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Biocorrosion of carbon steel by iron reducing bacteria

Héctor A. Videla[1], Sylvie Le Borgne[2], Juan M. Romero

Abstract

The role of Iron Reducing Bacteria (IRB) in biocorrosion is a controversial subject. According to some publications IRB are able to induce protection of carbon steel while others suggest an important enhancement of corrosion through the solubilization and removal of the passive films of iron oxides which facilitate the direct contact of other corrosive bacteria like SRB with the metal surface. In this paper it is supplied experimental evidence to support the last assumption by means of electrochemical laboratory experiments complemented with scanning electron microscopy (SEM) observations.

Key-words: iron reducing bacteria (IRB), carbon steel, biocorrosion, biofilms.

Introduction

Iron reducers derive benefit from reduction of Fe^{+3} by using this ion as a terminal electron acceptor in their metabolism. This can be done in two ways: either through the use of an electron transport chain in anaerobic respiration, or by the use of Fe^{+3} as an auxiliary "electron sink" during fermentation.
Reduction of Fe^{+3} is growth linked and for some of these bacteria significant anaerobic growth does not occur in the absence of Fe^{+3}. Many of the bacteria using anaerobic respiration for reduction of ferric ion can also use nitrate as a terminal electron acceptor (1). The iron reducers which use ferric ion as a terminal electron acceptor in anaerobic respiration have been of greatest interest in steel corrosion studies. A good example is *Shewanella putrefasciens* (2).
For most organisms which can grow in the absence of oxygen, a fermentative mechanism is used and the bacteria usually use an organic compound as their final electron acceptor. To augment the limited amount of ATP produced under fermentation, Fe^{+3} can be used under anaerobic conditions by many fermenting bacteria as an auxiliary electron acceptor or "electron sink" during fermentative processes (3).
Like most bacteria, and like the denitrifiers and SRB in particular, the iron reducers prefer neutral pH. Thus acid conditions which enhance chemical corrosion do not assist them. Some

[1] Full Professor in Biodeterioration of Materials -UTN-FRLP. Senior researcher and consultant, La Plata, Argentina.
[2] Professor and researcher. Universidad Autónoma Metropolitana-Unidad Cuajimalpa, D.F., México.

of the marine bacteria are halotolerant and capable of reducing ferric ion in the presence of high chloride concentrations. *Shewanella algae* is an example of one of these bacteria (4). IRB can be found in cold temperature and mesophilic conditions. Also, thermophilic members of the group have been found.
Amongst several explanations for a contributing role of iron reducers in corrosion of steel, it has been assumed that their reduction of ferric ion promotes the solubilization and removal of the protective passivating film of oxide which forms on exposed iron alloy surfaces, or that they are involved in biofilms which act to set up differential electrical cells which promote corrosion (5). Moreover, it is also argued that reduction of ferric ion by dissimilatory iron reducers in biofilm are able to retard the reduction process inducing metal protection (6). Contact between bacteria and ferric compounds should be necessary to achieve iron reduction This assumption has been supported by the results of laboratory experiments using *Shewanella oneidensis* (7) in which the contact between the microorganisms and the iron oxides was impeded by means of a semipermeable membrane. Results of these experiments showed that metal reduction required a direct contact between the cells and the metal surface. Moreover, the rate of reduction was directly related to surface area.
The aim of this paper is to describe a laboratory case where IRB influence SRB induced corrosion of carbon steel by using a batch fermentor where a mixed culture of a marine vibrio (*Vibrio alginolyticus)* and SRB are grown in saline Postgate C medium (8).

Experimental

SRB were isolated from circulating water in a petroleum distillery cooling system and purified by successive cultivation in Postgate C medium *Vibrio alginolyticus* (*V. alginolyticus*) was isolated from water collected from the port of Mar del Plata, Argentina. The water of this port is heavily polluted by fishing activities (9).
Bacteria were grown as batch cultures at 30^{o}C in a laboratory batch fermenting unit using a 5 l vessel with pH controlled between 6.0 -7.0 by the addition of a 0.5 M sulfuric acid solution. Growth was monitored by the rate of sulfuric acid addition required to maintain the pH. Dissolved oxygen concentration was monitored with an oxygen probe. In the early stages of inoculation the dissolved oxygen concentration dropped to 8 %. After 14 h the redox potential (*vs.* standard hydrogen electrode, SHE) was -0.190 V and after 36 h – 0.260 V. Anaerobic conditions created by *V. alginolyticus* respiration allowed SRB growth. Several carbon steel specimens were incubated in the culture vessel and removed in pairs at intervals during incubation. One specimen was used for SEM observations and the other for ex-situ potentiodynamic polarization experiments. Temperature was fixed at 30 +/- 0.1^{o}C. The open circuit potential of carbon steel was monitored against a standard calomel electrode (SCE). Table 1 shows the effect of inorganic components (NaCl, Na_2S) and microorganisms (*V. alginolyticus*, SRB) on the breakdown potential (E_b) of carbon steel.
These data show that *V. alginolyticus* alone is able to corrode carbon steel. When SRB are added to the culture during the logarithmic phase of growth, lower breakdown potential values indicate enhanced localized corrosion of the steel. Finally, the addition of sodium sulfide decreases the breakdown potential although less significantly than SRB does.
The sequence of events occurring on the metal surface can be described in this way: after a few hours of immersion, carbon steel surface was covered by a surface film of oxide above which a complex layer of amorphous corrosion products could be seen by SEM. Isolated bacterial cells colonized the layer of corrosion products. After longer periods of immersion (48-76 hours) many areas of carbon steel surface appeared densely covered by different layers of corrosion products impeding a direct observation of the microorganisms. Generally, these corrosion products correspond to spheres of dense colloidal goethite (hydrated iron oxides)

and some accumulation of crystals of hematite ($Fe_2 O_3$). In spite of the highly irregular topography of the metal surface, bacterial colonies could be seen between crystalline accumulations. Under these experimental conditions electrochemical anodic polarization curves revealed a decrease of breakdown potentials (Table 1) and a highly negative and unstable open circuit potential vs. time recordings. The localized attack appeared preferentially in the areas that were covered by microbial colonies. This attack could be explained as a sum of the following effects: a) differential aeration effects between covered and uncovered metal surface by microbial colonies; b) despassivation of the metal surface by microbial reduction of Fe^{+3} deposits into soluble Fe^{+2} compounds as it has been reported in the literature (10) This effect can be enhanced by microbial consortia with SRB within the biofilm thickness leading to an increase in concentration and variety of metabolic corrosive products.
SRB influenced corrosion of steel is markedly affected by the nature and the structure of the sulfide films produced during the metal dissolution (10, 11) The environmental characteristics of the metal/biofilm/ medium interface and its surroundings (pH, ionic composition, oxygen levels, extracellular polymeric substances (EPS) distribution control the chemical and physical nature of corrosion product layers and may change their effects on the metal behavior from corrosive to protective.(12) In chloride media the impact of sulfur compounds on corrosion is enhanced by chlorides, already present in the medium.
The entrance of oxygen into the anaerobic environment could accelerate corrosion rate, mainly through a change in the chemical nature of iron sulfides and elemental sulfur production. Both chemical species can provide additional cathodic reactants to the corrosion process, acting as electron carriers between the metal and the oxic interface within the biofilm.
The main mechanisms of corrosion inhibition by bacteria are always linked to a marked modification of the environmental conditions at the metal/solution interface by biological activity. It must be stressed that in practical situations, the inhibitory action of bacteria can be reversed to a corrosive action in the bacterial consortia structured in the biofilm. A proper understanding of the identity and role of microbial contaminants in the specific environment of a metal surface may be used to induce corrosion inhibition by bacteria as a useful tool to prevent frequent biocorrosion effects encountered in practice. Such cohesive effect of EPS in a biofilm will depend on several environmental and biological factors and will finally determine the extent of corrosion product/biofilm interactions. The last effect can be enhanced by microbial consortia within the biofilm thickness leading to an increase in concentration and variety of metabolic corrosive species.

Conclusions

The corrosive or the inhibitory action of bacteria are developed at biofilmed metal surfaces where complex biofilm/protective films interactions occur. The main mechanisms of corrosion inhibition by bacteria are always linked to a marked modification of the environmental conditions at the metal/solution interface by biological activity
The iron reducing bacteria *V. alginolyticus* tested in this work, may promote chemical or biological SRB-induced corrosion of carbon steel by removing protective corrosion products (insoluble Fe^{+3} compounds) from the metal, allowing corrosive species such as sulfides and chlorides to attack the surface.
Biocorosion and corrosion protection occurs in the presence of complex microbial biofilms in which different physiological types of microorganisms interact in a complex way, the global effect of such interactions is difficult to predict. The effect of the presence of biofilms on metallic surfaces should therefore be preferentially evaluated in the presence of consortia instead of pure cultures, such consortia should be representative of those colonizing the

monitored systems. Recent molecular biology tools allowed the identification of microorganisms present in such consortia.

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TABLE 1

E_b of carbon steel in Postgate medium C with different inorganic components and microorganisms additions

Addition to sterile medium	pH	E_b (V, SCE)
None	8.0	- 0.21
None	7.0	- 0.23
3 % Na Cl	8.0	- 0.37
3 % NaCl + Vibrio	7.8	- 0.43
3 % NaCl + vibrio + 0.001 M Na_2S	7.5	-0.52
3 % NaCl + vibrio + SRB	7.3	-0.60