J Indian Inst. Sci , Nov –Dec 1999, **79**, 485–495.

Recent research in microbial fouling and corrosion

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Abstract

Characterization of biofilms that develop as a result of microbial fouling in varied operational and environmental conditions has been the subject of extensive research in recent years Biofilms increase fluid frictional resistance, impair heat-transfer efficiency, influence larval settlement and more importantly accelerate corrosion of materials.

The primary consideration of microbially influenced corrosion is the determination of the ability of microorganisms to actively attack the materials. Development of various surface analytical and electrochemical techniques has made it possible to quantify the influence of microbes on electrochemical phenomenon, to elucidate corrosion mechanisms and to monitor metal loss. This has helped in developing measures to ensure satisfactory performance of the material and its protection, under various operational and service conditions, particularly in tropical environment.

The paper gives an account of several simple and reliable monitoring techniques that are presently in use to detect, enumerate and monitor the influence of microbes on material performance and the designing approaches to cope with material biodeterioration.

Keywords: Microfouling, biofilm, microbiologically influenced corrosion

1. Introduction

Several reports on the involvement of microorganisms in fouling and corrosion of metal surfaces have appeared over the last few years. The way in which microbes influence material performance and behaviour is increasingly being recognised. It is now widely accepted that microbial adhesion processes lead to modification of metal–solution interface accounting for serious failure and loss of energy due to biofilm accumulation and biocorrosion in different types of industrial systems.[1]

Microbial deterioration of metallic surfaces mainly depends on the type of metal and alloy, operational and environmental conditions and the microorganisms involved. It is now well established that knowledge of these principal factors[2] and mechanisms of attack is important to identify appropriate material for a given application and to predict its performance to minimize the risk of material failure. Rates of microbial fouling and corrosion have generally been found higher in tropical waters. In many instances, it has been noted, severe operational problems can be overcome by accurate assessment of the conditions of service, appropriate selection and treatment of materials and/or suitable treatment of working fluids.

In recent years, service failures have been reported in practically all common engineering metals and alloys including carbon steel, nickel, alloys and aluminium due to biofilm development and microbially influenced corrosion.[3–7] In studies to date, only titanium has proven to be immune to microbially influenced corrosion. The global impact of the failures due to microbial growth runs to billions of US dollars each year.[8]

2. Microbial fouling (Biofilm formation)

Biofilms are known to mediate interactions between metal surface and the environment. Depending upon environmental conditions and available nutrients, the microfouling film may comprise a wide range of aerobic, facultative and anaerobic microorganisms that together hydrolyze and ferment carbohydrate, proteins and many other primary nutrients.[9] Consumption of oxygen by the aerobes results in the formation of anaerobic pockets and the growth of sulphate-reducing bacteria (SRB) which accelerate localized corrosion of surfaces.

In the recent past, several cases of engineering failure due to biofilm accumulation have been reported.[10–12] There is an increasing recognition of the problems caused by microbial fouling. Some of the areas identified are industrial cooling systems, sea-water flood system, offshore oil platforms, oil and gas reservoirs, and ocean thermal energy conservation plants (OTEC) and reinforced concrete structures. The failures attributed to these biofilms are impairment of heat-transfer efficiency,[13] increased frictional resistance,[14] clogging of valves and filters[15] and accelerated localised corrosion.[16]

It has been observed that although the conventional antifouling paint prevents the settlement of macrofouling, it fails to offer protection against the biofilms comprising bacteria, diatoms and protozoans. Recent restrictions on the use of chromate-based inhibitors as well as the use of biocides have resulted in extensive growth of microbial films on the immersed surfaces.

A considerable body of data exists on the development of biofilms on various metallic materials under different environmental and working conditions. However, the study of biofilm formation is an emerging scientific activity in India. In the recent past, institutions like Naval Materials Research Laboratory, Mumbai,[16–20] National Institute of Oceanography, Goa,[21, 22] Indira Gandhi Centre for Atomic Research, Kalpakkam,[23] and Central Electrochemical Research Institute, Karaikudi[24, 25] have carried out studies on marine microbial fouling and corrosion. This has greatly contributed to our understanding of biodeterioration in the Indian coastal waters particularly with respect to structural and engineering materials.

3. Microbially influenced corrosion (MIC)

One of the most important implications of biofilm accumulation is the accelerated corrosion of metallic surfaces. Biofilm formation which involves microorganisms, their metabolic products, exopolymers, trapped detritus and the other organic matter changes the physical and chemical nature of the metal surface. Thus, microbial film affects significantly both the kinetics of corrosion and the type of corrosion the metal suffers.

In recent years, microbially influenced corrosion has received increased attention of corrosion scientists and engineers. A detailed survey indicated that MIC costs industries in USA between 16 and 18 billion dollars a year.[8] Chemical processing and oil and gas industries,[26] power generation industry[27] and US military[28] have acknowledged the prevalence of MIC in their operating systems. Case studies have demonstrated MIC in a wide variety of environmental conditions; in salt, brackish and freshwater, under stagnant and flowing regimes; in oil and gas facilities, pulp and paper plants, chemical process industries, water-treatment facilities and fossil and nuclear power plants.[29] The gravity of this situation is highlighted by marked increase in research funding by government and industry. Different types of bacteria colonizing a biofilm cause corrosion by various mechanisms, varying from formation of differential aeration cells to production of aggressive environments through chemical changes. Consumption of oxygen by the aerobes in biofilm results in oxygen-depleted conditions favoring the growth of SRB which substantially accelerates localized corrosion of surfaces causing serious maintenance problems.[30] Metals like aluminium and its alloys, stainless steels and copper alloys having a stable oxide film for their corrosion resistance are susceptible to this form of corrosion due to damage in oxide film or oxygen depletion on the metal surface by the biofilm. Corrosion can also be stimulated by the chemistry which develops within the biofilm and the exopolymers produced with metal-binding abilities.[31] Chelation of metal ions results in the formation of galvanic cells. Copper and its alloys are reported to be susceptible to this effect.[32] Corrosion by the release of aggressive microbial metabolites, such as inorganic or organic acids, is another potential hazard. Ferrous and some non-ferrous metals like aluminium integral fuel tanks in aircraft are susceptible to this form of attack. In some cases, particularly when iron-oxidizing bacteria are involved, corrosion tubercles are produced providing a suitable habitat for SRB which are probably most damaging to metal structures. Biogenic sulphide generated by these organisms is also a factor in corrosion fatigue of offshore structures and has been reported to stimulate the rate of crack growth.[33]

It is thus increasingly being recognised that interactions of resident bacteria in microbial fouling film results in accelerating corrosion ranging from general pitting, crevice and stress corrosion cracking to enhancement of corrosion fatigue, inter-granular stress and cracking. These represent a cross-section of the kinds of phenomena, which are being studied by microbiologists and corrosion scientists.[34]

4. Implications of recent research and future needs

Over the past two decades, enormous progress involving multi-disciplinary efforts has been made to assess, predict and monitor microbial fouling and corrosion-related problems of metals and alloys. This involved both laboratory and field investigations and development of methodologies comprising techniques, sophisticated instrumentation and test assemblies.

Test parameters have been evolved for physical and chemical characterisation of microbial fouling film in terms of biofilm mass, wet film thickness, total organic carbon and nitrogen contents, total carbohydrates and lipid phosphate. The two latter named parameters have been monitored with a view to using them as indicators of microbial participation in the films.[19] Microbiological techniques have been developed to estimate the cellular components, including characterisation of exopolymer produced by a fouling bacterium[35] as well as to measure microbial metabolism such as respiratory (ETS) activity.[36] Fatty-acid fingerprinting has been resorted to detect specific bacteria in the biofilm present on surfaces.[37] Immunological and radiotracer techniques have also been used to determine community structure and bacterial activity including metabolic pathways.

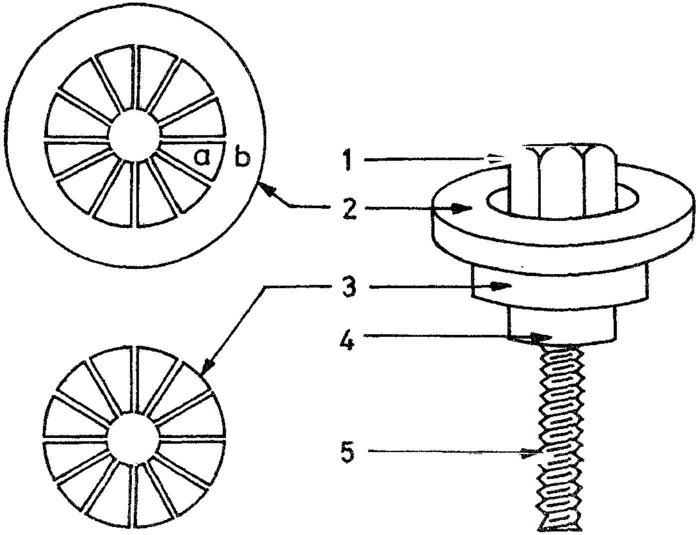

FIG. 1. Schematic drawing showing various elements of multiple crevice assembly for assessment of microbiologically influenced corrosion in stainless steel. 1 PVC bolt head, 2 304 stainless steel test coupons, 3 Teflon multigroove disc, 4: PVC nut, 5. PVC bolt. Here a grooved Teflon disc (3) is juxtaposed to 304 stainless-steel test coupon (2) creating a crevice effect over area marked as (a); area marked as (b) is free from crevice effect

Microbiologists have also introduced kits for onsite testing and monitoring of some of the important corrosion-causing bacteria from the biofilm. Culture media for specific detection of these bacteria are now available. Several new and sophisticated techniques such as ATP photometry, radiorespirometry, fluorescent antibody, epifluorescence and scanning electron microscopy as well as atomic microscopy, bioprobes and geneprobes have been developed. Some of the surface analytical methods such as energy-dispersive spectroscopy (EDAX), X-ray diffraction (XRD) and metallographic techniques are being used to identify the type of corrosion induced by the biofilm (pitting or crevice) and for the analysis of corrosion products present in the biofilm deposited on metallic surfaces.

Test systems have also been developed that enable the evaluation of bacterial biofilm formation and metabolic activity under conditions simulating those of the *in-situ* environment. The laminar flow adhesion cells designed for studies of biofilm formation and determination of antifouling coating efficacy have been used with online bioluminescence measurement systems.[38] With a view to creating crevice effects, a multiple crevice assembly (Fig. 1) is designed and used under laboratory conditions to study the accelerated crevice corrosion in presence of mixed bacterial cultures. For this, grooved Teflon discs were juxtaposed firmly to circular test stainless coupons by applying 3 KN force with the help of a torque wrench.

Tests using sophisticated electrochemical cells and corrosion-monitoring approaches such as monitoring of potential changes (indicating tendency of metal to corrode in the presence of biofilm), potentiodynamic polarisation, linear polarisation resistance, AC impedance (giving insight of corrosion processes occurring at metal/biofilm interface) and electrical noise have been used by various workers.[39] Impedance principle has been utilized for enumerating microbial populations.[40] Metabolic activity within biofilm such as organic acid production inducing corrosion can be studied by using zero-resistance ammetry.

Morton and Surman[41] give an account of biofilm contributing to corrosion as influenced by the availability of oxygen in the environment. Microelectrodes have been used to measure the redox potential within the biofilm matrix[42] with a view to determining the real oxidising or reducing characteristics of a biologically conditioned interface. Several studies have demonstrated the involvement of biofilm-containing SRB flourishing in low oxygen or oxygen-free environments[43] in accelerating corrosion of mild steel and copper.[44, 45] Innovative techniques such as environmental SEM ensuring structural reproducibility with hydrated specimens,[46] confocal laser microscopy and atomic force microscopy to study the fine details of individual cell surfaces[47] and differential interface contrast (DIC) for opaque and relatively flat surface[48] have been used. The development of redox-sensitive dyes has enabled the detection of respiring bacteria in aquatic environments.[49] The viability of the bacteria isolated from corrosion pits underneath barnacles in a biofilm settled on 304 stainless steel was determined using metabolic fluorochrome indicator INT.[20] INT and CTC dyes have proven extremely useful for the detection of bacteria possessing a functional electron transport system (ETS) in biofilms and have important implications for direct deterioration of surfaces beneath metabolically active bacteria.[36] More frequent use of these types of microelectrodes, fluorochromes and microscopic techniques should be encouraged in MIC studies.

A few studies have been conducted on microfouling and corrosion on surfaces immersed in polluted sea water.[50] It was observed that the biofilms generated on copper-base alloys unlike those on titanium are hard, tenacious, difficult to remove and also develop black coatings in polluted waters receiving untreated sewage.[19] Microbial fouling generated under once-through flow conditions on coupons and tubular metallic specimens have been estimated in a sea-water exposure assembly (Fig. 2) designed for exposing the coupons and tubes at desired flow rates of sea water. The assembly was employed on a pontoon in harbour waters to carry out field experiments. The biofilms formed were rich in bacteria and diatoms and the metal loss due to corrosion was 3–5 times higher in polluted water than in clean water (Table I). These studies have important implications for environment monitoring and safety of engineering facilities and should be pursued further for performance assessment of different metallic materials used as structural components or constructional materials under various environmental and operational conditions.

There are obvious difficulties in studying corrosion brought about by a consortium of two or more biofilm bacteria under laboratory conditions.[51, 52] The aerobic and anaerobic bacteria in combination have been demonstrated to be more aggressive than the individual species in

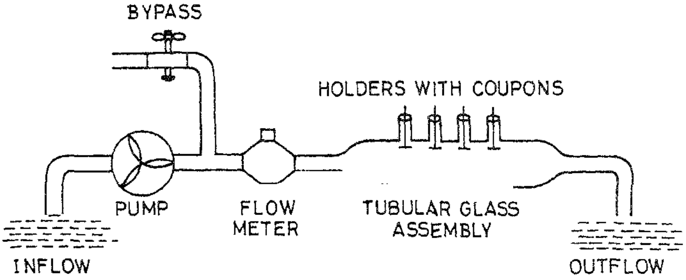

FIG. 2. Line diagram of 'once-through system' used for the exposure of test coupons for assessment of biofilm formation under field conditions.

inducing corrosion of 304 stainless steel.[16] Since the actual service conditions usually involve mixed systems, there is a need to develop new test methods with a view to establishing standard procedures. This approach would allow more appropriate evaluation of the performance of new materials.

The modification of the metal–solution interface structure through biofilm accumulation is now widely acknowledged in the literature. Different types of biofilm/inorganic passive-layer interactions have been reviewed with the help of three different corrosion behaviours as exemplified by a corrosion-resistant surface (stainless steel), an intermediate behaviour surface (90:10, copper–nickel alloy), and an easily corrodible surface (mild steel). However, the modification of the protective effect of inorganic passive films by microfouling processes is an important area in metal biodeterioration which deserves special consideration in future MIC research.

Table I
Metal loss and wet film thickness of biofilm generated on the metallic coupons and tubes exposed to quiescent and flowing waters

Test piece	Sea water state	Environment/Material					
		Film thickness (in μ) in clean water			Film thickness (in μ) in polluted water		
		Ti	Al–Brass	Cu–Ni 70.30	Ti	Al–Brass	Cu–Ni 70 30
Sheet coupon	Quiescent	160±18.88	120±13.31	100±20.67	240±14.81	145±21.0	165±12.43
	Flowing	27.55±4.41	50.22±2.82	39.06±2.56	41.29±1.09	101.52±6.68	68.11±1.41
Tubular	Quiescent	—	—	—	—	—	—
	Flowing	22.0±0.7 ND	42.2±1.7 [0.125±0.023]	32.2±2.4 [0.147±0.023]	35.5±2.7 ND	78.2±5.3 [0.656±0.154]	62.3±1.3 [0.396±0.134]

Abbreviations Ti = Titanium; Al–Brass = Aluminium brass, Cu–Ni 70 30 = Copper–Nickel 70 30, ND = Not detected.
Exposure period Quiescent = 15 days, Flowing = 130 h (velocity 5 ft/s).
Figures in parentheses denote metal loss due to corrosion expressed in mg/cm^2/day.

For prevention and control of MIC, upgrading and selection of improved alloys is the option, which is often considered, but in many cases it has been reported that the material might not have been evaluated with respect to its resistance to microbial corrosion. However, the impact of alloying elements of MIC has been reviewed for stainless steels, copper, nickel, aluminium and titanium alloys.[53] Cathodic protection is perhaps the most popular approach but the efficacy of this technique to control SRB-induced corrosion problems (due to demand for more negative potential to counteract the depolarisation effect) has been questioned.[54]

Considerable work has been done on the use of coatings and biocides[55] where biocides are applied; we have now become aware of the necessity to monitor and regulate the dosage and timing of biocide addition.[56] Although a large number of biocides are available with the ability to inhibit or kill planktonic bacteria, very few are able to penetrate the biofilm and kill sessile bacteria. Traditionally, the biocidal activity has been assessed in the free-floating (planktonic) state which tended to give results which were not relevant to bacteria embedded in biofilms on surfaces and pipe walls. Currently, the use of bioprobes, in which the bacteria are allowed to grow on metal studs in sessile mode, has become widespread.[57] This also has important implications with regard to the ability of the microbes to colonise replica test substrates reproducibly, which is a necessary component of microfouling research. For this, the use of Robbins device for laboratory and field applications has been described.[58] Annular-type reactors for the study of biofilm fluid-frictional resistance have also been developed.[59]

Recently the composition of microfouling film has been studied on stainless-steel weldments exposed to Mumbai harbour waters. Diatoms and bacterial settlement including SRB were found relatively high on the weld zones. *Amphora caffaeformis* which has been recorded consistently predominating among diatom species has been earlier reported as a very tolerant species to wide varieties of pollutants and toxicants.[60] Presently, a laboratory test device (biofilm generator) is under development at this laboratory, which will allow screening of biocidal agents against sessile causative microorganisms. This will aid in the search for cost-effective, safe, efficient and environmental-friendly options for preventing microbial fouling and corrosion. Improved field and laboratory-testing techniques and development of standard test methods for studying specific system and evaluating the performance of new alloys should help resolve many of the potential material protection problems which may arise in future.

5. Conclusion

Microbial fouling films or biofilms develop on all surfaces in contact with aqueous environments. MIC is caused by the presence of microorganisms within the biofilms. The modification of the metal solution interface structure through biofilm accumulation significantly affects both the kinetics and type of corrosion. Corrosion induced by sulphate-reducing bacteria residing under biofilm has particularly been recognised as a serious maintenance problem. The findings of a detailed survey have indicated that MIC costs industries in USA between $16 and 18 bn per annum.

Over the past two decades, significant advances have been made towards an understanding of the nature, mechanism and control of biofilm development and microbially influenced corrosion. Practical techniques for biofilm monitoring and assessment of microbiological activity in industrial systems have become sophisticated. Innovative electrochemical cells and advanced techniques such as AC impedance, electrical noise and many other improved surface analytical techniques are being used for field and laboratory studies. However, for prevention and control, a number of options have to be considered since no universal approach is available. In India, biofilm and MIC research is an emerging scientific activity. It is now established that the development of microbial film on immersed structures is very severe in tropical waters and more so in polluted waters. Many of the presently adapted microbial fouling and corrosion-preventive measures have been empirically derived and may not be compatible with materials and technologies of the future. Continued progress in understanding and preventing microbial fouling and corrosion problems aimed at increased material and system capabilities can be achieved by improved collaboration among microbiologists, chemists and practising engineers.

Acknowledgements

I am grateful to my colleagues who have contributed in studies mentioned in this review, particularly Dr S. N. Gaonkar, Shobhana Chongdar and Dr Susan Titus. I thank Dr A. A. Karande and Dr M. B. Deshmukh for valuable discussions and help in analysing the data. I thank Dr P. C. Deb for encouragement. Prof. G. N. Mathur provided ample support and has taken keen interest in the work. I thank him for his involvement and useful suggestions from time to time. Thanks are also due to Shri Anil Kumar for typing the manuscript and to Shri Nandlal for artwork.

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