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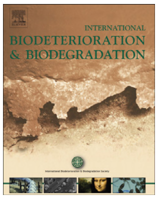

Microorganisms: Induction and inhibition of corrosion in metals

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A B S T R A C T

Corrosion occurs due to chemical or electrochemical reactions between the environment and metal. It can cause dangerous and expensive damage to a wide range of industries. However, it is difficult to evaluate the economic impact of corrosion, particularly when microorganisms are involved in the corrosion mechanism. Microbes change the electrochemical reaction at the biofilm/metal interface and either inhibit or accelerate the process of metal corrosion. The high cost, toxicity, and sometimes ineffectiveness of present physical and chemical strategies to control corrosion have called for the use of microorganisms in inhibitory mechanisms, and this has generated great interest. Although the microbial inhibitory mechanism is environmentally friendly, the predictability of the results is not yet affirmed, as sometimes the same bacteria with an inhibitory property may also become aggressive. This review discusses different mechanisms by which microbes induce or inhibit corrosion in metals. Further, as the corrosive or inhibiting behaviors of microorganisms vary considerably depending on environmental factors, the roles of these factors are also emphasized.

1. Introduction

Metal in its natural state is in the form of ore and it is present in combination with other elements. To strip away these elements and produce pure metal, a large amount of energy is required. As the energy content of metals and alloys gets higher, they become unstable and hence discharge the additional energy. The process by which the metal reverts to its lower energy state is termed corrosion (Schweitzer, 2010).

Corrosion is the interaction between the metallic material and its environment leading to the deterioration of the metal (Hamilton, 1985). It is an electrochemical phenomenon in which electrons are released from the metal at anodic sites and the released electrons are gained at cathodic sites. The cathodic reaction can vary according to the environment of the solution. The predominant reaction at the cathode is an oxygen reduction, which occurs at neutral or alkaline pH. However, under acidic conditions protons may act as cathodic reactants. Typical examples are:

$$M \rightarrow M_2^+ + 2e^- \text{ Anodic reaction}$$

$$1/2O_2 + H_2O + 2e^- \rightarrow 2OH^- \text{ Cathodic reaction at neutral or alkaline pH}$$

$$2H^+ + 2e^- \rightarrow H_2 \text{ Cathodic reaction at acidic pH}$$

According to DIN EN ISO 8044 (1999), standard corrosion may often lead to impairment of the function of the metal, the environment, or the technical system in which these form a part. Billions of dollars are spent annually for the replacement of corroded structures and machinery parts. Although assessment of the cost of corrosion is difficult, corrosion's annual cost worldwide is estimated to exceed U.S. $1.8 trillion, which translates to 3-4% of the gross domestic product of industrialized countries (Schmitt, 2009). Therefore, there is a need to explore new strategies to prevent corrosion and to improve existing corrosion management techniques.

Corrosion is visualized as a purely chemical process or one that is influenced by microbes. Microbially influenced corrosion (MIC) is a type of corrosion in which the deterioration of metallic as well as non-metallic material occurs due to the presence and activities of microorganisms. Microorganisms such as bacteria, fungi (Geweely, 2011), and algae (Javaherdashti et al., 2009) can influence corrosion. Major bacteria involved in MIC are sulfate-reducing bacteria (SRB) (Enning et al., 2012), manganese/iron oxidizing bacteria (Rajasekar et al., 2005), iron-reducing bacteria (Herrera and Videla, 2009), and acid-producing bacteria (Li et al., 2008). These bacteria are commonly present in communities as biofilm and influence the electrochemical process as a consequence of their metabolic activity.

The biofilm process begins when the physiochemical interaction takes place between bacterial cell and the conditioned surface. Following the production of bacterial exopolysaccharides, the cells

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get firmly attached to the metal surface and other surface-bound organisms. There will be an increase in cell density as well as in the complexity of the biofilm. Finally the cells get detached from the outermost layer of the biofilm when a critical mass is reached (Dunne, 2002). Biofilm gives protection to its inhabitants to some extent against certain environmental threats such as biocides and antibiotics (Roberts and Stewart, 2005). However, it actively participates in corrosion through several mechanisms, which include the formation of differential concentration cells, generation of corrosive substances, alteration of anion ratios, and inactivation of corrosion inhibitors.

2. Mechanisms of microbiologically influenced corrosion

2.1. Differential concentration cells

Differential concentration corrosion occurs when two or more areas of a metal surface are in contact with different concentrations of the same solution. There are three general types of concentration cell corrosion: oxygen concentration cells, metal ion concentration cells, and active-passive cells (France, 1972).

An oxygen concentration cell can develop if there is a difference in oxygen concentration between two points; the area of the metal that is in contact with the low concentration of oxygen will be anodic and the area of metal in contact with high oxygen concentrations will act as a cathode. One factor that encourages the formation of differential aeration cell is the nonuniform biofilm layer. Biofilm acts as a barrier, preventing diffusion of oxygen to the metal surface. However, the patchy and heterogeneous way biofilms get distributed creates differences in oxygen concentration between coated and uncoated areas of metal. Another factor that may contribute to the formation of differential aeration cell is the bacterial aerobic respiration. During aerobic respiration, areas of metal under the respiratory colonies act as anodes, while areas away from these colonies, with higher oxygen concentration serve as cathodes.

Differential oxygen concentration cell accelerates the formation of tubercles (round deposits, compact at the edge and loose in the center) (Herro, 1991). This structure in turn promotes more oxygen concentration cell. In the compact area of the tubercle, little oxygen diffuses to the bottom of the surface, whereas the loose deposits in the center will have a higher concentration of oxygen. Ray et al. (2009) investigated the structure and mineralogy of corrosion products formed on carbon steel coupons in the Duluth Superior Harbor. They observed iron-oxidizing bacteria within the tubercles. Iron-oxidizing bacteria present in the tubercle can also encourage the formation of more tubercles (Tiller, 1982). This bacterium oxidizes ferrous ions to ferric ions to get energy, which results in the formation of an iron oxide deposit. In some of the iron-oxidizing bacteria, such as *Leptothrix* sp., iron oxide deposits on the bacterial sheath form a membrane that is impervious to oxygen, and this decreases the oxygen content inside the tubercle (Rao et al., 2000).

When microorganisms colonize on a metal surface they produce extracellular polymeric substances (EPS) that contain different functional groups. These groups with different affinities for metal ions give rise to the formation of metal concentration cell. Those areas underneath exopolymers with high affinities for the metal act as anodes while areas underneath exopolymers with low affinities act as cathodes. Dong et al. (2011) conducted a study to understand the effect of isolated EPS on corrosion of carbon steel. They observed that a small amount of EPS retarded corrosion by inhibiting the mass transfer of oxygen. However, at a high EPS concentration, corrosion inhibition decreased due to the binding of more iron ions to EPS.

Corrosion is also accelerated by the formation of active-passive cells. When the passive layer (usually an oxide film) is broken and an active metal beneath the film is exposed to corrosion attack, an electrochemical reaction takes place between the larger area of the cathode (passive film) and the smaller area of the anode (active metal). Microbes break the passive film by producing metal-chelating agents such as siderophores. Siderophores bind to metal cations which exist in the oxide film and promote iron oxide dissolution, thereby stimulating corrosion. Apart from the siderophore, dissimilatory metal-reducing bacteria also directly degrade passive films. Videla et al. (2008) studied the role of *Vibrio alginolyticus*, an iron-reducing bacterium (IRB), and SRB in the corrosion of carbon steel in chloride-containing media. Though the maximum rate of pitting corrosion was observed in the presence of mixed IRB and SRB biofilm, the rate of corrosion was high in the presence of *V. alginolyticus* alone. The corrosion rate increased in the area covered by the *V. alginolyticus* colony due to the formation of differential aeration cells or the formation of active-passive film. Iron-reducing bacteria can dissolve insoluble ferric oxide to extract the iron necessary for their Fe-dependent anaerobic respiration, which leads to the breakdown of passive iron oxide layers (Herrera and Videla, 2009).

2.2. Generating corrosive substances

Multiple species of bacteria within the biofilm act symbiotically. Some bacteria produce metabolic byproducts that might support the growth of other bacteria. One common example of a symbiotic relationship is that between aerobic sulfide-oxidizing bacteria and anaerobic sulfate-reducing bacteria.

Thiobacillus, a sulfide-oxidizing bacterium, obtains its energy by the oxidation of sulfides and produces sulfuric acid, which could affect the electrochemical reaction and accelerate corrosion. These sulfide-oxidizing bacteria can also oxidize sulfide into elemental sulfur, which is not corrosive at near-ambient temperatures, although it does deposit on the metal surface. Anaerobic areas are formed under these deposits that are conducive to the growth of SRB. The SRB are anaerobic bacteria that use sulfate as terminal electron acceptors and reduce it to sulfide. To achieve this reaction they remove hydrogen from the cathode and stimulate a cathodic reaction (von Wolzogen Kuhr and van der Vlugt, 1934). This produces hydrogen sulfide, as shown in the following reactions.

$$8H_2O \rightarrow 8H^+ + 8OH^- \quad \text{Dissociation of water}$$

$$8e^- + 8H^+ \rightarrow 8H \quad \text{Cathodic reaction}$$

$$SO_4^{2-} + 8H^+ \rightarrow S_2^- + 4H_2O \quad \text{Cathodic depolarization}$$

$$4Fe \rightarrow 4Fe^{2+} + 8e^- \quad \text{Anodic reaction}$$

$$Fe^{2+} + HS^- \rightarrow FeS + H^+ \quad \text{Corrosion product}$$

Hydrogen sulfide is a corrosive agent and can react with the metal to form metal sulfide and atomic hydrogen, which would force more iron to get dissolved at the anode. The generated hydrogen can either combine to form molecular hydrogen and leave the surface as bubbles or enter the metal and cause sulfide stress cracking. The latter process is more probable because hydrogen sulfide prevents hydrogen recombination and thus promotes entry of atomic hydrogen into steel (Kim et al., 2008). Iron sulfides co-produced with hydrogen get precipitated on the surface of metal and accelerate corrosion by creating a new electrochemical active-passive cell, where the layer of the iron sulfide acts as a cathode and the exposed metal surface as an anode (Lewandowski and Beyenal, 2009).