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Transient early and longer term influence of bacteria on marine corrosion of steel

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There are essentially two periods when microbiological activity is important for the corrosion of steel coupons in marine environments. The first commences soon after first exposure but becomes ineffective after some months, for reason(s) not yet elucidated. The second period commences when sufficient rust layers have built-up on the corroding surface to permit new microbiological activity under suboxic and anoxic conditions. Since microbiological activity depends on the availability of appropriate micro-environments and on the rate of supply of necessary nutrients, it is argued that the first period concludes as a result of the changing micro-environment caused by the build-up of corrosion products. This interferes both with the metabolite flux and the availability of iron as a necessary nutrient for bacterial metabolism. A model consistent with field observations is proposed.

Keywords: MIC, Corrosion, Bacteria, Nutrients, Steel, Seawater

Introduction

The influence of microbiological activity on the corrosion of steel in marine environments consists of essentially two periods.¹ The first period commences almost immediately the metal surface is exposed to seawater. It is the result of the biofilm that develops and grows on the metal surface eventually providing an appropriate habitat for bacteria that can influence corrosion. Although the biofilm remains on the surface, the corrosion effect typically lasts only a few weeks–months, for reasons not yet elucidated.

The biofilm is a complex system composed of microbial cells, their extracellular polymeric substances and inorganic components derived from the seawater and the corroding steel.² It grows in volume and hence in thickness with time and eventually provides localised anoxic (and suboxic) niches. It is these that can provide suitable environments for obligatory anaerobic bacteria such as the sulphate reducing bacteria (SRB). They have been implicated extensively in the early corrosion process.³ In addition, in the suboxic niches other bacteria, such as ferrous oxidising bacteria (FOB), may be able to flourish and hence to contribute to corrosion. Certainly not all aspects of bacterial surface colonisation, development and contribution to early corrosion are fully understood at this time and research activity continues unabated.⁴

There is a second, later and long term, period during which SRB (and also FOB) activity may be involved in the marine corrosion of steel. Again, suboxic and anoxic conditions are necessary. In this second period, these

conditions result by the ferrous rust layers as their increasing thickness gradually causes a reduction in the diffusion of oxygen from the external environment. For steels exposed to immersion conditions, SRB in particular have been detected in the rust layers and have been implicated in the development of the rusts, including the production of iron sulphides (FeS).⁵ Moreover, from field observations over 16 years in the tropics SRB have been implicated in the long term marine immersion corrosion of steel.⁶ Bacterial activity has been associated also with the longer term corrosion of steels exposed in the tidal zone and in the coastal atmospheric zone.^{7,8} Evidence for the involvement of other bacteria, such as the FOB, also has been found.

The matter of interest for the present paper is the relationship between the two periods of microbiologically influenced corrosion and in particular the reason for the period of early bacterial influenced corrosion appearing to die out. This question was raised earlier without resolution.^{1,9}

Background

The context of the two periods of bacterial activity described above is shown in the idealised model for corrosion loss as a function of exposure time (Fig. 1).¹ This model has been shown to be applicable to immersion, tidal and coastal atmospheric conditions⁷ and for each there is now sufficient evidence that bacterial activity is involved particularly in longer term exposures.⁸

There are five sequential phases involved in the corrosion process (Fig. 1). Here it is sufficient to note that the corrosion process changes from involving a complex mix of activities including chemical kinetics and often biofilm formation and biological activity (phase 0), through some further biological activity and also

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1 Model for corrosion loss as function of time, showing sequential phases (0-4)

oxidation of the iron component of the steel with constraint on oxidation diffusion from the external environment provided initially by concentration control (phase 1) and later (phase 2) by diffusion control exerted by the build-up of rust layers. The first period of bacterial activity, if it occurs, commences and discontinues through these phases.

The second period of bacterial activity occurs during phases 3 and 4 of the model in Fig. 1. In phase 3 the rate of corrosion is a function of nutrient availability, including those stored in the rust layers. In phase 4 the rate of corrosion results from a balance between the rate of nutrient supply from the environment, controlled by diffusion through the rust layers and the rate of erosion of the rust layers. Models for these and for the transition from earlier oxidation processes have been developed.¹⁰

Corrosion caused by bacterial activity is generally considered to depend on the rate of bacterial metabolism. For SRB it is the result of metabolite production, principally H_2S acting on the steel to produce FeS .¹¹ For other bacteria, such as the FOB, although metabolism is considered to be involved, the precise mechanisms are less clear.¹² In all cases, the rate of bacterial metabolism (and hence the rate of corrosion) depends on the rate of availability of appropriate nutrients. Normally seawater has an abundance of sulphates and, provided diffusion or other transport mechanisms permit it, the corrosion of steel provides iron. Thus neither of these is likely to be limiting. Organic carbon tends to be available from decomposing organic matter in seawater or can be metamorphosed from inorganic carbon by other bacteria acting in bacterial communities.¹³ As a result, the limiting nutrient for seawater corrosion of steel typically is nitrogen, available as ammonia, nitrate and, to a lesser degree, nitrites.¹⁴

Empirical correlation between enhanced marine immersion corrosion losses and nutrient pollution has been demonstrated for the early period of exposure.¹⁵ It has been demonstrated also for corrosion in phases 3 and 4 of the model, i.e. for longer term corrosion.¹⁶ Since nutrients are available in the external environment throughout, it follows that the change from earlier to later microbiological activity cannot be a function of the environment. The reason must be sought elsewhere. It will be shown in the next section that it is the result of changing conditions at the corroding surface.

Model for intermittent bacterial influence

The changing nature of the environment immediately adjacent to the corroding surface as a function of time

a biofilm with anoxic niches potentially containing SRB provided with nutrients from external environment and production of bacterial metabolites that cause localised corrosion (oxygen diffuses from external environment through biofilm to cause oxidation of metal substrate); b increasing thickness of rust layer reduces ability of metabolites to diffuse to metal surface and also reduces Fe ions (nutrient) reaching bacteria (oxygen flux is gradually reduced as rust layer increases in thickness); c eventually anoxic niches develop in rust layer and scenario of a is repeated but now within rust layer

2 Schematic of development of bacterial activity with time

can be idealised as shown in Fig. 2. Almost immediately upon exposure the metal surface is colonised by biofilm and this continues to grow with time.¹⁷ Typically, sub-oxic and anoxic niches develop in the growing biofilm, shown schematically in Fig. 2a. These can harbour bacteria. The following remarks are confined mainly to SRB.

Figure 2a shows the SRB located somewhat away from the corroding surface. At the corroding surface pH levels around 1.5-2 have been recorded but the tolerance of and metabolic activity of SRB is known to be optimal around circum neutral pH.¹³ Thus the bulk of the SRB are likely to be located at locations with suitable pH levels as given by the pH gradient (Fig. 2a).

As shown in the inset to Fig. 2a, the metabolites from SRB activity can diffuse through the biofilm separating the anoxic niches and the metal surface. The metabolites are principally H_2S ,¹¹ and cause localised corrosion by a conventional electrochemical reaction with S^{2-} or HS^- as the electron acceptor. The result will be localised pitting and the production of FeS as the corrosion product. However, this reaction is not the only one occurring at this time. Oxygen can diffuse through the biofilm elsewhere and act as the electron acceptor to create conventional iron oxihydroxides. The combined effect is the creation of a rust layer heterogenous both in thickness and spatially.

As the corrosion processes continue, the rust layer will increase in thickness and become increasingly more difficult a barrier for the diffusion of metabolites from

3 Typical example of highly pitted, bright steel localised corrosion surface caused by bacterial metabolites, as revealed by simple removal of exterior rusts: photograph size covers 50×25 mm

the SRB and for the diffusion of oxygen from the exterior environment. Also, the increasing thickness of the rust layer is likely to impede the movement of ferrous ions (i.e. an essential nutrient) from the steel to the SRB. Although the relative concentration gradients and the relative diffusion coefficients are not known in general, it may be assumed, reasonably, that the diffusion of metabolites towards and of ferrous ions away from the metal surface is likely to decrease at a faster rate than the inward diffusion of oxygen, leaving the scenario shown schematically in Fig. 2b. It shows the increasing thickness of the rust layer having effectively stopped both the production (due to reducing Fe availability) and the diffusion of bacterial metabolites but still permitting the diffusion of oxygen. This can be equated with the later part of phase 1 and with phase 2 in the model of Fig. 1. Evidently the biofilm with its anoxic niches continues to exist exterior to the rust layer but the SRB that inhabit these niches now have little or no effect on the corrosion process, irrespective of their rate of metabolite production. The instantaneous rate of corrosion is now governed entirely by the rate of diffusion of oxygen acting as the only electron acceptor.

Consistent with the closing stages of phase 2 of the model of Fig. 1, eventually the rate of oxygen diffusion from the external environment will be much reduced, sufficient for localised anoxic niches to develop within the rust layer and in close proximity to the metal surface. SRB activity is now again possible but this time within the rust layer. This stage corresponds to the commencement of phase 3. As before, pH gradients limit the location of active SRB activity to anoxic niches removed some small distance from the low pH of the corroding surface. Again, the ferrous ions necessary for SRB activity are available also at this location. Figure 2c shows the resulting scenario schematically. At this stage there is considerable corrosion product over the metal surface and it will be inhibiting the diffusion of oxygen from the external environment. As a result, the spatial distribution of the anoxic niches parallel to the metal surface is likely to be considerable. However, their distribution through the thickness of the rust layer will be much more constrained owing to the considerable oxygen gradient through the rust layer. Now the metabolites from the SRB must diffuse through the relatively thin layer of rust between the bacterially active niches and the corroding surface, causing patchy, highly

4 Trends for variation of bacterial count data as function of exposure time for tropical Yulin site (based on data from Ref. 18)

distinctive bright steel pitted corroded surfaces. A typical example is shown in Fig. 3.

As the nutrients stored in the rust layer become depleted¹⁰ the overall corrosion situation gradually moves through phase 3 to stabilise eventually in phase 4 (Fig. 1). During this time, and subsequently, the essential mechanism remains as in Fig. 2c. Again, S^{2-} or HS^- acts as the electron acceptor.

Example

The transient nature of the bacterial activity in the biofilm that form on a metal surface upon exposure to seawater can be seen in the data reported by Peng *et al.*¹⁸ for bacterial counts taken for rusts on steels immersed over a 12 month period at Yulin (Fig. 4) and at Qingdao (Fig. 5) in China. Seawater pH and salinity at these sites were similar but seawater temperatures averaged 26.3 and 13.7°C respectively. Despite very significant differences in total bacterial counts and in the temporal

5 Trends for variation of bacterial count data as function of exposure time for temperate climate Qingdao site (based on data from Ref. 18)

variation of bacteria within the rust layers, similar bacteria were observed at the two sites, including SRB, heterotrophic bacteria, iron bacteria (most likely FOB), neutral sulphur oxidising bacteria (SOB) and acid SOB. Moreover, at both sites the rusts were found to contain traces of FeS after about one month exposure and this increased to around 6–8% after three months. This observation is consistent with the presence of SRB in the biofilm or in the rust layers or both.

The trends in Figs. 4 and 5 may be compared, approximately, with the model of Fig. 1 and the calibrated parameters for it as a function of seawater temperature.¹⁹ It may be compared also with corrosion loss data for these sites²⁰ and with subsequent interpretation of that data.²¹ For the Yulin site the transition from oxidation to long term bacterial corrosion as given by parameter t_a is approximately 0.8 years. In contrast for the Qingdao site t_a is about two years. This means that in both cases the rise and the fall of SRB activity is well within the period (phases 0–2) described by t_a , and is most likely within phases (0–1) of the model. The trends for the FOB and the other bacteria are not nearly as clear. The potential reasons for these observations will be discussed below.

Discussion

The above example shows that the SRB bacterial counts, and thus, presumably, the activity of the SRB rises and falls within a relatively short time after first exposure and that this appears to be inversely related to FOB activity. There is thus a change from predominantly anoxic bacterial to suboxic bacterial activity and this is reflected in the types of corrosion products formed.²² This behaviour is consistent with the model of Fig. 2, with SRB activity continuing whilst the environmental conditions are (semicontinuously) anoxic and necessary nutrients, including ferrous ions, are available. When the latter become difficult to obtain, as when the biofilm becomes increasingly further separated from the corroding steel surface, the activity of the SRB becomes inhibited, as seen in Figs. 4 and 5. This shows clearly that the early activity of SRB does not continue indefinitely but rather that it is transitory as modelled in Fig. 2.

Little has been said in the above about the role and action of FOB. These are known to require only low oxygen (suboxic) conditions¹² and to be much more tolerant to extreme (low) pH conditions. This suggests that they could be spread more diffusely both in the biofilm and in the rust layers. They also could exist in the immediate vicinity of the corroding surface. They have been detected there both after short term exposures and after many years of continuous immersion and atmospheric exposures.⁸ Because the corrosion products they generate are iron oxihydroxides or magnetite, all of which are normally generated also in abiotic environments, there is no immediately obvious rust 'signature' equivalent to FeS for SRB. This makes analysis for the influence of FOB more problematic.

Both Figs. 4 and 5 suggest that FOB activity may have a moderate increase with time although Fig. 4 suggests with considerable variability. It may be speculated that this is likely to be the result of the availability of suboxic conditions. It is unlikely to be the result of the rate of nutrient availability since if FOB can

exist close to the corroding surface owing to their pH tolerance, their iron nutrient supply is unlikely to be disrupted as the corrosion product layer increases. Clearly much remains to be understood about the mechanisms involved with the contribution of FOB to corrosion and of the factors involved. Nevertheless, given their repeated detection in association with the marine corrosion of steel it seems they are intimately involved in the process provided the environmental and nutrient conditions are suitable.

Figures 4 and 5 show that heterotrophic and SOB also are present in the rusts and biofilm examined. Evidently the SOB are not prominent early in the process but their numbers increase later. The heterotrophic bacteria appear to shadow the SRB and later the SOB. These observations presumably reflect the known fact that bacteria appear to flourish in bacterial consortia.

The observations of bacterial activity in Figs. 4 and 5 and the resulting correlations have all been obtained using data obtained from field experiments using natural *in situ* seawater. This is important because natural seawater is a biotic 'soup' that relies on the continual activity and interaction of its various components and with the atmosphere. The use of (even large) samples of seawater for laboratory experiments (transported seawater) does not produce the same results for corrosion loss and for pitting, as has been demonstrated a number of times.¹⁵ In contrast, the so called artificial seawaters lack biotic components and are therefore unsuitable for studying the influence of bacterial activity on corrosion.

Finally, the interpretations given in Fig. 2 regarding the location of anoxic niches suitable for SRB activity show that the nutrients from the external environment need diffuse through less than the full rust layer thickness and the SRB metabolites must diffuse to the corroding surface to have an influence on corrosion. These aspects were not considered in the mathematical modelling of phases 3 and 4 described by Melchers and Wells.¹⁰ Considerably deeper understanding of the mechanisms involved and various properties of the biofilm and rust layers will be required to add these refinements to the mathematical model.

Conclusion

1. A model is proposed herein to explain the declining influence of bacterially induced corrosion in the early stages of exposure of steels to seawater and marine environments. It is proposed that this phenomenon is the result of the changing micro-environment surrounding the relevant bacteria, with the gradual build-up of rusts increasingly impeding the diffusion of bacterial metabolites towards the corroding surface. The rust layer also impedes the diffusion of Fe ions towards the bacteria, thereby gradually reducing the rate of supply of this nutrient necessary for bacterial metabolism.

2. With increased exposure time the building-up of the heterogeneous rust layer allows the development of anoxic (and suboxic) niches. These permit the re-establishment of bacterial activity close to the corroding metal surface, thereby creating the conditions for long-term involvement of bacteria in the corrosion of steel in marine exposures.

3. Limited field trial observations suggest that consortia of bacteria are involved but that the sulphate

reducing bacteria play an important role both in the very early period and much later, causing characteristic bright metal corroded surfaces that are densely pitted.

4. The FOB appear to be most numerous during the oxidation phase 2, suggesting that even the iron oxidation processes are accompanied, if not assisted, by bacterial action.

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