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STABILIZATION OF LOCALIZED CORROSION OF CARBON STEEL BY SULFATE-REDUCING BACTERIA

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ABSTRACT

An attempt was made to simulate a pit by preconditioning a large area and a smaller area as a cathode and an anode, respectively. The effect of the presence of sulfate-reducing bacteria (SRB) on the resulting current between the cathode and the anode was then investigated. Observations showed that in the presence of SRB, there is a stable galvanic cell, whereas the coupling current is either unstable or very low in sterile conditions. The results suggest that the presence of SRB is necessary on both the anode and the cathode.

INTRODUCTION

The oil industry has often reported the presence of SRB on major field failures. These failures generally involved localized corrosion in deaerated conditions [1].

Usually, microbiologically induced corrosion (MIC) has been studied with electrochemical techniques providing surface-averaged measurements. Techniques such as electrochemical impedance spectroscopy (EIS) or linear polarization give results, such as uniform corrosion rate, which are not applicable to localized corrosion. Thus it was necessary to use a technique that would give an actual information on localized corrosion.

The literature commonly reports that the driving force of SRB MIC is the presence of these bacteria on the cathode. This theory which is called cathodic depolarization [2, 3, 4], and conflicts with modern electrochemistry [5], neglects anodic reactions. However, reactions occurring at the anode are at least as important as the cathode's and could be predominant in the case of SRB corrosion [6].

Localized corrosion could be defined as the stabilization of a galvanic cell between the large film protected areas (cathode) and the small active zones (anode) which corrode. For Stainless Steels, this is a matter of passive layers, chloride ions, acidification by the hydrolysis of chromium ions and pitting potential [11].It is widely accepted that bacteria such as SRB may interact in this process [5]. The high localized corrosion rates found in the oil industry suggest that SRB not only initiate a uniform which most of the time remains at a reasonable level, but also stabilize localized corrosion by maintaining a coupling current between the anode and the cathode. The question is then to experimentally check this assumption and imagine a driving force for such a mechanism [9]. Therefore, to study this type of corrosion, we developed a test vessel which artificially create a galvanic cell between a large cathode and a small anode by the use of either a potentiostat or a galvanostat. The potentiostat/galvanostat is later used as a zero resistance ammeter to measure the free coupling current. This was successfully done with CO_2 corrosion [7].

This study describes a technique that measures the local galvanic current, considers both the anode and cathode SRB population, and investigates the stabilization by SRB of an existing pit.

EXPERIMENTAL PROCEDURE

The electrodes were constructed of C1020-grade mild steel. They were made of two concentric electrodes separated by a Teflon insulator ring and embedded in epoxy. The surface ratio between the areas of the two electrodes was about 150. On each of the surfaces, an electrical wire was soldered and connected to a Sycopel DD100M potentiostat.

Glass reaction vessels with polypropylene tops containing deaeration, gas, inlet and outlet, reference electrode ports were used. The medium was American Society for Testing and Materials seawater (ASTM D-1141 "Standard Specification for Substitute Ocean Water") enriched with the necessary nutrients for the SRB to grow. The electrodes, medium, and vessels were sterilize by the appropriate methods. Deaeration was achieved by sparging 5% H2, 95% N2 gas both in the vessels and in the source. The medium was renewed at a rate of 10% per hour.

One vessel was left sterile while the others were inoculated with SRB. The bacterium was a Desulfovibrio Vulgaris from the laboratory's collection. D. Vulgaris is a dissimilatory anaerobic SRB. Bacterial counts were done using the most probable number (MPN) technique and acridine orange direct counts (AODC) using epifluorescent microscopy. The counts were performed by distinctively scraping off corrosion products/biofilm from the anode and the cathode.

The electrode was preconditioned by circulation of a current of microamps/cm^2/cathode between the anode and the cathode for three days. The SRB were inoculated on the second and third days of the experiment. One day is usually necessary to deaerate the medium in the vessels, and two days is necessary for the bacteria to grow and attach to the electrodes.

RESULTS

The potential of both the anode and the cathode was recorded during the preconditioning. As shown in Figure 1 the potential of the cathode was between -1.0 and -1.1 V/SCE before SRB inoculation. Following inoculation (17 hours), the potential of the cathode clearly increases (22 hours), while the anode's potential decreases slightly. This phenomenum has been reported by other authors [8] and was attributed to the formation of a biofilm. However, the same variations occur at 50 hours for the non-inoculated coupon, because of an accidental contamination of the medium as revealed by the cloudiness of the vessel and confirmed later on by the bacterial counts.

After three days of preconditioning, the potential difference between the centered anode and the cathode was typically 20 mV. The anode was covered with corrosion products, and the cathode usually remained relatively clean. A thin film was generally observed on the cathode, possibly magnesium hydroxyde caused by the polarization of the electrode as revealed by earlier studies [6].

Figure 2 shows the free current readings between the freely corroding anode and the cathode. The current densities are reported to the surface of the anode. The figure clearly shows the great instability of the coupling for the non-inoculated coupon during the first 20 hours. After which, the current more or less stabilized around zero. In the presence of SRB, the current sharply drops during the first 5 hours. Then it steadly increases to about 20 microamps, where it remains until the end of the experiment.

The SRB population was between 10E2 and 10E3 cells/cm^2 in the bulk and between 10E3 and 10E4 cells/cm^2 on both the anode and the cathode. Figure 3 shows an other current coupling plot. In this case, the coupling in the non-inoculated vessel reaches 10 microamps/cm^2/anode after a couple of hours and then steadly decreases to 5 microamps/cm^2 at the end of the experiment. Unexpected, out of three inoculated vessels only the first one shows a significant stable coupling at about 13 microamps/cm^2. The two other vessels behave in a manner similar to the one without SRB. The viable bacterial counts revealed the same amount of SRB in the bulk of the three vessels (between 10E2 and 10E4 cells/cm^2). However, no SRB were detected on the anodes of coupons 3 and 4 whereas between 10E3 and 10E4 cells/cm^2 were detected on the anode of coupon 1. The SRB population was identical on the cathodes of the three coupons (between 10E2 and 10E4 cells/cm^2).

DISCUSSION

Under sterile conditions it is possible to initiate a galvanic coupling between an anode and a cathode that simulates a pit. However, this coupling is unstable and will vanish or become infinite after a few hours. Neither the corrosivity of the medium (seawater on mild steel), nor the calcareous deposits on the cathode are capable of stabilizing the galvanic coupling. Therefore, corrosion pits would not grow in sterile deaerated seawater.

In the presence of D. Vulgaris, the galvanic coupling becomes stable and therefore dangerous. SRB stabilize the coupling current between the anode and the cathode; this stabilization is necessary for corrosion pits to grow. It is also clear that the SRB colonize the anode as well as the cathode. SRB must be present on both the anode and the cathode to obtain a stable galvanic coupling. The results show that no substantial growth of the pit would occur without the presence of SRB on the anode. In other words, the activity of the SRB on the anode (electrochemical or metabolic) could be more important than their activity on the cathode. This demonstrates that the driving force of this corrosion process could be at the anode and probably not at the cathode, as suggested by earlier studies [9, 10].

A similar experiment was carried out earlier [6], in which the same electrode was used, but the experiment was performed in initially aerated conditions. Three different bacterial possibilities were studied : sterile, monoculture of D. Vulgaris, monoculture of V. Natriegens, and coculture SRB/V. Nat. V. Natriegens is a slime-forming, acid-producing heterotrophic aerobe. The galvanic coupling between the anode and the cathode was initiated by cathodically polarizing the cathode to a potential of -1.2 V/SCE during two hours. This cathodic polarization induced the formation of calcareous deposits, as revealed by energy dispersive X-ray analysis (EDXA). The free coupling current resulting from this preconditioning was then recorded. Results from this experimental procedure are shown in Figure 4. There was a stable coupling only in the presence of a monoculture of D. Vulgaris, the two vessels inoculated with V. Natriegens behaving like the sterile one. The SRB population on both the anode and the cathode was about 10E7 cells/cm2.
This experiment showed that even an acid-producing bacterium (APB) like V. Natriegens would not stabilize localized corrosion and would prevent it even if SRB were present.

SRB are indeed believed to acidify the anodes by precipitating ferrous ions into ferrous sulfide [5]. This observation is not consistent with the theory of cathodic depolarization which stipulates that the bacteria on the cathode stabilize the galvanic coupling [2, 3, 4]. Rather, SRB MIC could be described on the basis of a specificity of their metabolism with respect to pH regulation [9]. This theory proposes that the SRB would acidify the anode and stabilize the pH of the cathode, thus inducing a galvanic coupling. This theory is consistent with our results because it accounts for the necessary presence of the SRB on both the anode and the cathode.

The results obtained in an earlier experiment [6] show that SRB corrosion is expected to be less dangerous in the presence of other bacteria. J. Guezennec also showed that a population density of about 10E7 cells/cm^2 on the anode could induce a corrosion current as high as 40 microamps/cm^2. Considering that in our experiment there were only 10E3 cells/cm^2 and that the presence of an other bacteria was detected (contamination); it can be predicted that in better conditions (i.e. no contamination, better SRB biofilm), a much higher coupling current would be reached.

CONCLUSIONS

The present work, and the earlier work performed by J. Guezennec, lead to several major conclusions.

- SRB do stabilize pitting corrosion of mild steel in deaerated seawater.

- Other bacteria such as Vibrio Natriegens are capable of preventing this localized corrosion.

- The value of the galvanic current could be correlated with the SRB population on the anode. The anode could be the driving force of this type to corrosion.

Future work should focus on increasing the SRB population on the electrodes and should be done achieving monoculture conditions throughout the experiment. Crolet et al. [9] suggest to study different possible metabolism (for instance, thiosulfate instead of sulfate) in order to recognize the most dangerous. Then it will be possible to assess the potential risks of SRB MIC and design appropriate bacterial/chemical treatments.

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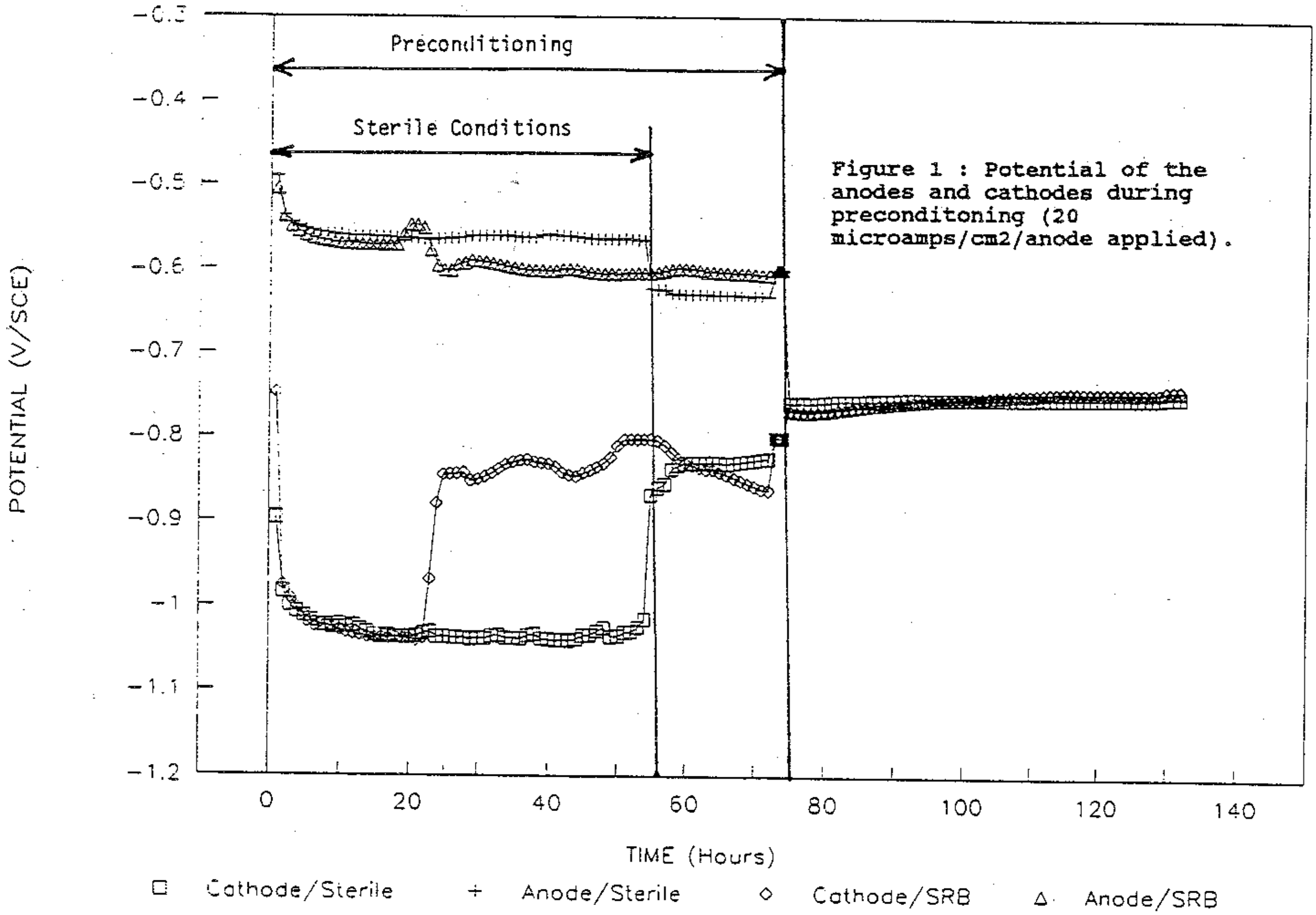

Figure 1 : Potential of the anodes and cathodes during preconditoning (20 microamps/cm2/anode applied).

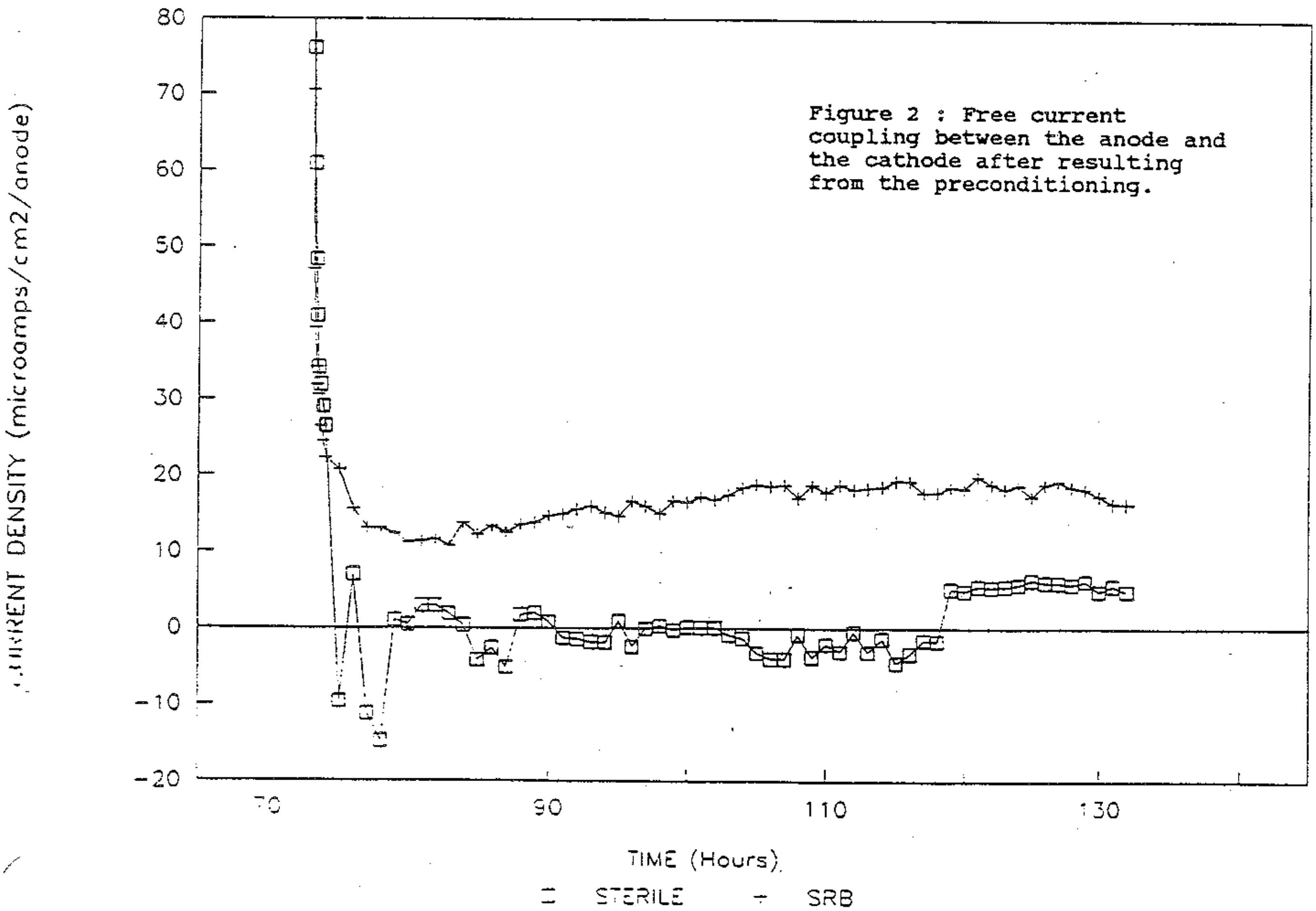

Figure 2 : Free current coupling between the anode and the cathode after resulting from the preconditioning.

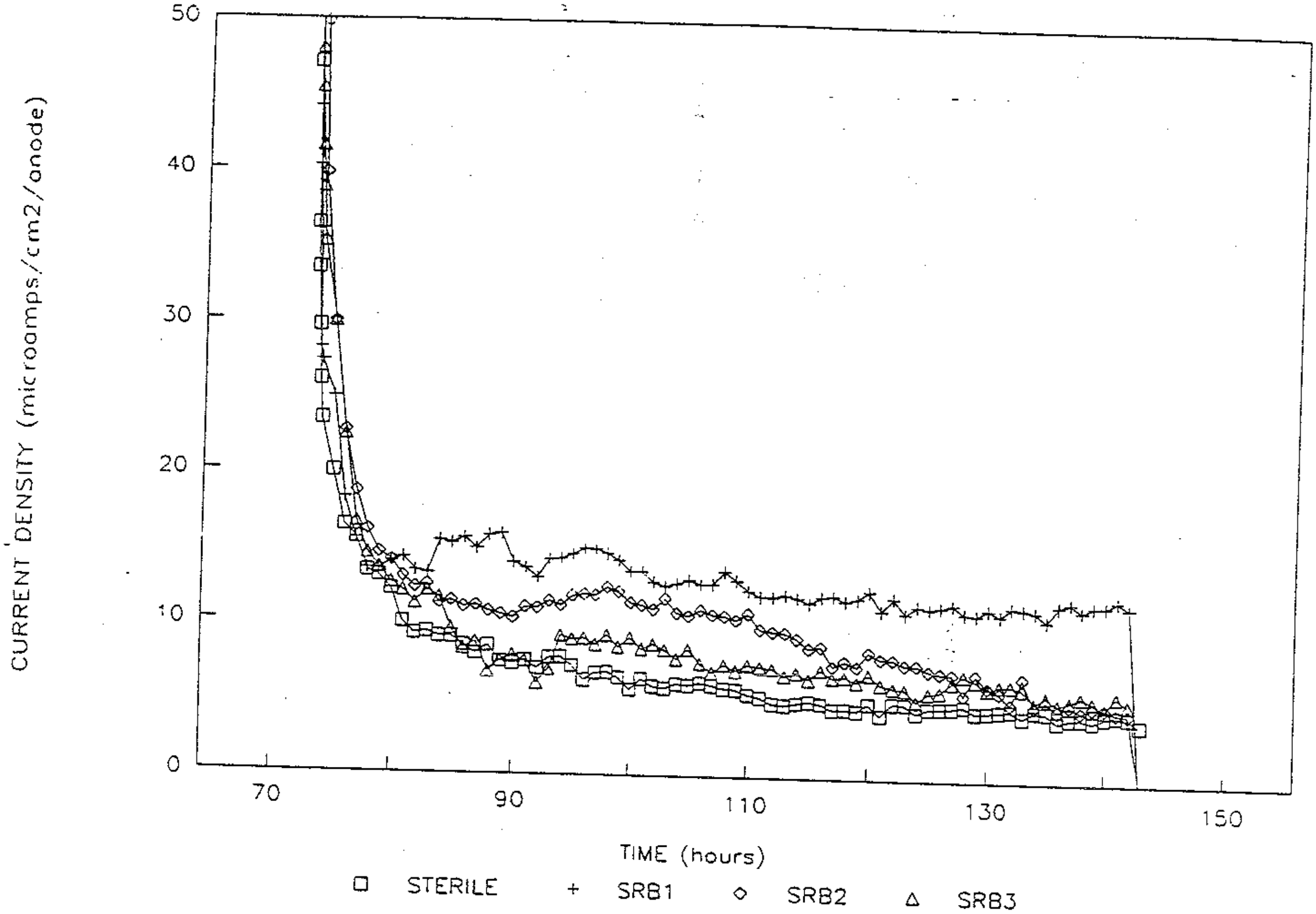

Figure 3 : Free current coupling between the anodes and the cathode - Effect of SRB population on the current -

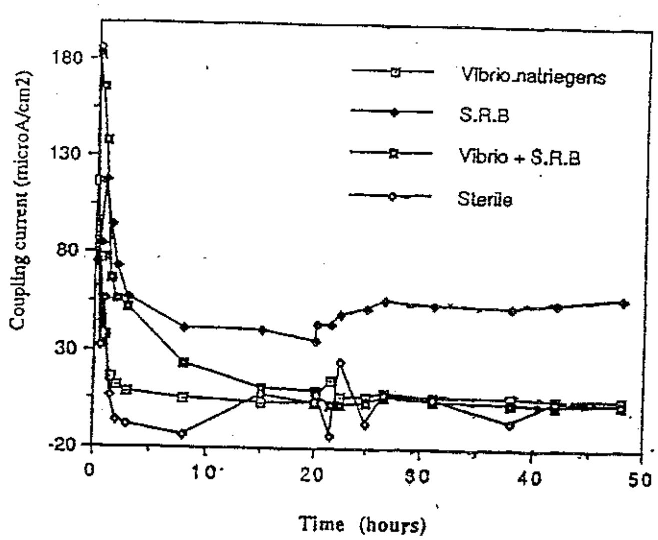

Figure 4 : Free current coupling resulting from preconditoning by applying -1.2V/SCE to the cathode [6].