Paper No.
265

CORROSION 94
The Annual Conference and Corrosion Show
Sponsored by NACE International

MIC OF MILD STEEL IN OILFIELD PRODUCED WATER

J. S. Luo
P. Angell, D. C. White
Center for Environmental Biotechnology
University of Tennessee
Knoxville, TN 37932-2567

and

I. Vance
BP Research
Warrensville Research Center
Cleveland, OH 44128

ABSTRACT

The effect of thermophilic anaerobes upon corrosion of AISI 1020 carbon steel in both natural and synthetic oilfield produced water was investigated. Electrochemical techniques such as: open circuit potential, linear polarization resistance, and electrochemical impedance spectroscopy associated with viable bacterial cell counts were applied to evaluate microbiologically influenced corrosion. The effect of glutaraldehyde upon MIC was also studied. Presence of thermophilic anaerobes in the produced water enhanced the corrosion of mild steel, and addition of glutaraldehyde in the water increased the corrosion rate during a short-term exposure (time < 5 hours).

Keywords: microbiologically influenced corrosion (MIC), oilfield produced water, thermophilic anaerobes, glutaraldehyde treatment.

INTRODUCTION

Microbiologically influenced corrosion (MIC) has been identified as a problem in oilfield systems during the past several years. It was reported[1] that microorganisms are associated with three deleterious effects in oilfield operations: i) corrosion of piping and equipment, ii) plugging

of the injection or disposal wells, and iii) souring of the fluids and the reservoir. A comprehensive review of MIC and biofouling in oilfield equipment[2] suggested that corrosion problems mainly arise from the presence of sulfate-reducing bacteria (SRB), slime-forming bacteria, iron-oxidizing bacteria, acid-producing bacteria, and other miscellaneous organisms, including algae, sulfur bacteria, yeasts, and molds. It was proposed[3-5] that the mechanisms of MIC can be categorized into three groups: i) production of differential aeration and concentration cells by biofilm formation resulting from the availability of dissolved oxygen at the metal/solution interface, ii) production of acidic metabolites, i.e., organic and/or inorganic acids or the end products of fermentation growth by bacteria, and iii) interference in the cathodic process under oxygen free conditions by obligate anaerobic bacteria and their metabolic sulfides.

In oil fields, corrosion problems have traditionally been thought to be associated with sulfate-reducing bacteria. However, other microbial species should also be considered to contribute to or possibly directly cause corrosion and well plugging. It is believed that mixed populations of bacteria contained in a biofilm are the most damaging[2]. The establishment of a biofilm on metal surfaces allows the creation of an anaerobic environment at the base of the film[6]. Anaerobes further exacerbate the corrosion by production of corrosive metabolites or by depolarizing cathodes. In the present study, thermophilic anaerobes were cultured from oilfield produced water and corrosion coupons at 60 °C; and MIC of mild steel was investigated by electrochemical techniques associated with viable bacterial cell counts. Specific attention has been focused upon the effect of glutaraldehyde upon MIC in the produced water.

EXPERIMENTAL PROCEDURE

Preparation of Microbial Cultures. Bacterial samples from oilfield produced water and corrosion coupons were cultured in two media: thioglycolate general anaerobe medium and lactate/acetate SRB medium. The thioglycolate general anaerobe medium, for general anaerobic bacteria (GAB) growth and enumeration, consists of (in g/l) yeast extract 5.0, casitone 15.0, dextrose 5.5, NaCl 2.5, L-cystine 0.5 and sodium thioglycolate 0.5. The lactate/acetate SRB medium, for sulfate reducing bacteria (SRB) growth and enumeration, contains (in g/l) sodium acetate 2.8, sodium lactate (60% solution) 2.91, yeast extract 1.0, ascorbic acid 0.1, $MgSO_4.7H_2O$ 0.5, Na_2SO_4 0.5, K_2HPO_4 0.5, NH_4Cl 0.5, $FeSO_4.7H_2O$ 0.1, NaCl 7.0 and sodium thioglycolate 0.1. The cultures were incubated at 60 °C for 4 days prior to inoculation and resulted in 1.0E+08 cells/ml GAB and 1.0E+05 cells/ml SRB.

Specimen. The test specimens, 16 mm diameter disks, were AISI 1020 carbon steel. The specified composition of this steel was 0.20 C, 0.47 Mn, 0.012 P, and 0.013 S, wt%. A four-sided working electrode[7] was fabricated to simplify experimental design by combining four steel disks into one probe as illustrated in Figure 1. It was reported that no interferences or crosstalk were observed between electrodes, and the interfacial chemistry at the metal/solution interface was reproducible[7].

Electrochemical Cell. A sterilized, flow-through electrochemical cell, as shown in Figure 2, consists of a 600 ml glass beaker and includes 1) a four-sided working electrode probe, 2)

a Pt coated Nb mesh counter electrode, 3) a saturated calomel reference electrode (SCE), 4) a solution inlet, 5) a solution outlet, 6) a 0.2 μm filter ventilation port and 7) a gas dispersion tube. Test solutions consisted of both natural and synthetic oilfield produced water. The synthetic produced water contained (in g/l) NaCl 17.03, Na_2SO_4 0.725, $CaCl_2$ 0.637, $MgCl_2.6H_2O$ 1.67, B_2O_3 0.354, KCl 0.2, $SrCl_2.6H_2O$ 0.064, $BaCl_2.2H_2O$ 0.003, KI 0.016, $NaHCO_3$ 2.26, $Na_2S_2O_5$ 0.434, $NaCH_3COOH$ 0.237 and NaC_2H_5COOH 0.033.

Test Procedures. Prior to the start of each experiment, all specimens were wet polished in sequence with 240, 400 and 600 grit SiC paper, ultrasonically cleaned with distilled water, degreased with acetone and sterilized with 70% alcohol for 20 minutes. The electrochemical cell was sterilized with ethylene oxide using the precautions defined previously[8]. All inlets and outlets of the cell were autoclaved to achieve sterilization. The synthetic produced water was sterilized by using capsule filters in sequence with 0.45 and 0.2 μm membrane filters. The pH of the water after adjustment with 0.1 M NaOH was 7.5. To achieve adequate anaerobic conditions, a stream of 5% hydrogen and 95% nitrogen gas was passed through a heated copper column and sparged in the test waters for 24 hours before starting an experiment. The redox potential of the waters after this period of degassing was measured at -150$\pm$10 mV. During the test period, test cells were inoculated with bacteria several times to achieve adequate microbial populations and accelerate MIC testing. The solution temperature was controlled between 55 and 60 °C by means of a water bath. The anaerobic conditions were maintained by continuously pumping 5% H_2 + 95% N_2 gas to the headspace of the test cells. A dual-channel peristaltic pump was used to control solution flow rate at 60$\pm$5 ml/hr.

Open circuit potential (OCP) of test specimens was monitored at intervals of 1 hour by a multimeter via a scanner controlled by a computer. DC measurements were conducted by a potentiostat. For linear polarization resistance, current densities were monitored within $\pm$30 mV versus OCP with a scan rate of 0.17 mV/sec. Electrochemical impedance spectroscopy (EIS) analysis was performed by a microcomputer, a frequency response analyzer, and a potentiostat. Sinusoidal potentials of 5 mV were applied between 5 mHz and 10 KHz at 5 steps/decade.

Bacteria cell counts from bulk solutions and specimen surfaces were performed by acridine orange direct counts (AODC) after fixation in 2.5% glutaraldehyde[9]. The most probable number technique[10] (MPN) was employed to calculate the total number of viable GAB and SRB.

A comparison of MIC of AISI 1020 carbon steel in natural produced water and the water containing an addition of lactate/acetate nutrients, i.e., a mixture of 90% natural produced water and 10% lactate/acetate SRB medium, hereafter referred to as PWLA, was investigated. To enhance microbial populations in the PWLA, inoculation of 30 ml of 4-day old GAB and SRB cultures into electrochemical cells was performed at specimen exposure time of 0 hour.

To investigate the effect of glutaraldehyde as a biocide upon corrosion of AISI 1020 carbon steel in oilfield produced water, experiments were performed in synthetic produced water containing GAB and SRB at 60 °C. Previous study[11] demonstrated that corrosion of mild steel in synthetic produced water is enhanced by the presence of thermophilic anaerobes after 640 hours of exposure. Therefore, prior to glutaraldehyde addition, the steel was immersed in the

inoculated synthetic produced water for 640 hours. After 640 hours, different doses of glutaraldehyde were added to electrochemical cells followed by continuous treatment for 5 hours. To study the corrosion behavior of treated coupons, specimens were left in contact with glutaraldehyde for another 20 hours. Glutaraldehyde treatment was carried out in this study at different concentrations: 0, 50, 150 and 250 ppm.

RESULTS AND DISCUSSION

Corrosion Behavior of Mild Steel in Natural Produced Water. Figure 3 shows the OCP versus time plots for specimens in the natural produced water and PWLA for up to 720 hours. A sharp increase in OCP from -775 mV (SCE) to -525 mV (SCE) was observed for a specimen in the natural produced water after 500 hours of exposure, while in PWLA, the OCP maintained steady at -800 mV (SCE) throughout the tests. Visual examination of specimens upon termination of the experiments indicated that elongated tubercles, as shown in Figure 4, were scattered on the coupon surfaces exposed to the natural produced water, but a relatively clean surface, as shown in Figure 5, was obtained for specimens immersed in PWLA.

The average corrosion rate, in terms of the reciprocal of polarization resistance Rp, measured by DC linear polarization resistance technique ($\pm$30 mV vs. OCP) for specimens in the natural and PWLA is given in Figure 6 as a function of time. During the first 500 hours, little corrosion was observed for specimens in both the natural water and PWLA. However, a significant increase in corrosion rate occurred for a specimen in the natural produced water after 500 hours of exposure. Such an observation is consistent with the OCP behavior as given in Figure 3.

It is generally recognized that under anaerobic conditions, there is very little, if any, corrosion of steel in neutral or alkaline solutions[12]. However, biotic hydrogen consumption can lead to corrosion of mild steel in anaerobic environments due to cathodic depolarization. In the natural produced water, the presence of an anaerobic biofilm produced by GAB and SRB associated with production of iron sulfide on the coupon surface could result in formation of tubercles and increased corrosion rates. However, additional nutrients in PWLA enhanced planktonic bacterial growth, and less extracellular polymeric substances production caused thin biofilm formation and little corrosion of the steel. AODC supported this hypothesis that there are 5.0E+07 cells/cm^2 bacteria on the coupon surface and 7.0 E+06 cells/ml in the bulk solution for a specimen in the natural produced water after 720 hours of exposure, while 2.0E+06 cells/cm^2 and 3.0E+07 cells/ml are found as a specimen was exposed to PWLA.

Figures 7-8 show the Bode plots measured by EIS for specimens in the natural produced water and PWLA at various immersion times. It was noticed that the phase angle at the lowest frequency (5 mHz) for a specimen in the natural produced water (Figure 7) increased from 15 to 40 degrees after 30 days of exposure. While in PWLA (Figure 8), the angle varied between 15 and 25 degrees. Previous studies[11,13] suggested that an increase of the phase angle at the lowest frequency may reflect the formation of a biofilm. Therefore, it is possible to infer that a thicker surface film (including biofilm) formed on the coupon exposed to the natural produced

water, but less film accumulation occurred for a specimen immersed in PWLA. Such observations suggest that at a constant low flow rate a high nutrient concentration enhanced the growth of the organisms in the bulk liquid, thereby resulting in thin biofilm formation on the coupon surface[14].

MIC of Mild Steel in Synthetic Produced Water. To confirm bacteria contribute to the corrosion of mild steel in natural produced water, AISI 1020 carbon steel was immersed in the sterile synthetic produced water with and without inoculation of bacteria. Inocula of 20 ml of 4-day old GAB and SRB cultures into test cells were performed at specimen exposure time of 0, 120, 240, and 360 hours.

Figure 9 shows the OCP versus time plots for specimens exposed to the sterile synthetic produced water and the water containing bacteria. In both cases, the OCP of specimens remained approximately -800 mV (SCE) throughout the experiments. The average corrosion rate, in terms of the reciprocal of Rp, for specimens in both waters is given in Figure 10 as a function of time. It is apparent that the corrosion rate in the inoculated water increased with increasing exposure time, while a relatively low and constant corrosion rate appeared in the sterile control. Such an observation is consistent with microbiologically influenced corrosion[12,13]. Viable cell counts by MPN from coupon surfaces indicated that 1.0E+06 cells/cm^2 GAB and 1.0E+02 cells/cm^2 SRB were detected for a specimen in the inoculated water after 640 hours of exposure. It demonstrated that both GAB and SRB play an important role to influence steel corrosion in oilfield produced water.

Figures 11-12 present the phase angle versus frequency plots for specimens in the sterile and inoculated synthetic produced water at various immersion times. In the sterile control (Figure 11), little or no changes of phase angle at the lowest frequency (5 mHz) occurred, while in the water with the inocula of bacteria (Figure 12), an increase in the angle (at 5 mHz) was observed. It was reported[15] that the combination of microbial films and corrosion products often encountered in MIC causes the impedance to become very high at low frequencies, thus shifting the maximum phase angle to low frequencies. As a result, an increase of the phase angle at the lowest frequency could reflect the formation of biofilms.

Effect of Biocide upon MIC of Mild Steel in Synthetic Produced Water. Tables 1 and 2 show the effect of glutaraldehyde on the planktonic bacteria (GAB and SRB) measured by MPN in inoculated synthetic produced water before and after treatment. In general, 1.0E+07 cells/ml to 1.0E+08 cells/ml GAB and 1.0E+02 cells/ml SRB were detected from bulk solutions after 640 hours of exposure, while the addition of glutaraldehyde resulted in a decrease in cell numbers. For the 50 ppm glutaraldehyde treatment, planktonic GAB decreased from approximately 1.0E+07 cells/ml to 1.0E+03 cells/ml after 5-h treatment and dropped below the detection limit (1 cell/ml) at the end of the experiment (experiments were stopped 20 hours after the 5-h treatment). At 150 ppm and 250 ppm glutaraldehyde, the continuous 5-h treatment immediately reduced the GAB level to less than 1 cell/ml. Moreover, no SRB were cultured from the solutions treated with glutaraldehyde for 5 hours. Sessile bacterial numbers recovered from coupon surfaces at the end of experiments are given in Table 3. Essentially no bacteria were cultured from the coupon surfaces after glutaraldehyde treatment. These results indicated that glutaraldehyde is an effective biocide, acting against both planktonic and sessile bacteria in

synthetic produced water.

Figure 13 presents the OCP versus time plots for specimens in the inoculated synthetic produced water before, during and after glutaraldehyde treatment. In all cases, OCP was relatively constant before glutaraldehyde treatment but increased upon addition, followed by a decay to another steady state value. The corrosion rate of coupons for these experiments is shown in Figure 14 as a function of time. In general, corrosion rate increased upon addition of glutaraldehyde, and the increment of corrosion rate in the first 5 hours increased with increasing the concentration of glutaraldehyde. However, a slight decrease in corrosion was observed after a further 20-h contact time. A possible explanation could be that chemical reaction of glutaraldehyde in the test systems dominated corrosion process during the treatment. At a low dose of glutaraldehyde treatment the lack of penetration of glutaraldehyde through the biofilm could result in the lack of change in the corrosion rate.

Figures 15-17 show the phase angle versus frequency plots for specimens treated with different concentrations of glutaraldehyde at various immersion times. Before treatment, the variation of the plots for specimens is likely due to different interfacial conditions between coupons and solutions, since the accumulation of biofilms and the corrosion process were independent in each test cell. However, it is interesting to note that a decrease in the phase angle at the lowest frequency (5 mHz) took place after 5-h treatment, and the decrement was proportion to the concentration of glutaraldehyde. It may suggest that defects or damage of surface films (including biofilms) occurred during glutaraldehyde treatment. A high concentration of glutaraldehyde was able to interfere with bacterial activities on the coupon. Furthermore, a return of the phase angle (at 5 mHz) back to the original nontreated value at the end of experiments could indicate that an equilibrium condition has been reached between glutaraldehyde and coupon surfaces after the 20-h contact time.

CONCLUSIONS

1. Corrosion of mild steel in synthetic oilfield produced water is enhanced by the presence of thermophilic anaerobes.

2. Addition of the lactate/acetate nutrient to natural produced water did not enhance MIC of mild steel. Thin biofilm formation on the treatment amended coupon surface could be a reason contributing to the result.

3. Glutaraldehyde works as a biocide in the synthetic oilfield produced water. However, the corrosion rate of mild steel increased upon glutaraldehyde addition for a short-term exposure (time $<$ 5 hours).

ACKNOWLEDGEMENT

The authors are indebted to BP America Inc. for financial support and the supply of bacterial samples as well as natural oilfield produced water.

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Table 1. Planktonic GAB measured by MPN before and after treatment.

Glutaraldehyde Treatment (ppm)	Planktonic GAB (cells/ml)		
	Before treatment	After 5-h	After 25-h
0	1.0E+07	1.0E+06	1.0E+06
50	1.0E+07	1.0E+03	<1
150	1.0E+08	<1	<1
250	1.0E+07	<1	<1

Table 2. Planktonic SRB measured by MPN before and after treatment.

Glutaraldehyde Treatment (ppm)	Planktonic SRB (cells/ml)		
	Before treatment	After 5-h	After 25-h
0	1.0E+02	1.0E+01	1.0E+02
50	1.0E+02	<1	<1
150	1.0E+02	<1	<1
250	1.0E+02	<1	<1

Table 3. Sessile bacteria from coupon surfaces measured by MPN at the end of experiments.

Glutaraldehyde Treatment (ppm)	Sessile Bacteria (cells/cm^2)	
	GAB	SRB
0	1.0E+06	1.0E+02
50	<1	<1
150	<1	<1
250	<1	<1

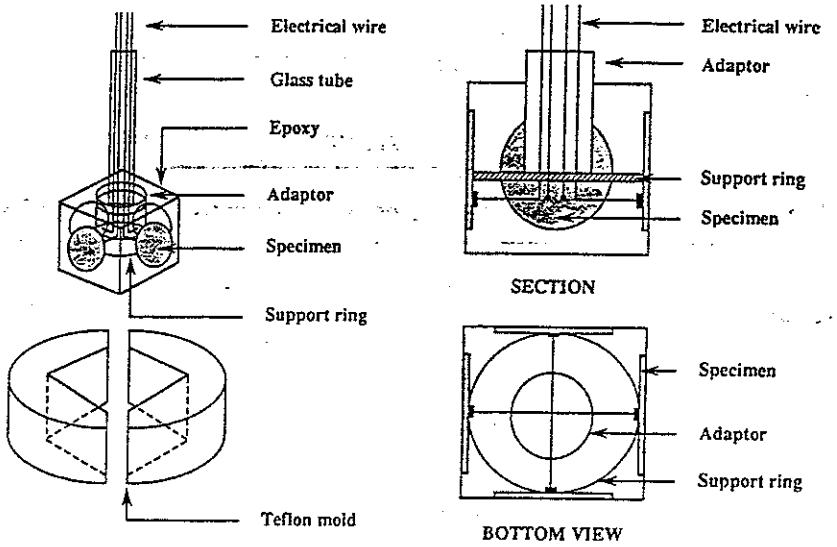

FIG. 1. Schematic illustration of a four-sided electrode probe.

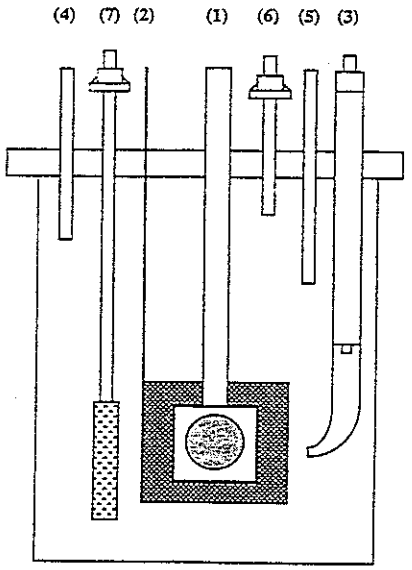

FIG. 2. Arrangement of electrochemical cells.

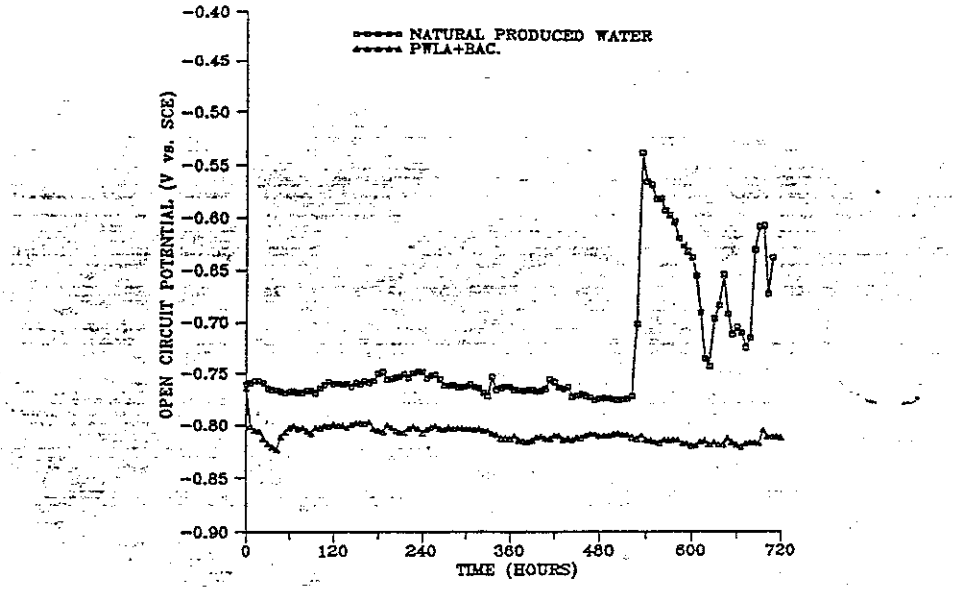

FIG. 3. OCP versus time plots for specimens in the natural produced water and PWLA + bacterial medium.

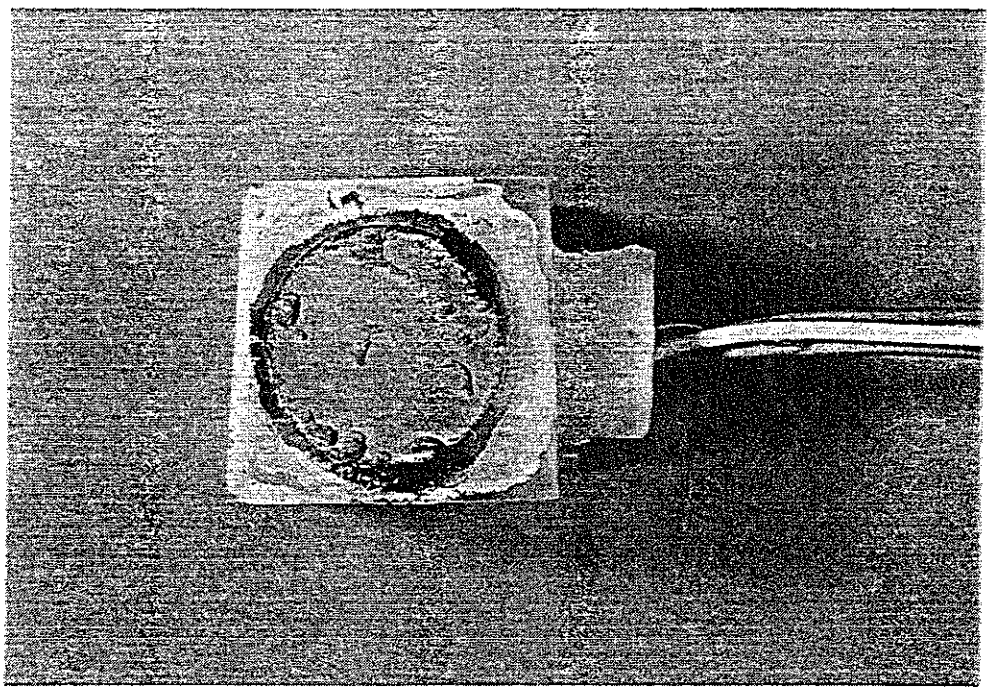

FIG. 4. Photograph of a specimen in the natural produced water after 720 hours of exposure.

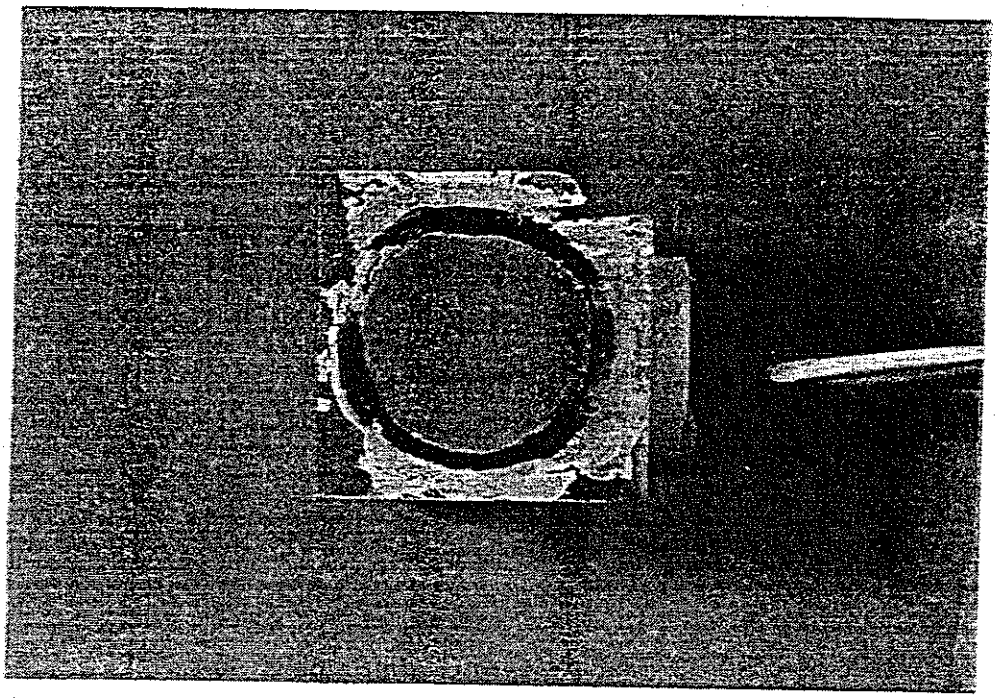

FIG. 5. Photograph of a specimen in PWLA + bacterial medium after 720 hours of exposure.

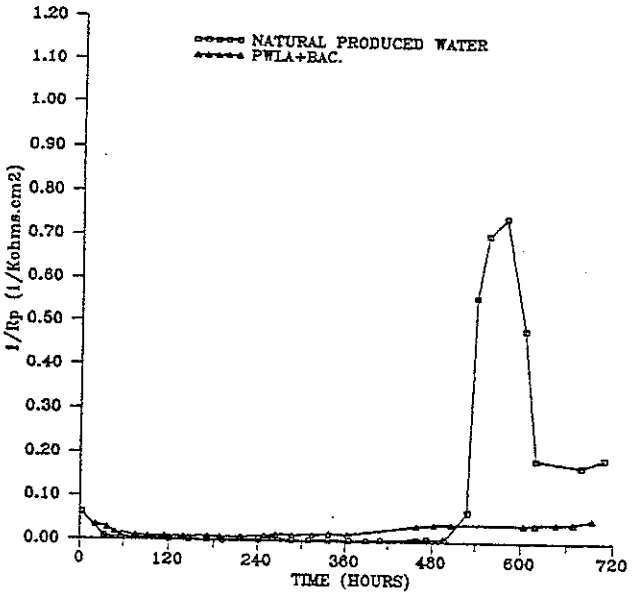

FIG. 6. Corrosion rate, in terms of the reciprocal of polarization resistance, versus time plots for specimens in the natural produced water and PWLA + bacterial medium.

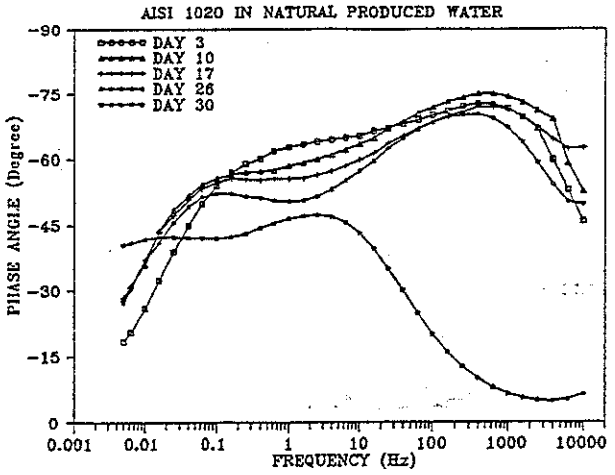

FIG. 7. Bode plots for a specimen in the natural produced water at various immersion times.

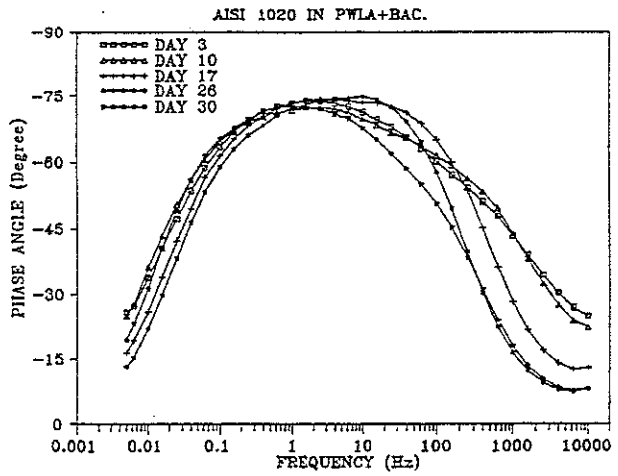

FIG. 8. Bode plots for a specimen in PWLA + bacterial medium at various immersion times.

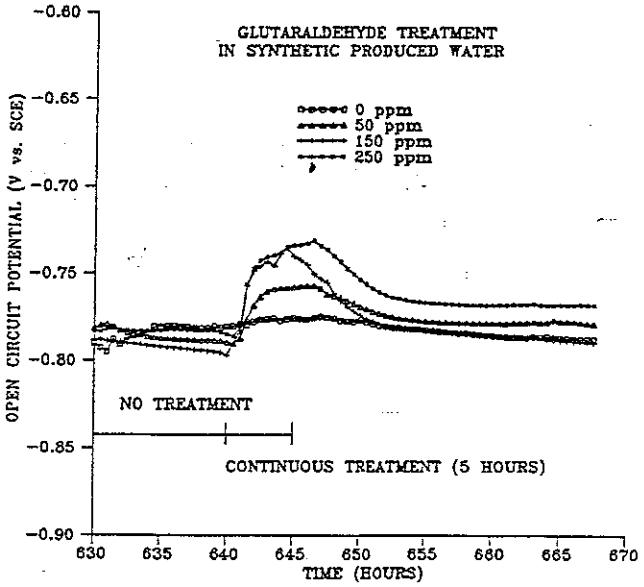

FIG. 13. OCP versus time plots for specimens in the inoculated synthetic produced water before, during and after glutaraldehyde treatment.

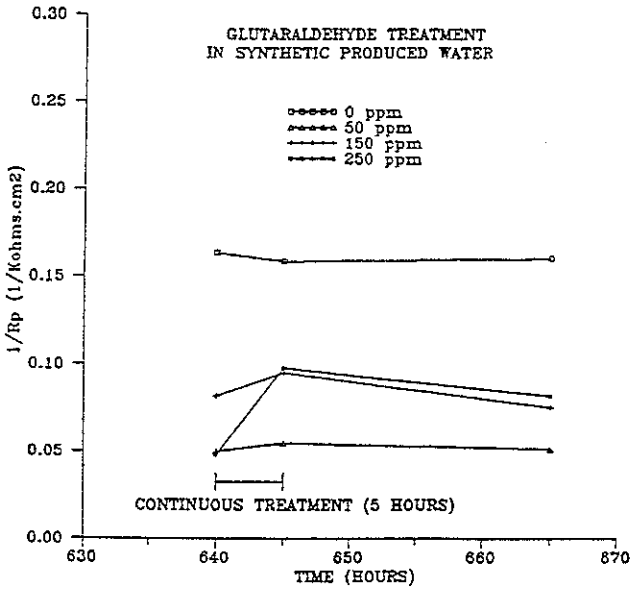

FIG. 14. Corrosion rate, in terms of the reciprocal of polarization resistance, versus time plots for specimens before and after glutaraldehyde treatment.

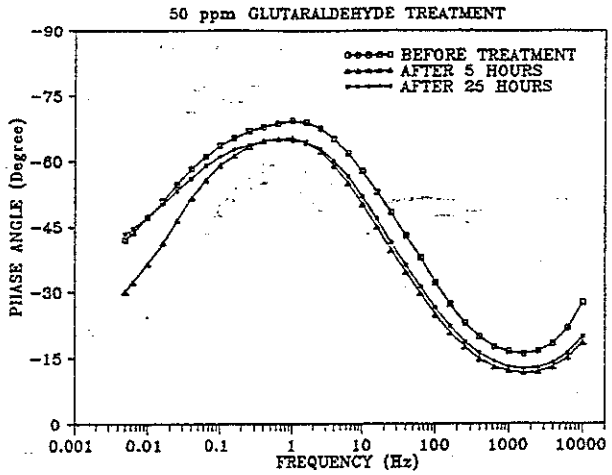

FIG. 15. Bode plots for a specimen in the inoculated synthetic produced water before and after 50 ppm glutaraldehyde treatment.

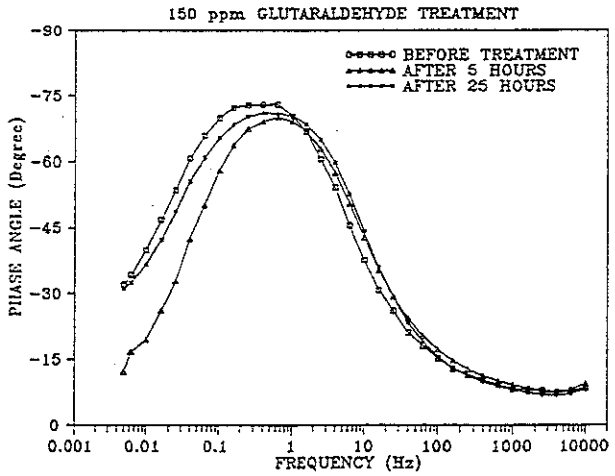

FIG. 16. Bode plots for a specimen in the inoculated synthetic produced water before and after 150 ppm glutaraldehyde treatment.

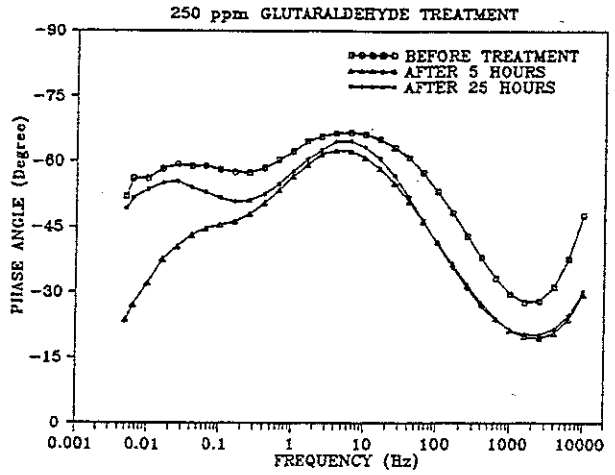

FIG. 17. Bode plots for a specimen in the inoculated synthetic produced water before and after 250 ppm glutaraldehyde treatment.