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A STUDY OF CARBON STEEL CORROSION INHIBITION BY PHOSPHATE IONS AND BY AN ORGANIC BUFFER USING A SCANNING VIBRATING ELECTRODE

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Abstract—The scanning vibrating reference electrode technique (SVET) has been used to map anodic and cathodic currents in solutions over freely corroding type C1020 carbon steel. All solutions contained millimolar concentrations of chloride and were sterilized. The effect of phosphate and an organic buffer on the corrosion of carbon steel in liquid media were studied because they were added to promote bacterial growth. Phosphate acted as an anodic inhibitor in the media, causing initiated pits to repassivate. If initiated pits did not repassivate, for example in a stagnant medium or when crevice corrosion initiated adjacent to the sample coating, the corrosion rates increased and the corrosion remained localized. Increased anodic current resulted in a drop in the open circuit potential and a decrease in the polarization resistance. The results show that phosphate can lead to lower average corrosion rates, than uninhibited steel, but as an anodic inhibitor can also lead to rapid penetration at localized sites.

INTRODUCTION

PITTING corrosion of iron in media containing one millimolar concentrations of chloride and sulfate ions has been studied.[1–3] The results suggested that in this poorly buffered medium, local pH was an important component in pit propagation and spreading of corrosion around the pit. Many aqueous environments are buffered and contain ions which inhibit or facilitate pit propagation. In a sterile medium containing similar concentrations of chloride and sulfate ions, as well as low concentrations of an organic buffer, glucose and other ions, carbon steel coupons remained passive for the nine days of exposure.[4] This was in contrast to the rapid pitting and corrosion propagation of pits observed for the pure iron, in the dilute chloride and sulfate containing media.[1–3] This study was carried out to ascertain, the corrosion inhibition by components in the complex medium used previously,[4] since trace ions can affect the corrosion rates of metals,[5–8] and buffering may be important in preventing the corrosion at pits from spreading.

The scanning vibrating electrode technique (SVET) has been used to obtain current density maps over freely corroding metal samples.[1,9–12] With the SVET, the time variations during localized corrosion can be evaluated without altering the progression of corrosion. Thus, the SVET and other scanning methods[13] provide a useful means for studying corrosion inhibitors.

In this study, the SVET, polarization resistances (R_p), and monitoring the open circuit potential (OCP), were used to study the specific effects of phosphate and an

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organic buffer on the propagation of pits in carbon steel in sterile solutions. The results indicated that phosphate ions in an air-bubbled solution caused repassivation of initiated pits. However, under certain conditions, phosphate addition could lead to highly localized corrosion.

EXPERIMENTAL METHOD

Electrolyte

The medium used in this study contained (in mg l^{-1}) 50 NH_4Cl, 50 $MgSO_4 \cdot 7H_2O$, 5 $CaCl_2 \cdot 2H_2O$, 27 KH_2PO_4, 50 glucose, 50 2-morpholinoethane sulfonic acid (MOPS buffer), and trace minerals (in μg l^{-1}) 0.1 $Na_2MoO_4 \cdot 2H_2O$, 50 $ZnSO_4 \cdot 7H_2O$, 7.7 $MnSO_4 \cdot H_2O$, 2 $CuSO_4 \cdot 5H_2O$, 1 $CoCl_2 \cdot H_2O$, 0.8 $NaB_4O_7 \cdot 10H_2O$, 0.5 $NiSO_4$. This medium has been used in a previous study of microbial influenced corrosion,[4,14] and was complex due to the growth requirements for the bacteria. The concentrated components of the medium were omitted as indicated in the results. All solutions were sterilized by autoclaving for 20 min.

Metal samples and electrochemical cells

The metal coupons of C1020 carbon steel were supplied by Metal Samples (Munford, AL). The steel contained; 0.17 C, 0.42 Mn, 0.009 P and 0.006 S, wt%. The coupons, with a spot welded electrical connection, were embedded in epoxy and finished with 600 grit silicon carbide paper. Thin, approximately 75 μm, pressure sensitive tape (3M Co. no 92) was used to insulate the sample except for an area in the center of the coupon approximately 25 mm^2. Microshield lacquer (Pyramid Plastics, Inc., Hope, AR) was painted at the edge of the tape to reduce crevice corrosion. For experiments where only the open circuit potential (OCP) was monitored over time, the working electrode and a salt bridge to a saturated calomel reference electrode immersed in a salt bridge were suspended in a beaker of medium. The media were stirred with a Teflon coated magnetic bar, controlled by a magnetic stirrer. The analog output of OCP from an electrometer was recorded by a strip chart recorder. The electrochemical cell for the SVET experiments had a working volume of 15 ml and contained a saturated calomel reference electrode emersed in a salt bridge, and a platinum wire for a counter electrode.

Current density maps

The vibrating electrode used to scan the working electrode consisted of an insulated platinum wire, 0.1 mm in diameter. The platinum wire was attached to a piezoelectric reed which was activated by applying a 10 V rms signal to the reed at 200 Hz, as described previously.[9,10] The peak to peak vibration was 0.04 mm. The vibrating electrode was positioned 0.09 mm from the working electrode surface. The alternating signal was analysed with a PAR model 124A lock-in amplifier with a model 116 plug-in unit, and a computer controlled data acquisition unit. The surface of the working electrode was scanned by moving the cell underneath the electrode in 0.2 mm increments with computer controlled stepper motors. The output voltage from the lock-in amplifier was calibrated with a known uniform current density.

Polarization resistance

For determining polarization resistance (R_p), the potential of the working electrode was ramped $\pm$25 mV around the open circuit potential at a rate of 5 mV s^{-1}. Polarization resistance was determined by the slope of the potential vs current line.

EXPERIMENTAL RESULTS AND DISCUSSION

OCP and corrosion of carbon steel in unbuffered media

The purpose of this study was to determine the effects of the more concentrated solution components on the early stages of corrosion of carbon steel in sterile solutions. The presence of buffers and phosphates are added to assist the growth of bacteria, but may themselves affect corrosion.

The carbon steel (OCP) in a medium containing 1 mM chloride and 1 mM sulfate is shown in Fig. 1, curve (A). The OCP decreased rapidly to approximately −510 mV(SCE) following immersion of the steel in the medium, and corrosion products were observed as the OCP decreased. The initial rapid decrease in OCP was followed by a slow decrease to approximately −540 mV(SCE), and then by another fairly rapid drop to approximately −620 mV(SCE), and then a slow continual decrease.

The results of the carbon steel corrosion in 1 mM NaCl and Na_2SO_4 solution were similar to those observed for pure iron in the same solution, as indicated by SVET and OCP vs time.[1] The OCP decreased rapidly to approximately −500 mV(SCE), and more slowly to −550 mV(SCE), as distinct pit sites remained localized. Below −550 mV(SCE) the anodic sites began to spread rapidly until the potential dropped to approximately −650 mV(SCE), where the size of the areas of corrosion began to stabilize.[1] The OCP was also similar in shape to those observed by Gatty and Spooner.[2] It therefore is apparent that the shape of the OCP decay curves remain the same but the rates change with many variables including surface preparation,[3] steel composition (compare Ref. 1 and Fig. 1A), and solution composition.

A map of pH, 0.04 mm over the iron surface, showed values which ranged from less than 6 over the anodic sites to greater than 10 over the cathodic sites,[1] suggesting that pH plays an important role in the spreading of anodic sites. The pH at the cathodic areas is increased by hydroxide formed during oxygen reduction, while the pH around the anodic areas is decreased by hydrolysis of ferrous or ferric ions. The model proposed for iron corrosion,[1] in the dilute chloride and sulfate solution suggested the spreading of the anodic area occurs as the potential and pH drop to values intersecting the value for the transition of passivity to general corrosion on the pH/potential diagram. As with pure iron, the pitting of carbon steel in unbuffered media may not be a serious problem, since the initial pitting corrosion developed into fairly uniform attack over most of the surface of the sample.

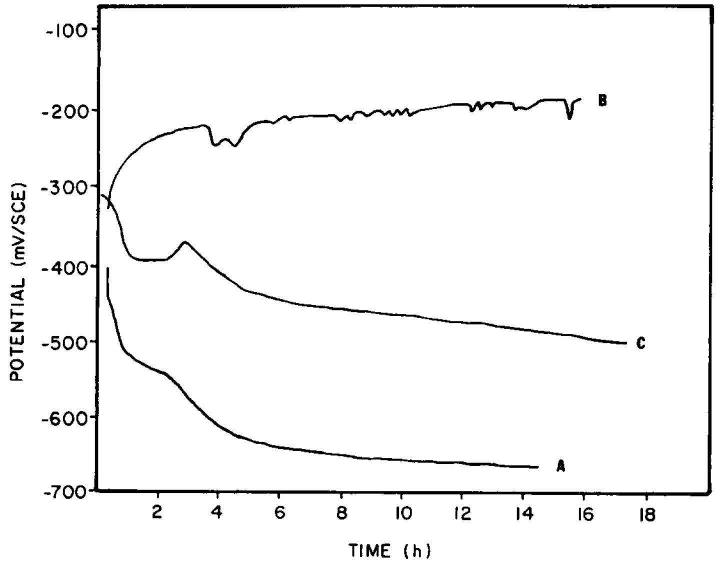

Fig. 1. Open circuit potential [mv(SCE)] over time for carbon steel electrode. Curve (A), carbon steel in 1 mM chloride and sulfate solution. Curve (B), carbon steel in stirred complex medium containing MOPS, an organic buffer, and ions. Curve (C), carbon steel in unstirred complex medium.

OCP in complex medium

In a previous study, with the same sterile complex medium used in this study, containing phosphate and an organic buffer, the OCP remained at approximately −200 mV(SCE) for the nine days of exposure, and little corrosion product was observed on the steel.[4] Figure 1, curve (B) shows the results of OCP vs time for the stirred complex medium. The OCP increased from approximately −350 mV(SCE) to approximately −200 mV(SCE). Drops in OCP of approximately 20 mV, followed by increases in OCP were observed throughout the experiment. The potential transients are characteristic of pit initiation, followed by pit repassivations.[13] Pit initiation and repassivation in this medium has been characterized by the SVET analysis in the absence and in the presence of active bacteria.[14]

Current density maps in unstirred medium

The increase in OCP was not observed when the complex medium was not stirred (Fig. 1, curve C). The OCP decreases rapidly to −400 mV(SCE), followed by a slow decrease in the OCP. The SVET was used to analyse the carbon steel corrosion in the unstirred complex medium. The results showed that four anodic sites formed after 0.08 h exposure of the steel to the medium (Fig. 2A). Two of the anodic sites were small, but could be detected by decreasing the scale of the z-axis. The corrosion pits were similar in appearance to pits previously described.[1] After 0.3 h of exposure, all but one anodic site close to the stop-off became inactive (Fig. 2B). This pit remained active throughout the remainder of the experiment (Fig. 2C). The OCP was monitored throughout this experiment (Fig. 2D). The OCP dropped with time, showing the same trend as curve (C), Fig. 1.

Polarization resistance measurements were made at the times indicated by the vertical lines in Fig. 2(D). The increase in anodic current density, determined by SVET, and the drop in OCP correlated with a decrease in the polarization resistance of the samples. After 2 h, when the potential of the steel in the unstirred medium had decreased to approximately −400 mV(SCE), the R_p was 3500 ohm cm^2. The area and the magnitude of the anodic site increased, as determined by the SVET, and the R_p decreased to 1500 ohm cm^2, as the potential continued to drop to approximately −500 mV(SCE) at 3.7 h.

Omission of MOPS buffer and glucose or phosphate

In order to establish the role of components of the complex medium on the pitting corrosion of the carbon steel, different combinations of phosphate and the organic buffer were omitted from the medium. The media were stirred in these experiments. Figure 3, curve (A) shows the OCP of the steel when the glucose, MOPS buffer, and phosphate were omitted from the medium. The OCP rapidly dropped to −450 mV(SCE) in less than 1 h and slowly to −590 mV(SCE) after 16 h. Figure 3, curve (B), shows the OCP of the stirred medium when phosphate was omitted and glucose and MOPS buffer were included. The potential dropped less rapidly after immersion than in case 3(A), but also reached −590 mV(SCE) in about 16 h. Figure 3, curve (C), shows the OCP when the glucose and the MOPS buffer were omitted, but the phosphate was included. The OCP initially increased from −320 mV(SCE) to −250 mV(SCE). The OCP remained around −300 mV(SCE) and fluctuations due to pit initiation could be observed after 11 h.

The results of this study suggested that buffering may contribute to localized

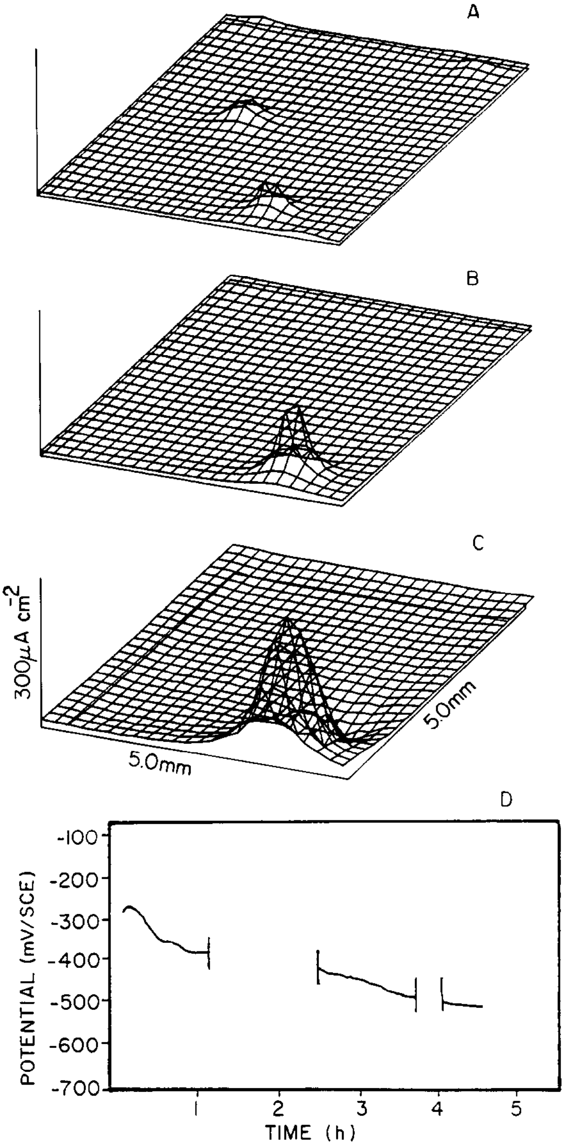

FIG. 2. Current density maps over carbon steel in unstirred complex medium: (A) 0.08 h; (B) 0.3 h; (C) 3.7 h; (D) open circuit potential for carbon steel in unstirred medium. Vertical lines indicate times at which polarization resistance measurements were made.

corrosion. The OCP diagrams for steel in medium containing MOPS buffer (Fig. 3, curve B) and for steel in medium containing MOPS buffer plus phosphate (Fig. 1) showed a slower drop in OCP than for the steel in 1 mM chloride and sulfate solution. This indicated that the corrosion was more localized for longer periods of time in the buffered solutions. This effect was more pronounced in the presence of phosphate than in the presence of MOPS, suggesting that phosphate had a greater effect on either pH or on dissolution kinetics. Hence it appears that in a medium which was well buffered, the buffering capacity of the medium inhibits the spreading of the pits,

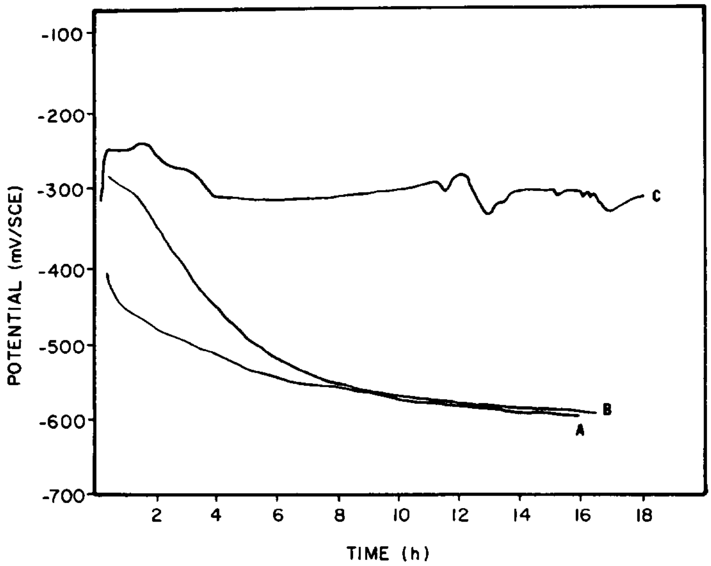

Fig. 3. Open circuit potential for carbon steel in stirred incomplete medium. Curve (A) carbon steel in medium lacking glucose, MOPES and phosphate. Curve (B) carbon steel in medium lacking phosphate. Curve (C) carbon steel in medium lacking glucose and MOPES.

by confining the low pH to the pit. This buffering capacity reduces spreading of the actively corroding areas and intensifies localized corrosion, rather than leading to a more general corrosion.

Current density maps in stirred complex medium

The complex medium was continuously bubbled with air to stir the solution during SVET analysis. In all but one experiment, pits initiated and the steel repassivated in stirred or aerated medium (Fig. 1, Ref. 14). The preferred location of the pits were adjacent to the lacquer. In one experiment, the lacquer coating was undermined as corrosion developed.

The results of the SVET analysis and the OCP vs time for the stirred medium where crevice corrosion developed are shown in Fig. 4. Figure 4 shows active pits at different locations for limited times during the first 9 h of exposure. After 9 h of exposure, one pit did not repassivate, but continued to grow over the remainder of the experiment. Figure 4(C) shows the position of the one anodic site, after 10 h of exposure. Figure 4(D) shows the current density map for the same sample after 22 h of exposure. The anodic site remained active in the same location, however, the magnitude of the current density increased. The OCP for this sample is shown in Fig. 4(E). The first 9 h of exposure showed potential transients due to pit initiation and repassivation.[13] After 9 h of exposure the OCP stabilizes at a value of approximately −340 mV(SCE), and the fluctuations stopped. The potential drops very slowly over the remainder of the experiment, as the single anodic site remains localized.

The spread of corrosion on carbon steel was rapid in a solution containing chloride and sulfate as shown by the fall in potential in Fig. 1(A). However, with the addition of inhibiting ions, the steel showed characteristics similar to those observed with stainless steels, where pit initiation was followed by repassivation (Fig. 1, Ref.

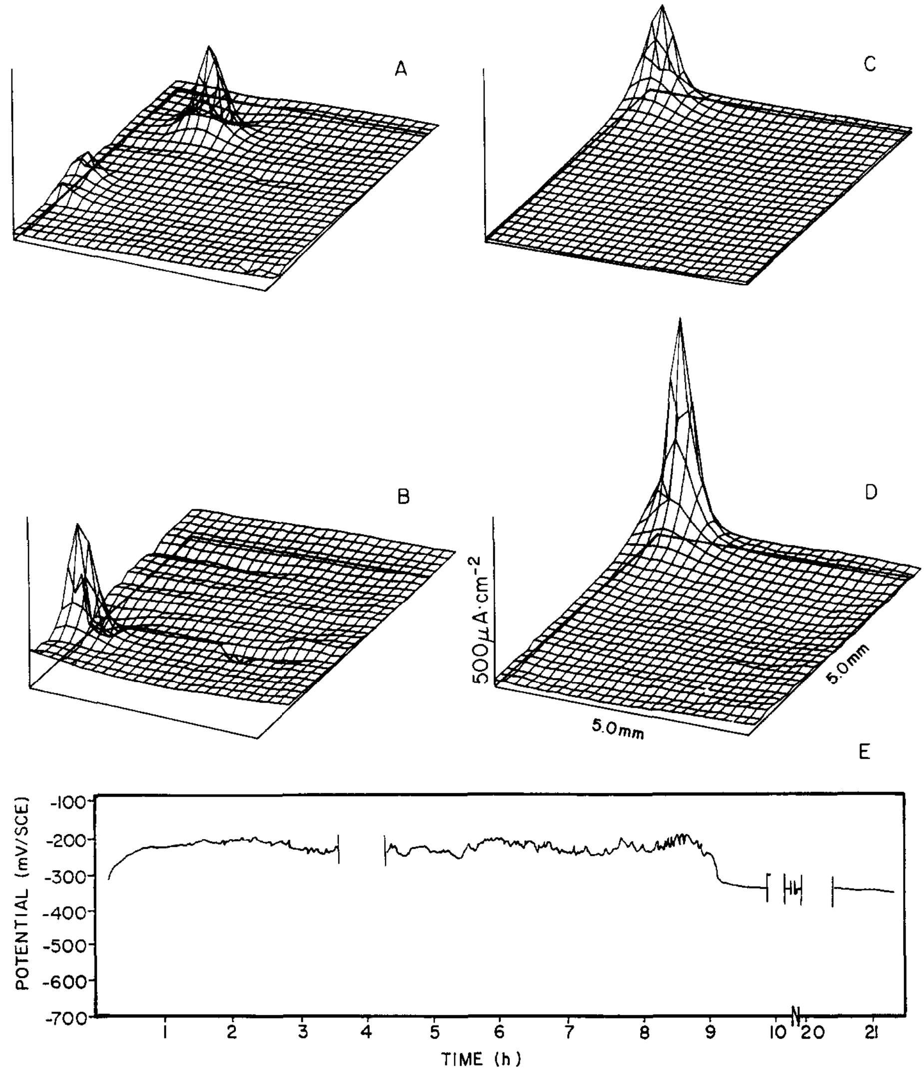

FIG. 4. Current density maps over carbon steel in air bubbled complex medium: (A) 3 h; (B) 6 h; (C) 10 h; (D) 22 h; (E) open circuit potential for the sample.

14). The combination of phosphate and convection had the greatest impact on repassivation of pits. The SVET analysis for the first 9 h in Fig. 4 also demonstrated this behavior. However, if conditions were not favorable for a pit to repassivate, aeration and phosphate can lead to enhanced localized corrosion. This was observed in the second 12 h in Fig. 4. Here, the crevice corrosion formed and the lacquer apparently inhibited repassivation. The crevice remained highly localized through the remainder of the experiment. The magnitude of the anodic current from the localized corrosion increased approximately two-fold over 12 h, but the area exposed to solution increased only slightly.

The polarization resistance measurements were obtained at the times indicated in Fig. 4(E). A decrease in R_p was observed in the sample as the size and magnitude of the anodic area increased. The R_p was 50000 ohm cm^2 at 3.5 h, when one small pit was observed using the SVET analysis. The value of R_p showed a marked drop to 9000 ohm cm^2 when a pit remained active for about an hour. However, only a relatively small drop was recorded after a further 10 h showing R_p had decreased to 5900 ohms cm^2. This was reflected in the small decrease in potential.

Addition of phosphate to corroding sample

The effect of phosphate addition to freely corroding steel was characterized by SVET analysis (Fig. 5). The steel was allowed to corrode in the medium without the

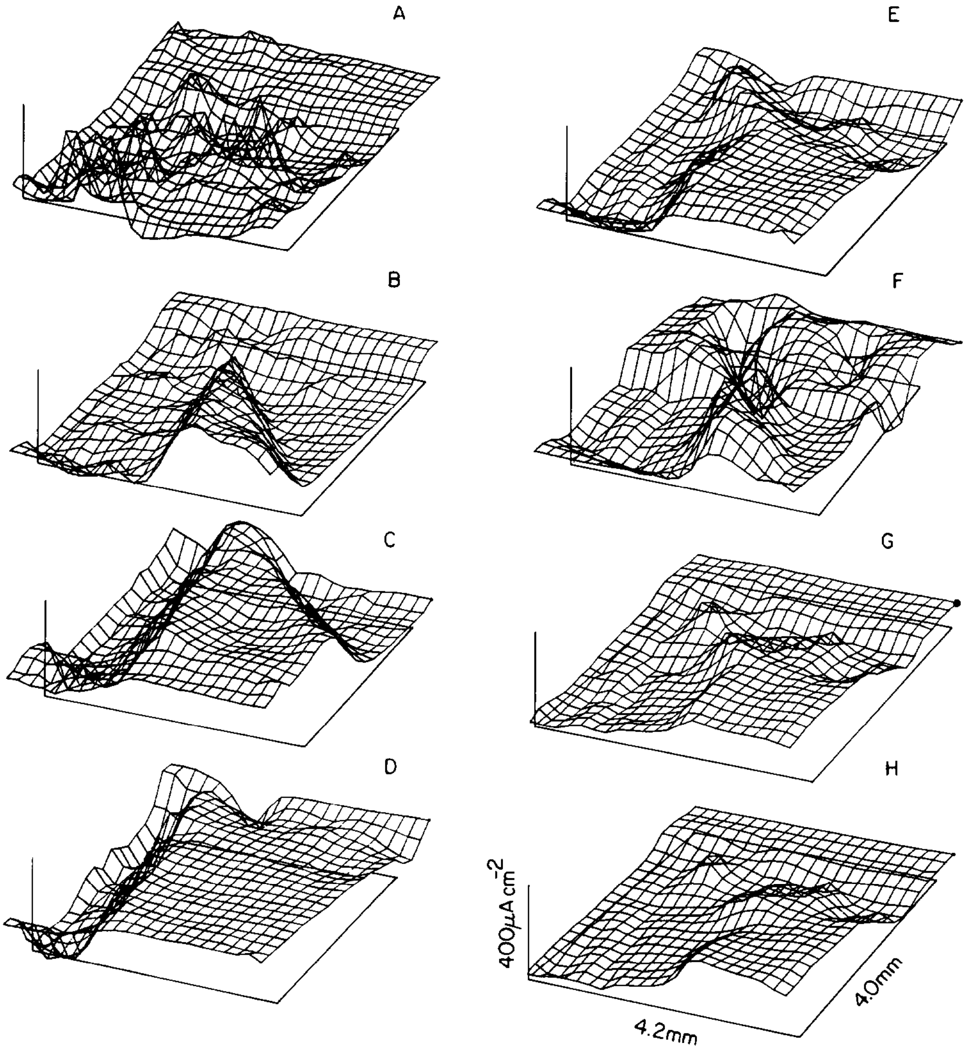

FIG. 5. Current density maps over carbon steel in medium lacking glucose, MOPS and phosphate: (A) 0.1 h; (B) 1 h; (C) 2.2 h; (D) 4.3 h. Current density maps after addition of phosphate to a final concentration of 0.2 mM: (E) 4.5 h; (F) 5.3 h; (G) 7.7 h; (H) current density map at 10 h after addition of phosphate to a final concentration of 0.8 mM.

MOPS buffer, glucose and phosphate. The OCP showed a trend similar to that observed when the steel was in 1 mM chloride and sulfate solution (Fig. 1, curve A). After 4.3 h, when the spreading of corrosion had virtually stopped, as indicated by SVET, and by a steady OCP of −690 mV(SCE), phosphate solution was added to bring the final phosphate concentration to 0.2 mM.

Figure 5 shows the spreading of corrosion from the current density maps over the steel prior to phosphate addition. Initially, after 0.1 h many distinct pits formed (Fig. 5A). After 1 h the anodic zone was confined to one area (Fig. 5B), and this zone spread (Fig. 5C) until approximately 70% of the sample was anodic, at 4.3 h (Fig. 5D). After the 4.3 h scan the potassium phosphate solution was added. Upon addition of the phosphate the size of the anodic zone decreased (Fig. 5E). This decrease continued until 5.3 h, and then was followed by very slow changes in the anodic zone (Fig. 5F,G). Although the changes were very pronounced on first adding the phosphate, the size of the anodic zone was not further decreased by the further addition of phosphate to a final concentration of 0.8 mM (Fig. 5H). The current density decrease in the area of the anodic zone was accompanied by an increase in the OCP from −690 mV(SCE) to −550 mV(SCE). The OCP did not increase above −550 mv(SCE), but gradually decreased with time as the corrosion slowly began to spread again.

The results indicated that phosphate acted as an anodic inhibitor, but the steel did not completely repassivate after the addition. The phosphate resulted in a decrease of the corroding areas. The smaller anodic site remained active with time, and addition of four-fold more phosphate did not further reduce the size of the anodic site.

CONCLUSIONS

The results showed that components of complex solutions, such as media used for microbially influenced corrosion studies, affected the corrosion rates and the corrosion propagation of steel samples. The results also demonstrated that the SVET is a useful technique for evaluating corrosion inhibitors. The current density maps obtained by SVET correlate with measurements of OCP and polarization resistance. In addition the SVET has been used to study corrosion inhibition when corrosion is highly localized. It has shown that when the corrosion is localized the phosphate inhibitor has difficulty penetrating the anodic environment, and thus produces highly active localized corrosion.

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