Laboratory testing of enhanced biocide mitigation of microbiologically influenced corrosion in enhanced oil recovery

Ru Jia, Dongqing Yang
Dept. of Chemical & Biomolecular Engineering
Institute for corrosion & multiphase technology
Ohio University
Athens, OH 45701

Intan Khalida Salleh, Jamal Momahad M. Ibrahim
Hydrocarbon Recovery
Group Research & Technology
Project Delivery & Technology
PETRONAS, Malaysia

Hasrizal Bin Abd Rahman, Pauziyah A. Hamid
Hydrocarbon Recovery
Group Research & Technology
Project Delivery & Technology
PETRONAS, Malaysia

Tingyue Gu (gu@ohio.edu)
Dept. of Chemical & Biomolecular Engineering
Institute for corrosion & multiphase technology
Ohio University
Athens, OH 45701

ABSTRACT

MIC is currently a prevalent problem in the oil and gas industry due to seawater injection in enhanced oil recovery (EOR). Biocides are often used to mitigate MIC. However, continued biocide dosing leads to resistance by microbes over time. In this work, D-amino acids were used to enhance the tetrakis (hydroxymethyl) phosphonium sulfate (THPS) biocide against a tough field biofilm consortium on C1018 carbon steel coupons. An equi-mass D-amino acid mixture ("D-mix") of four D-amino acids (D-methionine, D-tyrosine, D-leucine, and D-tryptophan) at a total concentration of 150 ppm (w/w) was tested. D-mix was injected with THPS and EOR chemicals (a polymer, a surfactant, a corrosion inhibitor, and a scale inhibitor) to treat the biofilm consortium and check the compatibility of the chemicals. After a 7-day biofilm removal test, the combination of 50 ppm THPS + 150 ppm D-amino acids achieved one extra log reduction in SRB and GHB sessile cell counts compared with using 50 ppm THPS alone. The combination also achieved lower weight loss and smaller maximum pit depths. The corrosion rates measured from linear polarization resistance were consistent with the weight loss data. The experimental data indicated that D-amino acids were compatible with the EOR chemicals.

Key words: microbiologically influenced corrosion, enhanced oil recovery, biofilm, biocide enhancer, D-amino acid

INTRODUCTION

Biocorrosion, also known as microbiologically influenced corrosion (MIC) is a major problem in the oil and gas industry.[1] Awareness of MIC is increasing in recent years especially after the 2006 Alaska pipeline leak.[2] Sulfate reducing bacteria (SRB) often cause corrosion and reservoir souring.[3, 4] Other bacteria such as acid producing bacteria (APB) and nitrate reducing bacteria (NRB) may also cause MIC.[5] Enhanced oil recovery (EOR) is practiced more often nowadays because of dwindling reserves.[6] Seawater injection can bring nutrients and microbes downhole. In the downhole environment, anaerobic microbes, especially SRB flourish. Nutrients and sulfate in seawater can be used by SRB to cause reservoir souring as well as MIC pitting against the downhole tubing.[7]

In the field, different types of microbes live in communities to form synergistic biofilm consortia.[8] Several mechanisms are used by biofilms to defend against biocides such as diffusional carrier for biocides,[9] slowed metabolic rates,[10] formation of persister cells,[11] and efflux pumps.[12] These mechanisms make it difficult to mitigate biofilm consortia. Therefore sessile cells in a biofilm are more recalcitrant to biocides than planktonic cells.[13] Tetrakis hydroxymethyl phosphonium sulfate (THPS) is a common biocide in field applications due to its broad-spectrum efficacy and excellent biodegradability. However, prolonged use of any biocide will promote microbial resistance, leading to dosage escalation over time. This increases cost and environmental impact. A more effective way to enhance existing biocides is desired to combat dosage escalation.

D-amino acids have been found to trigger biofilm disassembly presumably because they are signal molecules[14] or because they interfere with protein synthesis.[15] Xu et al. reported that 1 ppm (w/w) D-tyrosine (D-tyr) and 100 ppm D-methionine (D-met) enhanced THPS against the *Desulfovibrio vulgaris* biofilm.[13, 16] It was reported that an equi-mass mixture of D-met, D-tyr, D-leucine (D-leu), D-tryptophan (D-trp) was able to enhance THPS[8] and two other biocides[17] against a field biofilm consortium containing SRB and other microbes. EOR uses various chemicals such as surfactants and polymers to increase oil production.[6] Chemicals are typically applied in a single batch application in the oil field. EOR chemicals, biocides, biocide enhancers, corrosion inhibitors, and scale removers should be chemically compatible. Glutaraldehyde and D-amino acids are not compatible because glutaraldehyde is a protein cross-linking reagent.[18] In this work, an equal mass D-amino acid mixture (D-mix) of four D-amino acids (D-met, D-tyr, D-leu, and D-trp) was used as the biocide enhancer in combination with THPS to treat a corrosive field biofilm consortium.

EXPERIMENTAL PROCEDURE

A tough oilfield biofilm labeled as Consortium II was from an oil and gas field. [8, 17] Its metagenomics data indicated that the biofilm community contained SRB, fermentative microbes, and biodegradation microbes.[17] Artificial seawater was used to culture this biofilm.[19] The composition of the artificial seawater (g/l) was: NaCl 23.476, Na_2SO_4 3.917, $NaHCO_3$ 0.192, KCl 0.664, KBr 0.096, H_3BO_3 0.026, $MgCl_2$ $6H_2O$ 10.610, $SrCl_2$ $6H_2O$ 0.040, $CaCl_2$ $2H_2O$ 1.469, Tri-sodium citrate 0.5, $MgSO_4$ H_2O 0.4, $CaSO_4$ 0.1, NH_4Cl 0.1, K_2HPO_4 0.05, $Fe(NH_4)_2(SO_4)_2$ 0.5. The medium, 125 ml anaerobic vials, vial septa and caps, pipette tips, and tweezers were sterilized in an autoclave at 121°C for 20 minutes. Liquid solutions were sparged with filtered N_2 for 45 minutes to remove dissolved O_2. Coupons in this task were C1018 carbon steel square coupons with a top exposed surface area of 1 cm^2. All other surfaces were coated with inert Teflon. Coupons were polished with 180, 400, and 600 grit sandpapers, sequentially. Coupons were then cleaned with isopropanol and dried under UV light for 20 minutes. The biofilm Consortium II seed culture was grown in the artificial seawater enriched with 3.5 g/l sodium lactate and 1 g/l yeast extract. Before incubation, 5 coupons, 100 ml medium, and 1 ml seed culture were put into each 125 ml anaerobic vial in an anaerobic chamber. One hundred ppm L-cysteine was used as oxygen scavenger. Polymer, corrosion inhibitor, surfactant, and scale inhibitor chemicals were provided by our sponsor. Other chemicals used in this project were purchased from Fisher Scientific (Pittsburgh, PA, USA) or Sigma-Aldrich (St Louis, MO, USA).

Biofilms were first grown on coupons in the enriched artificial seawater for 4 days to achieve maturity. After that, the vials were opened in an anaerobic chamber and 1,000 ppm Polymer GLP-100, 5,000 ppm alpha olefin sulfonate (surfactant), 200 ppm Am 1554 (corrosion inhibitor), 15 ppm diethylene triamine penta (methylene phosphonic acid) (DTPMPA) (scale inhibitor), 50 ppm THPS, and 150 ppm D-mix were injected into the vials at the same time to treat the biofilms in a new 7-day incubation period at 37°C. The test matrix is shown in Table 1. After the additional 7-day incubation, coupons were taken out for assays. Sessile cells were enumerated by the most probable number (MPN) method. Three liquid culture media were used to count sessile cells according to three replicate serial dilution of NACE standard (TM0194-2014, standard test method-field monitoring of bacterial growth in oil and gas systems). They were modified Postgate's B (MPB) for SRB, standard bacterial nutrient broth for GHB, and phenol red dextrose (PRD) for APB, respectively. The MPN test culture media were purchased from Biotechnology Solutions† (Houston, TX). In a 10 ml pH 7.4 PBS solution, the biofilm was scraped off from a coupon using a small brush. The 10 ml PBS solution, the coupon, and the brush were put in a 50 ml centrifuge tube and vortexed for 30 seconds to distribute the sessile cells evenly in the solution. Then, the solution was serially diluted and incubated at 37°C. The cell counting was repeated at least twice. Live and dead cells were observed using a confocal laser scanning microscope (CLSM) (Model LSM 510, Carl Zeiss†, Jena, Germany). The abiotic control contains 1,000 ppm Polymer GLP-100, 5,000 ppm alpha olefin sulfonate, 200 ppm Am 1554, 15 ppm DTPMPA, 50 ppm THPS, and 150 ppm D-mix without inoculation. At least 4 coupons were weighed to get each weight loss data point. The weight of each coupon was measured before and after of the initial 4-day and the additional 7-day incubation periods with biofilms and corrosion products removed and cleaned using the Clark's solution for 30 seconds, which is a standard practice. The impact of the acidic Clark's solution on weight loss was negligible due to the short exposure time. Corrosion pit images were obtained by a scanning electron microscope (SEM) (Model JSM-6390, JEOL†, Tokyo, Japan). The deepest pit depth was obtained from an infinite focus microscope (IFM) (Model ALC, Alicona Imaging GmbH†, Austria).

Open circuit potential (OCP), linear polarization resistance (LPR), and electrochemical impedance spectroscopy (EIS) were performed using a potentiostat (Model VersaSTAT† 3, Princeton Applied Research, TN) to test a carbon steel coupon's electrochemical responses under different treatments. A saturated calomel electrode (SCE) was used as the reference electrode and a platinum plate (10 mm × 10 mm × 1 mm) was used as the counter electrode. LPR was scanned at a rate of 0.167 mV/s in the range of −20 mV to +20 mV vs. the OCP. EIS was obtained at OCP by applying a sinusoidal voltage signal of 10 mV in a frequency range of 10^{-2} to 10^{5} Hz with a scan rate of 5 mV/s.

Table 1
Test matrix for biocide treatment

| Microbes	Consortium II
Liquid medium	Enriched artificial seawater
Liquid volume	100 ml in 120 ml anaerobic vials
Biocide mixture	THPS + a quaternary mixture of D-amino acids
Biocide mixture concentration	50 ppm THPS, 150 ppm D-amino acid mixture
Temperature	37°C
Duration	4 days for initial biofilm growth + 7 days for biocide treatment
Coupon	C1018 coupons placed in vials

†Trade name

RESULTS

Coupons were first incubated in the enriched seawater at 37°C for 4 days to allow biofilm Consortium II to mature on C1018 coupons before initiating biocide treatment. Figure 1 shows sessile cell counts in the additional 7-day biofilm removal test using THPS and D-mix. In the additional 7-day biofilm removal test, 50 ppm THPS treatment alone achieved 1-log in APB, GHB, and SRB sessile cell counts reduction compared with the no treatment control. The combination of 50 ppm THPS + 150 ppm D-mix achieved one extra log reduction in GHB and SRB sessile cell counts compared with the 50 ppm THPS alone treatment. Sessile cell counts showed that D-amino acids enhanced THPS in the 7-day biofilm Consortium II removal test. The result also showed that D-amino acids had good chemical compatibility with the other chemicals as these chemicals did not harm the efficacy of the D-amino acids.
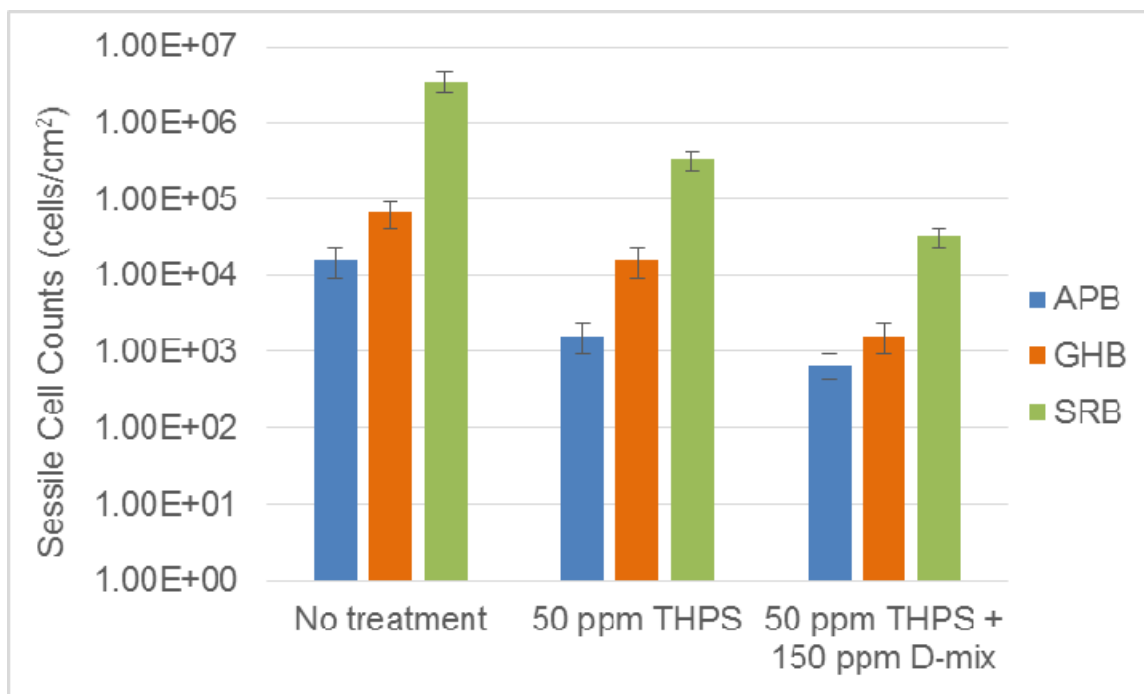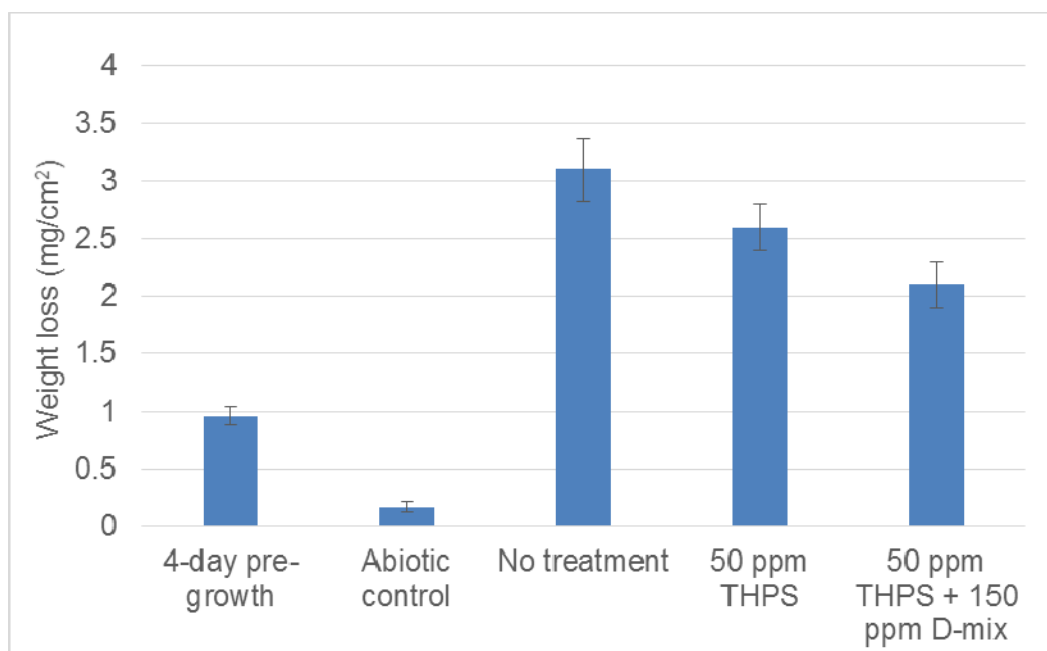

Figure 1. Sessile cell counts on C1018 coupon surface after the additional 7-day biofilm removal test. (Error bars represent standard deviation, statistical reference point n=6.)

CLSM was used to observe live and dead sessile cells on coupons. Figure 2 shows the CLSM images after different treatments. Coupons were washed using a pH 7.4 phosphate buffered saline (PBS) solution to remove planktonic cells, culture medium, and treatment chemicals before CLSM observation. The biofilms were then stained with the Live/Dead BacLight† Bacterial Viability Kit L7012 (Life Technologies†, Grand Island, NY, USA). In CLSM images, live cells show up in green color and dead cells red. After the additional 7-day biofilm removal test, the sessile cells on the no treatment control (Figure 2A) were almost all live cells. With the 50 ppm THPS treatment alone (Figure 2B), more dead cells showed up. After the treatment with 50 ppm THPS + 150 ppm D-mix, dead cells in Figures 2C far outnumbered live cells showing the effect of D-amino acids. The results were consistent with the aforementioned sessile cell counts.
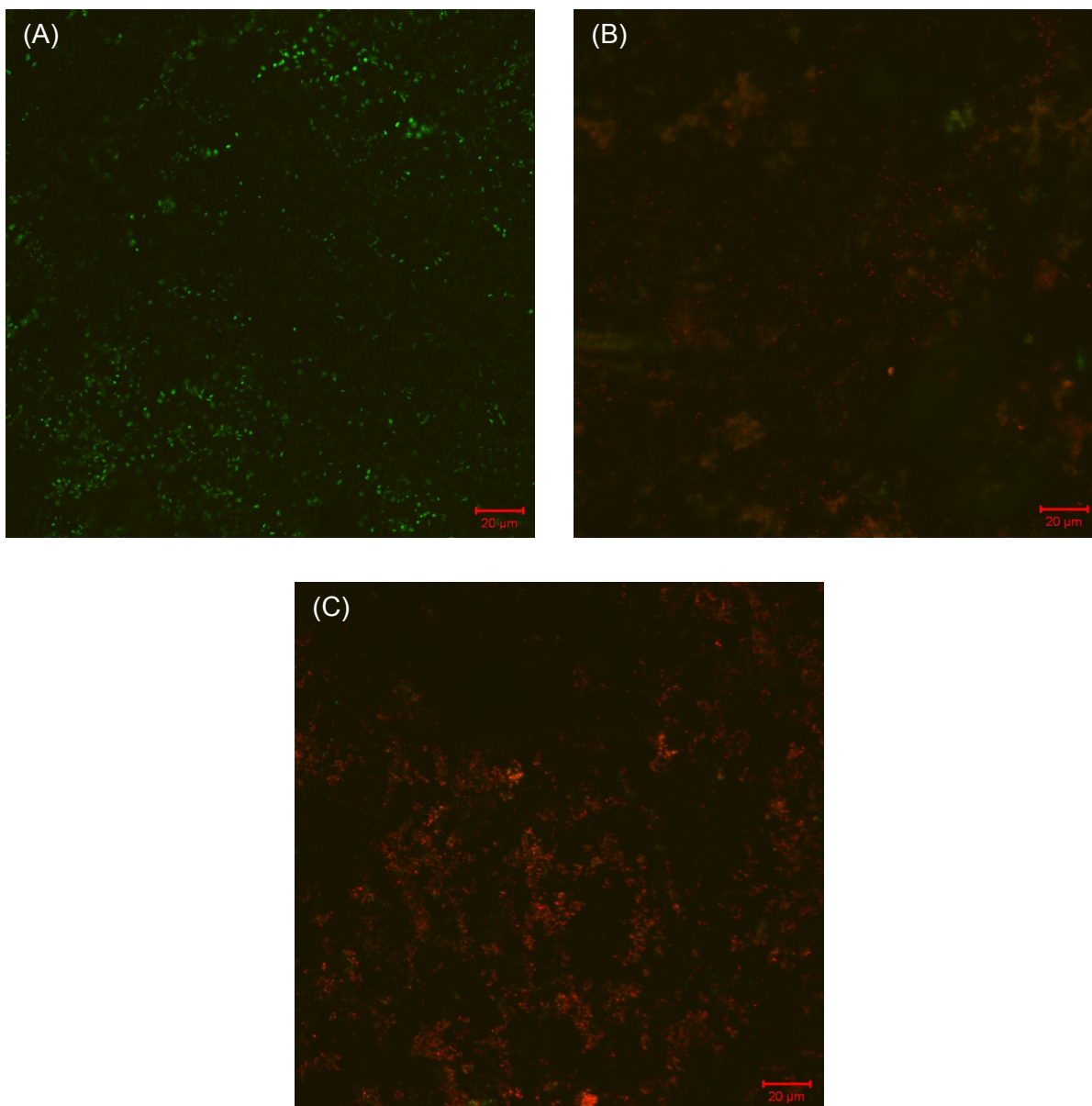
Figure 2. CLSM images after the additional 7-day biofilm removal test: (A) no treatment (control), (B) 50 ppm THPS, and (C) 50 ppm THPS + 150 ppm D-mix.

Figure 3 lists the weight loss data for 4-day pre-growth, abiotic control and different treatments after the additional 7-day biofilm removal test. The result showed that the weight loss of the 4-day pre-growth was 0.96 mg/cm^2. Fifty ppm THPS reduced C1018 coupon weight loss compared with the no treatment control. The combination of 50 ppm THPS + 150 ppm D-mix led to a lower weight loss compared with 50 ppm THPS alone treatment. Thus, the combination was able to mitigate MIC. The weight loss in the abiotic control was negligible. Figure 4 shows the images of pits on the coupon surfaces of the 4-day pre-growth, abiotic control, and with biofilms were removed after the additional 7-day biofilm removal test. Figure 4A shows some pits after the 4-day pre-growth of matire biofilms were removed. Figure 4C shows some large pits on the no treatment control. The combination of 50 ppm THPS + 150 ppm D-mix led (Figure 4E) to fewer pits compared with 50 ppm alone treatment (Figure 4D). No obvious pits were observed in the abiotic control coupon surfaces (Figure 4B). The pit images were consistent with weight loss data.

Figure 3. Weight losses of the 4-day pre-growth without treatments, abiotic control and the additional 7-day biofilm removal test with THPS and D-amino acids. (Error bars represent standard deviation, statistical reference point n=4.)

MIC mitigation was also reflected by the pit depth data as shown in Figure 5. Figure 5 shows maximum pit depth data of coupons after 4-day pre-growth and additional 7-day biofilm removal test. The 4-day pre-growth caused a maximum pit depth of 4.2 µm. The no treatment control after the additional 7-day biofilm removal test led to a maximum pit depth of 64.8 µm. With 50 ppm THPS treatment alone, the maximum pit depths caused by biofilm Consortium II was 49.2 µm. However, the combination of 50 ppm THPS + 150 ppm D-mix resulted in the smallest maximum pit depth of 34.6 µm. It should be noticed that in MIC pitting corrosion, the maximum pit depth is important because MIC failures are typically caused by pinhole leaks.[2]

Figure 6 shows the change of OCP vs. time under different treatments. It can be seen that the OCP of the abiotic control slightly shifted upward during the additional 7-day incubation. The OCP of the no treatment control shifted slightly to the more negative direction. In the 50 ppm THPS alone treatment, OCP kept steady in the first 4 days and then shifted to the positive direction. In the treatment of 50 ppm THPS + 150 ppm D-mix, OCP changed little and kept almost steady with time. In the treatment using 50 ppm THPS alone, the take-off of OCP shift after 4 days could be due to the growth of sessile cells and build-up of corrosion products after the THPS inhibition effect tapered down.[20] This led to the increase of the OCP.[21] The increased OCP was not observed with the treatment of 50 ppm THPS + 150 ppm D-mix. This corroborated the better treatment efficacy of this cocktail compared with the 50 ppm THPS alone treatment.
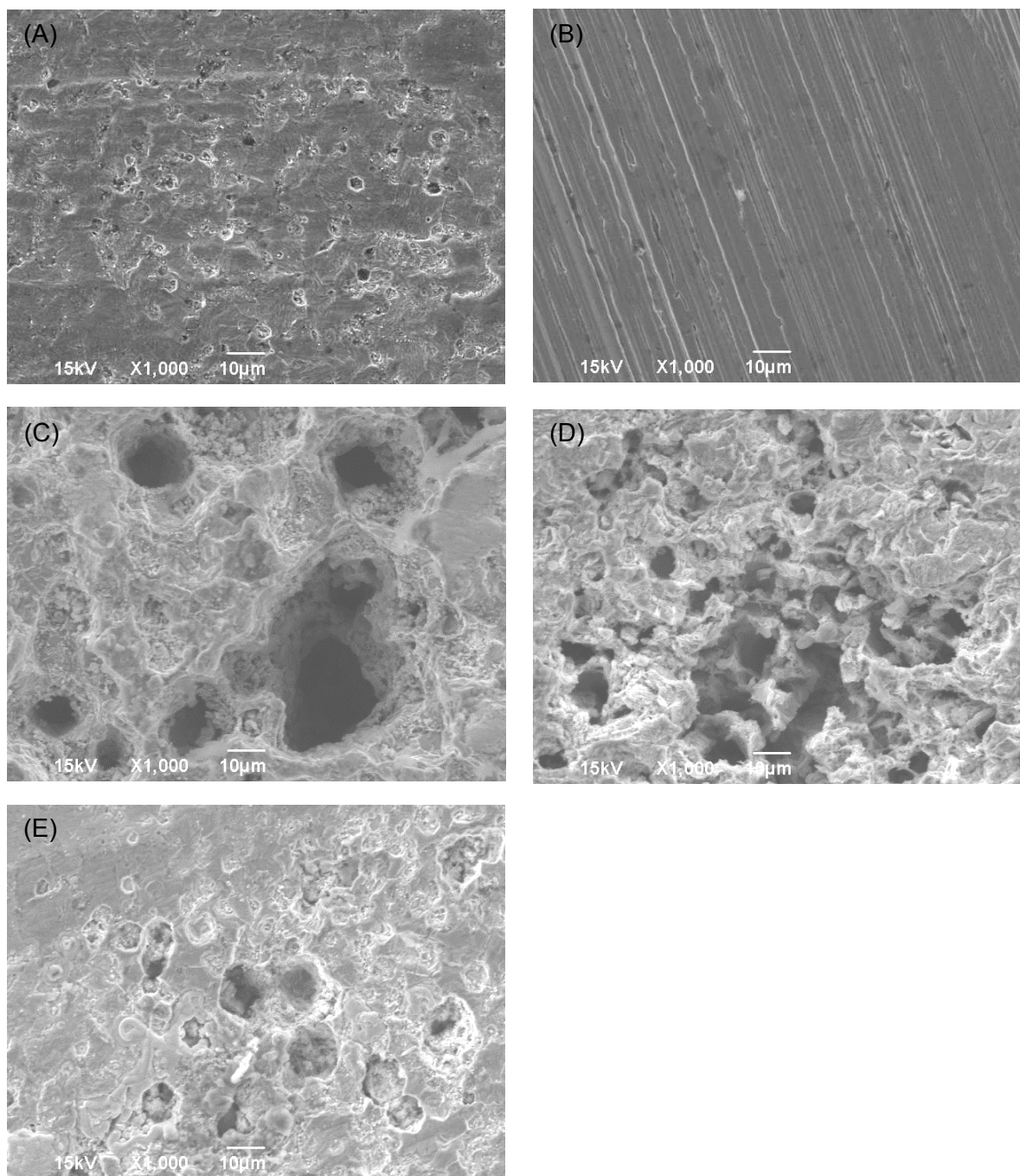
Figure 4. Pit images of the pre-growth before treatments, abiotic control and the additional 7-day biofilm removal test: (A) 4-day pre-growth without treatments, (B) abiotic control for 4 + 7 days, (C) no treatment (control), (D) 50 ppm THPS, and (E) 50 ppm THPS + 150 ppm D-mix. (C to E images were taken after additional 7 days of incubation.)
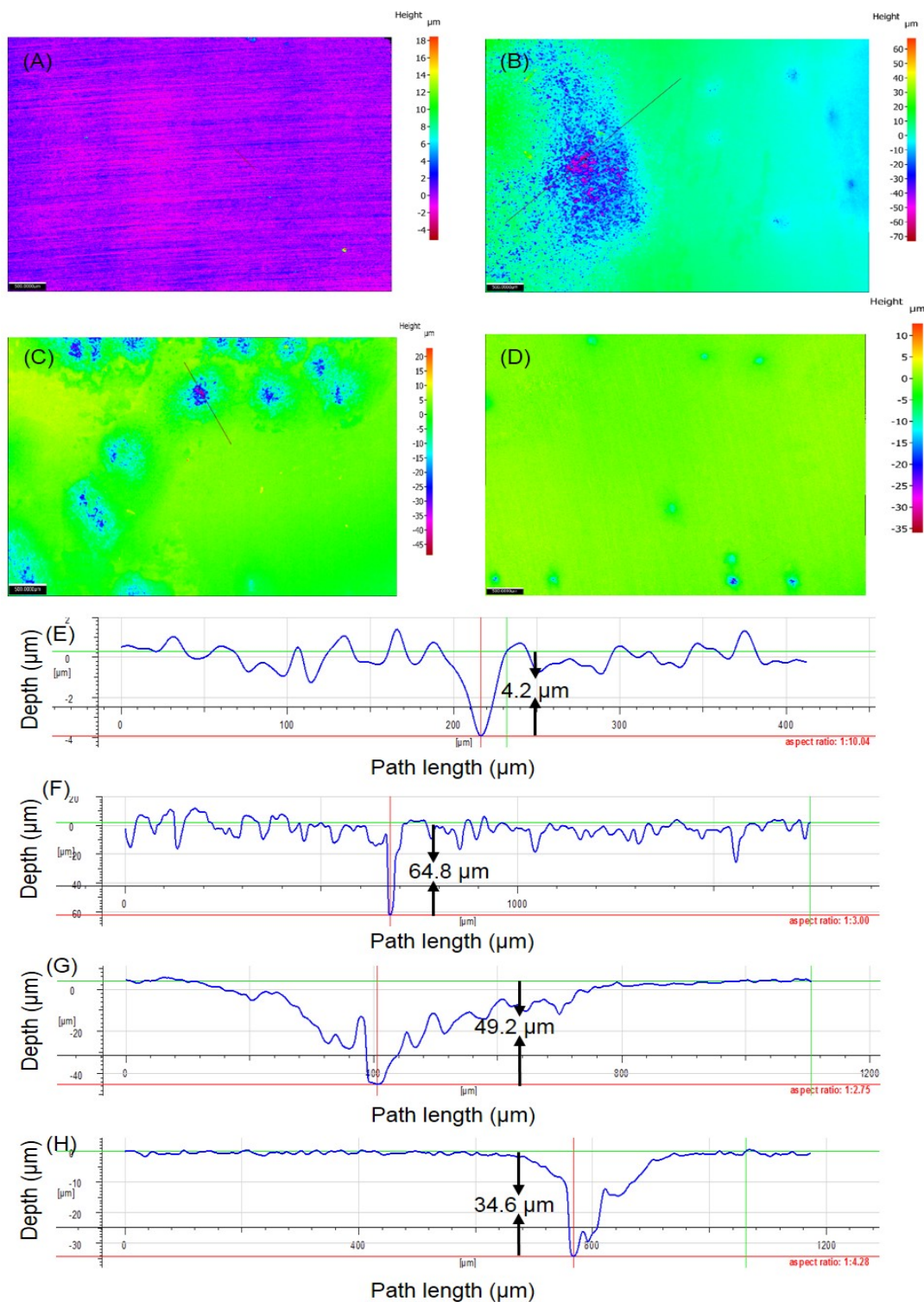
Figure 5. Coupon images under IFM: (A) 4-day pre-growth, (B) no treatment (control), (C) 50 ppm THPS, and (D) 50 ppm THPS + 150 ppm D-mix. (B to D images were taken after additional 7 days of incubation.) Maximum pit depths: (E) 4-day pre-growth, (F) no treatment (control), (G) 50 ppm THPS, and (H) 50 ppm THPS + 150 ppm D-mix. (F to H images were taken after additional 7 days of incubation.)
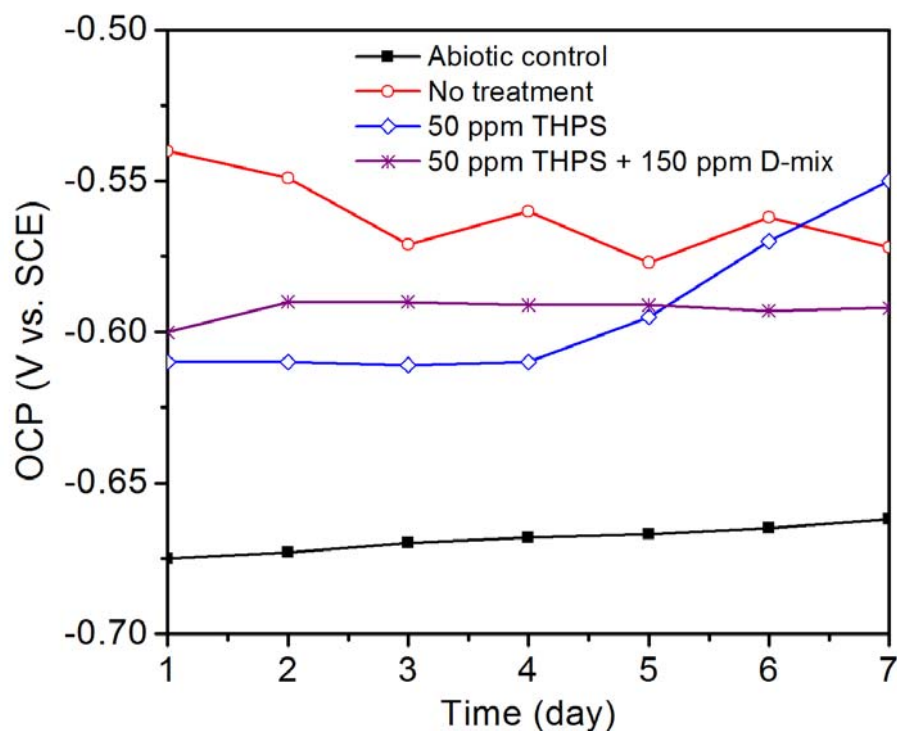
Figure 6. Variation of OCP under different conditions vs. time during additional 7 days of incubation.

LPR is a non-destructive electrochemical method for fast corrosion analysis.[22] The corrosion rates measured from LPR are shown in Figure 7. Figure 7 shows that the corrosion rate was considerably lower in the abiotic control medium. The corrosion rate of the no treatment control slightly decreased during the first 4 days and then increased sharply. The corrosion rates of both 50 ppm THPS alone treatment and treatment of 50 ppm THPS + 150 ppm D-mix gradually decreased from the first day during the biofilm removal test. The combination of 50 ppm THPS + 150 ppm D-mix achieved lower corrosion rate compared with the 50 ppm THPS alone treatment. The LPR results corroborated with the weight loss shown in Figure 3.
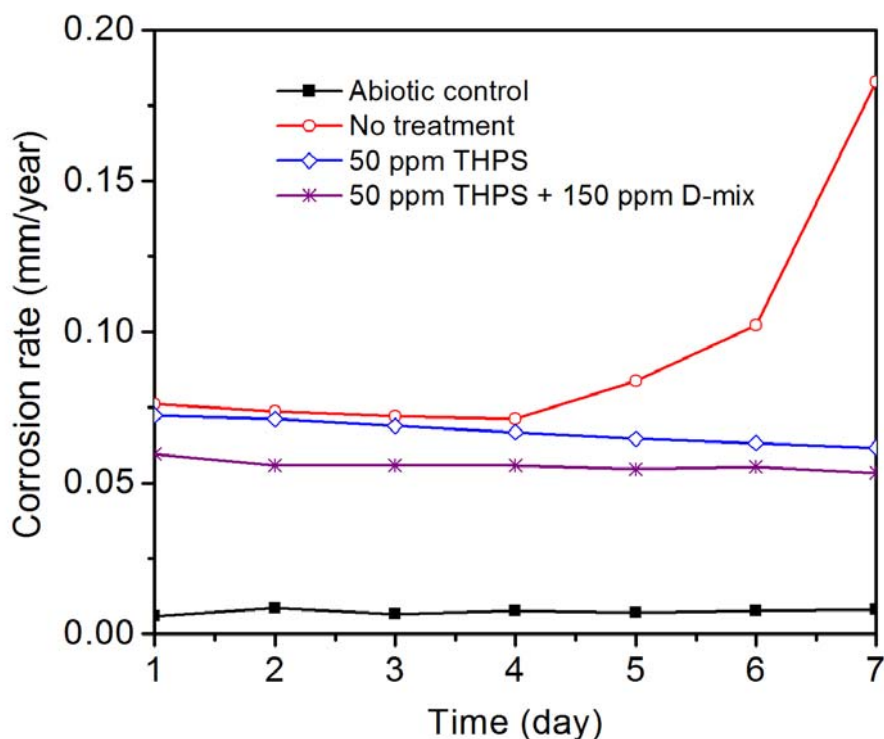
Figure 7. Variation of LPR corrosion rates under different conditions vs. time during additional 7 days of incubation.

EIS is another nondestructive technique that may be applied to study MIC.[22] It was found that the repeated use of EIS did not harm the biofilms and caused no change in the OCP.[23] The EIS analyses were carried out under a stable OCP. Nyquist plots of the coupons exposed to different treatments vs. incubation time are shown in Figures 8-9. The impedance of the abiotic control was significantly higher than the others in the inoculated media. The impedance in the biocidal treatments were higher that than the no treatment control. After the additional 7-day incubation, the Nyquist plot diameter of the no treatment control became significantly smaller compared to the other cases. The Nyquist plot diameter in the treatment of 50 ppm THPS + 150 ppm D-mix was larger than that of the 50 ppm THPS alone treatment. These results suggested that the addition of D-amino acids enhanced the charge transfer resistance and decreased the corrosion rate.
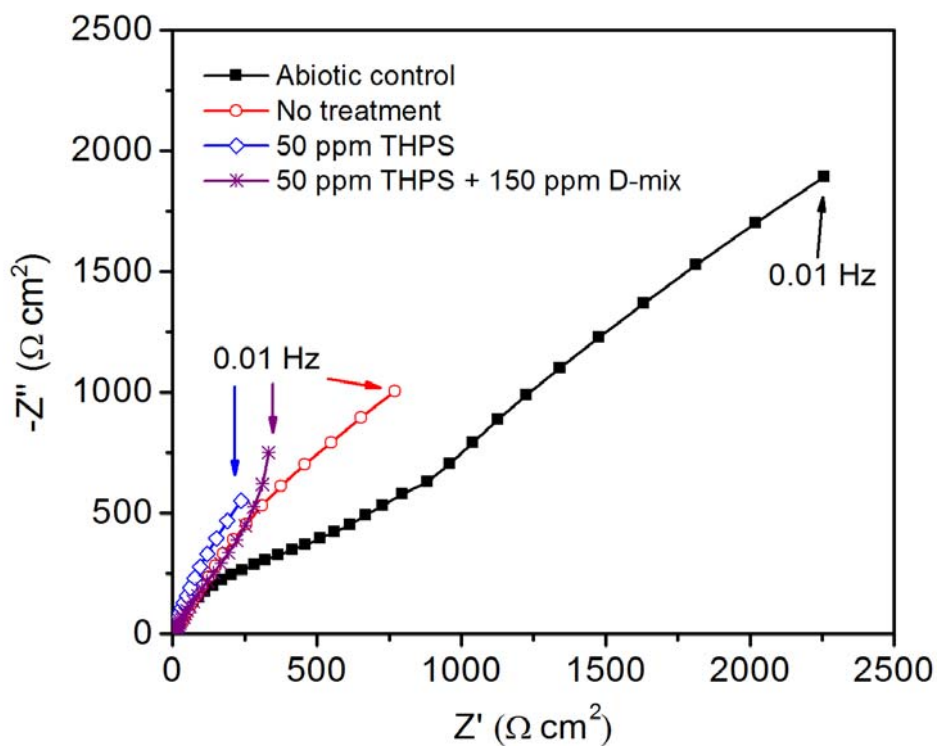
Figure 8. Nyquist plots for coupons under different treatments on the 4th day during additional 7 days of incubation.
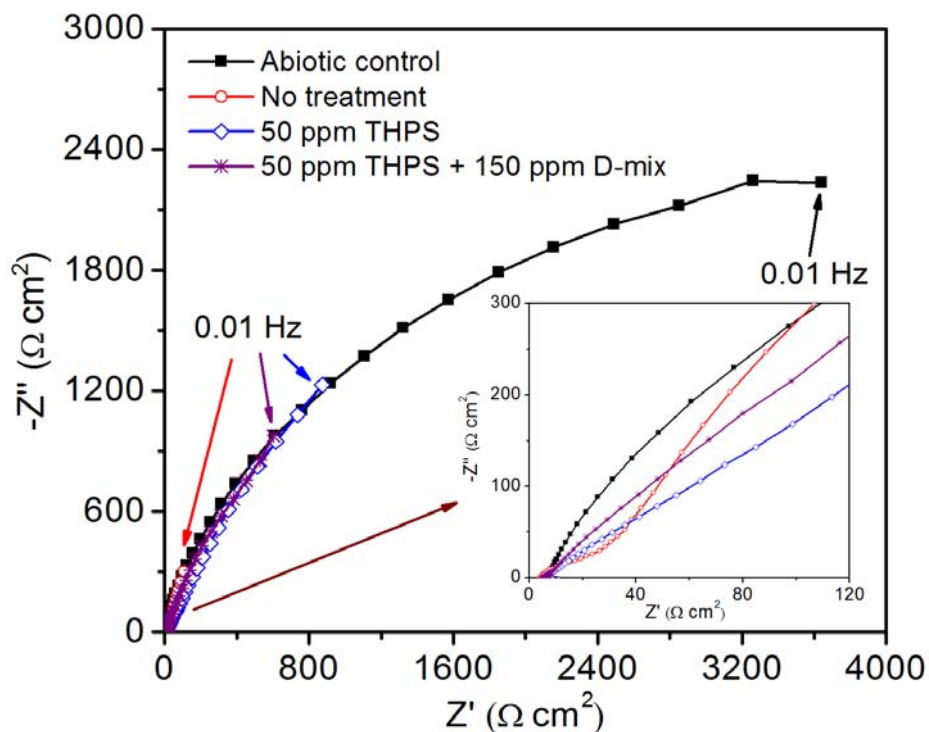

Figure 9. Nyquist plots for coupons under different treatments on the 7th day during additional 7 days of incubation.

CONCLUSIONS

The results in this work showed that a mixture of D-amino acids had good compatibility with EOR chemicals and it enhanced 50 ppm THPS in the biofilm removal test against a corrosive field biofilm consortium. The combination of 50 ppm THPS + 150 ppm D-mix achieved one extra log reduction in SRB and GHB sessile cell counts compared with using 50 ppm THPS alone. In addition, the combination led to a lower weight loss and a smaller maximum pit depth. The electrochemical corrosion test results were consistent with weight loss data.

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