ppm)	1580	Strontium (ppm)	ND
Iron (ppm)	140	Sulfate (ppm)	80.2
Magnesium (ppm)	ND	Sulfide, liquid (ppm)	6.2
Manganese (ppm)	0.0184	Total Dissolved Solids (ppm)	3640

ND = Not Detected at the reporting limit