

Investigation of the Impact of an Enhanced Oil Recovery Polymer on Microbial Growth and MIC

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ABSTRACT

In the oil and gas industry, water flooding, often with a polymer additive, is used in enhanced oil recovery (EOR) to increase reservoir pressure because reservoirs are aging. This practice causes operational concerns because water flooding brings nutrients and microbes downhole, which may allow microbes to flourish. Polymers such as carboxymethyl cellulose sodium are used in EOR to increase the viscosity of the injection water. However, there is a possibility that EOR polymers may be utilized as a carbon source by microbes downhole causing reservoir souring and microbiologically influenced corrosion (MIC). In this work, carboxymethyl cellulose sodium (3,000 ppm by mass) was found to be utilized by an oilfield biofilm consortium containing various microbes including sulfate reducing bacteria (SRB) and biodegradation microbes during a 30-day anaerobic incubation test at 37°C. The polymer utilization increased the planktonic cell count and SRB sessile cell count in anaerobic vials with 100 ml artificial seawater. After the 30-day incubation, the polymer utilization led to 16% viscosity loss. The utilization also slightly increased weight loss and pitting corrosion on C1018 carbon steel.

Key words: microbiologically influenced corrosion, biofilm, enhanced oil recovery, reservoir, polymer, biodegradation

INTRODUCTION

In the oil and gas industry, enhanced oil recovery (EOR) is utilized very often nowadays because reservoirs are aging.¹ Water flooding with added EOR chemicals is used to increase reservoir pressure.² Seawater is often injected. This practice brings oxidants (e.g., sulfate), nutrients and microbes downhole.³ A reservoir is strictly anaerobic.⁴ Oxygen is usually removed during water flooding to avoid oxygen corrosion of downhole tubing. In this environment, anaerobic microbes such as sulfate reducing bacteria (SRB) flourish.⁵ SRB can produce biogenic H₂S causing reservoir souring.⁶ Fermentative microbes can also grow.⁷ In the field environments, microbes live in synergistic biofilm consortia.⁸ Biofilms can cause biocorrosion in many industries, especially in the oil and gas industry.^{9–12} This kind of corrosion is also known as microbiologically influenced corrosion (MIC).¹³ MIC is gaining more concerns since the Trans-Alaska Pipeline leak in 2006.¹⁴ It is important to investigate whether EOR polymers can be used by microbes as organic carbons thus worsening reservoir souring and MIC.

Adding a polymer in EOR is an efficient way to increase fluid viscosity.¹⁵ Xanthan gum, partially hydrolyzed polyacrylamide (HPAM) and cellulose-based polymer are commonly used in EOR. Xanthan gum was popular in the old days. However, it was found that it is susceptible to microbial degradation which leads to the loss of viscosity.¹⁶ It is a polysaccharide¹⁷ that is widely used as a food additive.¹⁸ HPAM is inexpensive and commonly used in recent years. Reports showed that HPAM can also be utilized by microbes.¹⁹ It was found that HPAM can be utilized by a sulfate reducing bacterium as a carbon source resulted in viscosity loss.²⁰ *Bacillus cereus* was found to utilize the amide group and the carbon backbone of HPAM as their nitrogen and carbon sources, respectively.²¹ Cellulose-based polymers have been adopted as polymer flooding materials in EOR in recent years.²² Some reports showed that the fermentation products of cellulose such as organic acids can be used as organic carbon and contribute to SRB growth.^{23,24} There is no literature reporting direct utilization of cellulose-based polymers by SRB. However, microbes live in biofilm consortia in the field. It is expected that other microbes can digest it and then provide organic nutrients to SRB. So far, there is a lack of reports showing the utilization of cellulose-based polymers that affects microbial growth and MIC.

In this work, a commercial cellulose-based polymer (carboxymethyl cellulose sodium) at 3,000 ppm (w/w) was tested in 125 ml anaerobic vials to see whether it could be utilized by an oilfield biofilm consortium containing SRB and biodegradation microbes during a 30-day incubation period. Planktonic cell count, SRB sessile cell count, pitting data and weight loss data were analyzed to check its effects on the microbial growth and MIC of C1018 carbon steel.

EXPERIMENTAL PROCEDURE

A corrosive oilfield biofilm consortium labeled as Consortium II containing SRB, fermentative microbes and biodegradation microbes was used in this work. Its metagenomics data are reported previously.⁷ Consortium II was cultured in artificial seawater for testing. The composition of artificial seawater was (g/l): NaCl 23.476, Na₂SO₄ 3.917, NaHCO₃ 0.192, KCl 0.664, KBr 0.096, H₃BO₃ 0.026, MgCl₂·6H₂O 10.610, SrCl₂·6H₂O 0.040, CaCl₂·2H₂O 1.469, tri-sodium citrate 0.5, MgSO₄·H₂O 0.4, CaSO₄ 0.1, NH₄Cl 0.1, K₂HPO₄ 0.05, Fe(NH₄)₂(SO₄)₂ 0.5. The artificial seawater was enriched with 3.5 g/l sodium lactate and 1 g/l yeast extract only for the seed culture of Consortium II and 1 ml of it was used to inoculate 100 ml artificial seawater. The medium, vials and other lab tools were sterilized at 121°C for 20 min. One hundred ppm L-cysteine was used as an oxygen scavenger to counter any potential oxygen ingress. All liquid solutions were deoxygenated by sparging with filtered N₂ for at least 0.5 h before use. Square C1018 carbon steel coupons were used in this task. Only a 1 cm² top surface was exposed while the others were coated with inert Teflon. Coupons were polished sequentially with 180, 400 and 600 grit sandpapers. After that, coupons were cleaned with pure alcohol and then dried under UV light. A commercial cellulose-based polymer (carboxymethyl cellulose sodium) (100%) was provided by Petronas of Malaysia. Other chemical reagents were from Fisher Scientific (Pittsburgh, PA, USA) or Sigma-Aldrich (St Louis, MO, USA).

Table 1 shows the test conditions. Five replicate coupons and 100 ml culture medium were added to each 125 ml anaerobic vial (Wheaton Industries Inc., Millville, NJ, USA) before inoculation using 1 ml seed culture. Carboxymethyl cellulose sodium was added to the culture medium to reach 3,000 ppm. The uninoculated artificial seawater with 3,000 ppm polymer was used as the abiotic control. The initial pH of the culture medium was 7.5 before inoculation. The initial planktonic cell concentration was 10^6 cells ml^{-1} following inoculation. After inoculation, sealed anaerobic vials were incubated at 37°C without shaking. The planktonic cell count was obtained using a hemocytometer.²⁵ After 7, 14, 21 and 30 days, coupons were retrieved for various analyses. The most probable number (MPN) method in this work used modified Postgate's B liquid medium (Biotechnology Solutions[†], Houston, TX, USA) for SRB sessile cell count.⁸ The viscosity was measured using a falling ball viscometer at 23°C. After 30 days of incubation, biofilms were examined under scanning electron microscopy (SEM) (Model JSM-6390, JEOL[†], Tokyo, Japan) and confocal laser scanning microscopy (CLSM) (Model LSM 510, Carl Zeiss[†], Jena, Germany).⁵ At least 4 coupons were used for each weight loss data point. Biofilms and corrosion products were removed and cleaned using Clarke's solution for 0.5 min before weighing the coupons. Corrosion pit images were obtained under SEM.

Table 1
Text Matrix of impact of cellulose-based EOR polymer on microbial growth and corrosion

Microbe	Biofilm Consortium II
EOR polymer	Carboxymethyl cellulose sodium
Concentration	0 ppm polymer 3,000 ppm polymer
Liquid medium	Artificial seawater
Liquid volume	100 ml in 125 ml anaerobic vials
Temperature	37°C
Duration	30 days
Assay	Planktonic cell count, SRB sessile cell count, medium viscosity, biofilm images, coupon weight loss, pit image

RESULTS

Figure 1 shows planktonic cell counts during the 30-day incubation in the culture media with and without the polymer. The planktonic cell count in the inoculated artificial seawater with 0 ppm polymer decreased during incubation continuously due to a shortage of organic carbon in the medium. With 3,000 ppm carboxymethyl cellulose sodium in the medium, the planktonic cell amount decreased in the first 6 days. Then, it started to increase. The results showed that biofilm Consortium II adapted during the first few days and then started to utilize carboxymethyl cellulose sodium as an organic carbon source for growth. The adaption period is a typical phenomenon because cells need time to synthesize new enzymes to digest a new organic carbon. The SRB sessile cell count data in Figure 2 show that the utilization of carboxymethyl cellulose sodium contributed to the increase of the SRB sessile cell count. The SRB sessile cell count in the medium with 0 ppm polymer decreased during the 30-day incubation. However, the SRB sessile cell count in the medium with 3,000 ppm polymer did not decrease during the incubation period. SRB benefited from the metabolic products of carboxymethyl

[†]Trade name

cellulose sodium.²⁴ In this work, only SRB sessile cell count was assayed because SRB dominated biofilm Consortium II for the growth condition used in this work.⁷

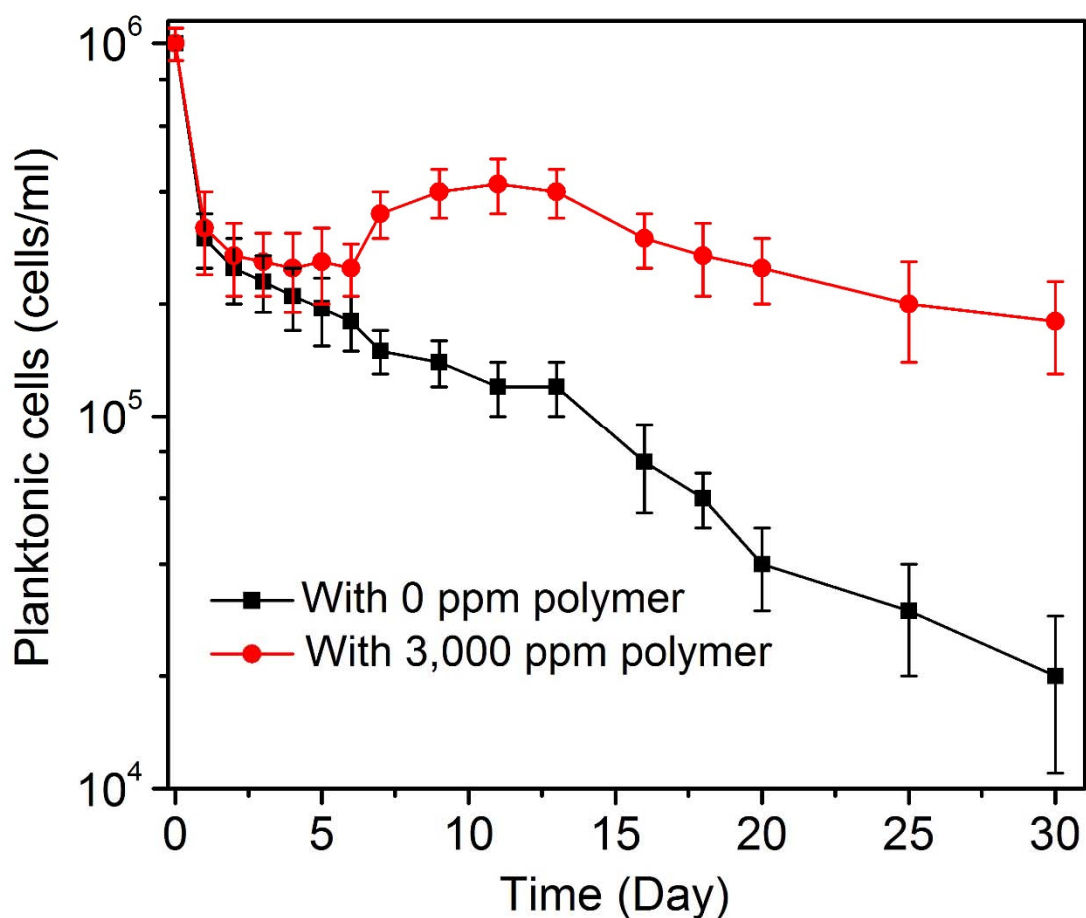


Figure 1. Planktonic cell counts in inoculated artificial seawater with and without polymer. (Error bars represent standard deviations from 4 independent samples.)

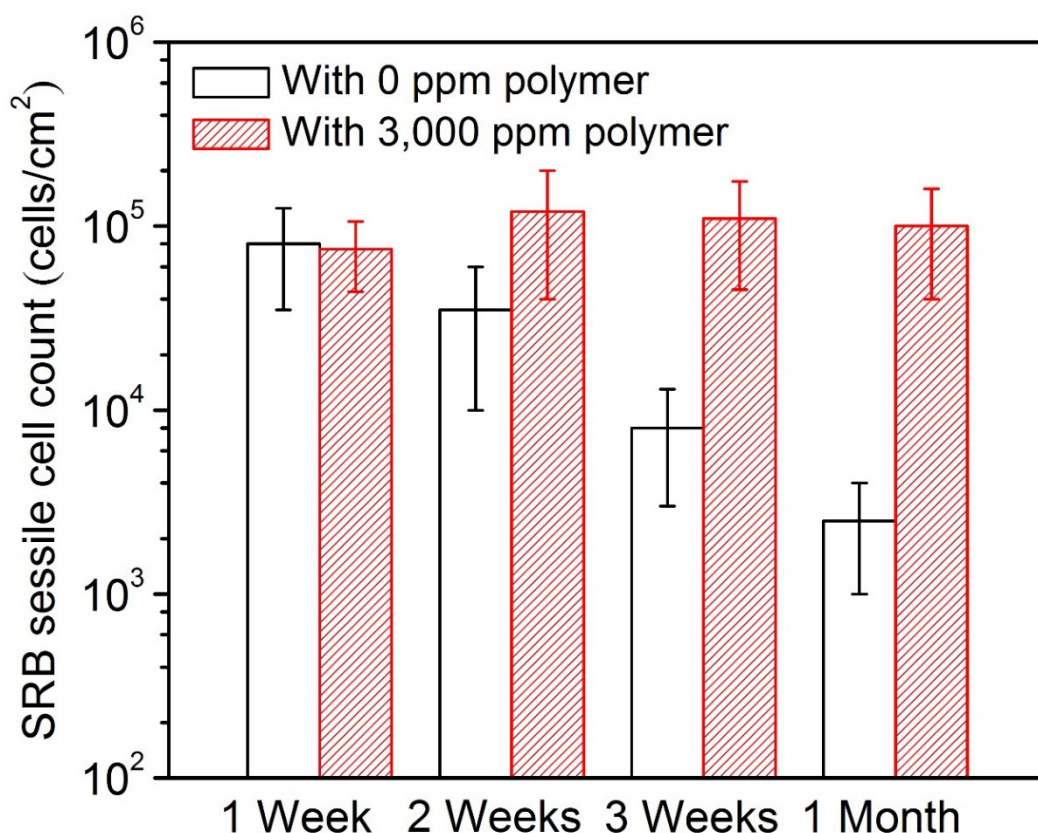


Figure 2. SRB sessile cell counts in inoculated artificial seawater with and without polymer for different incubation lengths. (Error bars represent standard deviations from 4 independent samples.)

The polymer utilization promoted cell growth especially SRB growth. This is visually verified by Figure 3. More Fe^{2+} ions were precipitated by biogenic sulfide as black FeS precipitates in the medium with 3,000 ppm polymer compared with that having 0 ppm polymer. This was because more cell growth produced more HS^- to precipitate Fe^{2+} . Figure 4 shows the viscosity change of the culture medium with 3,000 ppm carboxymethyl cellulose sodium in the abiotic medium and in the inoculated artificial seawater during the 30-day incubation time. In the abiotic control, the viscosity remained almost constant as expected during the incubation. However, in the inoculated medium, the viscosity of the culture medium decreased by 16% after the 30-day incubation. The results further confirmed that microbes in Consortium II degraded some carboxymethyl cellulose sodium. This polymer utilization was consistent with the planktonic cell count (Figure 1) and the SRB sessile cell count (Figure 2).

Figure 5 shows biofilm images under SEM and CLSM after 30 days of incubation in inoculated culture media with and without carboxymethyl cellulose sodium. SEM images of biofilms on coupons from the media with 0 ppm and 3,000 ppm polymer show that biofilm Consortium II was a mixed culture in Figure 5A and Figure 5B. However, biofilm SEM images only showed that there were numerous sessile cells without distinguishing live and dead cells. Figure 5A' shows that sessile cells on the coupon from the medium with 0 ppm polymer after 30 days of incubation were mostly dead cells (red dots), whereas sessile cells on the coupon incubated with 3,000 ppm polymer were mostly live cells (green dots). The

biofilm thickness on the coupon incubated with 3,000 ppm polymer was larger than that on the coupon incubated with 0 ppm polymer.

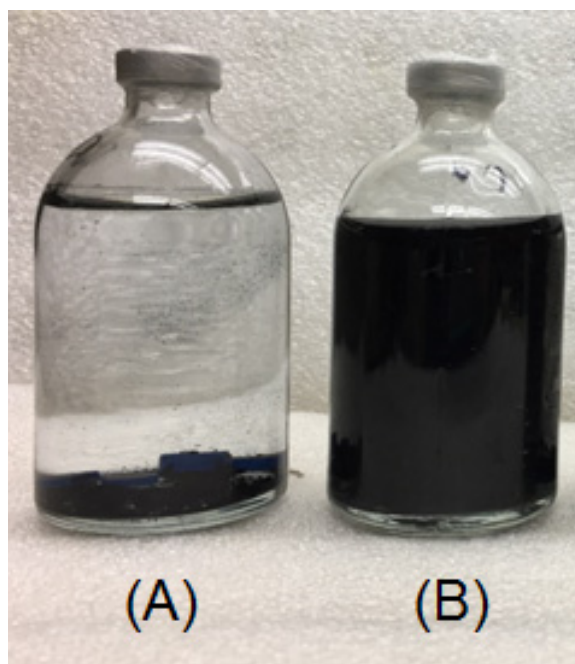


Figure 3. Images of anaerobic vials after 30-day incubation in artificial seawater: (A) with 0 ppm polymer, and (B) with 3,000 ppm polymer.

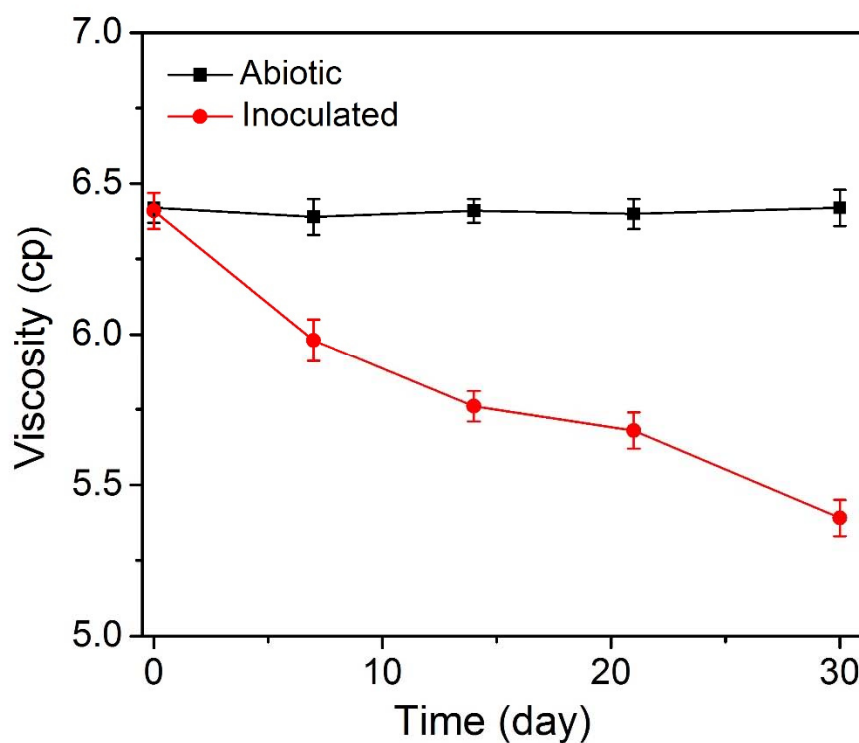


Figure 4. Viscosities of the abiotic artificial seawater and inoculated artificial seawater, both with 3,000 ppm polymer. (Error bars represent standard deviations from 3 independent samples.)

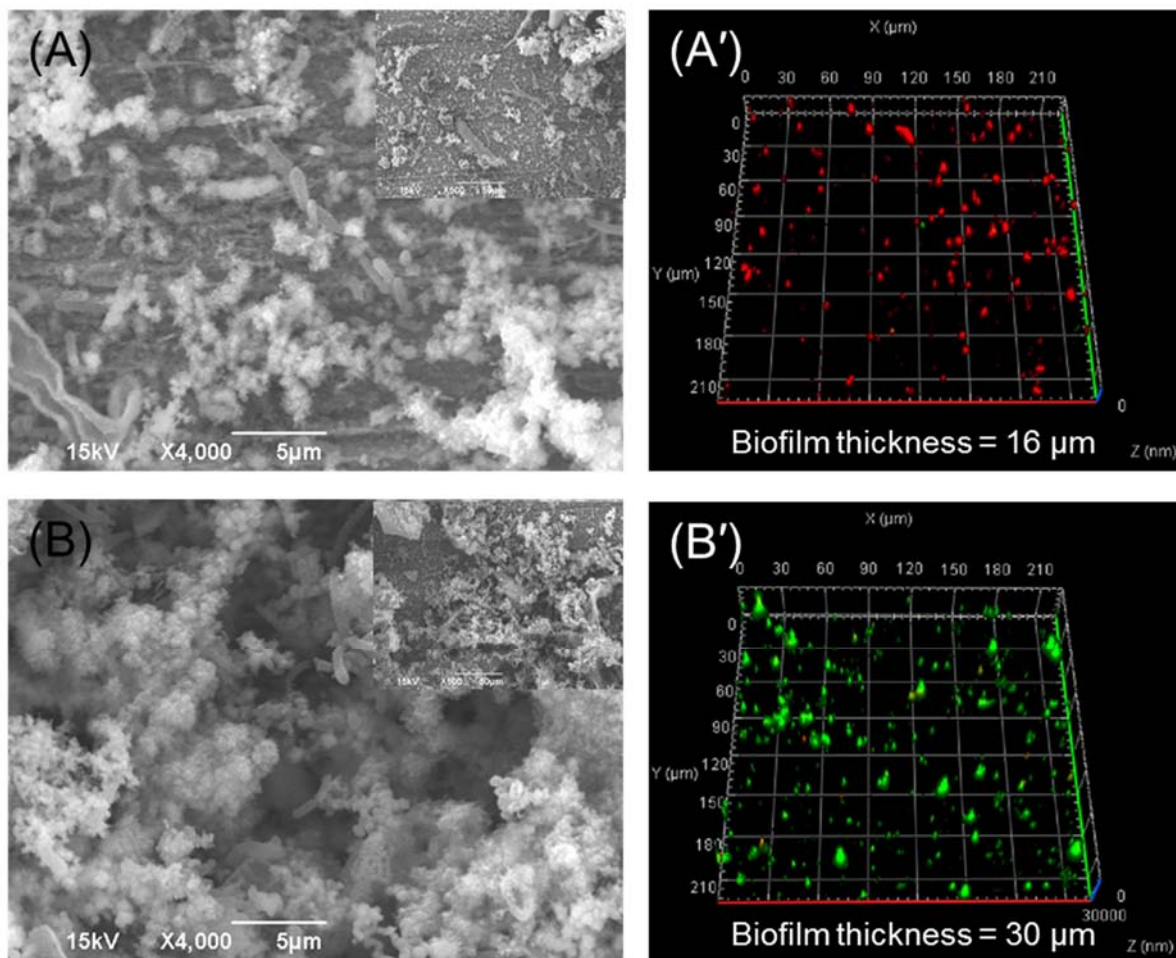


Figure 5. Biofilm SEM and CLSM images on the surfaces of coupons after the 30-day incubation in inoculated artificial seawater with 0 ppm polymer (A, A'), and with 3,000 ppm polymer (B, B').

The weight losses of coupons incubated after 30 days in the abiotic artificial seawater with 3,000 ppm polymer and in the inoculated artificial seawater with and without polymer are shown in Figure 6. The coupon incubated in the abiotic medium showed negligible corrosion indicating that chemicals in the abiotic culture medium caused almost no corrosion under anaerobic condition. The small weight loss could be attributed to coupon cleaning. The coupons incubated in the inoculated medium with 3,000 ppm polymer showed slightly more weight loss than that of coupons incubated in the inoculated medium with 0 ppm polymer. However, they were not statistically significant. The culture medium pH for the abiotic medium was still 7.5 after 30 days of incubation. The culture medium pH values of the inoculated medium with 0 ppm polymer were more than 7.5 during the 30-day incubation as shown in Figure 7. The pH values of the inoculated medium with 3,000 ppm polymer were more than 6.5 and slightly increased during the incubation. The organic acid attack was not a significant factor in corrosion with this kind of pH. Negligible pitting corrosion was found on the coupons incubated in the abiotic control with 3,000 ppm polymer as shown in Figure 8(A, A'). More pits are seen on the SEM image for the coupon from the inoculated medium with 3,000 ppm polymer (Figure 8C') compared to that with 0 ppm polymer (Figure 8B'). The pitting data corroborate the weight loss data in Figure 6.

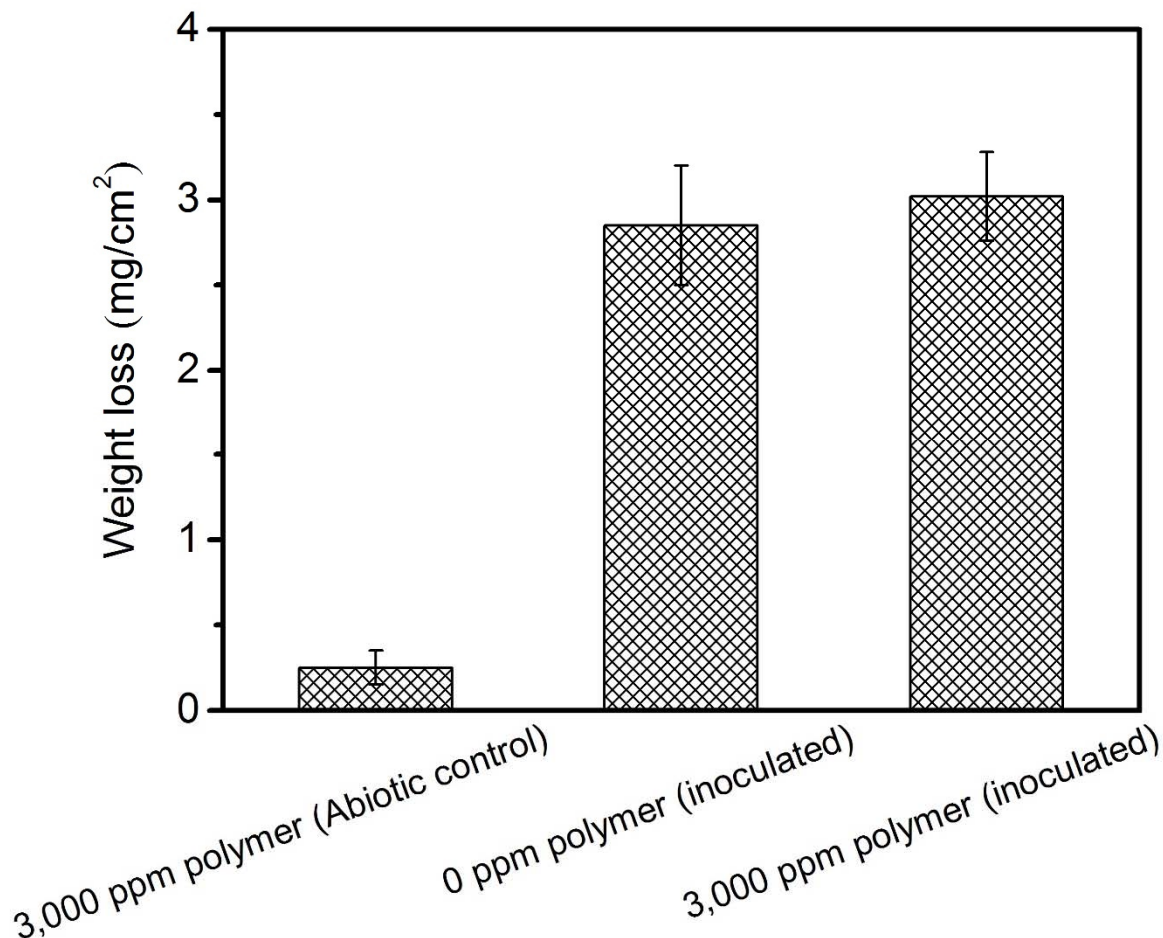


Figure 6. Weight loss of coupons after 30 days of incubation in inoculated artificial seawater with and without polymer. (Error bars represent standard deviations from 6 independent samples.)

Biofilms are responsible for MIC.²⁶ The biocatalytic cathodic sulfate reduction (BCSR) theory explains the SRB MIC with sulfate as the terminal electron acceptor.²⁷ The following two reactions in BCSR explained the bioenergetics of MIC because of the utilization of extracellular electrons by SRB in EET-MIC with extracellular electron transfer (EET).^{28,29}



The equilibrium potential for Fe^{2+} reduction and sulfate reduction are -447 mV and -214 mV, respectively versus standard hydrogen electrode at 25°C , pH 7, 1 M solutes (1 bar gases).³⁰ The $\Delta E'$ of the redox reaction coupling Reactions 1 and 2 is $+233$ mV, which means the reaction is thermodynamically favorable.³¹ However, in the abiotic control, negligible corrosion was found although it contained sulfate. This was because the actual reaction rate depended on kinetics which needed biocatalysis of SRB. More corrosion was found in the inoculated medium judging from the weight loss and pitting corrosion. The results show that biocatalysis was necessary for SRB MIC. As more FeS precipitation was observed in the inoculated medium with 3,000 ppm polymer as shown in Figure 3.

Reaction 3 below explains the lower pH observed in the inoculated medium with 3,000 ppm polymer compared to that in the medium with 0 ppm polymer.²⁸

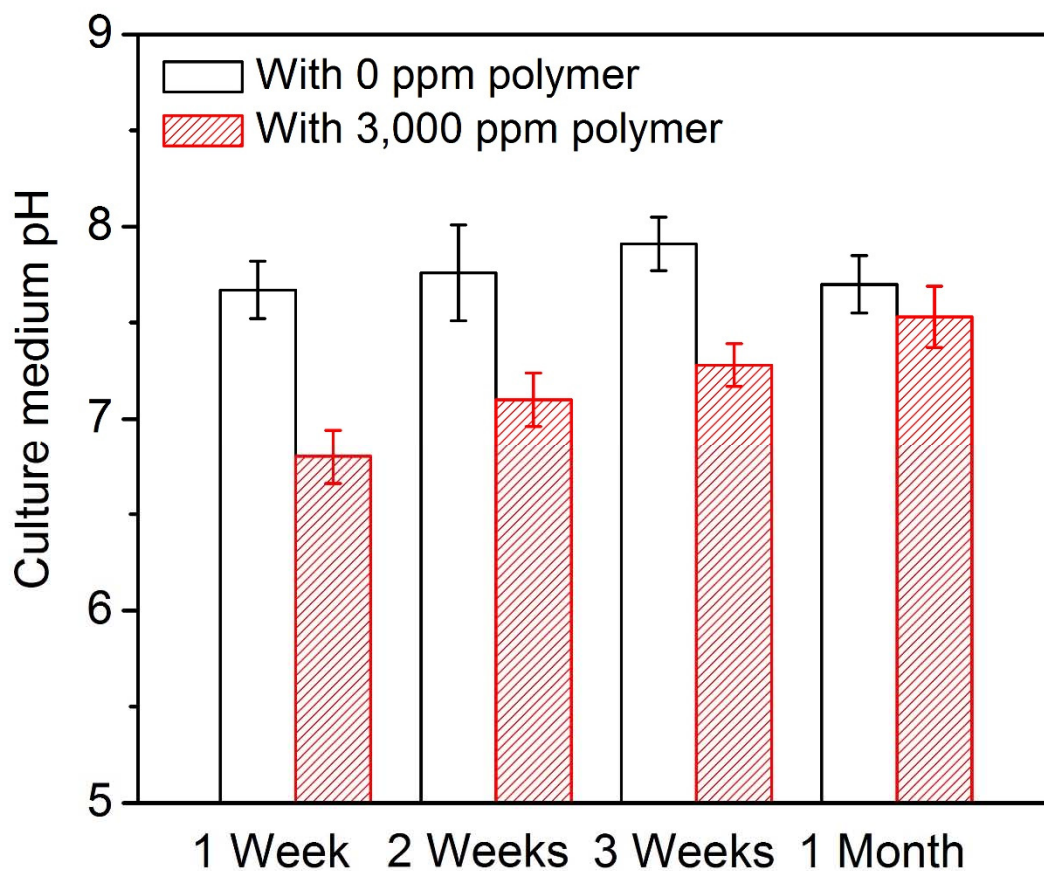


Figure 7. Culture medium pH values in inoculated artificial seawater with and without polymer. (Error bars represent standard deviations from 3 independent samples.)

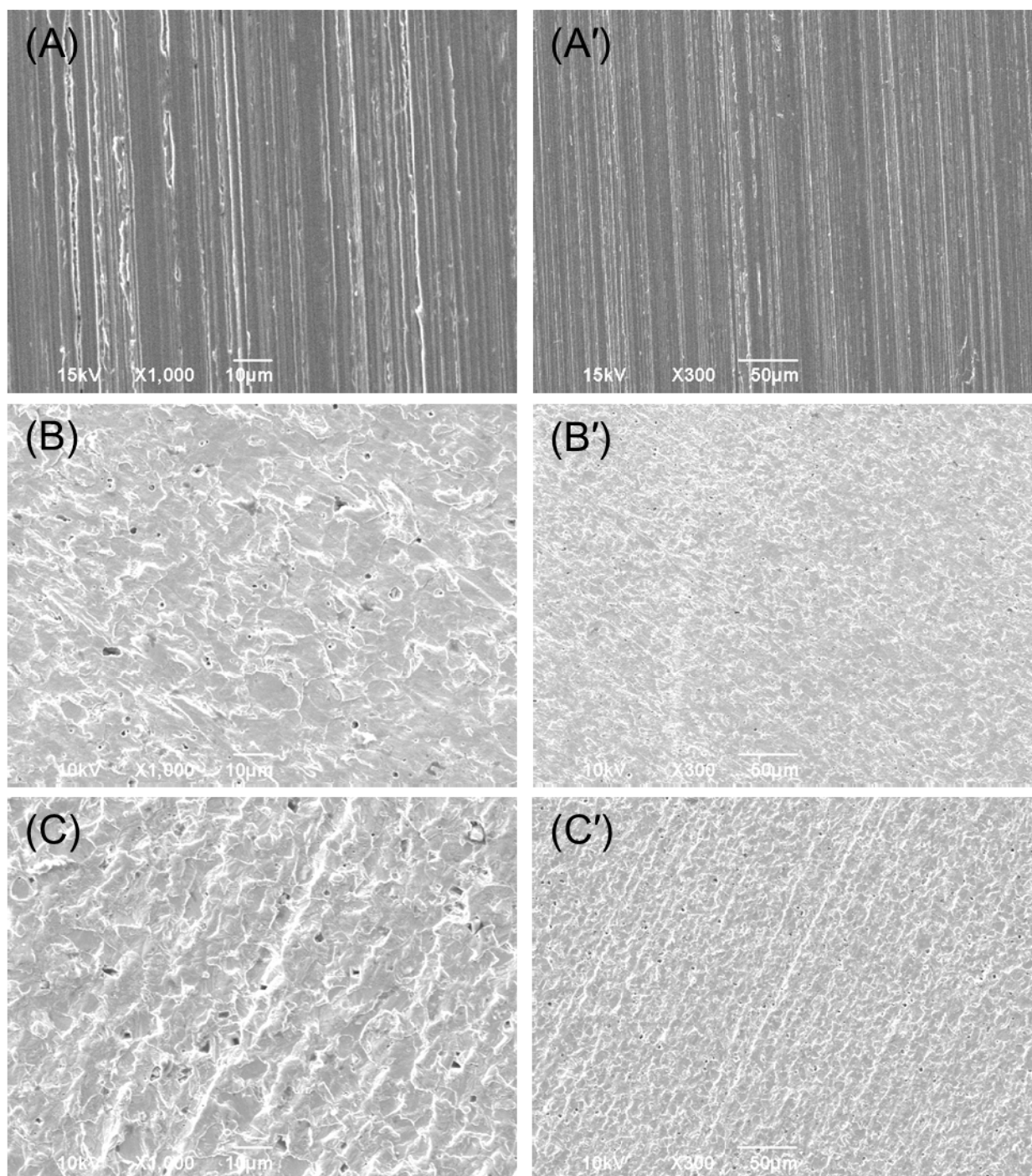


Figure 8. Pit images (apostrophe indicates lower resolution images) for coupons after 30 days of incubation in artificial seawater with and without polymer: (A) 3,000 ppm polymer (abiotic control), (B) 0 ppm polymer (inoculated), and (C) 3,000 ppm polymer (inoculated).

CONCLUSIONS

The results in this work showed that carboxymethyl cellulose sodium present as the sole organic carbon in the artificial seawater at 3,000 ppm was utilized by biofilm Consortium II during the 30-day anaerobic incubation test. The polymer utilization increased the planktonic cell count and SRB sessile

cell count in 125 ml anaerobic vials. After the 30-day incubation, viscosity decreased by 16% in the inoculated culture medium containing 3,000 ppm polymer. The utilization also slightly increased weight loss and pitting corrosion on C1018 carbon steel. A future project evaluating biocide efficacy in the mitigation of MIC in polymer flooding is recommended.

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