ROLE OF INHOMOGENEITIES AND MICROBIAL DISTRIBUTION IN MIC ATTACK AND PROGRESSION

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ABSTRACT

Concentric electrodes of carbon steel were created with a large circumferential area separated from a small central area by a narrow teflon ring. These electrodes were then incubated in an aerobic seawater medium and exposed to Vibrio natriegens and Desulfovibrio vulgaris as monocultures or as a co-culture. The large area was cathodically polarized at -1100 Mv/SCE for two hours and the galvanic coupling between the central anode and the circumferential cathode monitored. In both the sterile control and in the inoculated systems there was a rapid fall in the coupling current with time. The sterile control, the V. natriegens monoculture and the co-culture repassivated within 12 hours with a marked decrease in coupling current. The system inoculated with D. vulgaris however maintained a significant coupling current throughout the experiment. The same responses occurred if the cathodic polarization was initiated prior to the inoculation except that the period of increased coupling current was shortened significantly. Again the monoculture of D. vulgaris allowed generation of a continuing coupling current. Acridine orange direct microscopic counts of anodic and cathodic surfaces showed equivalent amounts for the V. natriegens monoculture and the co-culture but elevated numbers of D. vulgaris on the anodic surface in both situations where the coupling current persisted.

INTRODUCTION

Localized corrosion implies a passive surface acting as a cathode and small areas acting as anodes. The destruction of the passive films at the anodic areas allows the corrosion to

progress. Localized corrosion requires at least three conditions 1) the presence of a passivating layer associated with most of the surface; 2) localized areas acting as anodes that can be initiated by an external factor such as bacterial metabolism or some surface inhomogeneity; and 3) a stable galvanic coupling between the anodic and cathodic sites.

Bacteria form films which could act as nuclei for localized breakdown of the passive layer which can persist and lead to material degradation. These experiments were designed to directly test the capacity of bacteria to initiate localized corrosion and to maintain a coupling current between the anode and cathode as the corrosion persists.

EXPERIMENTAL PROCEDURES

Electrodes

Electrodes were constructed of C-1020 carbon steel in which a large circumferential cathode was separated from a central anode by a teflon washer. The relative areas were 4.87 cm^2 for the circumferential cathode and 0.031 cm^2 for the anode. The anode and the cathode were galvanically coupled through a Sycopel DD10M potentiostat (London, England) used as a zero resistance ammeter.

Generation of the Cathode and Anode

Localized corrosion was initiated by a preliminary cathodic polarization of the circumferential area with the generation of a calcarious scale. The circumferential cathodic area was polarized to -1100 Mv/SCE for 2 hours. The effects of bacterial biofilms were examined by inoculation prior to the application of the cathodic polarization and inoculation of the bacteria following the period of cathodic polarization.

Test Apparatus

Test vessels of glass reaction kettles[1] with polypropylene tops containing aeration and electrode ports were utilized. The medium was a seawater ASTM with the addition of 20 $meql^{-1}$ of carbonate as calcium carbonate. The carbonate potentiated the rapid formation of a homogeneous calcareous film on the cathodic surface. Two vessels were maintained under sterile conditions and each of the others inoculated with Vibrio natriegens ATCC 14048, or Desulfovibrio vulgaris ATCC 29579, or a co-culture of the two organism. V. natriegens is a slime-producing and acid producing heterotrophic aerobe. D. vulgaris is a dissimilatory anaerobic sulfate-reducing bacterium.

Analysis

The coupling current between the anode and cathode was measured with the Sycopel potentiostat utilized as a zero resistance ammeter. At the end of the experiments the scales and corrosion products were scraped from the electrodes and the bacterial densities determined by direct counting of dilutions of the microbes stained with acridine orange with the epifluorescent microscope. The composition of the scale was determined with X-ray diffraction.

RESULTS

COMPOSITION OF THE SCALE RECOVERED FROM THE CIRCUMFERENTIAL CATHODES

After the 2 hour polarization treatment a thin homogeneous film was visible on the surface. X-ray diffraction analysis of the film showed it to be a mixture of calcium carbonates and magnesium hydroxide with aragonite as the predominant calcium carbonate.

EFFECT OF BACTERIA IN INITIATING ELECTROCHEMICAL ACTIVITY

Inoculation of the systems with bacteria followed by the generation of the carbonate film on the circumferential portion of the electrode led to the generation of large initial coupling currents (Figure 1). The coupling current is expressed in uA cm^{-2}. The potential difference between the center anode and the cathode was 15 mV with the larger circumferential area being the cathode. In the sterile vessels the coupling current fell to essentially negligible values in 12 hours. The system containing the aerobe V. natriegens and the co-culture inoculated prior to polarization showed patterns similar to the sterile control. The vessel inoculated with the anaerobe D. vulgaris apparently survived the aerobic inoculation and grew on the electrode and maintained a coupling current between the anode and cathode of 65 uA cm^{-2}. Both the anode and cathode contained communities of 3.0×10^8 cells cm^{-2}. The monoculture of the sulfate-reducing bacteria produced biofilms of 4.0×10^6 on the cathode and 8.0×10^7 cells cm^{-2} on the anode.

EFFECT OF GENERATION OF CATHODIC AND ANODIC AREAS ON BACTERIAL GENERATION OF COUPLING CURRENTS.

The inoculation of bacterial monocultures and co-culture after the generation of scale formation on the cathode produced results (shown in Figure 2) similar to those generated by inoculation followed by electrochemical formation of the cathodic carbonate scale in Figure 1. The residual coupling currents were negligible at the end of the two day experiments for the sterile controls, the monocultue of V. natriegens and the co-culture. A residual current of 30 uA cm^{-2} was seen with the D. vulgaris monoculture. With the preformed scale on the cathode

the time for passivation and depression of the coupling current was much decreased from the previous experiment. The monoculture of V. natriegens and co-culture were 3.5 x 10^8 cells cm^{-2} on the anode and cathode. The cathode of the D. vulgaris monoculture showed 1.0 x 10^6 cells cm^{-2} compared to 5.0 x 10^7 cells cm^{-2} recovered from the anode.

DISCUSSION

In the experiments reported in this paper a microbial biofilm of the anaerobic sulfate-reducing bacteria D. vulgaris can form in the aerated bulk phase. When the cathode and anode are then generated by the application of potential difference between the circumferential cathode and center anode, these bacteria form a self-sustaining biofilm that generates a current of 65 uA cm^{-2} between the two sections of the electrode that continues after the cathodic polarization potential was stopped (Figure 1). The scale formed on the cathode offers sufficient protection from the aerobic bulk phase that the obligate anaerobe can grow and function. On the anode the organism thrives and generates a biofilm more dense than on the cathode. Possibly the acid generated with anodic reactions are particularly favorable to the growth of monocultures of this sulfate-reducing bacteria. If the cathodic scale is formed prior to inoculation the same general reaction ensues with the D. vulgaris monoculture (Figure 2). Again there is differential concentration of bacteria between the anode and cathode with a greater density on the anode as well as persistence of metabolic activity between the anodic and cathodic sites as evidenced by the current of 30 uA cm-2.

When V. natriegens is grown as a monoculture or as part of a co-culture with these obligate anaerobes a more dense biofilm is formed that is equivalent on the anode and cathode. When the cathodic scale is formed after the inoculation or prior to the inoculation there is essentially no generation of a persistent current between the anode and cathode. The presence of the V. natriegens nullifies the corrosion potentiating metabolism of the D. vulgaris when in a biofilm co-culture and the system behaves essentially as the sterile control.

These experiments clearly demonstrate that localization with a specific anodic site can be initiated by bacterial metabolism of D. vulgaris when a cathodic scale is generated electrochemically. Once an anodic site is active the metabolism of these organisms can maintain the corrosion in the absence of cathodic polarization. In the presence of the aerobic bacteria V. natriegens, the anodic and cathodic sites are passivated and the corrosion is not facilitated even when the D. vulgaris is the biofilm.

ACKNOWLEDGEMENTS

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Figure 1: Evolution of the coupling current

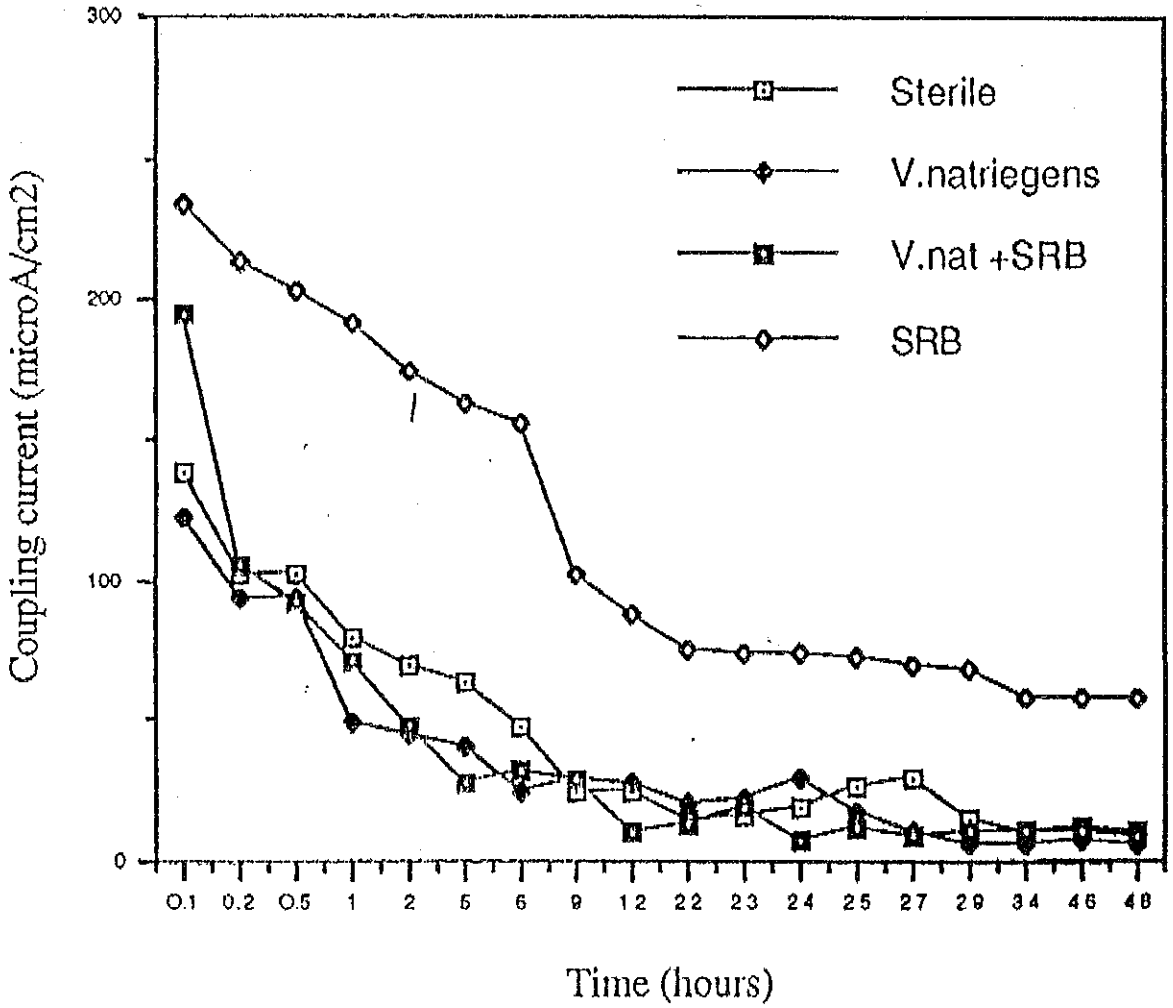

Figure 1. Coupling current between the anode and the circumferential cathode of carbon steel electrodes incubated in ASTM seawater medium inoculated with V. natriegens, D. vulgaris, a co-culture of both organisms, and the sterile control. The organisms were inoculated in the various culture vessels and a carbonate scale formed on the cathode by application of a potential of -1100 mV/SCE for 2 hours.

Figure 2: Evolution of the coupling current

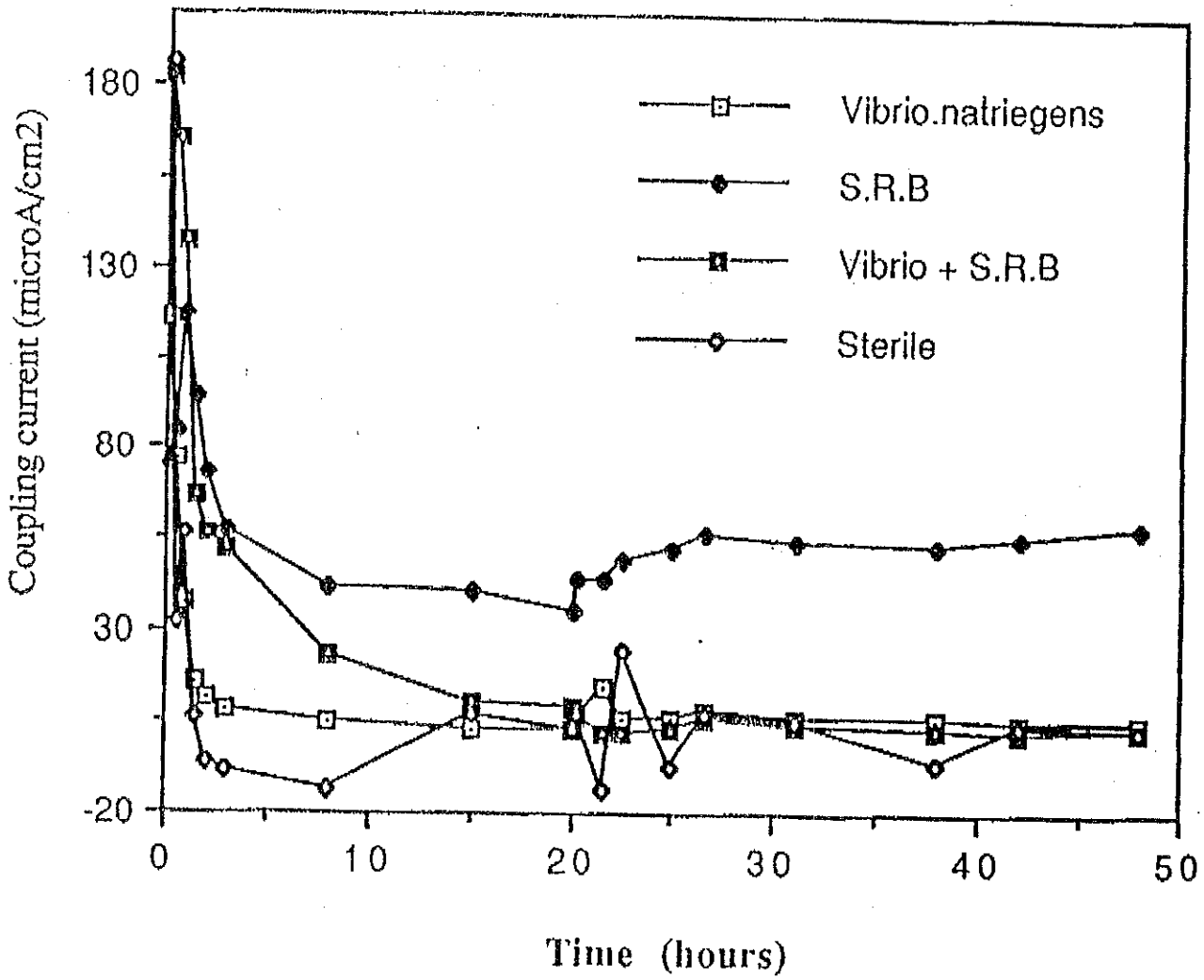

Figure 2. Coupling current between the anode and circumferential cathode after the generation of carbonate scale on the cathode prior to inoculation with the monocultures and co-culture used in Figure 1.