

Review

Biocorrosion control: Current strategies and promising alternatives

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Accepted 5 October, 2012

Metal corrosion is an electrochemical reaction between the environment and a metal, in which microbes are thought to play a very important role. The rates at which various types of metals corrode are dependent upon environmental conditions as well as on the type of metals. The most well studied bacteria involved in biocorrosion are the anaerobic sulphate reducing bacteria (SRB) and other bacteria such as methanogens, acid producers as well as the aerobic iron respirers and manganese oxidisers. The biofilm produced by the microorganisms facilitates biocorrosion by altering the chemistry such as pH, pressure, oxygen levels and nutrients at the interface between the metal and the bulk solution. Therefore biofilms can be used to alter the conditions at a metal surface, and to accelerate or inhibit corrosion. In this review, the proposed mechanisms of how bacteria contribute to the biocorrosion processes and the groups of bacteria involved will be included. Different strategies for biocorrosion control will also be discussed. Biological control strategies such as biocompetitive exclusion and the use of antimicrobial producing biofilm forming bacteria show increasing promise as more effective, environmental friendly and long term method of corrosion controls.

Key words: Microbially influenced corrosion, biocorrosion control strategies, biofilms, microorganisms, biocompetitive exclusion.

INTRODUCTION

Corrosion is an electrochemical reaction between the environment and a material, generally a metal, which alters the properties of the material and impairs its function (Fang et al., 2002; Garcia et al., 2012). Corrosion occurs spontaneously and can occur on most metallic materials. It is an old and problematic industrial dilemma, and is the main cause of the failures of metallic structures (Askeland, 2004). Electrochemical corrosion entails the oxidation and dissolution of a zero valent metal, at a point known as the anode, and a subsequent reduction at the cathode involving an external electron acceptor (Juzeliunas et al., 2006; Garcia et al., 2012). In aerobic conditions, the cathodic reaction involved the reduction of oxygen, whereas in anaerobic conditions, the

evolution of hydrogen usually occurs (Beech and Sunner, 2004). Deposition of matter, either organic or inorganic, can cause differential aeration pitting (particularly of austenitic stainless steel) and erosion/corrosion of some alloys (Rajasekar and Ting, 2011). Microbial growths on the surface on the metals can promote the formation of corrosion cells (Saravia et al., 2003); the by-products of some organisms such as hydrogen sulphide from anaerobic corrosive bacteria, are corrosive (Zuo et al., 2004; Rajasekar et al., 2010).

In industry, microbes are thought to play a very important role in the corrosion of metals such as iron and steel (Saravia et al., 2003). Microbially influenced corrosion (MIC), also called biocorrosion, is a process in which microorganisms initiate, facilitate, or exacerbate the corrosion reaction (Videla, 1986; Javaherdashti, 1999; Parande et al., 2005), and they perform this function in the form of a biofilm. A biofilm can be thought of as a gel composed of 95% water, containing extracel-

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llular polymeric substance (EPS), and a suspension of cells and inorganic matter (Saravia et al., 2003). Biofilms modify the properties at the interface between the metal and the bulk solution, such as by changing the types and concentrations of ions and oxygen and the pH, leading to a change in the electrochemical behaviour of the metal (Videla and Herrera, 2007). Microorganisms perform redox reactions that also have a significant effect on the properties of minerals in the environment (Choi et al., 2002).

The rates at which various types of metals corrode are dependent upon environmental conditions including the biotic and abiotic factors. Metal surfaces can be quickly colonised by aerobic bacteria present in the medium, forming a biofilm (Zuo et al., 2004). The upper areas of the biofilm are aerobic whereas the lower layers will be anaerobic due to bacterial respiration, allowing for the colonisation of SRB within these niches even in aerobic environments (Zuo et al., 2004). The most well studied bacteria involved in biocorrosion are the anaerobic sulphate reducing bacteria (SRB), although other bacteria such as methanogens and acid producers, as well as the aerobic iron respirers and manganese oxidisers may also be involved (Rajasekar et al., 2010). SRB have been implicated in the corrosion of metals in many different industries, such as sewage treatment facilities and pipelines, offshore oil rigs, power generation equipment and cooling water-recirculation systems, due to the production of the highly corrosive and toxic hydrogen sulphide (Zuo et al., 2004).

In the oil industry, hydrogen sulphide leads to reservoir souring as well as corrosion (Zuo et al., 2004). MIC is therefore a serious industrial problem that affects a diverse range of metals and industries including sugar, dentistry, paper and pulp, shipping, petroleum and gas industries (Rajasekar et al., 2010). The annual costs with regards to corrosion related problems worldwide are estimated to cost as much as \$1.8 trillion US dollars (Lieser and Stek, 2010), with MIC estimated to contribute to approximately 50% of this total (Fang et al., 2002; Hamilton, 2003). Therefore, the control of biocorrosion is of uttermost importance, and many different strategies are used. The currently used strategies in industry will be discussed in this review, as well as potentially more effective and environmentally friendly strategies.

MICROBIALY INFLUENCED CORROSION

Due to their opportunistic behaviour, microorganisms are known to influence the energy yielding corrosion reaction, often enhancing corrosion in order to harvest the energy released (Fang et al., 2002) known as microbiologically influenced corrosion (MIC). It has been postulated that microorganisms can accelerate the corrosion process by as much as 1000 to 10,000 times, as abiotic corrosion is often a relatively slow process (Fang et al., 2002).

Various metals are submitted to MIC in natural waters where the microbial population is estimated to be around 10^3 to 10^9 CFU/ml. Within a relatively short time, depending on the environment, EPS production and microbial growth will result in a mature biofilm. The biofilm facilitates MIC by altering the chemistry such as pH, pressure, oxygen levels and nutrients at the interface between the metal and the bulk solution (Beech and Sunner, 2004; Videla and Herrera, 2005). This leads to major changes in the concentration and type of ions, redox potentials, pH, and oxygen levels, resulting in an alteration of the active or passive properties of the metal as well as the corrosion products formed (Videla and Herrera, 2005).

Biofilms consists of many compartments; the surface to which the microbes attach, the biofilm, the nutrient solution and the gas phase (Lewandowski and Beyenal, 2008). The products of reactions occurring on the metal surface reacts with products of microbial metabolic processes in a complex way. Some of these processes may accelerate corrosion (Microbially influenced corrosion acceleration) or inhibit corrosion (microbially influenced corrosion inhibition) (Lewandowski and Beyenal, 2008). Therefore biofilms can be used to alter the conditions at a metal surface, and to accelerate or inhibit corrosion.

A wide variety of mechanisms have been attributed to biocorrosion, which reflects the wide variety of physiological activities carried out by different microorganisms. A single mechanism cannot be attributed to MIC, nor can a single species. The mechanisms by which a biofilm can influence MIC involve: (i) The creation of oxygen heterogeneities; (ii) increasing mass transport resistance at the metal surface; (iii) Generating corrosive substances such as acids; (iv) Removal of protective films during detachment thus changing the structure of passive protective layers or increasing their dissolution from the surface of the metal; and (v) Changing redox conditions at the interface of the metal and bulk solution that can act as cathodic reactants (Lewandowski and Beyenal, 2008).

Biofilms are composed of microbial cells held together by a thick mucilaginous slime known as the extracellular polymeric substance (EPS). The biofilm acts as a protective layer, reducing the contact of the colonised surface to the external environment. The EPS is important in maintaining the structural integrity of the biofilm, but may also be directly involved in the degradation of the metal (Fang et al., 2002). The EPS is composed of polysaccharides, lipids, uronic acids, DNA as well as proteins containing functional groups including carboxylic and amino acid groups, which are able to bind metallic ions. Therefore, the EPS is able to affect the electrochemical nature of the metal surface and may significantly affect the corrosion process (Fang et al., 2002).

A study by Chan et al. (2002) showed that the increase

in EPS production by sulphate reducing bacteria, containing 84 to 92% proteins and 8 to 16% polysaccharides, resulted in an increase in the corrosion of mild steel coupons. The inhibition of corrosion was also observed by bacteria due to biofilms in aqueous environments such as artificial seawater. Decreases in corrosion rate of aluminium by *Bacillus* sp. biofilms have been reported (Videla and Herrera, 2005 b; Zuo et al., 2005; Morikawa, 2006; Juzeliunas et al., 2006). However *Bacillus* sp. which decreased in corrosion rate of aluminium, could increase in corrosion rate when colonising zinc, and indifference when colonising mild steel (Juzeliunas et al., 2006). These results also showed that MIC not only depends on environmental conditions as well as the type of microorganism, but also on the type of metal colonised.

Numerous mechanisms for MIC have been proposed, such as metal reduction or oxidation, sulphuric acid reduction etc, each implicating a different microorganism (Kan et al., 2011). Therefore, recently, the identification and biochemical characterisation of the properties of microbes isolated from corrosion sites have been of high priority. Knowing the general species and the mechanisms of MIC would provide a basis for the control, detection or monitoring of MIC (Kan et al., 2011).

Microbially influenced corrosion acceleration by bacteria

Microbiologically influenced corrosion acceleration (MICA) in nature is not caused by one type of microorganism, nor is it limited to one mechanism. MICA occurs due to the synergistic action of a number of different bacterial groups that share a common environment (Chongdar et al., 2005). The most well studied bacteria with regards to MICA are the anaerobes, including the sulphate reducing bacteria (*Thiobacillus*) and the acid producing bacteria (*Clostridium*), and the aerobe bacteria and fungi including manganese and iron oxidisers (*Gallionella*; *Shewanella*, *Geobacter*) and the extracellular slime producers (Rajasekar et al., 2007; 2010). Some studies even suggest that SRB need not be present in all bacterial communities responsible for MIC (Rajasekar et al., 2007). Biocorrosion often results due to synergistic interactions between the surface of the metal, corrosion products, the bacteria and metabolic products, which include organic and inorganic acids and compounds such as ammonia and hydrogen sulphide (Chongdar et al., 2005).

Sulphate reducing bacteria (SRB)

Sulphate reducing bacteria (SRB) belong to the group Deltaproteobacteria and include species such as *Desulfovibrio* and *Desulfomaculum*. SRB are the most

known and studied bacteria implicated in the biocorrosion of copper alloys, nickel alloys, cast iron, carbon steels, stainless steels and low alloy steels (Zuo et al., 2004). They have been frequently found in facilities such as transportation, storage and oil and gas producing facilities and are the most probable cause for corrosion and problems such as souring and biofouling in these areas (Beech and Sunner, 2004).

SRB are able to oxidise organic matter and utilise sulphite, lactate or tetrathionate as a terminal electron acceptor (Bermont-Bouis et al., 2007, Kan et al., 2011). The main end product due to their metabolism is the production of sulphides, which build up at the metal surface and acidify the environment, and catalyse the corrosion process (Kan et al., 2011). SRB though, are not the sole group of bacteria able to produce sulphide, nor the only cause of biocorrosion (Kan et al., 2011).

The mechanism studied with regards to SRB induced biocorrosion involves the transfer of electrons from the metal surface to the sulphate reduction pathway with the use of a hydrogen intermediate, which requires the use of hydrogenase enzymes (Beech and Sunner, 2004). Hydrogenase enzymes are therefore the most extensively studied groups of enzymes involved in anaerobic biocorrosion. Recent studies report that purified hydrogenase enzymes isolated from *Ralfstonia eutropha* were shown to directly influence the cathodic reaction on stainless steels even in the absence of viable cells (Beech and Sunner, 2004). SRB are able to participate in MIC even in aerobic environments, when they are present in biofilms. Dissolved oxygen concentrations have been shown to decrease to zero from as little as 180 micrometres from the metal surface (Videla and Herrera, 2005). Therefore, SRB are able to grow at the bottom of biofilms, despite the presence of large concentrations of oxygen in the bulk solution (Videla and Herrera, 2005). Indications of SRB attack of mild steel and stainless steel are the formation of black FeS films on the surface and pitting corrosion (Zuo et al., 2005). The nature and structure of the sulphide films produced by the bacteria during metal dissolution was also shown to affect the MIC of steels by SRB (Videla and Herrera, 2005).

Mn oxidising bacteria (MOB)

All known manganese oxidising bacteria are aerobes which form manganese oxides within the cell envelope or extracellularly (Landoulsi et al., 2008). Many studies have established a relationship between the deposition of manganese oxides/hydroxides and the corrosion of stainless steels in natural waters (Landoulsi et al., 2008). The deposition of these manganese accumulations were attributed to the presence of Mn oxidising chemolithotrophic bacteria, such as *Leptothrix* and *Siderocapsa* (Pacini et al., 2005).

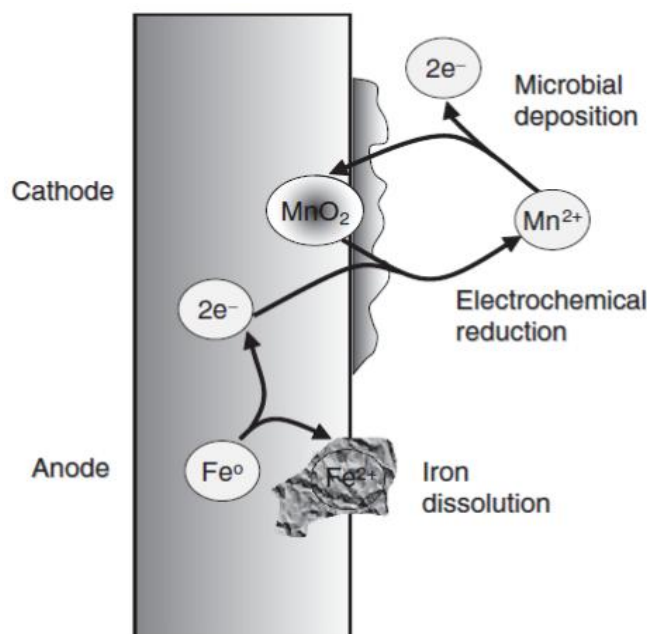


Figure 1. Hypothetical mechanisms by which metal oxidising bacteria participate in biocorrosion (Lewandowski and Beyenal, 2008).

Manganese oxidisers are categorised into three groups: (a) Those that are involved in the oxidation of dissolved Mn^{2+} ; (b) Those that are involved in the oxidation of Mn^{2+} bound to solids; and (c) Those that are involved in the oxidation of dissolved Mn^{2+} by the metabolic H_2O_2 using catalase (Rajasekar et al., 2007). Lewandowski and Beyenal (2008) suggested a mechanism by which MOB catalyse biocorrosion. The mechanism results in pitting corrosion as is summarised in Figure 1. Divalent manganese (Mn^{2+}) are oxidised to manganese oxyhydroxide ($MnOOH$), then oxidised to manganese dioxide (MnO_2), which are also deposited onto the metal surface. The corrosion process catalysed by MOB requires the direct contact between the Mn oxides and hydroxides and the metal surface (Hamilton, 2003). These oxides on the metal surface are then reduced back to Mn^{2+} using electrons released at anodic sites. However, the ennoblement process does not terminate there, as the soluble Mn^{2+} is then reoxidised by the MOB in a continuous cycle, producing renewable reactants such as $MnOOH$ and MnO_2 that act as cathodic reactants (Lewandowski and Beyenal, 2008).

Species such as *Bacillus* have been found in water pipelines and galvanised steel and have been shown to be capable of manganese and iron oxidation as well as acid production (Kan et al., 2011). *Bacillus* spp. are able to oxidise manganous ions to manganic ions onto the metal surface resulting in the deposition of manganese dioxides on the metal surface which subsequently promotes corrosion (Rajasekar et al., 2007). Fungi are also known to cause biocorrosion due to the oxidation of

manganese (Gadd, 2010). These organisms oxidise dissolved Mn^{2+} to form enriched mineral encrustations. Manganese oxide depositions can form on many submerged substances such as metal, plastic, glass and stone in environments with manganese concentrations as low as 10 to 20 parts-per-billion (Lewandowski and Beyenal, 2008). It has also been shown that on non-passivating metals such as mild steel, where the oxides are reduced as rapidly as they are deposited, an increase in corrosion rate may occur without evidence of microbial activity (Zheng et al., 2007).

Iron oxidising bacteria (IOB)

Iron oxidising bacteria (IOB) have been implicated in biocorrosion since the 1960s (Costello, 1969). These bacteria gain energy through the oxidation of ferrous iron (Fe^{2+}) to ferric iron (Fe^{3+}), which occurs at near neutral pH and may result in the formation of iron oxides. IOB are micro-aerophilic and therefore are found commonly associated with other microorganisms in aerobic environments in the presence of reduced iron (Coetser and Cloete, 2005).

The first step in biocorrosion caused by iron oxidising bacteria is the production of EPS and the formation of a biofilm. At the metal solution interface, the iron oxidising reactions have taken place (Chongdar et al., 2005). The oxidation of Mn^{2+} is commonly closely linked to the Fe^{2+} oxidation (Rajasekar et al., 2007). Ferric ions present in the environment can serve as strong oxidising species which may accelerate corrosion (Tamura, 2008).

The IOB species that have been studied most extensively in biocorrosion are *Gallionella*, *Leptothrix* and *Siderocapsa* (Rajasekar et al., 2007). The mechanism presented is due to the formation of a differential aeration cell in which the bacteria form iron oxide deposits. The area under the deposits is excluded from oxygen, and thereafter serves as the anode and the areas uncovered by the deposits and exposed to oxygen serve as the cathode. The metal under the deposits dissolve and form cationic species that then undergo hydrolysis.

IOB corrosion in freshwater environments is much better understood than in marine environments. In the presence of chloride ions, IOB activity may result in the formation of ferric chloride, which is highly corrosive and may concentrate under ferric oxide deposits (Rajasekar et al., 2007). Studies have indicated the role of *Mariprofundus ferroxydans*, which is a stalk forming bacteria commonly isolated in iron rich microbial mats in deep sea hydrothermal vents (Edwards et al., 2011). Studies have also shown that carbon steel submerged in a saline medium, experienced localised pitting corrosion (Videla and Herrera, 2005). This occurred beneath microbial colonies formed due to the formation of differential aeration cells and the depassivation of the surface of the metal due to the reduction of insoluble iron deposits into soluble iron compounds by IOB.

Acid producing bacteria (APB)

Acid producing bacteria are a group of heterotrophic bacteria that are able to produce organic acid metabolic products when grown under reductive environmental conditions (Wilkie, 2005). Acids are produced during the fermentation of organic materials to cause a drop in pH from neutral to pH values of 3.5. These acidic conditions are aggressive enough to affect the integrity of any metal materials, causing corrosion. APB is normally found within biofilms, tubercles, nodules or encrustations under reductive conditions and is generally found at the metal biomass interface (Thomas, 2002). It is widely recognised that acid producing bacteria are in fact significant contributors to biocorrosion due to rapid depolarisation of the cathode (Thomas, 2002).

A study by Rajasekar et al. (2010) detected the presence of *Klebsiella oxytoca*, *Bacillus cereus*, *Pseudomonas stutzeri* and *Serratia marscesens* in corrosion sites suggesting the contribution of acid producing bacteria in MIC. *K. oxytoca*, which is commonly found in nature in soil and water and is involved in nitrogen fixation under micro-aerophilic or anaerobic conditions, was detected in diesel pipelines (Rajasekar et al., 2010). It is known to produce nitrates and nitric acid which may play a role in biocorrosion (Rajasekar et al., 2010).

Both SRB as well as APB are known to propagate in reductive conditions, although SRB thrive in the presence of high sulphate concentrations whereas APB tend to thrive in conditions which are rich in organic matter. The corrosion caused by APB can be characterised as shallow depressions, which differs from the corrosion caused by SRB, which normally cause deep pitting attacks (Thomas, 2002). Acid producing bacteria grow in the absence of oxygen, therefore is generally considered that these bacteria may be partners to the SRB in the biocorrosion process (Setareh and Javaherdashti, 2003), especially in the oil and gas industries. Sulphate may also have been produced by the APB in the water due to sulphur oxidation, which may allow for the propagation of SRB. Due to these findings, biocorrosion management commonly involves the assessment of both SRB and APB activity (Setareh and Javaherdashti, 2003).

Extracellular slime producers (ESPs)

Upon exposure of a material to an aqueous solution containing nutrients, the surface properties of the material is altered due to the adsorption of organic materials to the surface, called a conditioning film (Sheng et al., 2008). This conditioning film thereafter has an effect on the attachment of bacteria to the surface. It is thought that bacteria show a propensity to grow in areas of nutrient abundance (Sheng et al., 2008). Therefore in a nutrient deficient liquid, bacteria will be inclined to attach to a

solid surface due to the ability of the solid material to adsorb trace nutrients. Studies have shown that certain bacteria, such as *Burkholderia* sp. show a propensity to attach to solid surfaces in oligotrophic conditions rather than in eutrophic conditions (Sheng et al., 2008). In oligotrophic conditions, bacteria also turn on the production of EPS, which have been shown to promote hydrophobic interactions and increase the adsorption of nutrients to the surface (Sheng et al., 2008).

Bacterial EPS is considered one of the most significant contributors to the MIC of metals (Chongdar et al., 2005). This material that allows for attachment of bacteria to the metal surface has been shown to bind to and crosslink with metal ions with strong affinity (Chongdar et al., 2005). These reactions between the EPS and metal ions occur due to weak electrostatic interactions between hydroxyl groups such as carboxyl, glycerate, succinate, phosphate and pyruvate in neutral polymers or through the formation of salt bridges between carboxyl groups in acidic polymers (Sheng et al., 2008; Lewandowski and Beyenal, 2008). The propensity of multidentate anionic functional groups found on the EPS to attach to multivalent metal ions such as Ca^{2+} , Cu^{2+} , Mg^{2+} and Fe^{2+} can be particularly strong (Beech and Sunner, 2004). Therefore in principle, if a corrosion site is covered in EPS, cross linking can occur between the polysaccharides of the EPS and the metal ions and alter the equilibrium between the metal and the metal ions, and may lead to corrosion acceleration (Lewandowski and Beyenal, 2008).

The metal ions bound to the EPS may therefore act as electron shuttles and may lead to new redox reaction pathway occurring in the biofilm as shown in Figure 2. For example, the EPS can direct the transfer of electrons from a metal or biomineral (Sheng et al., 2008). These pathways may also lead to cathodic depolarisation in the presence of a suitable electron acceptor such as oxygen in aerobic conditions or nitrate in anaerobic conditions, which may lead to corrosion acceleration (Beech and Sunner, 2004). The metal binding nature of the EPS is not the only mechanism by which the EPS can contribute to MIC. The EPS of *Pseudomonas alcaligenes* was shown to contribute to the biocorrosion of mild steel due to its acidic nature, by lowering the interfacial pH and promoting acidic conditions which are conducive to corrosion (Chongdar et al., 2005).

Microbially influenced corrosion inhibition by bacteria

The acceleration of corrosion by bacteria could occur due to the encouragement of the anodic reaction by bacterial acidic metabolites or the production of a different cathodic reactant such as H_2S (Juzeliunas et al., 2006). Increase in biocorrosion could also occur due to the breakdown of protective films by the bacteria or an

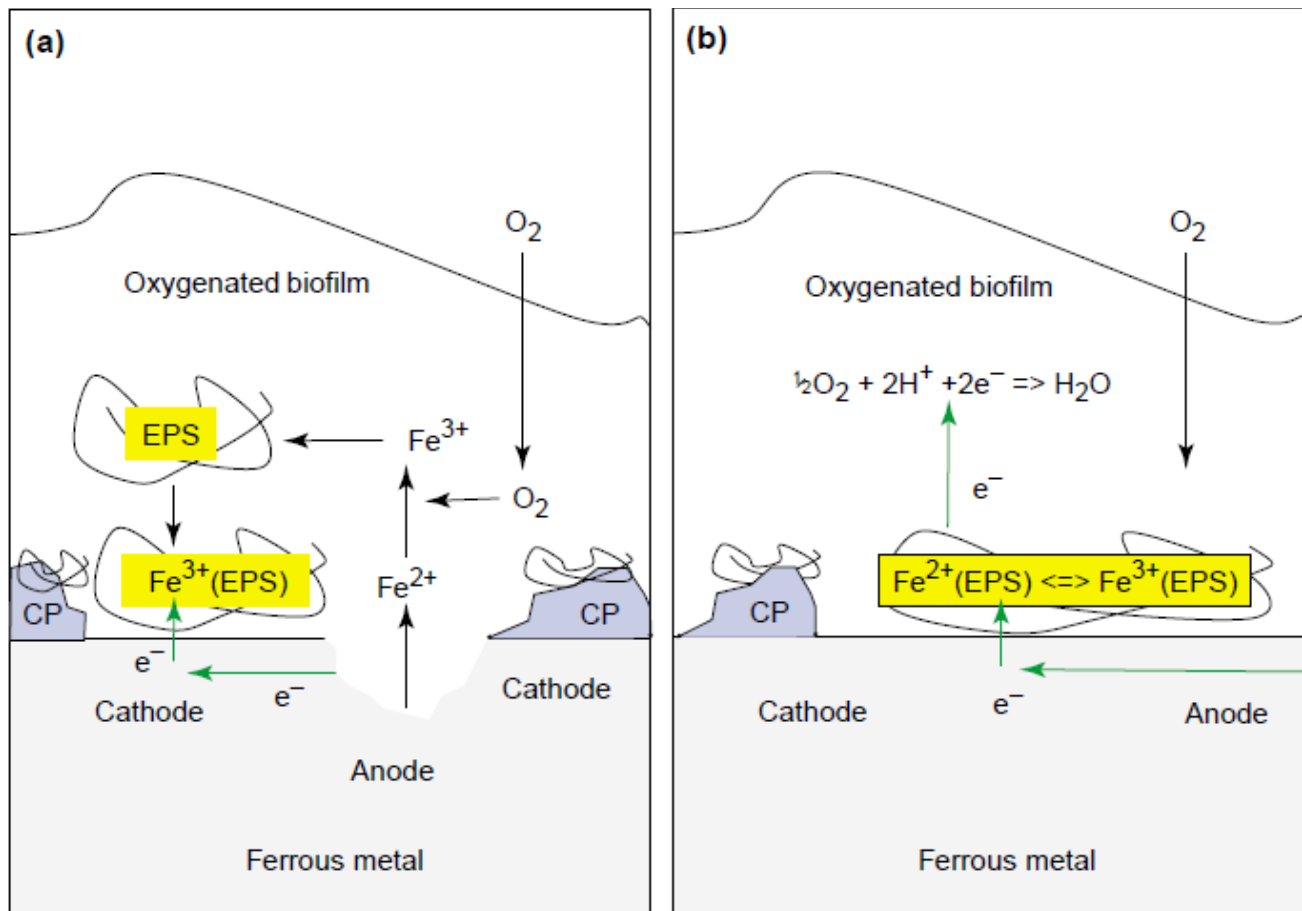


Figure 2. Mechanism by which EPS has been shown to contribute to MIC (Beech and Sunner, 2004).

increase in the conductivity of the surrounding liquid. Corrosion inhibition, on the other hand, is the decrease in the rate of corrosion. It is generally performed by substances known as corrosion inhibitors which, when added in minute amounts, are able to decrease the rate of the dissolution of the metal due to attack by environmental factors (Dahmani et al., 2012). The effect of microorganisms, whether it is an increase or decrease in the rate of corrosion, occurs on colonised surfaces in the presence of biofilms (Juzeliunas et al., 2006).

The most significant mechanisms by which bacteria cause an inhibition of corrosion are always due to a change in the environmental conditions at the metal-bulk solution interface due to the activity of the microorganisms (Akpabio et al., 2011). The inhibition of corrosion by bacteria is often accomplished by: (i) A decrease in the corrosive action of the medium in restricted parts of the metal-bulk solution interface, such as by neutralising the acidity of the medium; (ii) the formation of protective films on the metal surface or providing new protective films such as through the production of EPS with metal binding abilities and; (iii)

decreasing the cathodic reaction due to the consumption of a cathodic electron acceptor by microbes (Juzeliunas et al., 2006; Akpabio et al., 2011).

The formation of biofilms on the surfaces of metals has been shown to decrease the rate of corrosion due to the consumption of the cathodic reaction, oxygen, therefore rendering it unavailable for the corrosion reaction (Lewandowski and Beyenal, 2008). The rate of mild steel corrosion was shown to be markedly decreased due to the formation of a uniform biofilm layer (Lewandowski and Beyenal, 2008). The decrease was attributed to the microbial respiration occurring within the biofilm, which resulted in a decrease in the availability of oxygen at the surface of the metal and thus a decrease in the cathodic reaction. However, the inhibition of corrosion by this mechanism requires the biofilm to uniformly cover the entire surface of the metal and have a uniform microbial activity (Lewandowski and Beyenal, 2008). Therefore, the inhibitive effect of microbial biofilms is difficult to predict because biofilms in nature are not uniformly distributed and do not have uniform microbial activity (Lewandowski and Beyenal, 2008).

However, Garcia et al. (2012) showed, using Scanning Electron Microscopy and EN analysis that bacteria isolated from copper electrode surfaces prevented corrosion due to biofilm formation which acted as a protective anticorrosive coating (Garcia et al., 2012). It was postulated that the exopolysaccharides produced by the bacterial strains reduced the corrosive activity as it prevented the interaction of the metal surface with the external environment. The protective action of the biofilms of *P. fragi*, *E. coli* and *B. brevis* as well as Actinomycetes has also previously been shown (Garcia et al., 2012). The presence of *B. subtilis* biofilms formed a protective layer allowing Al 2024 to be passive in artificial seawater (Zuo et al., 2005). When the cells within the biofilm were killed upon the addition of antibiotics, pitting corrosion was observed within hours. These results showed that live biofilms were necessary for the decrease in corrosion rate by biofilms (Zuo et al., 2005). The decrease in corrosion rate was due to a decrease in reduction at the metal surface by oxygen and biofilms may cause a reduction in corrosion due to a decrease in the rate of the reaction at the anode and an increase in pitting potential (Zuo et al., 2005). It may also be possible that corrosion inhibition occurs due to the negative charge of the bacteria as well as the EPS, which are able to repel corrosive chloride ions.

BIOCORROSION CONTROL STRATEGIES

An understanding of the microbial communities involved as well as the role of different species is important and may be exploited to induce microbial inhibition of corrosion as a method to prevent the occurrence of MIC encountered in the various fields (Videla and Herrera, 2005). Many factors affect the corrosion rates in a given system. Dissolved oxygen, pH, total dissolved solids, temperature are few important factors. Oxygen dissolved in water is essential for the cathodic reaction to take place (Garcia et al., 2012). Low alkalinity waters that have little pH buffering capability can pick up acidic gases from the air and can dissolve metal and the protective oxide film on metal surfaces. Water containing a high concentration of total dissolved solids has a high conductivity, which provides a considerable potential for galvanic attack. Dissolved chlorides, hydrogen sulphide and ammonia are particularly corrosive even when total hardness and alkalinity are relatively high (Garcia et al., 2012). Therefore, the age old concept for keeping an industrial system free of the harmful effects of biocorrosion is to keep it clean. Many strategies have been used (Videla and Herrera, 2005) and these strategies can be grouped into physical, chemical and biological methods.

A better corrosion management can be achieved using preventive strategies in nontechnical and technical areas. The principle methods to prevent or minimizing corrosion

include: (a) Selecting suitable materials of construction to resist corrosion; (b) Adding protective film or applying protective coatings such as paints, metal plating, tar or plastics on external surfaces; (c) Controlling scaling and micro-biological growth and; (d) Protect cathodically, using sacrificial metals.

Physical control strategies

Physical protection methods are very common for lower temperature use. As mentioned earlier, in an aqueous medium, the electrical conductivity of the medium becomes important in causing corrosion. Wide use is made of applying potential differences between medium and metal to reduce the corrosion that is, cathodic and anodic protection. Among the physical control methods, flushing is considered the most simple however, it is of limited efficiency (Videla and Herrera, 2005). To increase effectiveness, flushing can be performed using cleaners or chemical agents that would induce the detachment of biofilms (Videla and Herrera, 2005). Sponge balls that are abrasive or non-abrasive are frequently used, however abrasive sponge balls may damage protective passive films, and non-abrasive sponge balls are not very effective with regards to biofilms (Videla and Herrera, 2007). Finally, a general method to enhance corrosion resistance is to apply protective coatings. Various organic coatings have been studied for corrosion protection (Chou et al., 2002; Avci and Abanoz, 2004; Shimura and Aramaki, 2008). SiO₂ is practically useful in enhancing organic coating and supports the paint in aggressive environment (Li et al., 2007; Wang and Bierwagen, 2009). Ag/SiO₂ nanoparticles could enhance long-term corrosion protection and has a strong potential use in environmentally friendly antimicrobial coatings (Le et al., 2010).

Chemical control strategies

Biocides, either oxidising or non-oxidising agents, have been used in controlling biocorrosion. Due to the environmental concerns, the combination of electric field with the antimicrobial agents (Blenkinsopp et al., 1992; Costerton et al., 1994; Wellman et al., 1996) and coupling a more easily corroded sacrificial metal (Saravia et al., 2003; Orfei et al., 2006) have been used to reduce the biocorrosion. Other unusual corrosion inhibitors such as tobacco extract (von Fraunhofer, 2000; Martin, 2003; Loto and Popoola, 2011b) and the combination of KI and molasses are also reported (Martin, 2003).

Biocides

Chemical control strategies used to control bioorrosion entails the used of biocides (Saravia et al., 2003). A

biocide is any chemical agent that is able to kill living organisms. Biocides could be used in conjunction with other substances such as dispersive or penetrating agents that are able to increase the efficiency of the treatment (Saravia et al., 2003). These substances are commonly used in closed systems, such as cooling towers and storage tanks, due to their toxic nature (Bartolomé and Sánchez-Fortún, 2005).

Biocides can be either oxidising or non-oxidising agents (Videla and Herrera, 2005). Oxidising agents, such as chlorine, chlorinating compounds, choramines and bromine are commonly used in freshwater systems, with the most practical being chlorine compounds. However, the effectiveness of chlorine compounds depends on factors such as pH, temperature as well as light. They are also not very effective when used to control biofilms. Currently, there is a trend to use strong oxidizing biocides like chlorine dioxide in cooling systems and ozone in water distribution systems as low levels of chlorine have been found to be ineffective against biofilms (Murthy and Venkatesan, 2009).

Non-oxidising biocides include quaternary salts, anthraquinones, amine-type compounds and aldehydes. Non-oxidising biocides are more stable than oxidising biocides and can be used in a variety of different environments. They have also been shown to be effective against a broad range of microorganisms such as bacteria, fungi and algae as well as a greater persistence in the environment (Videla and Herrera, 2005). There, activities are usually pH independent (Videla and Herrera, 2005). In most cases, combinations of both oxidising as well as non-oxidising biocides are used to increase the microbiological control of the system (Videla and Herrera, 2005). Other biocides that are commonly used are glutaraldehyde, isothiazolones and quaternary ammonia compounds and heavy metals such as chromates due to their effectiveness and ability to act over a wide range of environmental conditions (Videla and Herrera, 2005).

A study by Rajasekar et al. (2010) showed that the widespread use of ester based or toxic biocides or inhibitors in the petroleum industry has led to the growth and dominance of *Bacillus* species, due to their ability to form resistant spores (Rajasekar et al., 2010). Many of these biocides may also be degraded by certain types of *Bacillus* species (Russell, 2003).

Therefore the choice of the biocide/inhibitor is very important. Response of the bacteria to the chemical agent is dependent on the type of bacterium as well the type of chemical agent (Rajasekar et al., 2010). Therefore, due to the formation of resistant spores by genera such as *Bacillus* and *Clostridium*, higher concentrations of biocide are needed to effectively control biocorrosion (Rajasekar et al., 2010). Biocide usage in industry is also very expensive (Licina, 2010) and may cause pollution of the environment. Some biocides, if used at concentrations greater than a few parts per

million, may even cause metal corrosion themselves (Jayaraman et al., 1999a). Additionally, biocides are not very effective at eradicating biofilms as they are at killing planktonic populations (Jayaraman et al., 1999a). Therefore, the popularity of certain biocides is decreasing, due to increasing legislative criteria as well as the need for more environmentally friendly biocides (Choi et al., 2002; Videla and Herrera, 2005). This has led to the need for the development of new biocides or the careful selection of currently used biocides, and a trend towards more environmentally benign "green chemicals" (Choi et al., 2002; Videla and Herrera, 2005).

The biocide, tetra-kis-hydroxymethylphosphonium sulphate (THPS), is one of the most promising non-oxidising biocides in recent years (Videla and Herrera, 2005). It has a broad spectrum, being effective against a wide range of microorganisms such as bacteria including SRB, fungi and algae (Videla and Herrera, 2005). When used with a surfactant, THPS is effective in eradicating biofilms. THPS has been used in industrial cooling systems and paper making industry as well as oil field operations due to its ability to dissolve ferrous sulphide (Videla and Herrera, 2007). However, Martin (2003) reported that under certain conditions THPS can be a corrosion aggravator.

Ozone

Ozone has received a lot of interest in recent years due to its effectiveness and lack of toxic product accumulation (Saravia et al., 2003). Ozone rapidly attacks bacterial cell walls and is more effective against the thick-walled spores of plant pathogens and animal parasites than chlorine at practical and safe concentrations (Suslow, 2003). It has been used in industry such as in cooling water systems. With regards to environmental concerns, the use of ozone has many advantages over conventional biocides (Saravia et al., 2003). The highly toxic nature of ozone and non-toxic by-product discharge makes ozone a very promising biocide for the future. Zuma et al. (2009) and Jonnalagadda et al. (2009) demonstrated the efficiency of ozonation on the disinfection of *Pseudomonas* sp. and *E. coli*. Ozone aeration also significantly decreased the BOD levels of natural and *B. subtilis* spiked waters (Zuma and Jonnalagadda, 2010). However, high running costs complex system control has limited its uptake to only small-capacity production and in developed countries.

Bioelectric effect with antimicrobial agents

The effectiveness of using antibiotics as biocides at preventing metal corrosion has been difficult to predict due to diffusing resistance to the antibiotic as well as due to the drastically lower growth rates of the cells in the biofilms (Costerton et al., 1994). Many studies have

shown that bacteria within a biofilm are 500 to 5000 times more resistant to antibiotics than planktonic bacteria of the same species (Eng et al., 1991; Costerton et al., 1994).

However, application of a relatively small direct current electric field in addition to biocides drastically increases the killing action of the biocides (Wellman et al., 1996). This effect is termed the "bioelectric effect". Blenkinsopp et al. (1992) and Wellman et al. (1996) reported that in the presence of an electric current flowing through the chamber in which the biofilm was present, the effectiveness of an antimicrobial agent such as glutaraldehyde was greatly enhanced up to 8 log orders. At the same time, far lower concentration of antimicrobials was needed than that to kill the more sensitive planktonic cells (Blenkinsopp et al., 1992).

Results showed that the current alone is unable to affect the biofilm suggesting a synergistic action between the antimicrobial and the electric current field density. Blenkinsopp et al. (1992) and Costerton et al. (1994) proposed that electric currents are able to disrupt the organisation of the biological membranes present in the cell as well as membrane analogs, both prokaryotic and eukaryotic metabolic and developmental processes and the shape and behaviour of the cell. Electrophoretic forces enable the antimicrobial agents to overcome diffusion barriers that prevent their access to biofilm cells (Costerton et al., 1994). This therefore disrupts the organisation and permeability of membranes to the antibiotics. Low strength electric fields have been shown to disrupt the resistance mechanisms of biofilms (Blenkinsopp et al., 1992). The results mentioned show that the bioelectric effect has potential to reduce the amount of biocides used in the control of biocorrosion without decreasing their effectiveness, and may be particularly attractive to industry, with concerns over the environmental impact of using large amounts of toxic biocides (Blenkinsopp et al., 1992).

Cathodic protection

Cathodic protection (CP) is another widely used and effective method to control corrosion (Saravia et al., 2003; Orfei et al., 2006). The metal structure can be protected by coupling a more easily corroded sacrificial metal (anode), or to an external direct current power source to change the amount of charge on the metal surface (Orfei et al., 2006; Loto and Popoola, 2011a). Cathodic protection is effected by forcing the potential to a negative region where the metal is completely stable. If designed properly, the corrosion rate of the structure can be completely prevented or drastically reduced to a negligible level. Cathodic protection is well suited to steel structures in marine or underground environments to prevent corrosion in water or fuel pipelines and many other facilities susceptible to corrosion (Orfei et al., 2006;

Loto and Popoola, 2011a). Cathodic protection techniques have been shown to be successful in preventing biocorrosion when used in conjunction with coatings (Zuo et al., 2004).

There are two commonly used types of cathodic protection systems, the impressed current and galvanic/sacrificial anode method (Loto and Popoola, 2011a). In both systems, the structure to be protected is forced to act as the cathode, preventing its dissolution (Orfei et al., 2006). The galvanic method involves the use of a more easily corroded sacrificial metal, which is usually composed of alloys of aluminium, magnesium or zinc (Loto and Popoola, 2011a). This method is relatively simple and inexpensive as it does not require the supply of an external power source (Orfei et al., 2006). It releases a somewhat uniform current distribution and requires very little maintenance. However, the current released might be very low and requires additional anodes to increase the current (Loto and Popoola, 2011a). Galvanic CP has been used in ships, offshore oil rigs, underwater and underground pipelines, and submerged concrete structure and production platforms (Loto and Popoola, 2011a).

The impressed current method involves the use of relatively inert anodes which are connected to an external DC power source (Orfei et al., 2006). This method is used for larger structures in which galvanic anodes are unable to deliver current large enough to provide adequate protection (Loto and Popoola, 2011a). Anodes used include silicon, mixed metal oxide, platinum, cast iron, nonium coated wire and graphite (Loto and Popoola, 2011a). Research into the use of solar power as the external power source is currently underway (Orfei et al., 2006).

Biological control strategies

Biological control strategies involve the use of microorganisms to control biocorrosion (Zuo et al., 2004). Biological control methods also have the advantage in that they are much cheaper as well as more environmentally friendly than physical or chemical control methods and have the potential to be much more efficient. The biological control strategy can be achieved by the biocompetitive exclusion (Videla and Herrera, 2007) and by bacterial species that can produce antimicrobial compounds within the biofilm or by the formation of bacterial biofilms alone (Jayaraman et al., 1999a; Zuo et al., 2004).

Biocompetitive exclusion

Biocompetitive exclusion (BE) strategies are becoming increasingly promising techniques in the control of

biocorrosion and reservoir souring by SRB (Videla and Herrera, 2007). This strategy has been shown to be successful at the laboratory and field scale and has been used in the oil industry (Videla and Herrera, 2005; Tabari et al., 2011). It involves the use of nutrients that stimulate the growth of competitive bacteria such as nitrate reducing bacteria (NRB) that are able to displace the SRB from the community (Tabari et al., 2011). The addition of nitrate has been shown to induce a shift in the dominant bacterial populations from the sulphate reducing bacteria to nitrate reducing bacteria, which thereafter prevents the production of hydrogen sulphide and SRB growth (Videla and Herrera, 2007). The actual microbiological basis is not very well understood and it is still not known whether autotrophic or heterotrophic NRB have the most significant role (Videla and Herrera, 2007). However, it has been shown that the enrichment of NRB in the system inhibits the growth of SRB due to the production of toxic by products such as nitrite as well as by increasing the redox potential (Bødtker et al., 2008). In systems where carbon is limited, NRB are also able to out-compete SRB due to the more favourable energy output of nitrate compared to sulphate. In most cases, the inoculation of NRB into the site is not necessary as the addition of nitrate stimulates the growth of already present NRB (Videla and Herrera, 2005). In some cases, the addition of nitrate was even shown to encourage the SRB to shift from sulphate metabolism to the nitrate reduction pathway (Beech and Sunner, 2004).

The effect of low nitrate concentration treatment on the microbial communities and on corrosion of an oil weld at Veslefrikk and Gullfaks during a 7 to 8 years continuous nitrate injection was investigated (Bødtker et al., 2008). A rapid reduction in number and activity of the SRB was observed in response to the nitrate treatment at both welds. A reduction in corrosion rate of up to 40% was observed when compared to biocide treatment. Results from 16S rRNA gene based Polymerase Chain Reaction and Denaturing Gradient Gel Electrophoresis (PCR-DGGE) revealed that the dominant populations were formed by the populations of NR-SOB *Sulfurimonas* spp. The biofilm community during the long term treatment remained highly diverse and relatively stable. This study has shown that nitrate injection has the potential to provide a stable and long term method of SRB inhibition, when compared to the use of biocides (Bødtker et al., 2008).

However, although proving to be successful in the laboratory and field scale to reduced hydrogen sulphide production as well as biocorrosion, nitrate injection does have its drawbacks, including the following (Videla and Herrera, 2007). An increase in localised corrosion could occur due to nitrate treatment through the production of polysulfide and thiosulfate by the simultaneous oxidation of sulfide and reduction of nitrate. Certain species of SRB are also capable of nitrate reduction and may be quantified by both SRB and NRB quantification methods.

Corrosion inhibition from within the biofilm

SRB are naturally resistant to a wide spectrum of antimicrobial agents. Furthermore, the corrosion products produced due to SRB activity further limits the effectiveness of the antimicrobials used (Videla and Herrera, 2007). Once biocorrosive bacteria become established and form biofilms, it becomes extremely difficult to remove or kill them (Jayaraman et al., 1999b; Zuo et al., 2004). Instead of killing all SRB and other biocorrosive bacteria in the system, a strategy can be developed to prevent the colonisation of SRB from within the biofilm itself (Jayaraman et al., 1999b).

Bacillus sp. are able to form biofilms and efficiently secrete a wide range of antimicrobial peptides such as polymyxin B and gramicidin S, these microbes seem promising candidates to produce antimicrobials against SRB (Jayaraman et al., 1999a). This strategy may also have the additional advantage of being able to decrease generalised corrosion due to oxygen reduction by as much as 40-fold (Jayaraman et al., 1997). Jayaraman et al. (1999a) and Zuo et al. (2004) reported that *Bacillus* species (naturally or genetically constructed) can produce antimicrobial compounds within the biofilm, resulting in inhibiting the growth of corrosion-causing SRB and decrease in corrosion rate of mild steel. Supernatants of the gramicidin S producers, as well as purified gramicidin S were shown to inhibit the growth of the SRB (Zuo et al., 2004).

The mechanism of action of these antimicrobial substances was shown to involve outer and cytoplasmic membrane disruption. Therefore, the use of bacteria which produce antimicrobial peptides within the biofilm complex to inhibit SRB colonisation from within the biofilm is an attractive and promising preventative technique. Its successful implementation would provide massive saving in practical applications due to the decreased use of high biocide and corrosion inhibitor concentrations (Ornek et al. 2002a). Ornek et al. (2002b) also reported that some microorganisms can secrete corrosion inhibitors such as polyaspartate or polyglutamate in the biofilm thereby protecting the metal surface from corrosion.

An increase in depth of biofilm is known to correspond to a greater reduction in corrosion (Jayaraman et al., 1999b). Aerobic *P. cichorii* was able to inhibit corrosion of mild steel due to a layer of passive oxide products formed during corrosion which was trapped in the biofilm (Chongdar et al., 2005). Bacterial metabolic activities can contribute to oxygen removal by biofilms (Dubiel et al., 2002). Biofilm formed by *B. mycoides* increased the charge transfer resistance of the aluminium that slowed down the corrosion rate (Juzeliunas et al., 2006).

CONCLUSIONS

Biocorrosion is a very problematic phenomenon which

causes billions of dollars of losses in monitoring and control every year. MIC has relevance in almost every major industry, with various physical and chemical strategies used for their control. The control of MIC has largely been dominated by the use of biocides however, the formation of biofilms and development of antibiotic resistance has restricted their effectiveness in eradicating biocorrosive bacteria. The need for environmentally safe substances has reduced the use of certain biocides and led to the need for controlled use of biocides or development of more environmentally benign alternatives.

Biological control strategies such as biocompetitive exclusion, show increasing promise as a more effective long term method of corrosion control. This strategy has been shown to be successful at the laboratory and field scale. The use of antimicrobial producing biofilm forming bacteria to prevent SRB colonisation is another attractive alternative to provide a cheaper, more effective control. These techniques show immense potential to reduce the effects of MIC, rather than through the use of environmentally toxic biocide doses.

ACKNOWLEDGEMENTS

This research was funded by the National Research Foundation of South Africa. The authors are grateful to the NRF for the award of Honours student bursary.

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