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Studies of Microbiologically Influenced Corrosion Using a Coupled Multielectrode Array Sensor

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ABSTRACT

A newly developed multielectrode array sensor (MASS) was used to conduct a series of abiotic and biotic tests to determine if the probe can detect corrosion induced by microbial activity. The probe was able to determine the maximum corrosion rate in the presence of sulfate reducing bacteria (SRB) and showed that this rate was at least a factor of 10 greater than in the absence of SRBs. In addition, the corrosion rates obtained using the probe were much higher than those determined using linear polarization resistance further demonstrating its inherent better sensitivity to localized corrosion.

INTRODUCTION

Microbiologically influenced corrosion (MIC) is a problem in many engineering applications, including seacraft, process equipment and cooling water systems. MIC is usually manifested in the form of localized corrosion, and like abiotic localized corrosion, it tends to be catastrophic in effect. Of concern in many applications (e.g., process streams, cooling water systems, pipelines) is monitoring for corrosion and in particular MIC. Monitoring enables the operator to determine if the mitigation schemes, such as corrosion inhibitors and biocide applications, are effective. Furthermore, monitoring can provide an indicator to establish the dosing schedule and importantly can serve as a gage of system integrity. That is, the monitoring scheme can focus on microbial activity as well as corrosion activity. The ideal situation would be to have a method capable of monitoring the corrosion rate and corrosion mode (particularly localized corrosion) that could sensitively monitor system integrity and the net effects of inhibitors and biocides.

Several methods have been employed to monitor corrosion processes in various process stream-type applications, including electrochemical noise (EN), linear polarization resistance (LPR), and electrical resistivity probes (ER). Each of these methods has been utilized to some degree of success in various situations. EN offers an advantage over LPR and ER in that it may be sensitive to localized corrosion, as might occur in the presence of microorganisms. However, EN has been shown in some cases to not detect pitting[1]. This observation can be easily explained by considering two pits that form nearly simultaneously on each electrode such that there is no net current exchange between them. A slightly different approach to monitoring specifically for MIC is used in the BioGeorge probe and has shown the potential for determining the presence of a biofilm and the effects of subsequent antimicrobial remedial actions[2-4]. Though this approach provides valuable information, just because a biofilm is detected, however, does not mean that MIC is occurring or that MIC is even a risk. Considering the

ubiquitous nature of microbes, it is easy to misinterpret corrosion processes as MIC based solely on the detection of microbial activity as demonstrated recently for double-hulled transport barges.[5]

To mitigate some of the possible limitations of currently available localized corrosion monitoring tools, we have developmented a Multielectrode Array Sensor System (MASS). This sensor has been successfully used to monitor corrosion processes in both laboratory tests and industrial process stream applications.[6-9] The MASS probe consists of multiple miniature electrodes made of metals to be studied (Figure 1). The miniature electrodes were coupled together by connecting each of them to a common joint through independent resistors, with each electrode simulating an area of a corroding metal. In a localized corrosion environment, anodic currents flow into the more corroding electrode, and cathodic currents flow out of the less or non-corroding electrodes. These currents are measured from the voltages across the resistors. The current from the most anodic electrode or the degree of variation among the currents from the different miniature electrodes, which is represented by the standard deviation of the currents from the different miniature electrodes, is used as an effective indictor for localized corrosion. Figure 2 is a picture of the MASS probe in different configurations.

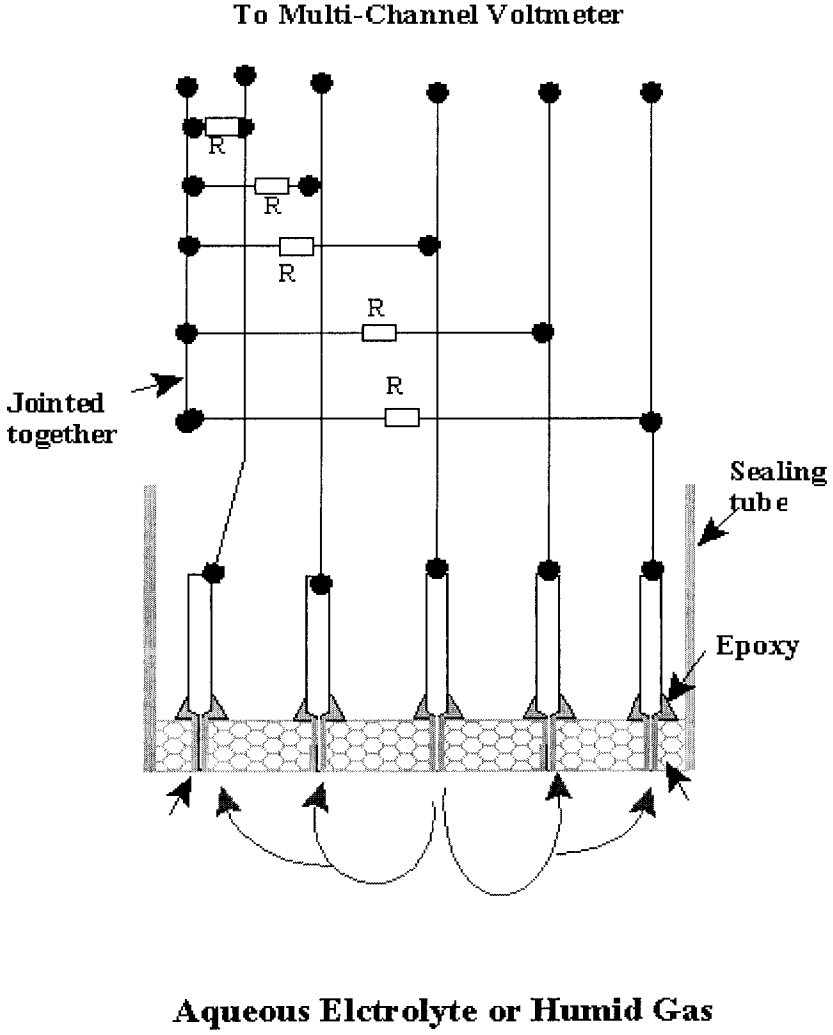

Figure 1: Schematic of MASS probe.

Figure 3 shows a typical standard deviation signal of a 25-electrode stainless steel UNS S30400 MASS probe (electrodes 1 mm in diameter) in different localized corrosion environments.[6] The standard signal responded well to the severity of the localized corrosion environment. Figure 3 also shows the effectiveness of $NaNO_3$, a well known corrosion inhibitor,[10] in reducing the corrosion of stainless steel in the 0.25M $FeCl_3$ solution. The MASS probe was highly sensitive and was able to measure the current in deionized water for stainless steel UNS S30400. This work reports efforts to use the MASS probe to monitor for MIC.

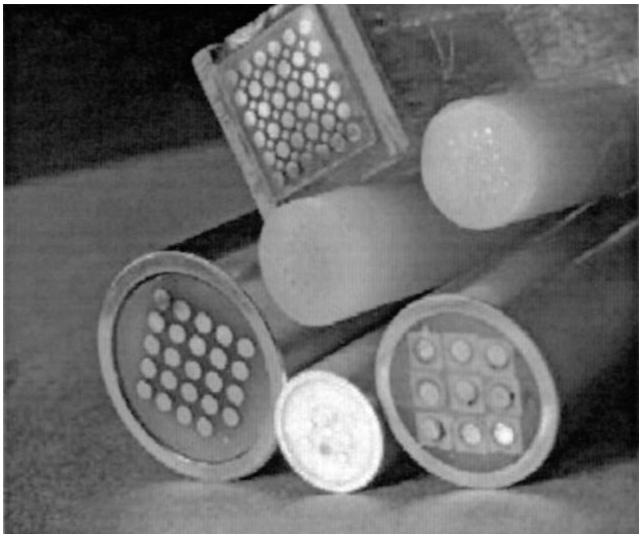

Figure 2: Different configurations of MASS probes.

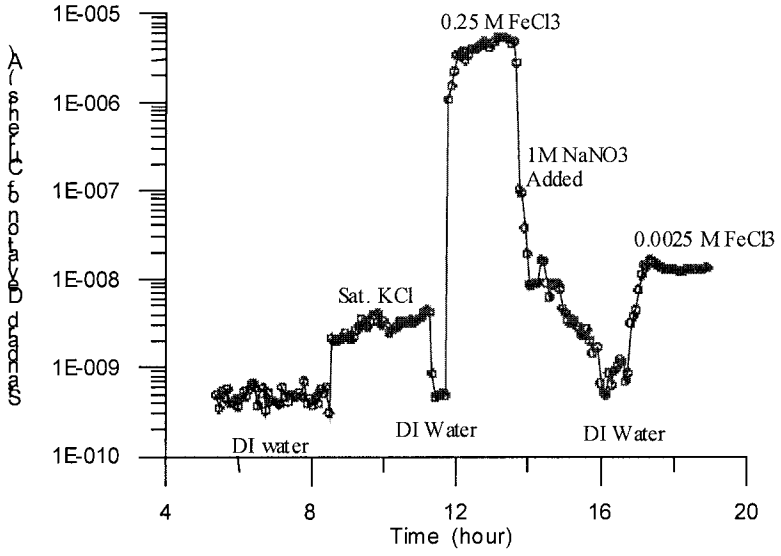

Figure 3: Typical standard deviation signal of a stainless steel UNS S30400 MASS probe in different localized corrosion environments (from Ref 6)

EXPERIMENTAL APPROACH

Two type 1010 carbon steel (UNS G10100) and two Type 304 stainless steel (UNS S30400) MASS probes, each having 16-sensing electrodes made from 1 mm diameter wires, were mounted into two cells (a test cell and a control cell) filled with a 0.5% NaCl solution and deaerated with nitrogen (Figure 4). Both the test cell and control cell were then immersed in a deaerated container, also filled with 0.5% NaCl. One MASS probe was used as an abiotic control with only sterile nutrients injected. The biotic test MASS probe was injected with nutrients along with a slime former (*Vibrio natriegens*) and a sulfate reducing bacteria (*Desulfovibrio vulgaris*).

Bacterial injections were conducted on sequential days for 3 days to ensure adequate inoculation. Then periodically, aliquots of the solution near the probe were extracted and plated on Brucella blood agar plates to confirm the presence of viable *Vibrio natriegens* and on Modified Baar's agar plates to confirm viable *Desulfovibrio vulgaris*. In addition, commercially available molybdate (inhibitor A) and nitrite (inhibitor D) based corrosion inhibitors were added as were gluteraldehide (biocide A) and isothiozoline (biocide B) as biocides. The response of the abiotic and biotic probes was compared during each step. For comparative purposes, several test cells were constructed using flat coupons that could be monitored using LPR to determine corrosion rates under similar conditions to those used in the MASS probes. After testing, the probes and the samples were examined visually for signs of corrosive attack. LPR tests were also conducted in deaerated 0.5% NaCl.

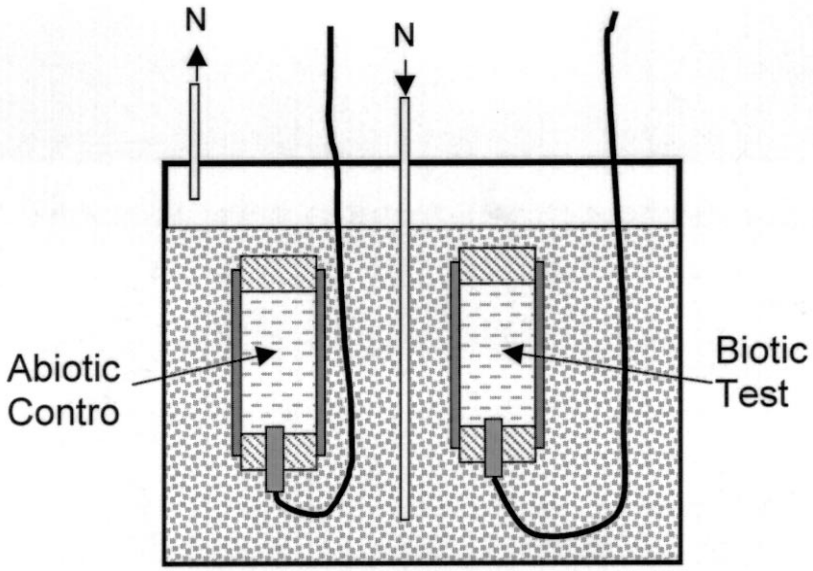

Figure 4: Configuration for MIC tests using MASS probe.

RESULTS AND DISCUSSION

The response of the MASS probes in the abiotic and biotic test conditions is shown in Figure 5, where Test_CS, Ctr_CS, Test_SS, and Ctr_SS are the signals from the carbon steel probe in the test cell, the carbon steel probe in the control cell, the stainless steel probe in the test cell, and the stainless steel probe in the control cell. Also shown is the effect of various biocide and corrosion inhibitor additions. Very little difference was noted between the response of the abiotic control and the biotic test Type 304 MASS sensors with the standard deviation currents measured between 10^{-11} and 10^{-8} A which correspond to low corrosion rates based on other laboratory and field tests of the sensor probes (Figure 3). Furthermore, examination of the probe member surfaces after testing showed little corrosive attack and the existence of prior polishing scratches still evident. A significant difference between the abiotic and biotic carbon steel sensors was noted however, typically a factor of 10 or greater with biotic standard deviation currents as high as 10^{-6} A compared to currents less than 10^{-8} for the abiotic case in some instances. Post-test examination (Figures 6 and 7) of the carbon steel MASS probes revealed evidence of pitting corrosion on the biotic sample and only general corrosion and surface roughening on the abiotic probe. It should also be noted, that the effects of biocide and corrosion inhibitors were also examined. Additions of gluteraldehide (biocide A) at increasing doses over time did not significantly alter the measured response of the biotic carbon steel probe. However, culturing of extracted fluid showed that after the second inoculation of the test cell with gluteraldehide the viable SRB population was nil but the slime former was still viable. Continued injections of the gluteraldehide in combination with isothiazoline did eventually kill the slime former as well. However, the currents measured remained high, even after the addition of inhibitors (and in some cases actually increased). Though not confirmed at this time, it is felt that the continued high currents on the MASS probe result from the formation of a biofilm that was not altered by the addition of biocides and acted as a barrier for the ingress of the corrosion inhibitors. Another possible explanation for the lack of efficacy for the corrosion inhibitors is the lack of oxygen. In previous tests examining these particular inhibitors for use in cooling

water systems revealed that very little inhibition was observed in deaerated systems whereas decreases in corrosion rate by several orders of magnitude were noted under conditions in which oxygen was present.[11]

To serve as a basis for comparing the results from the MASS probe, LPR tests were conducted on coupon samples under similar conditions. The measured corrosion rates using LPR are shown in Figure 8. As can be seen, the corrosion rates measured for carbon steel in the biotic test are greater than those in the abiotic test, similar to the results observed using the MASS sensor. For example, the average corrosion rate measured using LPR for carbon steel was ~ 4.5 μm/yr for the biotic test and ~ 4 μm/yr for the abiotic case. The corrosion rates measured for stainless steel were < 0.7 μm/yr. For the MASS probe, the average maximum corrosion rates for carbon steel were 800 and 50 μm/yr for the biotic and abiotic case and for stainless steel were less than 5 μm/yr for both cases. The difference in the measured corrosion rates using the two methods can be understood in the following way. The MASS sensor is designed to measure the maximum corrosion rate, and thus given the small size of each electrode is more conducive to measuring localized corrosion. For LPR, even if the same processes are occurring, because the corrosion is localized in nature and the area of the sample was considerably larger, the corrosion rates determined represent an underestimation of the actual rates. Furthermore, only a single inoculation with SRBs had been conducted and as yet it has not been verified that viable organisms are present.

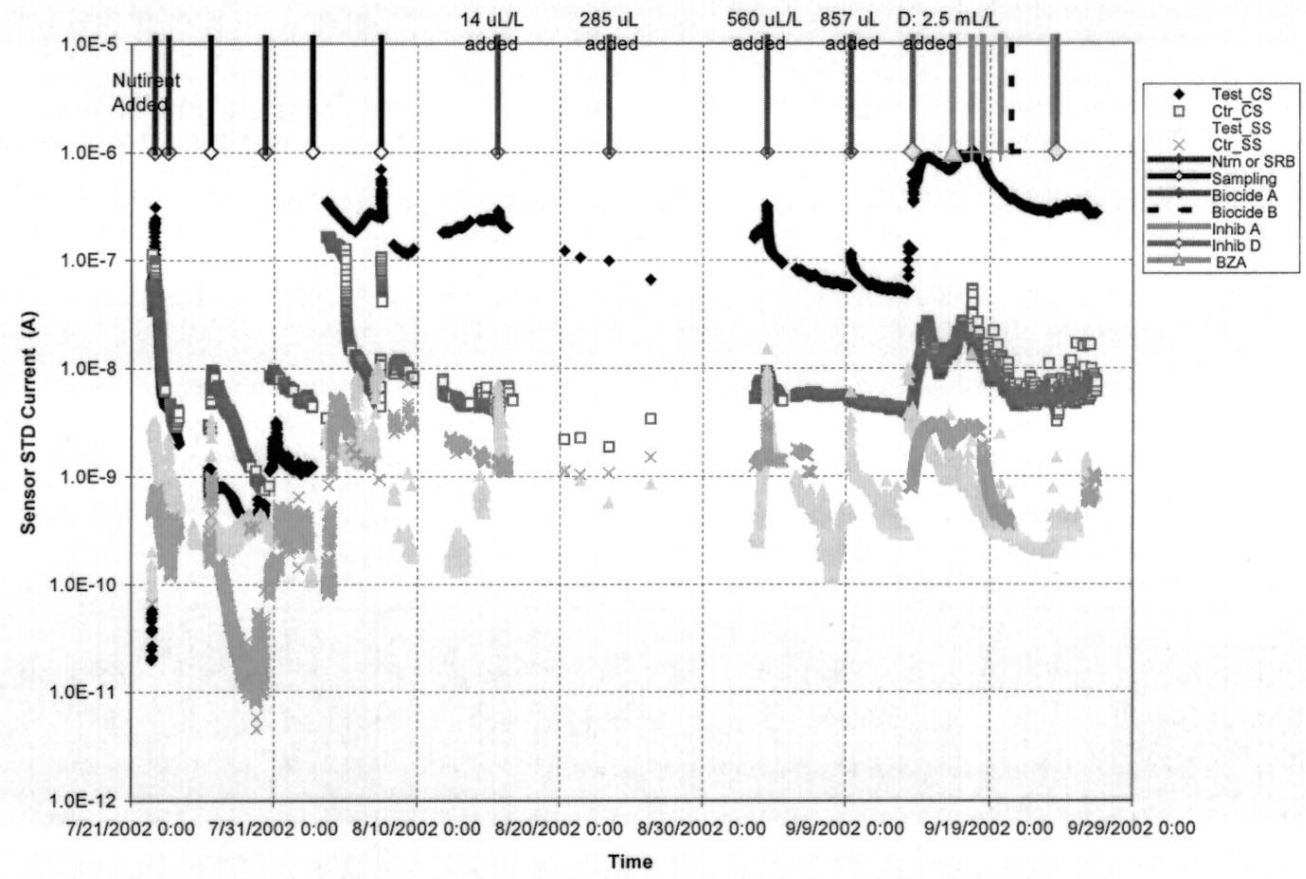

Figure 5: MASS sensor probes responses during MIC testing.

One surprising observation thus far in this study was the lack of significant corrosion noted on Type 304 stainless steel in the presence of SRBs. Numerous authors have studied the corrosion behavior of stainless steels in the presence of SRBs. For example, Webster et al.[12] compared and contrasted the pitting noted on stainless steel in the presence of SRBs and possible inorganic sulfur compound analogues (e.g., thiosulfate). They found that the anodic dissolution reaction was catalyzed by the presence of either inorganic or organically

generated H_2S and also that chloride was needed in sufficient concentration to induce pitting. Sinha et al.[13] reviewed failures of stainless steel components used in nuclear power plants that were attributed to MIC. Similar failures of stainless steel components have been attributed to MIC by others as well.[14-17] Thus, the lack of notable localized corrosion in the case of the stainless steel MASS probes is perplexing. One key observation that was noted by Webster et al.[12], however, was a clear requirement of an oxygen cathode inducing a sufficiently high corrosion potential to induce pitting of stainless steel in the presence of SRBs. Alternatively, the potential could be raised by other cathodic oxidants or through the use of a potentiostat. Though SRBs are strict anaerobes, they have been known to thrive in aerobic systems under the biofilms formed by slime forming bacteria that consume oxygen creating anaerobic conditions. Thus, one possible explanation for the lack of response for the stainless steel MASS sensor is that the corrosion potential was not sufficiently high (i.e., not greater than the repassivation potential) in the deaerated system that was investigated thus far.

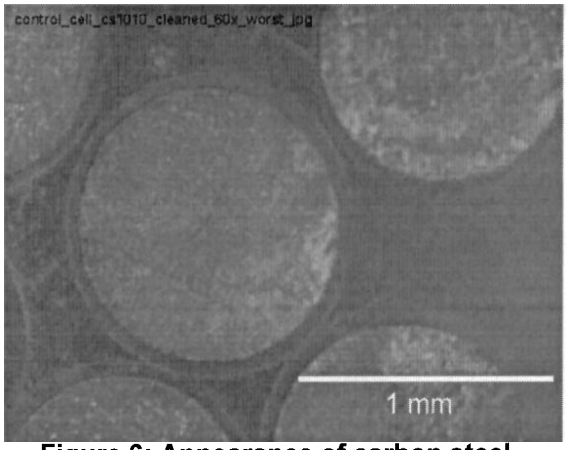

Figure 6: Appearance of carbon steel MASS probe after abiotic test.

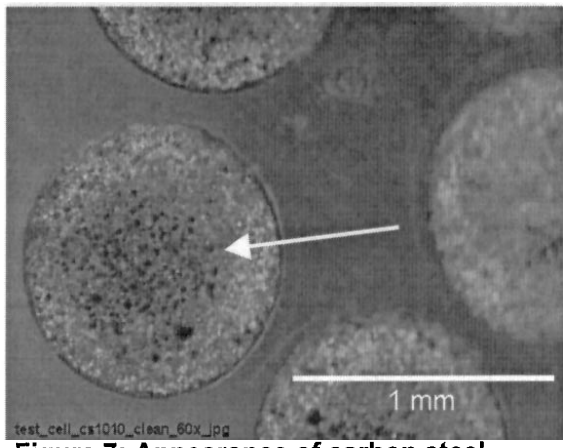

Figure 7: Appearance of carbon steel MASS probe after biotic test. Note small pits on electrode noted by arrow.

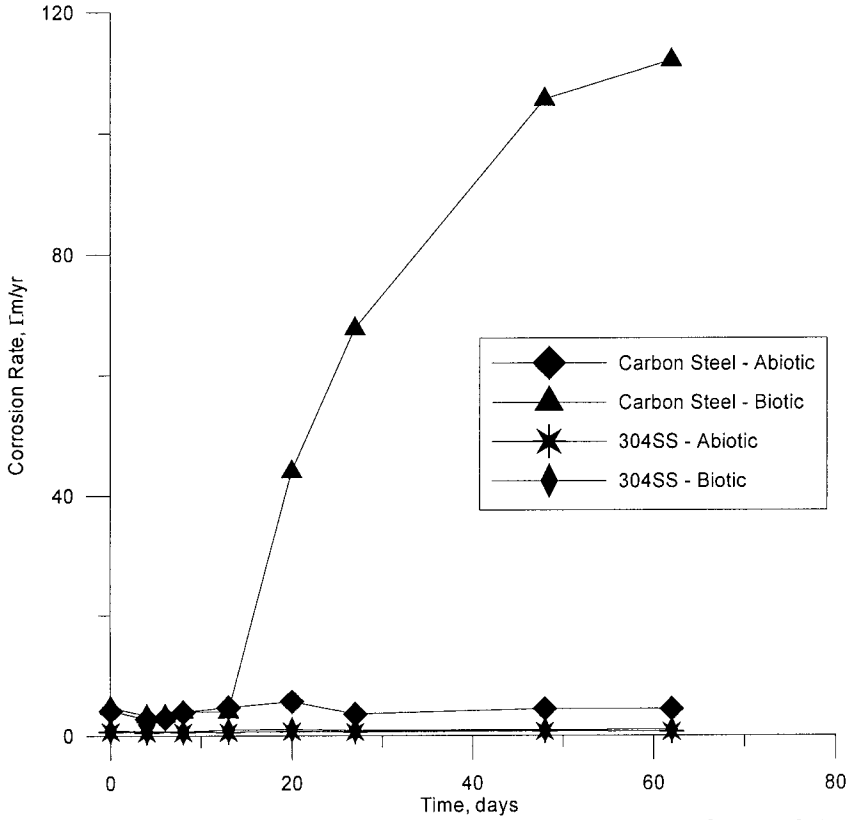

Figure 8: Corrosion rates determined using linear polarization resistance.

Based on testing conducted to date, the MASS probe can sensitively detect localized corrosion and give an indication of the maximum corrosion rate for the system of interest. This capability is not limited to abiotic systems as clear differences between biotic and abiotic conditions can be clearly discerned where the only difference between the conditions is the presence/absence of bacteria. Though it can detect localized corrosion and provide information on corrosion rate, it cannot strictly distinguish between abiotic and biotic pitting. That is, the MASS probe at present cannot distinguish if the pitting that is detected results from microbial activity. Additional testing is on-going to explore this possibility further.

CONCLUSIONS

The MASS sensor probe was used to conduct a series of abiotic and biotic tests to determine if the probe can detect corrosion induced by microbial activity. The probe was able to determine the maximum corrosion rate in the presence of SRBs and showed that this rate was at least a factor of 10 greater than in the absence of SRBs. In addition, the corrosion rates obtained using the probe were much higher than those determined using LPR further demonstrating its inherent better sensitivity to localized corrosion. The probe, however, cannot at this time distinguish between biotic and abiotic pitting. Additional work is on-going to evaluate the probe further.

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