



A COMPREHENSIVE APPRAISAL OF MICROBIOLOGICALLY INFLUENCED CORROSION: ITS DETECTION, PREVENTION AND ROLE OF GREEN CORROSION INHIBITORS

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Abstract

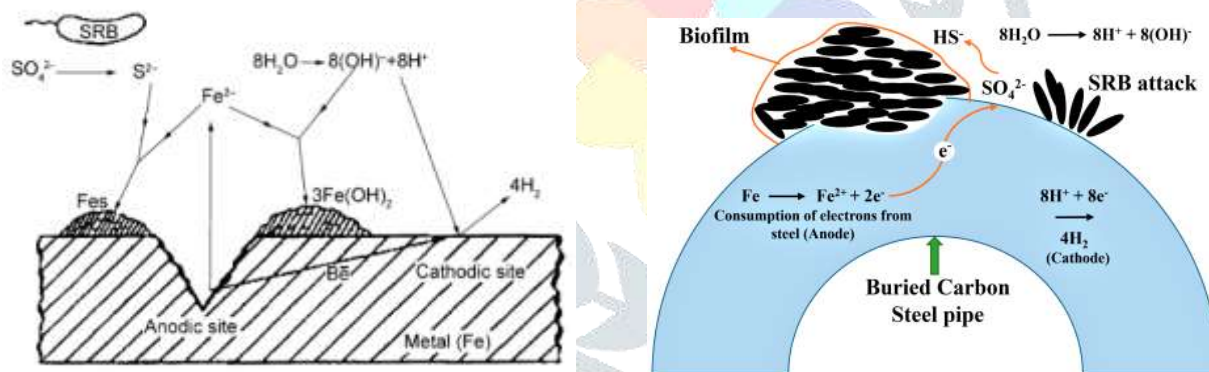
This review discusses the state-of-the-art of research into biocorrosion and the biofouling of metals and alloys of industrial usage and finishes with suggestions on what needs to be done to further our understanding of MIC (Microbiologically influenced corrosion) which is a major concern in a wide range of industries, with claims that it contributes 20% of the total annual corrosion cost. The focus of this present work is to review critically the most recent proposals for MIC mechanisms, with particular emphasis on whether or not these make sense in terms of their electrochemistry. It is determined that, despite the long history of investigating MIC, we are still a long way from really understanding its fundamental mechanisms, especially in relation to non-sulphate reducing bacterial (SRB) anaerobes. Nevertheless, we do know that both the cathodic polarization theory and direct electron transfer from the metal into the cell are incorrect. Electrically conducting pili also do not appear to play a role in direct electron transfer, although these could still play a role in aiding the mass transport of redox mediators. However, it is not clear if the microorganisms are just altering the local chemistry or if they are participating directly in the electrochemical corrosion process, albeit via the generation of redox mediators. The key concepts needed to understand the main effects of microorganisms on metal decay, and current trends in monitoring and control strategies to mitigate the deleterious effects of biocorrosion and biofouling are also described. Several relevant cases of biocorrosion studied by our research group are provided as examples: (i) biocorrosion of aluminum and its alloys by fungal contaminants of jet fuels; (ii) sulfate-reducing bacteria (SRB)-induced corrosion of steel; (iii) biocorrosion and biofouling interactions in the marine environment; (iv) monitoring strategies for assessing biocorrosion in industrial water systems; (v) microbial inhibition of corrosion; (vi) use and limitations of electrochemical techniques for evaluating biocorrosion effects. Future prospects in the field are described with respect to the potential of innovative techniques in microscopy (environmental scanning electron microscopy, confocal scanning laser microscopy, atomic force microscopy), new spectroscopic techniques for the study of corrosion products and biofilms (energy dispersion X-ray analysis, X-ray photoelectron spectroscopy, electron

microprobe analysis) and electrochemistry (electrochemical impedance spectroscopy, electrochemical noise analysis). This manuscript brings into focus the problems posed by microbial infestations in industrial cooling water system and the other water handling equipments along with monitoring, diagnostic procedures, preventive measures and investigation strategies, and role of green corrosion inhibitors.

Key words: [MIC](#), CIM, SRB, EPS, Biofilms, Biocides, EFAMCs, TEM, XRD

Introduction

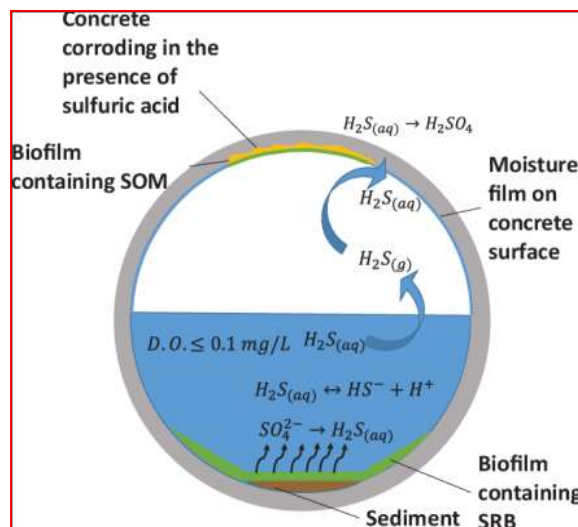
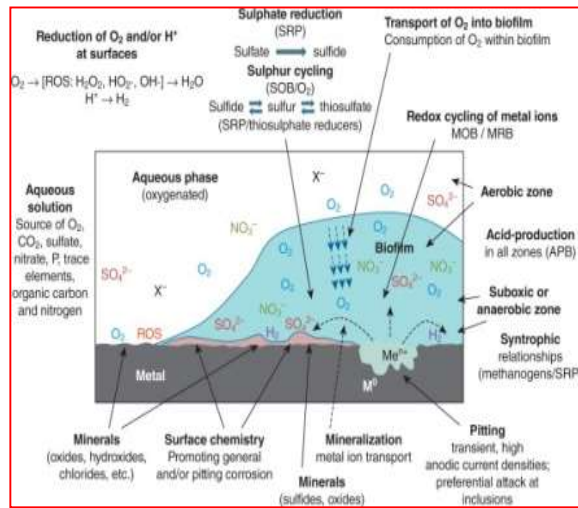
Microbially influenced corrosion (MIC) or biocorrosion is recognized as an important category of corrosion leading to important economical losses in many industries and services. Although almost impossible to quantify precisely, because it is still difficult to differentiate MIC from normal corrosion cases, some authors estimate that around 20% of all corrosion failures are due to microorganisms (Flemming, 1996; Beech and Gaylarde, 1999). Microbes can interact in the environment with materials/surfaces in so many ways that make the complexity of the system too high to be evaluated by standard corrosion model predictions. Nevertheless, biofilm formation is considered as the primary step to start a biocorrosion process, allowing the cells to be in close contact with the surface and creating a microenvironment that can be totally different from the bulk with distinct properties: pH, dissolved oxygen, and the presence of organic and inorganic species (Beech *et al.*, 2005; Hamilton, 1985). A biofilm is an elaborated tridimensional structure, with complex composition providing nutrient gradients (Beech and Sunner, 2004). A biofilm is recognized as being composed of a consortia of microorganisms, and sulphate-reducing bacteria are the most targeted ones, as they have been implicated in the corrosion of ferrous metals in several habitats and represent the main concern to many industrial operations due to their capacity to produce biogenic sulphide (Coetser and Cloete, 2005). A biofilm is composed of four compartments: (1) the surface to which the microorganisms are attached, (2) the biofilm (the microorganisms and the matrix), (3) the solution of nutrients, and (4) the gas phase (Lewandowski and Beyenal 2007). Each compartment consists of several components, and the number of components may vary depending on the type of study.



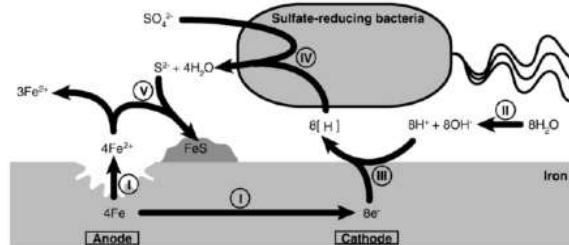
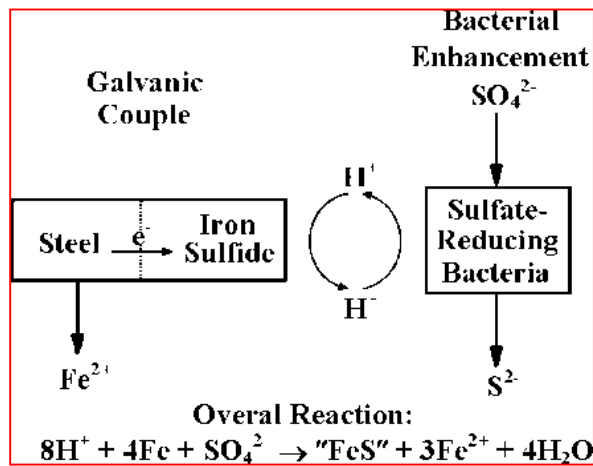
For example, in some MIC studies it is convenient to distinguish four components of the surface: (1) the bulk metal, (2) the passive layers, (3) the biomineralized deposits on the surface, and (4) the corrosion products. Microorganisms can modify each of these components in a way that enhances corrosion of the metal surface. In addition, components of the other compartments of the biofilm can be modified in ways that affect the corrosion reactions as well. Modifications in the solution compartment may include the chemical composition, hydrodynamics and mass transfer rates near the metal.



Different Aeration corrosion Resulting from Variations in Soil Conditions



Microbial life affects everything including many industrial systems. The microbes inhabiting the industrial systems adversely affect the efficiency of the operation by their sheet number and diversity. Metabolic wasters of microbes depositing on metallic surface result in corrosion which is emerging as a serious problem in various industrial organizations. The treatment includes complete synergistic approach for controlling the corrosion/bio-fouling taking place. A specific microorganism control program is considered to be a part of routine operation and maintenance of the industrial system. It is of paramount importance to understand corrosion-influencing microbes (CIM), not as a unique or different type of corrosion but as a part of the corrosion process which is to be recognized and corrected whenever occurs.



Physicochemical interactions between a metallic material and its environment can lead to corrosion. Electrochemical corrosion is a chemical reaction involving the transfer of electrons from zero-valent metal to an external electron acceptor, causing release of the metal ions into the surrounding medium and deterioration of the metal. This process proceeds through a series of oxidation (anodic) and reduction (cathodic) reactions of chemical species indirect contact with, or in close proximity to, the metallic surface. Microbial activity within biofilms formed on surfaces of metallic materials can affect the kinetics of cathodic and/or anodic reaction and can also considerably modify the chemistry of any protective layers, leading to either acceleration or inhibition of corrosion. Deterioration of metal due to microbial activity is termed MIC (Microbially Influenced Corrosion) or Biocorrosion. Which is a type of corrosion where microorganisms are the main perpetrators in the degradation process of a wide range of metals and alloys, and is a major concern to a wide range of industries, from oil and gas to aviation [1,2]. It has been estimated that MIC constitutes about 20% of the total annual corrosion cost [3], although there has never been any real numbers presented to support this figure. Nevertheless, notable MIC-related cases include the 2006 Prudhoe Bay oil spill and the corrosion of deep-sea tsunami early warning systems [4]. A wide range of microorganisms has been associated with MIC, including protozoa, algae, archaeons, diatoms and fungi, but bacteria, especially sulphate-reducing bacteria (SRB), have received the most attention because these are economically the most destructive [5]. In addition to directly causing corrosion, microorganisms can metabolize certain corrosion inhibitors [6], as well as lubricating oils, with the latter leading to fretting and fatigue corrosion. There have been a number of good reviews on MIC over the years [5,7,8]. However, despite this volume of work, we are still not certain of the fundamental interactions between microorganisms and metallic substrates that ultimately lead to the observed rapid corrosion. Therefore, the major focus of this present work will be to review critically the most recent proposals for MIC mechanisms, with particular emphasis on whether or not these make sense in terms of their electrochemistry.



MIC is caused by sessile cells within a biofilm adhered to the metal's surface, rather than planktonic (free-swimming) cells in the solution. The main driving forces for biofilm formation, as opposed to remaining planktonic, are: access to uninterrupted nutrient sources; adhesion as a way to remain in a favourable environment; shielding from harmful environmental conditions; and benefiting from cooperative relationships with other species [40]. Typically, when a metal is immersed into seawater or any other nature water, the attachment of organic and inorganic molecules occurs within a few hours and a biofilm forms within days after immersion, with the latter consisting of bacteria, diatoms and micro-organisms in an extra-cellular polymeric substances [41,42]. The strength of the attachment is a strong function of the surface roughness and surface energy of the material on which the biofilm develops [43,44]. Porous weld-joints, crevices, grain boundaries and scratched edges are better sites for colonization than smooth surfaces, which are also the sites most prone to abiotic corrosion [45,46]. Corrosion can start in the early stages of biofilm formation and, once formed, biofilms have the capacity to locally alter the concentrations of dissolved oxygen, chloride and other ionic species as well as pH levels, all of which impact corrosion rates [47,48].

Unfortunately, the nature of the microorganisms that comprise the biofilm are likely to be vastly different from their planktonic counterparts. This causes difficulties in assessing the degree of threat posed by the local microbiological community, as it is easy to collect solution samples for analysis but much harder to take swabs from the inside walls of a long pipeline. This is a task made more complicated by the fact that the ecology of the biofilm can be altered by small oil leaks, which allow hydrocarbon-degrading microorganisms to thrive and in turn provide the nutrients required by corrosive species [27]. Even if the microorganisms are non-corrosive in themselves, the presence of a biofilm will impede the diffusion of chemical species across it and this can lead to the formation of differential oxygen concentration cells. This is especially likely if the biofilm contains voids or channels surrounding micro-colonies, through which oxygen diffusion is faster or at least not consumed by the microorganisms. As a result, the anaerobic zones under respiring colonies become the anodes and the surrounding volume works as the cathode [48]. Naturally, differential oxygen cells could also form if the biofilm only partially covers the metals surface. However, in many cases a biofilm that consists of non-corroding microorganisms may actually reduce corrosion rates, since it acts as a diffusion barrier layer [8,49]. For example, Pedersen and Hermansson [50] found that axenic cultures of *Pseudomonas S9* and *Serratia marcescens EF190* decreased the corrosion rate of SIS 1156 (UNS G10080) carbon steel.

Although a biofilm can consist of just a single species, most naturally occurring biofilms contain consortia of multiple species, the actions of which may combine to generate much more serious corrosion problems than the single species biofilms that are usually found in laboratory conditions [51,52]. For example, as well as being corrosive in their own right, aerobic acid-producing bacteria can produce metabolic products, such as acetates, which act as a carbon food source for SRB that can then also significantly accelerate the corrosion rate [5,53]. Even if the aerobes are not corrosive themselves, they will still consume oxygen allowing an anaerobic environment to develop at the biofilm/metal interface where the SRB or other corrosive anaerobic microorganisms can thrive. However, the situation is complicated by the fact that in a consortium the corrosive SRB have to compete for resources with other

non-corrosive anaerobic microorganisms. For example, Duan et al., [54] reported accelerated corrosion of carbon steel in a single SRB culture, but the corrosion was inhibited when a mixed anaerobic bacteria culture was tested. This highlights the great difficulty of replicating the MIC rates recorded in the field under laboratory conditions. Furthermore, in their recent work, Deutzmann et al. [55] suggested that certain extracellular enzymes, held in the biofilm matrix, could also lead to corrosion that further complicates matters.

Microbiologically Influenced Corrosion (MIC) is a localized pitting corrosion mechanism that was first identified within the Oil and Gas industry in the early 20th century but is still not fully understood. MIC can not only cause rapid corrosion but also cause operational issues, decrease equipment life and devalue production fluids. It occurs throughout production facilities but most commonly water injection systems, closed drain systems, re-injection wells and produced water systems as well as pipelines and storage tanks. As a consequence, frequent repairs or replacement and associated downtime occur as MIC can cause pinhole leaks in a relatively short period of time in comparison to other corrosion mechanisms. Corrosion rates of 2-3 mm per year are not unusual but there have been published cases of corrosion at significantly higher rates. In addition, to the operational challenges posed by MIC, there is also the issue of hydrogen sulfide gas, a by-product of the process in many cases, which is not only poisonous and flammable but can also affect the value of the inventory and create additional integrity threats.

Oilfield bacteria come in different forms and types. Identifying each type of bacteria present in a system is a complex process, with no single analysis technique able to verify the differing families of bacteria present due to the differing conditions they can exist. Bacteria are commonly split into aerobic or anaerobic bacteria, and this article focuses on the bacteria commonly found in the Oil and Gas industry. Different forms of bacteria can be present in a processing system, depending on factors such as temperature, pressure, oxygen levels, nutrients, pH and salinity.

Sulfate Reducing Bacteria (SRB) are the most common and problematic type of bacteria in oil and gas systems. They are typically found in pipelines, dead legs on small bore pipework or stagnant flow areas, ratholes and under deposits of scale and other accumulated debris. They metabolize sulfate to sulfide through anaerobic respiration. SRB can remove molecular hydrogen from the surface of metallic materials, leading to cathodic depolarization of the metal surface. Iron sulfide or scale is accumulated on these surfaces, which accelerates the dissolution of the iron. The sulfide ions that are produced react with dissolved iron to produce iron sulfide (black deposits) and/or hydrogen sulfide. Hydrogen sulfide gas is a waste product of the sulfate reducing bacteria; its rotten egg odor is often a marker for the presence of sulfate reducing bacteria.

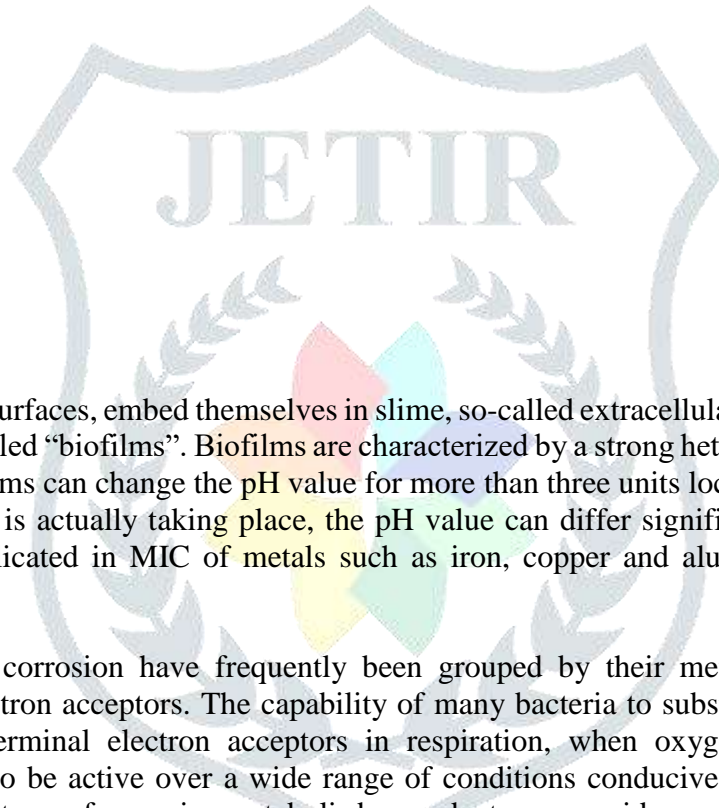
Figure 1: SRB mechanism [1]

Most sulfate reducing bacteria can also reduce other oxidized inorganic sulfur compounds, such as sulfite, thiosulfate, or elemental sulfur. In addition to the associated corrosion, there can also be significant biofouling by the accumulation of biomass which has caused numerous wells to become plugged by heavy bacterial growth over the years. Other forms of bacteria include acid producing bacteria (ACB) which are commonly found in storage tanks and platform legs. They produce organic and inorganic acid in the absence of sulfates and nitrates. The acids produced are trapped under the biofilm where they deteriorate the oxide film from the surface of a variety of metals resulting in very high pitting rates, with 10 mm per year not uncommon. Slime-forming bacteria can be found in supply wells, surface equipment and storage tanks. Slime-forming bacteria have a slimy coating over their surface which assists in protecting the bacteria from the harsh environment and chemical treatments. They also allow the bacteria to adhere to one another, which can result in a substantial biofilm. Biocides are grouped into two chemical classes: oxidizers and non-oxidizers. Oxidizing biocides are the most widely used biocides worldwide due to their fast kill rates and are common to treat seawater for water injection in the oil and gas industry. These oxidizing biocides normally take the form of sodium hypochlorite to kill microscopic bacteria such as fungi, which is commonly seen as mold or yeast growths. Non-oxidizing biocides are used in the oil and gas industry due to their less corrosive properties in comparison to oxidizing biocides. Common non-oxidizers include filming amines, aldehydes and formaldehydes.

When it is suspected that a material failure was caused by microbial corrosion, it is reasonable to ask: "How do we know that the corrosion process was influenced by microorganisms?" To address this question, many research groups Springer Series on Biofilms, doi: 10.1007/7142_2008_8 35 © Springer-Verlag Berlin Heidelberg 2008 Z. Lewandowski Department of Civil Engineering and Center for Biofilm Engineering, Montana State University, Room 310, EPS Building, Bozeman, MT 59717, USA e-mail: ZL@erc.montana.edu 36 Z. Lewandowski and H. Beyenal have attempted to find a fingerprint of microbially influenced corrosion (MIC), i.e., specific characteristics distinguishing microbially stimulated corrosion from ordinary galvanic corrosion (Beech et al. 2005; Javaherdashti 1999; Lee et al. 1995; Little et al. 2000, 2007; Mansfeld and Little 1991; Videla and Herrera 2005; Wang et al. 2006). Despite significant research effort, no such fingerprint characteristic of MIC has yet been found, and there are good reasons to believe that a universal mechanism of microbially stimulated corrosion does not exist (Beech et al. 2005; Flemming and Wingender 2001; Miyanaga et al. 2007; Starosvetsky et al. 2007). Instead of a universal mechanism, several mechanisms by which microorganisms affect the rates of corrosion have been described, and the diversity of these mechanisms is such that it is difficult to expect that a single unified concept can be conceived to bring them all together. From what we now understand, and what has been demonstrated by numerous researchers, accelerated corrosion of metals in the presence of microorganisms stems from microbial modifications to the chemical environment near metal surfaces (Beech et al. 2005; Geiser et al. 2002; Lee and Newman 2003; Lewandowski et al. 1997). Such modifications depend, of course, on the properties of the corroding metal and on the microbial community structure of the biofilm deposited on the metal surface (Beech and Sunner 2004; Dickinson et al. 1996b; Flemming 1995; Olesen et al. 2000b, 2001). The conclusion that there are many mechanisms of MIC, rather than a single one, is generally accepted in the literature and can be exemplified by the paper by Starosvetsky et al. (2007), who concluded that to uncover MIC in technological equipment failures requires an individual approach to each case, and that an assessment of the destructive role of the microorganisms present in the surrounding medium is possible only by analyzing and simulating the corrosion parameters found in the field (Dickinson and Lewandowski 1998). Quite succinctly, Beech et al. (2005) describe MIC as a consequence of coupled biological and abiotic electron-transfer reactions, i.e., redox reactions of metals enabled by microbial ecology. Hamilton (2003) attempted to generate a unified concept of MIC and has found common features in only some of the possible mechanisms. It is unlikely that a unified concept of MIC can be generated at all.

MIC (Microbially Influenced Corrosion) or Biocorrosion

Microbially Influenced Corrosion refers to the influence of microorganisms on the kinetics of corrosion processes of metals, caused by microorganisms adhering to the interfaces (usually called "biofilms"). Prerequisites for MIC is the presence of microorganisms. If the corrosion is influenced by their activity, further requirements are: (I) an energy source, (II) a carbon source, (III) an electron donator, (IV) an electron acceptor and (V) water“ • A role of MIC is often ignored if an abiotic mechanism can be invoked to explain the observed corrosion. In principle, corrosion is an interfacial process - kinetics of corrosion are determined by the physico-chemical environment at the interface, e.g., by the concentration of oxygen, salts, pH value, redox potential and conductivity. All these parameters can be influenced by microorganisms growing at interfaces. This mode of growth is preferred by most microorganisms on earth (Costerton et al., 1987).



The organisms can attach to surfaces, embed themselves in slime, so-called extracellular polymeric substances (EPS) and form layers which are called “biofilms”. Biofilms are characterized by a strong heterogeneity. Metabolic activity of clusters of biofilm organisms can change the pH value for more than three units locally. Directly at the interface, where the corrosion process is actually taking place, the pH value can differ significantly from that in the water phase. Microorganisms implicated in MIC of metals such as iron, copper and aluminium, and their alloys are physiologically diverse.

Bacteria involved in metal corrosion have frequently been grouped by their metabolic demand for different respiratory substrates or electron acceptors. The capability of many bacteria to substitute oxygen with alternative oxidisable compounds as terminal electron acceptors in respiration, when oxygen becomes depleted in the environment, permits them to be active over a wide range of conditions conducive for corrosion of metals. The ability to produce a wide spectrum of corrosive metabolic by-products over a wide range of environmental conditions makes microorganisms a real threat to the stability of metals that have been engineered for corrosion resistance. Sulphate-Reducing Bacteria are a group of ubiquitous, divers anaerobes that reduce oxidised sulphur compounds, such as sulphate, sulphite and thiosulphate, as well as sulphur to H₂S. Although SRB are strictly anaerobic (obligate anaerobes), some genera tolerate oxygen and are even able to grow at low oxygen concentrations. The activities of SRB in natural and man-made systems are of great concern to many different industrial operations. In particular, oil, gas and shipping industries are seriously affected by the sulphides generated by SRB. Biogenic sulphide production leads to health and safety problems, environmental hazards and severe economic losses due to reservoir souring and corrosion of equipment.

Since the beginning of the investigation into the effect of SRB on corrosion of cast iron in 1930s, the role of these bacteria in pitting corrosion of various metals and their alloys in both aquatic and terrestrial environments under anoxic as well as oxygenated conditions has been confirmed. Several models have been proposed to explain the mechanisms by which SRB can influence the corrosion of steel. These have included cathodic depolarisation by the enzyme hydrogenase, anodic depolarisation, production of corrosive iron sulphides, release of exopolymers capable of binding Fe-ions, sulphide-induced stress-corrosion cracking, and hydrogen-induced cracking or blistering. Recent reviews clearly state that of predominant mechanism may not exist and that a number of factors are involved. Metal-

Reducing Bacteria promote corrosion of iron and its alloys through reactions leading to the dissolution of corrosion-resistant oxide films on the metal surface. Protective passive layers on e.g. stainless steel surfaces can be lost or replaced by less stable reduced metal films that allow further corrosion to occur. Despite of their wide spread occurrence in nature and likely importance to industrial corrosion, bacterial metal reduction - recently.

Numerous types of bacteria including those from the genera of *Pseudomonas* and *Shewanella* are able to carry out manganese and/or iron oxide reduction. It has been demonstrated that in cultures of *Shewanella putrefaciens*, iron oxide surface contact was required for bacterial cells to mediate reduction of these metals. The rate of reaction depended on the type of iron oxide film under attack. Metal-Depositing Bacteria Participate in the biotransformation of oxides of metals such as iron and manganese. Iron-depositing bacteria (e.g., *Gallionella* and *Leptothrix*) oxidize Fe^{2+} , either dissolved in the bulk medium or precipitated on a surface, to Fe^{3+} . Also capable of oxidizing manganous ions to manganic ions with concomitant deposition of manganese dioxide. Promote corrosion reactions by the deposition of cathodically-reactive ferric and manganic oxides and the local consumption of oxygen caused by bacterial respiration in the deposit. Fungi are well-known producers of organic acids, and therefore capable of contributing to MIC (e.g., *Aureobasidium pullulans*).

Much of the published work on biocorrosion of aluminum and its alloys has been in association with contamination of jet fuels caused by the fungi *Hormoconis* (previously classified as *Cladosporium*) *resinae*, *Aspergillus spp.*, *Penicillium spp.* and *Fusarium spp.* *Hormoconis resinae* utilizes the hydrocarbons of diesel fuel to produce organic acids. • Selectively dissolve or chelate the copper, zinc and iron at the grain boundaries of aircraft aluminum alloys. • Forming pits which persist under the anaerobic conditions established under the fungal mat. Acid-Producing Bacteria (APB) produce inorganic or organic acids as metabolic by-products. Microbially-produced inorganic acids are HNO_3 , H_2SO_3 , H_2SO_4 , HNO_2 and carbonic acid H_2CO_3 . • Sulphurous acid and sulphuric acid - bacteria of the genera *Thiobacillus*. Other bacteria, such as *Thiothrix* and *Beggiatoa spp.* *Thiobacilli* are extremely acid tolerant and can grow at a pH value of 1. • Nitric acid and nitrous acid - bacteria belonging to the groups of ammonia- and nitrite-oxidising bacteria. • Sulphuric and nitric acid corrosion resulted salts are water-soluble and, hence, a formation of a protective corrosion product layer is not possible. - Due to the lowering of the pH, protective deposits formed on the surface, e.g., calcium carbonate, can dissolve. Some bacteria e.g. *Pseudomonas aeruginosa* elaborate extracellular acidic polysaccharides such as alginic acid, during biofilm formation on metal surfaces. These acids can be highly concentrated at the metal-biofilm interface by the diffusional resistance of the biofilm exopolymers, making it impossible to accurately assess the acid concentration at the metal surface from measurements made in the overlying bulk aqueous phase. Microsensors (ultramicroelectrodes) which have been used to probe the pH gradients within microbial biofilms, revealed both horizontal and vertical variations in pH values at the biofilm / metal interface.

Enzymes and Bio corrosion Enzymatic activities are readily detected in biofilms, nonetheless, the importance of reactions mediated by these enzymes has only recently been considered as relevant to biocorrosion. Mechanisms that increase the free corrosion potential of stainless steel, widely reported in oxygenated natural waters and referred to as 'ennoblement', brought enzymes into focus. A lack of ennoblement was observed when a biofilm was treated with sodium azide, which is an inhibitor of the microbial respiratory chain and enzymes such as catalases, peroxidases and superoxide dismutases. These enzymes are involved in reactions of oxygen reduction, therefore, in principle, they might facilitate corrosion by accelerating the overall cathodic reaction. The effect of extracellular catalase produced by *Pseudomonas* species on the ennoblement behaviour of aluminium brass is the best example of such a relationship. Biocorrosion occurs in aquatic and terrestrial habitats - differ in nutrient content, temperature, pressure and pH. Results in the presence and physiological activities of microbial consortia on the metallic surfaces. Such biofilms promote interfacial physicochemical reactions, not normally favoured under abiotic conditions. Mechanisms proposed as pertinent to biocorrosion reflect the range of physiological activities carried out by diverse types of microorganisms found within biofilms. These mechanisms vary with microbial species.

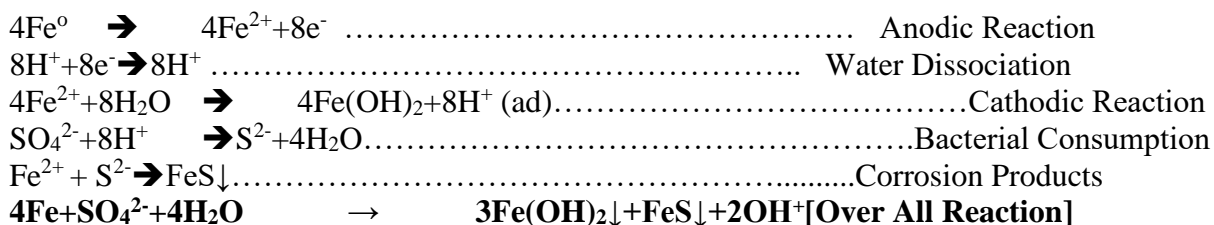
2. Historical background of MIC

Microbiological Influenced Corrosion has a long history, the effect of microbes on corrosion being noted by Gaines in 1910 [9]. However, it was probably only after the 1934 work of Kühr and Vlugt [10], on the graphitization of cast irons in anaerobic soils, that significant research was first devoted to this field. Nevertheless, industry was not totally convinced that MIC was a real phenomenon, so for the years leading up to the early 1970s research on MIC was mainly focused on the corrosion of steels by SRB (e.g., *Desulfovibrio* species) and validating the now largely discredited cathodic depolarization mechanism [11- 15]. The 1980s and 1990s marked the period where industrial attention to MIC problems increased significantly and consequently spurred further studies. There were a number of intensive works that focused on understanding the complex interactions that occur at the biologically conditioned interface between the metal and the biofilm, with microbiological and material characterisation techniques being coupled with electrochemical monitoring programmes [5,16,-22]. Moving into the 21st century, with improved accuracy and a wider range of sophisticated techniques becoming available, especially with advances in microbiological identification techniques, researchers are now capable of analysing in great detail the microbial populations found in marine environments and petroleum -reservoirs, revealing that populations are much more diverse than solely containing SRB [23-27]. As a result, it has been increasingly evident that the phenomenon of MIC in anaerobic environments is not simply the result of the action of SRB, but heavily influenced by the presence of other microorganisms found commonly in industrial environments. These include nitrate-reducing bacteria (NRB), acid-producing bacteria (APB), sulphur-oxidizing bacteria (SOB), iron-oxidizing bacteria (IOB), iron-reducing bacteria (IRB) and methanogens, an archaea species [7,8,28,29-36]. Some actions of these microorganisms are also suggested to be protective against the corrosion of steels [37-39].

Cathodic depolarization/H₂S production

This mechanism for most localized industrial corrosion associated with sulphate reducing bacteria viz. *Desulphovibrio-desulphuricans*, *Desulphovibrio-vulgaris* [-in presence of sulphate and organic matter & anaerobic condition, pH -8., 10-40⁰C], *Desulphotomaculum-nigrificans* [-in presence of sulphate(SO₄²⁻) and organic matter & anaerobic condition, pH -8., 45-70⁰C] affect metallurgies of aluminium(Al), copper(Cu), iron(Fe), Steel. These bacteria contain enzyme hydrogenase that uses elemental hydrogen generated at cathodic sites for reduction of SO₄²⁻ to sulphide (S²⁻)². water potential zones ranging from Nil to Excellent. In this study area, the geomorphic unit Pediplain with moderate weathering indicates high groundwater potential. Pediplain with shallow weathering indicating medium groundwater potential which is observed in major part of the study area. The other geomorphic units such as pediments, inselbergs and residual hills indicate low groundwater potential.

Chemical reactions involved



Libration of Corrosive Metabolites :

During the metabolic reactions number metabolites like *HNO₃, *H₂SO₄, *NH₃, CO₂, H₂S and some *organic acids area resulted by micro-organisms {viz. *nitrifying bacteria such as *Nitrosomonas- sps*, *Nitrosococcus- sps*, *Nitrobacter- sps*, *Nitrocystic- sps* [-in presence of NH₃& aerobic condition], *sulphur oxidizing bacteria such as *Thiobacillus- thiooxidans*, *Thiobacillus- thioparus*, *Thiobacillus- ferrooxidans* [-in presence of sulphur reducing compound & aerobic conditions, pH 0.5-8, 10-40⁰C], *nitrate reducing bacteria such as *Clostridium-prefrigens*,

Propionibacterium- sps [-presence of organic matter & nitrate], nitrogenous compound fermentation bacteria such as Clostridium- sps, Escherichia- coli [-in presence of protein/amino acid & anaerobic condition], Bluegreen algae [-in presence of sun light, CO, pH 7-9, 20-40⁰C], *organic matter/cellulose degrading bacteria such as *Desulphovibro- sps Clostridium-sps, Ervinia-sps Shigella-sps* [-presence of organic compounds/cellulose& anaerobic condition, pH 3-9, 20-40⁰C], fungi such as *Clodosporium-resinae, Aspergillus-niger, Aspergillus-fumigants, Penicillium-cyclopium* [-presence of organic compound and aerobic conditions, pH 3-6., 10-40⁰C; best 30-35⁰C] respectively} which affect a variety of metallurgies of (viz. Fe, Steel, Copper alloys; Fe, Steel, Copper alloys, Al; Cu, Copper alloys; Fe, Al, Cu, Copper alloys respectively) leading to substantial damage to systems³.

•Metal oxidation/reduction

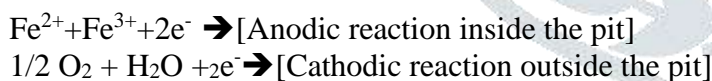
Some bacteria viz. *Gallionella-sps, Sphaerotilus-sps, Crenothrix-sps, Leptothrix-sps, Clonothrix-sps* [-in presence of Fe⁺²ions and aerobic conditions, pH 7-10., 20-40⁰C] directly oxidize ferrous (Fe⁺²) to ferric (Fe⁺³)ion which precipitates in sheath around the cell. These accumulate as tubercle in pipeline. Some species of *Pseudomonas* [-in presence of Fe⁺³ion & aerobic conditions, pH 4-10] reduce ferric oxide (Fe₂O₃) coatings to Fe⁺²ion exposing base metal Fe⁺² to corrosion.

•Oxidation concentration cell due to microbial growth: Bio-films (fine microbial coating on natural surfaces) and tubercles form deposit on metal surface. The metal outside deposit becomes assessable to oxygen. While that under deposit remain shielded from it. These results in formation of corrosion cell, with the liberation of metal ion in anodic region under deposit leading to pitting. The type of cell is referred to as oxygen concentration cell.

•Bacteriological attack resulting in breaking down/disruption of protective film: Bacteria growing in contact with metal surface usually interface with protective film formation that would result in pitting, and it might be very severe if acids and alkalis are produced.

Some corrosion inhibitors have nutritive value to bacteria, e.g. corrosion inhibitor based on nitrite (NO₂⁻), nitrate (NO₃⁻), phosphate (PO₄³⁻) and benzoate (C₆H₅O⁻) are often metabolized by bacteria and are rendered ineffective as corrosion inhibitors.

Interaction among the above factors: In the eating away of metal inside a developing pit beneath the deposit on steel cooling water pipe, the corrosion reactions⁵ considered are mentioned below.
Chemical reactions involved



As the dissolved oxygen in water inside the pit is depleted, the metal surface becomes anodic to the metal outside the pit and corrosion begins. The first corrosion product to be formed in Fe⁺²ion which can then further be oxidized to Fe⁺³ion by oxygen, iron oxidizing bacteria or be other reaction away from the metal surface. Both ferrous and ferric ions form corresponding chlorides which get hydrolyzed to produce ferrous and ferric hydroxides as depicted here.



Corrosion products are thus formed and the deposits expand. The ph of the water next to metal surface declines and thereby corrosion accelerates. Sulphate reducing bacteria, if present in the deposit, anaerobically reduce SO₄²⁻ions in the water to produce H₂S. Ferrous ions can react with H₂S and produce black iron sulphide (FeS) deposits at CIM sites along with more HCl as following.



The role of SO_4^{2-} reducing bacteria is to ensure that the ongoing under deposit corrosion reaction even more aggressive. Anaerobic environments also shelter a group of bacteria [collectively known as acid producing bacteria (APB)] that metabolize complex organic compounds into simple organic acid.

Aerobic bacteria are also involved in CIM. The role of aerobic bacteria is primarily to encourage the formation of deposits that provide protective sites for anaerobic bacteria in otherwise aerobic environments. The polysaccharides produced by slime forming bacteria in cooling water system acts as glue holding corrosion product and scale deposits on metal surface. Iron oxidizing bacteria oxidize Fe^{2+} to Fe^{3+} and help to form large tubercular deposits. The reactions are much more complex than they seem and many intermediate steps are involved. Corrosion induced by bacteria is a serious aggravating factor in normal under-deposit corrosion processes⁶.

MICROBIAL REACTIONS ASSOCIATED WITH TUBERCLES

What does CIM look like? Corrosion influenced by bacteria affects different materials in different ways viz. on mild steel CIM often leaves characteristics of concentric rings, visible after cleaning the surface indicating the growth of a S^2 producing (SO_4^{2-} -reducing) bacteria colony that produces H_2S . On stainless steel (SS*) it leaves a characteristic signs after the surface is cleaned. Pitting can be highly localized. Another typical characteristic is a deep penetration of the SS that is similar in appearance to the tunnelling caused by termites in wood. It can be of several type on Cu-alloys, Al-alloys and galvanized steel. Pitting can occur with S_2 - producing bacteria forming CuS -corrosion. Denitrifying or NH_3 -producing bacteria caused corrosion. A blue/black area at the site of the CIM identifies this type of corrosion.

BACTERIAL BIO-FILMS

Bacteria sticks to almost any surface in industrial water system and produce a slimy polysaccharide matrix which further entraps dirt, organic matter, precipitates, corrosion products and bacterial debris, Universally, this state is now called as bio-film. Physical, chemical and biological properties of bio-films are dependent on the environment to which the attachment surface is exposed. Physical and chemical environment combine to select prevalent bacteria, which interact in complex ways to produce a milieu at the bio-film/metal interface that is radically different from that of bulk medium in terms of pH, dissolved oxygen and organic & inorganic species⁷.

Bio-films pose numerous problems in water processes as mentioned below:

Corrosion: Bio-films produce highly localized concentrations of metabolites like corrosive gases and acids directly on metal surface causing severe pitting corrosion. **Sailing:** Organic acids and polymers produced by bacteria in bio-films combine with calcium (Ca) and Magnesium (Mg) ions to form insoluble formats [$(\text{HCOO}^-)_2$], oxalates [$-\text{OOC}-\text{COO}-$], acetates [$(\text{CH}_3\text{COO}^-)_2$] and insoluble polymer complexes of Ca and Mg. These insoluble compounds deposit along with the bio-films making them more impermeable. **Loss of heat transfer capacity:** Bio-films cause poor water distribution by plugging nozzles and holes in upper deck of towers and water boxes built over atmospheric sections. It has been estimated that most-cooling towers suffer an efficiency loss by 10% due to plugged distribution nozzles. Bio-films also impede flow through heat exchangers and pipelines⁸. **Health hazards:** Bio-films in cooling water system harbour harmful organisms like Legionella which cause a deadly disease known as Legionnaires' disease. In USA alone, out of 2.4 million cases of pneumonia that occur each year. An estimated 10,000 to 100,000 are actually the cases of Legionnaires' disease. Five% - fifteen % of these cases are fatal. An unknown additional number are infected but possess mild or no symptoms. The cases of Legionellosis have been recently identified worldwide⁹. These outbreaks have resulted in stringent regulations and clear guidelines for Legionella associated risk management in building HVAC systems and cooling towers in other countries. In India, there are so many incidents of pneumonia each year. However, none of them have identified as Legionellosis, although. Tropical conditions are highly favourable for the growth of the bacteria. Legionella testing is not a common practice in India industries. Probably most of the cases go unnoticed. There is a strong requirement for its awareness especially amongst communities of people handling HVAC system, cooling towers and evaporative coolers etc. **Monitoring of these systems for Legionella associated risk must be made mandatory**¹⁰. **Recalcitrance to chemical treatment:** The most practical difficulty encountered with bio-films is their recalcitrance to chemical treatment. As the bio-films increase in volume, the ability to penetrate the structure with conventional biocide treatment is highly reduced, therefore requiring high dose level and longest contact time of biocide to produce at best minimal results.

the bio-films also limits ability of bio-films inhibitors to reach the metal surfaces, therefore corrosion inhibition is compromised. The large surface area of bio-film absorbs surface active water conditioning chemicals; leading to increased dosage requirements¹¹. Development of biocide resistant strain: Bio-films also promote development of biocide resistant strains. The resistance is produced by sessile growth under and within deposits where limited amount of biocide are able to reach the bacteria cultures.

CIM MONITORING STRATEGIES

Biological corrosion monitoring can be divided into two main types according to the target

Early detection: the goal of early detection monitoring is to catch incipient CIM and change the process conditions, environment, or material before the problem becomes acute. The second category of CIM monitoring is based on biocide efficacy. Main goal of the program is to determine minimum quantity of biocide required to maintain acceptable bacteria which are compared with biocide levels in the system. It is impossible to maintain bacteria number to zero, but is often difficult to know how many is too many. Acceptable number are usually determined empirically. The factors that play crucial role in diagnosis of bio-fouling¹² and CIM in water handling system are water quality parameters: It is important to measure all water quality parameters viz. physical, chemical and microbiological, relevant to the growth of bacteria.

Physical and chemical parameters: The parameters, which should be monitored on frequent basis & corrected with microbial numbers, are included as Temperature(T), suspended solids(SS), dissolved solids(DS), pH, NO_3^- , NO^- , NH_3 , SO_4^{2-} , S^{2-} , Fe organic carbon and turbidity¹³. Bacteria may increase e.g. during influx of particulate matters, organics etc from external environment or the process. Some chemical indicators of bio-fouling are:

- Depletion of SO_4^{2-}
- Increase in/appearance of NO_3^- , NO_2^- , NH_3 , S^{2-} etc in water during circulation¹⁴.

Microbiological monitoring: For consistent monitoring, water should be analyzed for parameters like total visible count (TVC), APB/fungi, CO_2^- producing bacteria, S-oxidizing bacteria, Fe-oxidizing bacteria etc¹⁵. There should not be any change in the methodology of collection, culture, or measurement techniques unless necessary, if it's necessary, the effect of new condition should be checked by overlapping the two methods till the relationship between the results of both, is clear in the system.

The classic mistake is to measure only planktonic numbers which repeatedly have been shown to poor correlation with sessile bacteria on metal surface. The sessile bacteria should be sampled from area most susceptible to corrosion. For consistent monitoring of sessile bacteria removable in process probes in some side stream device like Robbins & Rena Probes, have been very successful. Planktonic bacteria can provide useful data if measured consistently. The samples should be collected from the same place, incubated from the same time, at the same T and counted using the same method¹⁶.

The culture medium should not be changed unless strictly necessary. In bacterial monitoring programs, the actual number is far less important than the trend which can be developed only if there is consistency in sampling and methods employed. the following information should be documented along with sample¹⁶.

- ✳ Conductivity, turbidity, organic loading, SS, pH, T etc both for circulation water sample and source¹⁸.
- ✳ Material of construction and history of performance in system.
- ✳ History and upstream condition for makeup water.
- ✳ Nature of contaminants and their source, if any
- ✳ Chemical treatment & point of collection.

Duration of monitoring: There should be sustainable monitoring i.e. for a long period as large seasonal and annual changes can occur in bacterial counts and bactericide demand.

DEPOSIT AND CORROSION PRODUCT MONITORING:

The deposit sample should be analyzed for chemical and microbiological parameters as well. If there is corrosion related failure in the system, the product should be collected both from the pitted area and area surrounding the pit. The deposit then is to be sealed in a plastic bag to retain moisture¹⁷.

CHIMICAL ANALYSIS: The deposit should be analyzed for chlorine (Cl⁻), manganese (Mn) pH etc that normally concentrate at under deposit corrosion sites. Deposits should also be examined for elemental-S, NO₃⁻, NO₂⁻, NH₃, SO₄²⁻, etc¹⁸. Onsite tests for S²⁻ with lead acetate [Pb(CH₃COO)₂] paper are useful. Don't expect large quantity of organic material even if they are biologically mediated¹⁹. Deposits that are 90% mineral have shown to be organically driven. While performing the chemical tests of a sample by x-ray fluorescence (XRF), energy dispersive x-ray analysis (EDXA) or atomic absorption spectroscopy (AAS); the total organic carbon of >20% leads to suspicion of CIM, Sulphur of ~1% or more, signals involvement of S²⁻-producing bacteria (if black and smelly) or S-oxidizing bacteria (if yellow and highly acidic). High Mn or Fe deposits on SS* and other non-Fe metallurgies indicate possibilities of Mn and Fe bacteria in CIM. High phosphorus (P) may also indicate S²⁻-producing bacteria. While preparing corrosion products for SEM examination, 2% buffered osmium tetroxide (OsO₄) in accordance with standard SEM examination techniques should be post fixed. The Os will be taken by living tissue and shows up an EDXA spike which helps identifying bacteria and distinguish them from similarly shaped artifacts²⁰.

MICROBIOLOGIC ANALYSIS:

The sample should be examined as quickly as possible both by microscopic technique and culture test as well, for bacteria like general aerobic bacteria count, APB/fungi, CO₂-producing bacteria, NH₃-producing bacteria, nitrifying bacteria, SO₄²⁻-reducing bacteria, S-oxidizing bacteria, Fe-bacteria and algae etc²¹.

EXAMINATION OF METAL SURFACES:

Examination of metal surface during planned (or unplanned) shut downs is an often ignored but extremely important component of biological corrosion monitoring. Direct examination of equipment surface is the best method to determine the successes or failure of biocide programs. As soon as vessels, equipment, pipes etc are opened, samples should be collected before the systems have a chance to change in condition, dry out and/or has been contaminated by exposure to air. Samples are to be collected for culturing, scanning electron microscopy and EDXA examination. The surface should also be monitored for corrosion pattern. CIM often but not always, produces characteristic patterns on metal surfaces. On mild steel, it often appears as shallow pit with concentric rings or small deep pit with larger pits. Tunnelling is characteristic of CIM on SS*. Morphological evidence although often convincing, is not conclusive and may lead to misleading result²².

ONLINE MONITORING:

Coupons installed in online corrosion monitoring rack should be examined for corrosive metabolites, pH, and microbes. Online bio-film monitoring is a helpful way to measure the growth of sessile bacteria in the system²³.

BIOCIDE MONITORING PROGRAM:

Non-oxidizing biocides generally are difficult to measure accurately, making it to determine exact levels in the system. Fortunately, they tend to be less volatile, although they may interact unexpectedly with other chemicals in the system. Correct feed doses usually are best determined by correlation with bacterial inferences. Oxidizing biocides are highly susceptible to unexpected fluctuations in effective dose. Chlorine (Cl₂) in particular must be checked regularly with safety, as only the free residual is an effective biocide. One important requirement is to measure the oxidizing biocides at the risked equipment. A second step to avoid problems caused by fluctuations is to measure oxidizing biocides immediately. It is to be taken to the sample-not the sample to the lab. Portable Cl₂/Br₂ check kits/online ORP monitor are major tools in oxidizing biocides monitoring program. Over a long period, efficacy is to be checked²⁴.

Diurnal and seasonal changes & periodic changes as well, in the process or operating conditions, which may affect T, nutrients etc. Change with time doesn't occur in biocide efficacy particularly with non-oxidizing biocides.

Bacteria, however, may adapt/mutate into more resisting strains. To maintain an acceptable kill rate, increasing amounts of biocides as indicated by long term monitoring, area required. When that happens it is necessary to change the biocide at least for short period.

TECHNIQUES EMPLOYED FOR DETECTION OF CORROSION CAUSING ORGANISMS

Some of the techniques which are of paramount importance are discussed as mentioned below.

CULTURE TECHNIQUES:

Depending on specific requirement of bacteria to be enumerated, bacteria are cultured on specific media. Enumeration is performed using either plate count or MPN technique²⁵.

ENZYME BASED ASSAY:

Enzymes possess important consecutive properties of bacteria/specific group of bacteria. Enzyme activity of enzyme concentration can correlated directly with bacterial numbers e.g. enzyme adenosine- phospho- surphate-reducase (APS-reductase), an intracellular enzyme found in all SRBs an hydrogenase-an enzyme found in some SRB that can be extracted from liquids or solids including bio-films corrosion products, and sludge. Both enzymes product calorimetric reaction with an intensity and development rate proportional to the amount of enzyme, which turn can be correlated to number of cells from which was extracted²⁶.

EPIFLUORESCENCE:

Organism on solid surface or liquid phase maybe directly count microscopically after sating with fluorescent dye or optical brightener²⁷.

IMMUNOASSAY:

This involves use of specific antibody directed against target organism. The technique like enzyme linked immunoassay (ELISA), are widely employed for detecting specific bacteria including legionella²⁸.

FATTY ACID PROFILE:

Analyzing fatty acid methyl esters derived from cellular lipids can fingerprint organisms rapidly. With confidence, organism in industrial and environmental samples can be identified provided pertinent profiles are known. In the short term, the impact of events such as changes in operating conditions or applications of biocides could be monitored by such analysis. in the long term, problem populations might be identified so that an appropriate management could be implemented in a timely fashion.

GENE PROBES:

For the detection of specific bacteria, gene probes are powerful tools. In this technique, deoxiribose nucleic acid (DNA) from organism previously isolated from the system is spotted on a master filter. From the field samples of interest, DNA isolated is then labeled with either a radioactive or fluorescent indicator and exposed to this filter, where complimentary strands of DNA are present, labeled DNA from the field sample sticks to the corresponding spot on the master filte²⁹.

METABOLITIES:

An overall assessment of bacteria activity can be obtained by measuring the amount of adenosine tri-phosphate (ATP) in field samples. This key metabolite drives many cellular reactions. Release of light by the firefly luciferin/luciferase with ATP, can be measured by a suitable instrument. The method is best suited to clean aqueous samples particulate in the mean time chemical quenching if present, can affect results. Detection of metabolites such as organic acids or gas compositions including CH₄ or H₂S by routine gas chromatography can also indicate involvement of industrial problems³⁰.

RESPIRATION:

The dye reduction test relies on the respiratory activity of bacteria in reducing a redox dye. The rate of dye reduction is directly correlated with bacteria number. More sensitive method for assessing respiratory activity involves incubation of sample with radio labeled substrate such as C*-14 glucose. Respired CO₂ can be collected in caustic soda (NaOH) and measured in scintillating counter. Difference between bacteria and fungi can be obtained by incorporating antibacterial and antifungal substances into incubation mixture³¹.

WHOLE CELL:

Approaches based on the conversion of radioisotopically labelled substrate can be used to assess the potential activity of bacteria population of samples. Selection of radioactively labelled substrate is a key to the interpretation of results but the procedure can provide insights into factors limiting growth by comparing activity in native samples with supplemented test samples under various conditions³².

CORRECTING AND PREVENTING STRATEGIES:

Control of bacterial fouling can be accomplished by the concerted efforts of physical and chemical methodologies³³.

PHYSICAL CONTROL METHOD:

They include side stream filtration, cooling tower air intake filters and elimination of sun light by shading. Side stream filtration is a often utilized to remove SS from cooling tower system. Control of bacteria requires engineering modifications like relocation of bleed offline, isolation of low velocity flow area and routine periodic flush outs.

CHEMICAL CONTROL METHOD: These methods and their application rely on the three categories as mentioned below.

OXIDIZING BIOCIDES:

In this category generally used biocides in industrial waters to control bacterial fouling are Cl₂, Br₂, halogen carries, chlorine dioxide and ozone (O₃). Chlorination, despite its drawbacks, still remains the method of choice for bio-fouling controlling cooling water systems, because of its low cost and broad spectrum activity. Apart from low dose continuous chlorination, and pulse chlorination (PC) have been developed with the objective to achieve better protection, while keeping Cl₂ discharge with stipulated limits³⁴.

Targeted chlorination is employed when normally used Cl₂ is insufficient to destroy slime (bio-film) growing on heat exchangers. Pulse chlorination is a relatively new concept for the control of mussel fouling and based on the principal that mussels have a recovery period after exposure to chlorine, before they open their shells and restart feeding. This takes advantage of this recovery time by employing precisely timed short pulses of chlorine with intervening periods without chlorine. Using PC, utilities can reduce their Cl₂ dosage (and thereby discharge) by half and yet achieve significantly improved bio-fouling control. This procedure has been accepted as best available technology under the European Community (EU) guidelines²¹. Recently other biocides like chlorine dioxide and O₃ are gaining acceptance and in coming years one may visualize more utilities switching over³⁵.

Non oxidizing biocide:

A large variety of no oxidizing biocides are available to control microbial fouling in industrial water. Selection of them depends upon type of cooling water system, water characteristics, plants past history, nature of treatment employed to control scale and corrosion and environmental restrictions³⁶.

Dispersants:

Use of bio-penetrant and dispersant is gaining big deal of attention and become a standard treatment protocol for bio-film and microbial deposit control purposes. Bio-dispersants function by penetration and displacement of the microbial deposit/bio-film from system surface resulting in their sloughing off. Additionally adhesion mechanism of bacteria may be affected by the integration of surfactants with attachment structure of the bacteria and making them more hydrophilic. The de-adhesion of organisms allows oxidants and microcides/biocides to more readily

interact with the organisms remaining at the surface as well as those released in the bulk water³⁷. Bio-dispersants improve both planktonic and sessile efficacy when employed in combination with non-oxidizing and oxidizing microbiocides. Chemically bi-dispersants are composed of amines and long chain fatty acid amides. They are used in conjunction with microcides to remove faunal, algal and bacterial deposit and associated debris from cooling water, air washer and air scrubber system³⁸.

Ideally bio-dispersants should be added prior to the feed of microcides which allow dispersants to achieve maximum exposure of organism to the effect of microcides. However, frequency of bio-dispersant addition varies depending upon the potential for bio-film/microbial deposit related problem and effectiveness of bio-dispersant used. It is recommended to use combination of oxidizing and non-oxidizing microbiocides together. Oxidizing biocide viz. Br₂ as hypobromous acid (HOBr) is of choice in system operating above pH 8. Non-oxidizing biocide formulations having penetration power along with bio-dispersants provide longer lasting residual protection. In oil transmission pipelines pigging is the most effective and economical strategy available to control CIM. Pigging disrupts bio-film communities, remove water, deactivate nascent pitting sites, and remove corrosive deposits. Pigging with biocides is particularly effective in controlling bio-corrosion in pipelines³⁹.

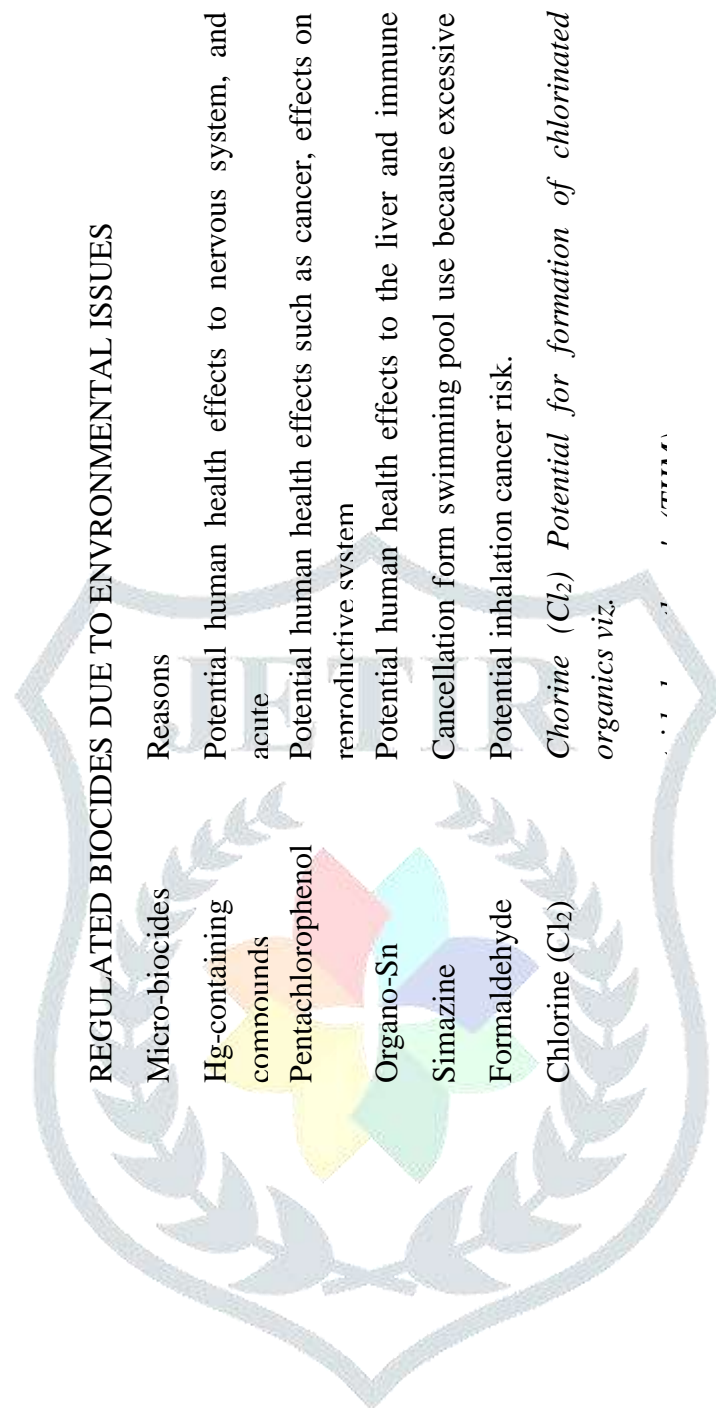
ENVIRONMENTAL CONCERNS

Until now, the country's most significant requirement for a biocide was that it should be effective against a broad spectrum of microorganisms, be cost effective, and be compatible with the product application environment (including no interference with the scale/corrosion inhibitors). However, with stringent environmental legislation and conscientious approach of industry to shoulder environmental responsibility as responsible corporate citizen, microcides are also required to meet following demands³⁹.

- ★ Broad spectrum of activity consistent with the application
- ★ Very low toxicity
- ★ Environmental acceptability
- ★ Cost-effectiveness
- ★ Safety, ease of use in handling and storage

With new environmental legislation initiative, it's being realized that efficacy of an active substance is only one aspect in future assessment of the acceptability of biocides. Comparison is driven by risk management of toxicology and eco-toxicity of each substance in question. The new microbe control approach focuses on environment friendly chemical treatment program that does not function merely by killing the microorganisms, but also keeping the microbes from attaching to the surfaces, or by dispersing them from the surface if they are already attached.

The dispersed microbes can then be easily killed with oxidizing biocides. Another approach receiving considerable attention is the use of enzymes to control microbial deposits/bio-films by catalyzing the hydrolysis of extracellular polysaccharides produced by microbes after they attach to the surface. Enzymes also disrupt the microorganisms' attachment to surfaces thus preventing of microbial deposits. Active research is being pursued in this field and promising new directions and strategies are indicated for control of bio-films and corrosion in water handling system. Following table lists a number of micro-biocides that have become limited or regulated due to environmental toxicity in several countries.



Nanoparticle-based corrosion inhibitors and self-assembled monolayers

Marine microbiological corrosion is responsible for considerable damage to all devices and vessels immersed in seawater, and this poses serious economic problems to maritime activities.¹⁴⁻¹⁶ Employing effective antifouling marine paints containing booster biocides at non-toxic levels is one approach to solving the issue of fouling.¹⁷⁻¹⁹ Copper and its oxides are common biocides in a large number of commercial antifouling marine paints. Commercially available antifouling coatings have cuprous oxide (Cu₂O) as the primary biocide, which typically varies from 20% to 76% copper content;²⁰ however, recent reports have shown that 26% of sampling locations/year in the UK exceeded the concentration of current Environmental Quality Standard (5 µg/l)²¹ for copper, and marine microalgae were able to take up copper very quickly in natural coastal seawater. Besides Cu, other metals such as Zn and Ag exhibit antifungal and antibacterial properties and have been widely utilized in advanced coating

technologies. Furthermore, silver has a remarkably low toxicity compared with other heavy metal ions, which makes it possible to manufacture more environmentally friendly antimicrobial paint additives than copper. Recent studies proved that the biocidal activity of the common biocides increased significantly with the decrease in particle size. Nanosilver particles have low toxicity, which makes them an environmentally friendly antimicrobial paint additive. Similarly to the inhibitors, biocides also can be released on demand using nanostructured carriers. The leaching rate of biocides should not be too fast, which would result in rapid and premature depletion of the antifouling activity of marine coatings and an unnecessarily high concentration in the sea. However, the release rate should not be too slow, since this would undoubtedly result in fouling.³⁶ In order to deal with both issues, the application of core-shell nano/microstructured materials was investigated, since the shells offer protection to the cores and introduce new properties to the hybrid structures. Up to the present time there have only been a few reports exploring marine corrosion protection based on core-shell structures employing biocides and corrosion inhibitors; however, there are still challenges, such as the stability of core-shell particles, uniform dispersity in a matrix and control of the release rate. Ke *et al.* have successfully prepared monodispersed Ag/SiO₂ core-shell nanoparticles with a facile pathway. Ag/SiO₂ core-shell nanoparticles within the size of 60 nm were applied to marine antimicrobial corrosion coatings. TEM (Transmission electron microscopy) and XRD (X-ray diffraction) results indicate that the Ag gets completely covered by SiO₂, and that its crystal form was not affected after being coated by SiO₂. The effects of Ag/SiO₂ nanoparticles in the microbial corrosion of acrylic-coated steel studied by ENA (electrochemical noise analysis) results 1 wt% Ag/SiO₂ nanoparticles exhibit better antimicrobial corrosion activity than conventional 40 wt% Cu₂O biocides. ICPOES (Inductively coupled POES (plasma optical emission spectrometry) showed very low numbers of Ag⁺ ions leaching from the matrix resin, whereas there was a much higher volume of Cu⁺⁺ ions leaching from the resin in the same period. It was concluded that Ag/SiO₂ core-shell nanoparticles could enhance long-term corrosion protection in comparison with the Cu -biocides. This composite has a great potential use in EFAMCs (environmentally friendly antimicrobial coatings).

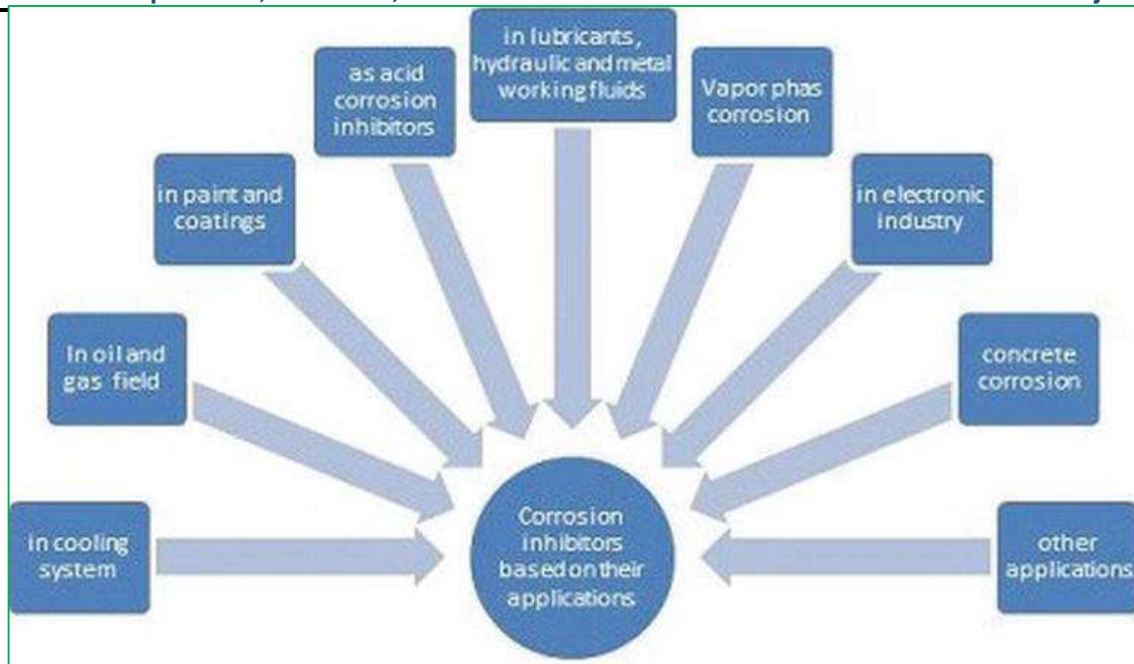


Metals are the pre-eminent important materials used in structural and decorative applications. The corrosion, deterioration or destruction of metals is an unavoidable but controllable process. The corrosion of metals has a significant impact on the development of a country, which can be compared to any natural disasters like earthquake, flood, etc. For example; the direct metallic corrosion cost in the US was estimated approximately \$276 billion on an annual basis, which is several times greater than the normalized loss incurred due to the natural disasters (\$17 billion per annum). It was also suggested that about 25-30% of the annual corrosion costs could be saved by means of optimum corrosion management practices. Several different methods can be employed to slow or prevent corrosion of metallic structures. The most commonly used methods are protective coatings on metals using organic molecules, plastics, polymers; and cathodic and/or anodic protection using organic or inorganic inhibitors. The initial report of corrosion inhibition by organic inhibitors is attributed to Speller, who examined the corrosion inhibition of scaled water pipes in HCl. Since then, many organic and inorganic compounds that are added to the corrosive fluids have been investigated for this purpose. There are growing concerns about certain compounds like chromates as inhibitors for corrosion processes, mainly due to the issue of toxicity. Green inhibitors like natural products from plant extracts and substances from other renewable sources are of the interest of the researchers who are interested in “green chemistry” or “eco-friendly” technologies. The literature contains a number of references on green corrosion inhibitors.

An inhibitor is a substance (or a combination of substances) added in a very low concentration to treat the surface of a metal that is exposed to a corrosive environment that terminates or diminishes the corrosion of a metal. These are also known as site blocking elements, blocking species or adsorption site blockers, due to their adsorptive properties. The term “green inhibitor” or “eco-friendly inhibitor” refers to the substances that have biocompatibility in nature. The inhibitors like plant extracts presumably possess biocompatibility due to their biological origin. Similar to the general classification of “inhibitors”, “green inhibitors” can also be grouped into two categories, namely organic green inhibitors and inorganic green inhibitors.

Redox Reactions involved in corrosion mechanism	
$2H^+ + 2e^- \rightarrow H_2$	E1
$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$	E2
$2H^+ + 2e^- \rightarrow H_{ads} \rightarrow 2H_2$	E3
$Inhibitor + nH_{ads} \rightarrow Inhibitor_{ads} + \frac{n}{2}H_2$	E4
$M^+ + nM^+ \rightarrow M^+ + nM^+$	E5
$M + X^- \leftrightarrow [(M)X]_{ads} \leftrightarrow [(M)X]_{ads}$	E6
$[(M)X]_{ads} + LsC^+ \leftrightarrow (M)X_{ads} + LsC^+$	E7
$M + \frac{1}{2}O_2 + e^- \leftrightarrow M_{ads} + \frac{1}{2}O$	E8
$M_{ads} + \frac{1}{2}O_2 + e^- \leftrightarrow M_{ads} + \frac{1}{2}O$	E9
$M_{ads} + M_{ads} \rightarrow H_2 + 2M$	E10
$M + LsC^+ + e^- \leftrightarrow M(LsC)_{ads}$	E11

The organic green inhibitors are the flavonoids, alkaloids and other natural products obtained from plants. It also includes synthetic compounds with negligible toxicity. Green corrosion inhibitors are of interest because there has been an increase in environmental awareness and a change in regulations that restrict regular corrosion inhibitors due to their toxicity. Natural products are a good source of green corrosion inhibitors, where most of their extracts containing the necessary elements such as O, C, N, and S, which are active in organic compounds, assist in adsorption of these compounds on metals or alloys to form a film that protects the surface and hinders corrosion. Numerous natural products and their application in different processes, especially in steel reinforcement embedded in concrete, are discussed. Development of green chemistry and green chemical technologies offers novel synthetic methods for ionic liquids, which are considered as new corrosion green inhibitors, and their mechanism of adsorption, how these green inhibitors act in different media, and their protective role for different metals and alloys are discussed. Finally, industrial applications of vapor-phase inhibitors and their mechanisms are presented.



IGIs (Inorganic green inhibitors)

Inorganic elements or metals have a crucial role in living organisms, when they are at trace amounts. The higher concentrations of many metals cause toxicity to all forms of lives. It is also applicable for the derivatives of metals. For example, chromium compounds, mainly chromates were widely used as potential corrosion inhibitors in aqueous systems due to their high efficiency. Besides the high inhibition efficiency, chromates exhibit high toxicity and consequently prohibited to use for industrial applications. In search of alternatives for chromate inhibitors, lanthanide salts are found to show excellent inhibition properties. Lanthanide salts like lanthanide chlorides were reported to possess toxicity that is comparable with sodium chloride. Hence lanthanide salts can also be considered as green inhibitor or eco-friendly inhibitor (Table 2).

IGIs	Metal	Medium	Reference
CeCl ₃	AA5083 Galvanized steel	NaCl	a
CeCl ₃ .7H ₂ O	Tinned iron	NaCl	b
La(NO ₃) ₃ ; Sm(NO ₃) ₃ ; LaCl ₃ ; SmCl ₃	AISI 434 SS	NaCl	c

Table 2. Inorganic green inhibitors

A few research studies were reported on the corrosion inhibition properties of lanthanides during the last decade. For example, Arenas et al reported the application of CeCl₃ as an inhibitor for an aluminium alloy (AA5083) and galvanized steel in aerated NaCl solutions. The study has provided evidence for the formation of an inhibitor layer on the surface of alloy as well on galvanized steel. The presence of Ce⁴⁺ was observed which was due to the oxidation of Ce³⁺. The phenomenon of “over precipitation” of cerium particles was observed on some areas of galvanized steel surface. This was attributed to the loss in the film coherence that occurs when it reaches critical thickness. The yellow coloration of the layer formed on the galvanized steel was not observed for the aluminium alloy, which may be due to the microscopic sizes of the precipitates. In another attempt by Arenas et al, CeCl₃.7H₂O was employed as corrosion inhibitor for tinned iron or tin plate in NaCl solutions. The coulometric studies revealed the cathodic nature of the inhibitor, which was similar to their previous report. Similarly, Bernal et al reported the inhibitive effects of lanthanum nitrate (La(NO₃)₃), samarium nitrate (Sm(NO₃)₃), lanthanum chloride (LaCl₃), and samarium chloride (SmCl₃) for corrosion of AISI 434 SS in sodium chloride solutions [49]. Even though the nitrate ion is considered as an anodic inhibitor, the studied rare earth nitrates (La(NO₃)₃, Sm(NO₃)₃) were demonstrated as mixed-type inhibitors, which was attributed to the presence of lanthanide ions in the solutions. Interestingly, for rare earth chlorides decrease in inhibition efficiency was observed on increasing the inhibitor concentration. This negative effect was interpreted as due to the increase in the concentration of the chloride ions.

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Natural Polymers

Polymers are the materials that have excellent adhesive properties on metal surfaces. A wide range of polymers has been studied for their anti-corrosive properties in the form of both pre-coating on the metal as well as inhibitor in a variety of corrosive fluids (Table 3). The inhibitory mechanism of mimosa tannin against corrosion of low-carbon steel in acid solution was reported by Martinez et al [56]. The adsorption mechanism of the mimosa tannin was studied at pH 1–3. It is interesting to note that at pH 1–2 the inhibitor adopts chemisorption mechanism, whereas the mechanism of inhibition switched to physisorption at pH 3. Table 3 List of natural polymers and derivatives studied as corrosion inhibitor.

Guar gum, a naturally-occurring polysaccharide was examined for corrosion inhibition of carbon steel in sulfuric acid solutions. An adsorption mechanism was proposed for the inhibitive nature of Guar gum. The increase in the concentration of the inhibitor had increased the resistance to pitting corrosion, which was supported by the shifts in the pitting potentials. The interaction between the oxygen atoms present on the side chains, and ferrous ions were probably impossible. Therefore, the possible mode of coordination type bonding was assumed to occur between the ferrous ions and the oxygen atoms present in the backbone of the polymer. In an attempt to compare the inhibition efficiencies of a natural polymers and synthetic

polymers, Umoren et al [58] studied gum Arabic and polyethylene glycol for corrosion inhibition of mild steel in sulphuric acid solutions. The synergistic effects of halide derivatives were also studied. The authors have also reported the inhibitive properties of exudate gum for aluminium corrosion inhibition in acidic medium [59]. Though the time dependence of the inhibition efficiencies of exudates gum followed almost similar trend to gum Arabic, the effect of temperature was different. The inhibition efficiency was increasing on temperature scale for the former, where as it was decreasing for the later. Therefore, the exudate gums was proposed to have physically adsorbed on the surface of aluminium. Cellulose is a most abundant waterinsoluble natural polysaccharide. Carboxymethyl cellulose is a water-soluble (semi-) synthetic analog of cellulose. The anti-corrosion properties of carboxymethyl cellulose (CMC) were studied for mild teel in different acid solutions [60-62]. Bayol et al have studied the adsorptive behavior of CMC on mild steel in HCl solutions [60]. Umoren et al reported the inhibition potential of CMC for sulphuric acid corrosion of mild steel and also the effects of synergism and antagonism of halide ions with CMC on corrosion inhibition. Another natural polymer, starch was investigated by Mobin et al [63], for inhibition of mild steel corrosion in sulphuric acid.

Inhibitor	Metal	Medium	Reference
Mimisa tanin	Low carbon steel	H ₂ SO ₄	e,f,
Guar gum	Carbon steel	H ₂ SO ₄	g,h,i.
Gum arabic	Mild steel	H ₂ SO ₄	I,k,
Exudate gum	Aluminium	HCl	L,m
Carboxymethyl cellulose	Mild steel	HCl	o
Carboxymethyl cellulose	Mild steel	H ₂ SO ₄	p

Table 3 List of natural polymers and derivatives studied as corrosion inhibitor

The synergistic effects of surfactants such as sodium dodecyl sulfate and cetyl trimethyl ammonium bromide on the corrosion inhibition behavior of starch was also studied. Similar to the previous reports on the anti-corrosion properties of natural polymers as described above, the inhibition mechanism of starch was proposed as physical adsorption. The synergistic effects of halide derivatives were also studied. The authors have also reported the inhibitive properties of exudate gum for aluminium corrosion inhibition in acidic medium. Though the time dependence of the inhibition efficiencies of exudates gum followed almost similar trend to gum Arabic, the effect of temperature was different. The inhibition efficiency was increasing on temperature scale for the former, where as it was decreasing for the later. Therefore, the exudate gums was proposed to have physically adsorbed on the surface of aluminium. Cellulose is a most abundant waterinsoluble natural polysaccharide. Carboxymethyl cellulose is a water-soluble (semi-) synthetic analog of cellulose. The anti-corrosion properties of carboxymethyl cellulose (CMC) were studied for mild teel in different acid solutions. Bayol et al have studied the adsorptive behavior of CMC on mild steel in HCl solutions. Umoren et al reported the inhibition potential of CMC for sulphuric acid corrosion of mild steel and also the effects of synergism and antagonism of halide ions with CMC on corrosion inhibition. Another natural polymer, starch was investigated by Mobin et al, for inhibition of mild steel corrosion in sulphuric acid.

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Bio-mimicking of Green Inhibitors

It is well known that green inhibitors like plant extracts contain numerous organic compounds. It is rather difficult to understand the mechanism of inhibition for a cluster of different compounds present in a plant extract. Investigation of the synthetic analogs of naturally occurring flavones, amino acids are very much dexterous to figure out the mechanisms involved in the inhibition process. For example, 3-hydroxy flavone, 2,3-dihydroxy flavanone were investigated by the authors for acid corrosion of mild steel (Table 4). The flavone derivatives were found to adsorb on the mild steel surface via both physical and chemical adsorptions. Similarly, amino acids alanine, cysteine, glutamic acid, glycine, leucine, serine, threonine, tryptophan were studied mainly for corrosion inhibition of steel and also for copper corrosion. Oguzie et al investigated the inhibition mechanisms of methionine for acid corrosion of mild steel along with synergistic effect of iodide ion. The results showed that the synergistic effect of iodide ion increased on increasing the population of specific adsorbed I⁻ ions for ion-pair formation with methionine cations. The adsorption of L-tryptophan on low-carbon steel was evaluated by Fu et al

Inhibitor	Metal	Medium	Reference
3-Hydroxyflavone	Mild steel	HCl	q
2,3-Dihydroxy flavanone	Mild steel	HCl	r
Methionine	Mild steel	H ₂ SO ₄	s
Tryptophan	Low-carbon steel	HCl	t
Cysteine, glycine, leucine, & alanine	Mild steel	HCl	u
Cysteine Copper	Copper	HCl	v

Serine, threonine, & glutamic acid	Copper	HCl	w
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Table 4 Model green inhibitors

The quantum chemical calculations determined the possible adsorption centers of L-tryptophan and also its flat orientation with respect to the Fe surface. Similarly, quantitative structural activity relationship for four amino acids namely, cysteine, glycine, leucine and alanine were studied. And cysteine was found to possess higher inhibition efficiency than the other studied amino acids. Khaled et al has examined cysteine for corrosion inhibition of copper. The synergistic effect of Cu^{2+} ions was investigated. At higher concentrations of Cu^{2+} ions, decrease in inhibition efficiency was reported in this study. And at very low concentrations (0.01 mM) of Cu^{2+} ions, the inhibition efficiency did not change, which may be due to the adsorbed layer formation by amino acid itself. Similarly, Zhang et al [68] examined the corrosion inhibition property of Serine, threonine and glutamic acid against copper corrosion. Glutamic acid showed higher inhibition potential due to the presence of carboxylate ions.

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CONCLUSION

Despite the long history of investigating MIC, we are still a long way from really understanding its fundamental mechanisms, especially in relation to non-sulphate reducing anaerobes. As presented here from an electrochemist's view, both the CDP theory and direct electron transfer from the metal into the cell are incorrect. Electrically conducting pili also do not appear to play a role in direct electron transfer, although these could still play a role in aiding the mass transport of redox mediators. However, it is not clear if the microorganisms are just altering the local chemistry or if they are participating directly in the electrochemical corrosion process, albeit via the generation of redox mediators. It is feasible that both are true, with the dominant mechanism depending on the actual microorganisms involved and the local environment. Going forward there is still much work to be done if we are to develop our understanding to the level where we can predict the degree of threat and model the likely corrosion rates. In particular, detailed investigations into how microorganisms impact the mineralogy of surface films are required. This will not be easy as many in situ techniques either cannot penetrate the biofilm or involve the use of lasers that will disrupt the very biological behaviour that needs to be studied. Likewise, for ex situ techniques, strict anaerobic environments need to be maintained during both sample preparation and characterization stages. Identification of the corrosion redox mediators that certain microorganisms are thought to generate when under stressful conditions, if they do indeed exist, would be another useful step as their detection could provide an early

warning of the onset of a MIC problem. The chapter demonstrates that biofilms can influence the corrosion of metals (1) by consuming oxygen, the cathodic reactant; (2) by increasing the mass transport of the corrosion reactants and products, therefore changing the kinetics of the corrosion process; (3) by generating corrosive substances; and (4) by generating substances that serve as auxiliary cathodic reactants. These interactions do not exhaust the possible mechanisms by which biofilm microorganisms may affect the corrosion of metals; rather, they represent those few instances in which we understand the microbial reactions and their effect on the electrochemical reactions characteristic of corrosion. In addition, we can use electrochemical and chemical measurements to detect one or more products of these reactions. An important aspect of quantifying mechanisms of microbially influenced corrosion is to demonstrate how the microbial reactions interfere with the corrosion processes and, based on this, identify products of these reactions on the surfaces of corroding metals using appropriate analytical techniques. The existence of these products, associated with the increasing corrosion rate, is used as evidence that the specific mechanism of microbially influenced corrosion is active. There is no universal mechanism of MIC. Instead, many mechanisms exist and some of them have been described and quantified better than others. Therefore, it does not seem reasonable to search for universal mechanisms, but it does seem reasonable to search for evidence of specific, well-defined microbial involvement in corrosion of metals. Generally green inhibitors are excellent inhibitors under a variety of corrosive environments for most of the metals. To explore natural compounds as effective green corrosion inhibitors because of their biodegradability, easy availability, and nontoxic nature has been mentioned. The literature revealed that natural plant extracts are effective green corrosion inhibitors against various metals and alloys. In addition, in this review, it has been revealed that why the efficiency of green and sustainable inhibitors of ionic liquids for the corrosion of metals and alloys is preferred compared to traditional corrosion inhibitors because of their advantageous physiochemical properties.

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