PREVENTION OF MICROBIAL CORROSION USING COATINGS MIXED WITH NATURAL ADDITIVES

M. M. Al-Darbi *
Chemical Engineering Department, Sexton Campus, Dalhousie University,
1360 Barrington Street, Halifax - N. S., B3J 2X4, Canada.
Z. M. Muntasser, A. R. Nouri and M. R. Islam
Civil Engineering Department, Sexton Campus, Dalhousie University,
1360 Barrington Street, Halifax - N. S., B3J 2X4, Canada.

Abstract Corrosion causes huge economical and ecological damage worldwide. Microbiologically influenced corrosion (MIC) refers to corrosion that is influenced by the presence and activities of microorganisms. MIC is extremely harmful to both the industry and the environment. It is estimated that 20-30 % of all corrosion is microbiologically influenced with a direct cost from 30-50 billions per year [Javaherdashti, 1999]. One of the most important microbial corrosion is that due to the presence of sulfate reducing bacteria (SRB), which is most common in petroleum operations because of the prevailing anaerobic environment [Phelps et al., 1991]. In this study, the influence of sulfate reducing bacteria (SRB) grown in lactate/sulfate culture medium on the corrosion of both uncoated and coated mild steel was evaluated. To achieve this, oil based coating (alkyd) was used with and without the addition of natural additives to protect mild steel in a sulfate reducing bacteria environment. Another objective of this study is to investigate the effects of SRB and/or their metabolites on the used coatings and the adverse effect of those coatings on the biofilm formation and bacteria growth rate. Bacteria populations were counted at the beginning and at the end of the tests using plate count method. After immersing the different coupons for three months in the SRB medium, it was noticed that the number of bacteria and their colonies were highly affected by both the environment and the used coating systems. Visual observations, scanning electron microscopy (SEM) analyses and image analyzer techniques were used to study the effects of SRB on the studied coupon surfaces. It was observed that the presence of coatings inhibited both the biofilm growth and bio-corrosion effects. Those results were much pronounced in dominant by the addition of natural products to the studied coatings.

Keywords: MIC, SRB, Coating, Additives.

INTRODUCTION

Microbiologically influenced corrosion (MIC) is of great importance from economical, conservation, safety and scientific points of view. Protection of structures against MIC has therefore become very critical in many industries including municipal pipelines, marine, storage vessels, sewage treatment facilities and so on [Geesey et al., 1994]. The study of microbiologically influenced corrosion (MIC) has progressed from phenomenological case histories to a mature interdisciplinary science including electrochemical, metallurgical, surface analytical, microbiological, biotechnological and biophysical techniques [Little and Wagner, 1994].

Microorganisms such as bacteria, algae and fungi under certain conditions can thrive and accelerate the corrosion of many metals even in otherwise benign environments. Biological organisms can enhance the corrosion process by their physical presence, metabolic activities and direct involvement in the corrosion reaction [Hamilton, 1985]. The occurrence of MIC is often characterized by: unexpected severe metal attack, the presence of excessive deposits and in many cases the rotten-egg odor of hydrogen sulfide [Lee et al., 1995].

For a microorganism to grow, environmental conditions must be favorable. Essential nutrients required by most microbes include carbon, nitrogen phosphorous, oxygen, sulfur and hydrogen. Other elements required in trace quantities include potassium, magnesium, calcium, iron, copper, zinc, cobalt and manganese. Carbon is required by all organisms for conversion into cell constituents [Tanji, 1999].

The main bacteria related to MIC are aerobic slime formers, acetate-producing bacteria, acetate-oxidizing bacteria, iron/manganese oxidizing bacteria, methane producers, organic acid producing bacteria, sulfur/sulfide-oxidizing bacteria (SOB), and sulfate-reducing bacteria (SRB).

The most important microbial corrosion is that due to the sulfate reducing bacteria (SRB). SRB thrive under anaerobic (no oxygen) conditions, for example deep in soils and underneath deposits. The best-known examples of SRB are Desulfovibrio and Desulfotomaculum. In many cases SRB derive their carbon (for incorporation into cell material) from low molecular weight compounds such as lactate and fumarate. SRB possessing the enzyme hydrogenase and can obtain their energy from the oxidation of molecular hydrogen. SRB are capable of growing over a wide pH range (4-8) and at temperatures from 10-40°C, although some thermophilic strains can grow in the temperature range 45-90°C, and a pressure up to 500 atm [Herbert and Stott, 1983].

There is no universal mechanism to account for the corrosive action of SRB. It is believed that the iron sulfide formed on the metal surface is an efficient cathodic site for the reduction of hydrogen [Pankhania et al., 1986]. This has the effect of accelerating the corrosion process. Another viewpoint suggests that oxygen made available from the sulfate reduction reaction:

$$SO_4^{2-} \rightarrow S^{2-} + 2O_2 \quad (1)$$

reacts with nascent hydrogen and therefore speed up the cathodic reaction. The overall reaction of the anaerobic corrosion of iron induced by SRB can be described by [Pankhania et al., 1986]:

$$4Fe + SO^{2-}_4 + 4H_2O \rightarrow FeS + 3Fe(OH)_2 + 2OH^- \quad (2)$$

Pankhania [Pankhania et al., 1986] proposed that hydrogen sulfide (H_2S) acts as the cathodic reaction. and showed that the sulfate reduction can occur with cathodically formed hydrogen.

Chen [Chen et al., 1997] discussed many instrumental analysis of microbiologically influenced corrosion. They emphasized that detection and monitoring of microbiologically influenced corrosion is essential for understanding the mechanistic nature of the interactions and for obtaining control methods. The techniques include electrochemical noise measurement, concentric electrodes, scanning vibrating electrode mapping, electrochemical impedance spectroscopy, atomic fore microscopy, confocal laser microscopy, Fourier transform infrared spectroscopy, x-ray photoelectron spectroscopy and auger electron spectroscopy.

Rainha and Fonseca [Rainha and Fanseca, 1997] studied the influence of the sulfate reducing bacteria (SRB) Desulfovibrio desulfuricans ATCC 27774, grown in a lactate/sulfate medium, on the anaerobic corrosion of mild steel. Higher corrosion rates as well as the transpassive dissolution of Fe(0) or Fe(II) compounds to Fe(III) were observed in the presence of bacterial culture. Moreno et al. [Moreno et al., 1992] studied the pitting of stainless steel by the sulfate reducing bacteria (SRB) and found that the biogenic sulfides enhanced the passivity breakdown in the presence of chloride anions.

Many workers studied the performance of different coatings exposed to biologically active environments [Jack et al., 1996]. Meehan and Walch [Jones-Meehan et al., 1992] studied coated steel exposed to mixed communities of marine microorganisms using EDS. The EDS analysis detected breaching of epoxy, nylon and polyurethane coatings applied to steel coupons. SEM and ESEM studies have shown that all coated surfaces of steel were heavily colonized with a diverse assembling of bacteria.

EXPERIMENTAL WORK

Sulfate reducing bacteria (SRB) Desulfovibrio desulfuricans culture medium was prepared with the composition: KH_2PO_4 (0.5 g/l), NH_4Cl (1.0 g/l), Na_2SO_4 (1.0 g/l), $CaCl_2$-$2H_2O$ (0.1 g/l), $MgSO_4.7H_2O$ (2.0 g/l), sodium lactate (3.5 g/l), yeast extract (1.0 g/l), cystein solution (1.0 ml/l) and ferrous ammonium sulfate (5.0 ml/l). Preparation of this media was performed by sequential addition of compounds to deionized water. The pH of the culture was adjusted to 7.6 , and the medium was sterilized at 130 °C for 25 minutes. The medium was kept in an incubator at 33 °C under anaerobic conditions (sealed containers). After 30 hrs of inoculation the population of SRB was counted using the plate count method and was found to be 6×10^6 cells/ml.

Oil based coating was used to protect the mild steel surfaces against MIC effects. Oil based coatings include materials that are based entirely on oil, such as linseed oil-based products, alkyds, alkyd enamels, oil based varnishes, and similar materials. One of the principal characteristics of this type of coatings, that it is generally applied in thin films. Another characteristic of these types of coatings is their wettability of most surfaces. On the other hand one of the oil coating disadvantages, that they are not highly corrosion resistant. This is due to the relatively high moisture vapor transfer rate and the transfer of ions through the coating.

In this study alkyd coating was used, because it has the broadest usage. Alkyds also can be modified to improve their properties mainly their corrosion resistance. The alkyd coating was applied on 800-grid hand polished mild steel surfaces using brush. The average coating thickness was measured and found to be in the range of 4-5 mils.

Natural products were added to the alkyd coating to study their effects on the modified coating protective properties compared to the basic ones. Nearly all the natural oils of both the animal origin like Manhaden fish oil and the plant origin like olive oil consist almost exclusively of the simple lipid class – triacylglycerols with the stereochemical configuration shown in Fig. 1.

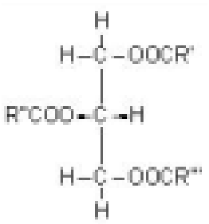

Fig. 1 Stereo-chemical structure and configuration of triacylglycerols.

The different metal coupons were then immersed in the SRB medium and kept in sealed containers for three months. The studied coupons were: uncoated mild steel, mild steel coated with alkyd, mild steel coated with alkyd mixed with Manhaden fish oil and mild steel coated with alkyd mixed with olive oil. After the three months incubation period, the samples were investigated using different microscopic and analytical techniques.

RESULTS AND DISCUSSION

It was found that the sulfate reducing bacteria (SRB) grew at different rates on the studied mild steel surfaces. This variation in the growth rate led to the formation of discrete biofilms and bacterial colonies attached to the coupon surfaces as shown in Fig. 2.

Within each biofilm, the local physical and chemical conditions created an environment that helped in the microorganisms attack. Those biofilms profoundly caused microbially influenced corrosion on the surfaces on which they grew in different rates. Scanning electron micrographs of mild steel surfaces showed heavy microbial colonization after exposure to the SRB culture for 3 months.

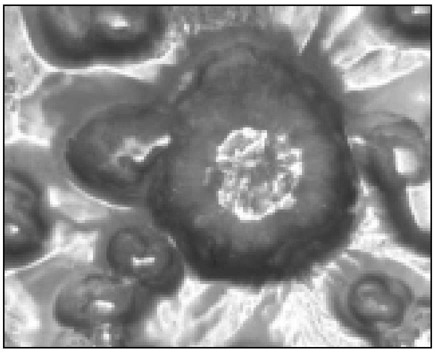

Fig. 2 SEM photomicrograph of the bacterial colonies attached to the coupon surfaces, 2000x.

Fig. 3 shows a scanning electron micrograph of uncoated mild steel coupon. Bacteria colonies and biofilm matrices were observed to be attached to the surface between the layers of the heavy and dense corrosion products. Small holes under the corrosion product deposits were observed and this can attributed to both the SRB and chloride attacks.

Most MIC, however, manifests as localized corrosion because most of the organisms do not form in a continuous film on the metal surface. Microscopic organisms tend to settle on metal surfaces in the form of discrete colonies or at least spotty, rather than continuous films, and this explains the localized (intergranular or pitting) corrosion on the metal coupons as shown in Fig. 4.

Fig. 3 SEM photomicrograph of uncoated mild steel shows the SRB attack on the coupon surface, 800x.

Fig. 4 SEM photomicrograph shows the localized attack (intergranular or pitting) on uncoated mild steel coupon surface, 2000x.

Fig. 5 shows a scanning electron micrograph of a mild steel coupon coated with alkyd without any additives. Bacterial colonies can be seen attached to the coating surface. Breaching of the coating was detected on the surface, which lead to pitting localized corrosion. Biodegradation of the coating was also detected as holes with bacteria in and around the holidays. Black ferrous sulfide deposits were detected underneath the breaches in the coating layer as shown in Fig. 6. Those effects were highly pronounced at the corners, edges, and around the suspension hole.

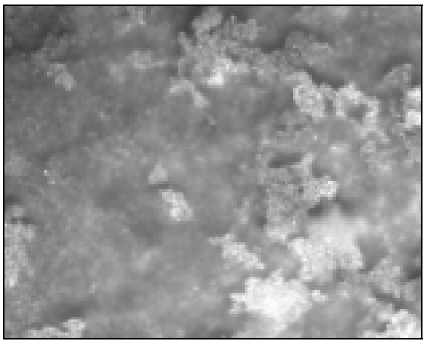

Fig. 5 SEM photomicrograph shows biofilms attached to the surface of mild steel coupon coated with alkyd, 1000x.

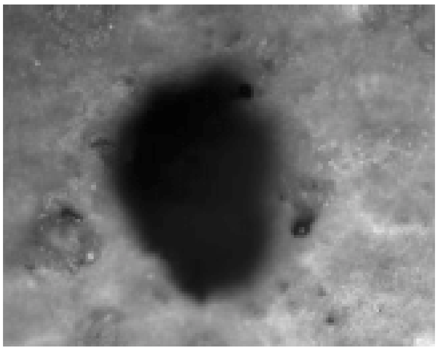

Fig. 6 SEM photomicrograph shows a hole in the surface of mild steel coupon coated with alkyd, 1500x.

Fig. 7 shows a scanning electron micrograph of a mild steel coupon coated with alkyd mixed with olive oil. No biofilms were detected on the surface, but on the other hand few spots were observed at different location on the surface. Blistering without rupturing of the coating where observed on the coated surface which is an indication of some microbial processes occurring beneath the coating.

Its worth mentioning here that the SRB existing in the slim layer (biofilm) convert sulfates in the sample into H_2S. The hydrogen sulfide, and carbon dioxide (CO_2) react with water to produce a mild acidic condition that affects the metal surface. This process lowers the pH of the substrate surface to levels favorable for the growth of bacteria that at the end creates a very acidic environment, thereby encouraging rapid corrosion.

Fig. 8 shows a scanning electron micrograph of a mild steel coupon coated with alkyd coating mixed with Manhaden fish oil. Few bacterial colonies and a very thin biofilm can be observed on the surface. No breaches, blistering or deterioration were detected on the surface. The coated surface was found to be well protected.

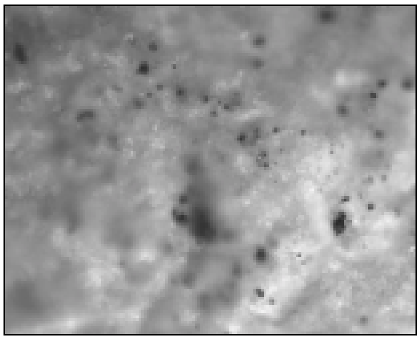

Fig. 7 SEM photomicrograph shows some pinholes on the surface of coated mild steel coupon with alkyd mixed with olive oil, 1000x.

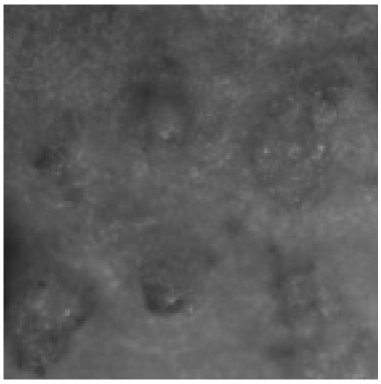

Fig. 8 SEM photomicrograph shows the surface of a well protected mild steel coupon coated with alkyd mixed with fish oil, 1000x.

CONCLUSIONS

The black ferrous sulfide detected on some of the tested coupons confirmed the activity of SRB on the surfaces and as a result MIC attack The presence of SRB reduced sulfate to sulfide, which reacted with iron and produced the black ferrous sulfide.

Bacteria and biofilms were heavily attached to the uncoated and coated surfaces without natural additives as discrete colonies rather than continuous films. This explains the fast propagation rate of localized (intergranular or pitting) corrosion on those surfaces..

The microbial influenced corrosion (MIC) attack appeared to proceed at a lower rate on the surfaces coated with alkyd mixed with the natural additives due to a marked inhibition of bacterial adhesion on those surfaces, and its believed that some of the additives increased the corrosion resistance properties of the modified alkyd.

Mixing natural products mainly fish oils with oil-based coatings like alkyd showed a positive result towards inhibiting both the biofilm formation and the microbial induced corrosion (MIC) effects on mild steel surfaces.

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