

MICROBIAL CORROSION OF METALS (A REVIEW)

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Abstract

Biocorrosion processes of metal surfaces are associated with microorganisms, or the products of their metabolic activities including enzymes, exopolymers, organic and inorganic acids, as well as volatile compounds such as ammonia or hydrogen sulphide. These can affect cathodic and/or anodic reactions, thus altering electrochemistry at the biofilm/metal interface. Various mechanisms of biocorrosion, reflecting their variety of physiological activities carried out by different types of microorganisms, are identified and recent insights into these mechanisms reviewed. Many recent investigations have centred on the microbial-influenced corrosion of ferrous and copper alloys and of particular interest are *Desulfurivibrio* species, *Thiobacillus* species, *Pseudomonas*, *Methanobacterium*, *Methanospirillum*, *Escherichia coli*, and *Ferrobacillus ferrooxidans*. Some of the factors that influence biocorrosion include; pH, temperature, oxygen, moisture and the nature and types of metal.

Keywords: Biocorrosion, sulphate reducing bacteria, enzymes, exopolymers, electrochemistry.

1. Introduction

Corrosion is a naturally occurring phenomenon which involves the deterioration of a substance (usually a metal) or its properties because of its physicochemical interaction with its environment (van Delinder, 1984). Microbes can cause and influence corrosion because of their ability to influence changes in their environment. If microorganisms are to alter their environment, there must be an adequate source of carbon and energy for growth and metabolism (Obiekwe, 1983). Microbiologically influenced corrosion constitute a dangerous and expensive industrial problem which affect diverse processes ranging from water distribution and waste water system to transport of natural gas and oil in steel pipelines (Jones and Any, 2002). Unlike many natural disasters however, there are proving methods to prevent and control corrosion that can reduce or eliminate its impacts on public safety, the economy and the environment.

Bacteria are considered the primary colonizers of inanimate surfaces in both natural and manmade environments. Therefore, the majority of microbial investigations have addressed the impact of pure or mixed culture bacteria biofilms on corrosion behaviour of iron, copper, aluminium and their alloys (Beech, 2004).

Corrosion of metals by microorganisms had been associated with two genera, the anaerobic *Desulfurivibrio* and the aerobe *Thiobacillus* (Obiekwe, 1983), iron oxidising/reducing bacteria, manganese-oxidising bacteria and bacteria secreting organic acids and slime (Beech, 2004). Their corrosive activities are from their metabolism of

sulphur/sulphur compound, manganese and iron compounds.

Under aerobic condition *Thiobacillus* species oxidise reduced sulphur compound to sulphur acid which corrode the metals. On the other, *Desulfurivibrio* species act anaerobically reducing sulphate to sulphide which reacts with iron to form the characteristic of corrosion product (FeS) (Beech and Coutinbo, 2003).

2. Mechanisms of microbial influenced corrosion

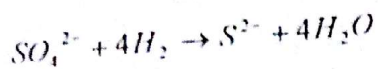
(a) Corrosion of metals under anaerobic conditions
In stagnant water containing materials such as oil, microbes may thrive, especially at conducive temperatures. Bacteria corrosion often proceeds in three stages

(i) Initial microbial proliferation: The oxygen that is normally dissolved in water is used up by bacteria and other microbes, at this stage, mildly acidic organic chemicals are produced by the microbial oxidation processes, which may accelerate ongoing electrolytic corrosion thus making the zone near the microbial growth becomes oxygen deficient and anodic.

(ii) In some cases, conditions are such that a second stage occurs, where one or few specialist species of anaerobic bacteria take over the scene, feeding on the acidic chemicals. The best known of these anaerobic species are the sulphate reducing bacteria. Their characteristic properties are that they utilise the oxygen in sulphate SO_4^{2-} for breathing and

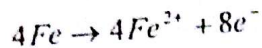
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reduce the sulphate to sulphides S^{2-} (Zhu *et al.*, 1994) as follows:

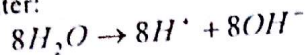


The detailed mechanisms are thus:

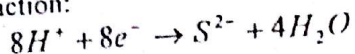
Anodic reaction:



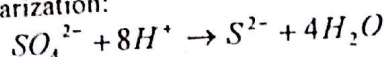
Dissociation of water:



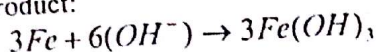
Cathodic reaction:



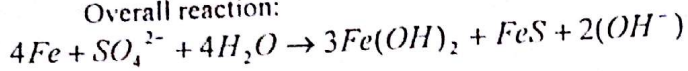
Cathodic polarization:



Corrosion product:



Overall reaction:



[This mechanism suggests that the ratio of the metal to the sulphide is 4:1. Thus, sulphate reducing bacteria which are hydrogenase positive bring about cathodic depolarization as illustrated above (Obiekwe, 1983). Therefore, no depolarization was observed with *Desulfotomaculum orientis* which is hydrogenase negative.

Besides sulphate reducing bacteria, the nitrate reducing bacteria (such as *Pseudomonas*, *Chromobacterium* and *Bacillus*) and methane bacteria (such as *Methanococcus*, *Methanobacterium* and *Methanospirillum*) are actively involved in anaerobic corrosion provided the organisms are hydrogenase positive. *Escherichia coli* is also implicated in anaerobic corrosion by the production of organic acids (Obiekwe, 1983).

(b) Microbial corrosion under aerobic condition

Corrosion due to the activity of microorganisms in aerobic conditions is often the result of the production of a corrosive metabolites, usually this is an acid; either mineral or organic. A wide range of organisms may be concerned in corrosion of this type, but the sulphur-oxidising bacteria are by far the commonest and most important (Beech, 2004). A prevailing theory of microbial influenced corrosion holds that biofilms promote corrosion by inducing the formation of corrosive cells. This is believed to occur as a result of aerobic respiratory activities within the biofilms that leads to the establishment of local cathodic and anodic regions on the steel surface which promote electron flow (Dubiel *et al.*, 2001). Recent evidence however suggests that aerobically respiring bacteria may protect steel from corrosion over the long term which raises questions regarding the extent to which aerobic respiration contributes to corrosion (Dubiel *et al.*, 2001). A

notable organism involved in aerobic biocorrosion is *Ferrobacillus ferrooxidans* that may directly oxidise iron into iron oxides or hydroxides, or oxidise ferrous iron in solution to the ferric state and effect the precipitation of ferric hydroxides (e.g. *Gallionella ferruginea*). Precipitated ferric hydroxides can build up on the surface of a metal component to form hard excrescences known as 'tubercles', which are firmly adherent to the metal surface and may set up an oxygen concentration cell leading to accelerated corrosion at the bottom of the tubercle. The problem is often aggravated by the fact that the anaerobic region at the base of the tubercle provides a suitable habitat for sulphate-reducing microorganism, they proliferate in this region and add their own contribution to the total corrosion (Beech, 2004). *Thiobacillus* species oxidise sulphur compounds to sulphuric acids which corrodes the metal (Obiekwe, 1983). Three species, *Thiobacillus thiooxidans*, *Thiobacillus thioparvus* and *Thiobacillus concretivorus*; found in muds, soil and water oxidise sulphur, thiosulphates, sulphites and several polythionates to sulphates, with the simultaneous production of strong acids. Other corrosive actions exerted by microorganisms also have to do with the formation of concentration cells, possibly in combination with fouling problems (Beech, 2004).

(c) Enzymes and biocorrosion

Catalases, peroxidases and superoxide dismutases are involved in reactions of oxygen reduction, therefore, in principle; they might facilitate corrosion by accelerating the overall cathodic reaction.

The enzyme, dissimilatory sulphite reductase (dsr) is widespread among bacteria sulphite reducers (Ansensden *et al.*, 1993) and is found in one thermophilic genus *Archaeoglobus fulgidus* (Dihl *et al.*, 1993). Dissimilatory sulphite reductase catalyses the central energy conserving step in the dissimilatory sulphate reduction pathway; the six-electron reduction of sulphite to sulphide (Odum and Peck, 1994). Dissimilatory sulphite reductase is either an $\pm 2^2 2$ or $\pm 2^2 2^2 2$ enzymes in the species characterised thus far (Dahl *et al.*, 1993), encoded by dsrA and dsrB (Hipp *et al.*, 1997), which are likely contained in one operon (Larsen *et al.*, 1999) and highly conserved in primary sequence.

The complete genome sequence of *Desulfovibrio vulgaris* encodes oxidases, oxidoreductases, plasmid-encoded catalases and superoxide dismutase (Heidelberg *et al.*, 2004). Furthermore, the analysis of the incomplete genome sequence of the gram positive sulphate reducing bacteria *Desulfotomaculum hafniense* showed genes encoding three catalases of which at least one is extracellular. These catalases are homologues of hydrogen peroxidases I and II (HPI and HPII) and manganese-containing catalases (Beech and Sunner, 2004). The following

enzymes also play a major part in sulphate activation and reduction; pyrophosphatase, ATP sulphurylase, bisulphate reductase, desulphoviridin, desulphorubidin and desulfuscidin (Gibson, 1990).

(d) Environmental measurement of sulphate reducing bacteria

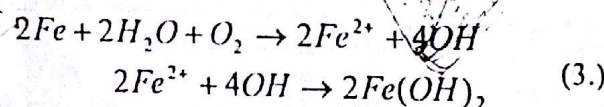
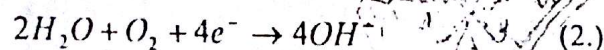
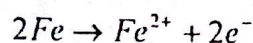
Most Probable Number (MPN) enrichment

The most probable number of sulphate reducing bacteria in environmental samples can be estimated using three tubes per dilution (Banwart, 1981). The MPN experiment were inoculated with water from the cartridges. The media are then prepared by strict anaerobic technique (Balch and Wolfe, 1976) and 9 ml aliquots were dispensed into Hungate screw-capped tubes and sealed with butyl rubber septa. Either lactate (10 mM) or hydrogen (10 %) was then added as the electron donor for sulphate reduction. H_2 is thought to be common energy source for deep surface communities (Stevens and Mckinley, 1995). Tubes containing H_2 were shaken at 200 rpm to overcome gas-transfer limitations. Samples were inoculated at mesophilic and thermophilic temperatures and under low saline (5 gl-1 NaCl) and high saline (50 gl-1 NaCl) conditions. Tubes were observed for growth and sulphide production after 7, 14 or 21 days.

3. Control of biocorrosion

Corrosion control involves the hindering the natural chemical reaction that occur between the metal and its environment (Sondalini, 2003).

In considering corrosion prevention methods, it is important to keep in mind the overall reaction for the corrosion of iron in reactions 1 and 2



From the above equations, it can be deduced that limiting the reaction from left to right will decrease corrosion of iron. In fact, the removal of any one of the reactants from the zone of reaction will prevent the reaction from occurring.

Alternatively, modification of the bulk-phase chemistry such as reducing the assimilable organic carbon concentration or increasing buffering capacity may be considered. It is also critically important to clean sprinkler system, eliminate water from dried sprinkler system, recharging of systems with water containing low concentration of nutrients, critical cleaning of newly installed piping systems to remove organic and inorganic debris and the addition of safe and compatible corrosion inhibitors, avoiding

accumulation of dirt; sludge and foul watery deposits, will reduce the risks. Effective testing, proper maintenance and prompt treatment can also stop MIC activity and prevent reversible damage to sprinkler piping and blockage of critical system components. Thus understanding the factors that contribute to microbial growth and associated corrosion activities is the key to MIC control and prevention (Beech, 2004).

(a) Conditioning the metals

Each metal and alloy has unique and inherent corrosion that can range from the high resistance of noble metals for example gold and platinum to the low corrosion resistance of active metals, for example sodium and magnesium. When the noble metals are metallurgically combined with those lower in the galvanic series, the resulting alloys takes on corrosion resistance properties. The resistance can come from the development of a protective oxide film on the outside surface or because the new alloy has a different voltage potential which acts to make it behave more noble (Sondalini, 2003). Furthermore, the corrosion resistance of a metal depends on the environment to which it is exposed, that is the chemical, temperature, velocity and so on (NACE, 2000).

The general relationship between the rate of corrosion, the corrosivity of the environment and the corrosion resistance of a material is;

$$\frac{(\text{Corrosivity of environment})}{(\text{Corrosion of metal})} = \text{rate of corrosion attack}$$

Passivation of a metal is a method of changing the potential difference of a metal surface. By removing the oxide normally present on a metal and exposing the bare metal directly with an acid, the acid will react with the metallic surface to make a new compound with more noble properties. The passivated layer covers the metal and provided the layer is not broken and the voltage remains favourable, it will protect the metal under it from corrosion (Sondalini, 2003). Thus, for a given corrosion resistance of the material, as the corrosivity of the environment increases, the rate of corrosion increases and as the corrosivity of the environment increases the corrosion resistance of the material decreases.

(b) Modification of the environment

In aerobic corrosion, removing oxygen from the environment prevents completion of the corrosion process by slowing the chemical reaction requiring electrons. The removal of oxygen could be achieved by the use of strong reducing agents e.g. sulphite or by the use of an inert atmosphere. However, for an

open evaporative cooling system, this approach to corrosion prevention is not practical since fresh oxygen from the atmosphere will have continual access. Besides, the pH in the 10-11.5 range slows corrosion or by the removal of oxygen from the water system in the pH range of 6.5-8.5, one of the required components for corrosion would be absent and corrosion will be prevented.

Also, if water is excluded from the metal surface, the corrosive action cannot occur. Research has shown that iron will not corrode in an atmosphere containing less than 30 % relative humidity (van Delinder, 1984).

(c) Corrosion inhibitors

Corrosion inhibitors are substances that combine with the corroding metal (anode) or the protected metal (cathode) to form barrier layer that reduces the flow of ions and electrons across it to very low values and virtually stops the corrosion. If the protective barrier is damaged, corrosion resumes (Obiekwe, 1983). Thus, it is necessary to keep an amount of the inhibitor in contact with the metals. Inhibitors can be incorporated in protective coatings or in a primer for a coating at a defect in the coating; the inhibitor leaches from the coating and controls the corrosion. Chromates, silicates, organic amines, organoborates and ethylene glycol monomethylether are common inhibitors.

The mechanism of inhibitor can be quite complex. In the case of the organic amines, the inhibitor is adsorbed on anodic and cathodic sites and stifles the corrosion current. Other inhibitors specifically affect the anodic process e.g. silicate, orthophosphates, nitrite and ferricyanide while the cathodic inhibitors act by causing a reduction of oxygen. Some retard corrosion by adsorption to form a thin, invisible film only one molecule thick. Others form bulky precipitate that coats the metal and protect it from attack (Koch *et al.*, 2001).

(d) Protective coatings

The metal can be completely covered with impervious coatings of paints, lacquer, resin, oil, ceramics or grease. This affords excellent protection as long as the coating can be maintained intact. Metallic coatings of less noble metal over more noble metal provide sacrificial protection. Galvanizing is a bonded, protective coat of zinc put over steel. The zinc protects the steel from corrosion in two ways; from the galvanic series, it can be seen that zinc will corrode before steel. Secondly, a protective layer of zinc oxide forms on the zinc. Thus as long as the zinc remains in contact with the steel it corrodes sacrificially and protects the steel. Non-metallic coatings put over metal can be of two types; they act as a physical barrier and bar access to the metal surface or they can introduce a very high resistance into the corrosion cell circuit and drastically reduce

the film of electron. The barrier type coatings protect the metal as long as there are no cracks. If a crack occurs, corrosion becomes intense at the metal surface. Resistance type coatings include additives that breakdown in the presence of water and oxygen into inhibiting agent (Koch *et al.*, 2001).

The metal may be coated by chemical action with an impervious film such as an oxide coating. Strong oxidizing agents such as fuming nitric acid cause iron to become passive or chemically unreactive, presumably because of the formation of a stable oxide film. Epoxy based primer coating applied on a properly washed and blast cleaned surface has shown good result. Moreover, the level of salt contamination on the surface should be kept as low as possible (NACE, 2000).

4. Factors influencing biocorrosion

There is an ongoing dispute as to which component: biotic or abiotic is of greater relevance to corrosion reactions (Pak *et al.*, 2003). Sulphate and organic concentrations, sedimentation rate, turbulence, temperature, salinity and hydrostatic pressure are the main environmental factors controlling the number and distribution of sulphate reducing bacteria and the rate of bacteria sulphate reduction (Wetrich and Bwerna, 1988).

Increase in oxygen increases the corrosion rate during aerobic biocorrosion. Anaerobic biocorrosion microbes will not occur in the presence of even a trace of oxygen. Flow rate, increased water rate increases oxygen access to the surface and remove protective surface film so usually increase corrosion but can sometime improve access for corrosion inhibiting reactants. Temperature also influence biocorrosion for instance, the *Desulfovibrio* grow well at temperatures between 25 °C and 45 °C. *D. nigrificans*, however, is thermophilic, with an optimum growth of 55 °C and growth occurs even at 65-70 °C, but the organism can adapt itself to grow at temperatures as low as 30-37 °C. Water type, in general low concentration rates are found with scale forming waters. Aggressive ions, which accelerated corrosion, are chlorine, sulphate ions but quite complex interaction may occur between the various deferred maintenance and extended useful life of buildings and equipment. In low iron concentration, the corrosion rate will depend on the growth rate but not so in iron-rich medium. In media sufficiently rich in iron, the sulphide will precipitate as FeS, thus suppressing the formation of protective surface film on the metal specimen. Once FeS is formed in culture, FeS depolarization activity can continue even in the absence of the bacteria. Although light can be a limiting factor, extreme low light adaptation in certain prototroph and their ability to oxidise ferrous iron might be of importance (Heising *et al.*, 1999). In the range of 4-1 %, corrosion rate is fairly

Independent of
pH falls below
sulphuric acids

Independent of pH but it increases rapidly when the pH falls below 4. This is because acids such as sulphuric acids especially in aerobic corrosion is involved actively in corrosion of the metals. *Desulfivibrio* grow well at pH values between about 5.5 and 9.0 (optimum pH = approx. 7.2). The pH range of the *Desulfotomaculum* is similar. Other factors which influence microbial corrosion of metals include; the condition of the metal surface and the nature of the metal.

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