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MIC ISSUES: COMMENTARY FROM THE CORROSION 2002 MIC PANEL DISCUSSION

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ABSTRACT

Invited panelists, prominent Microbiologically Influenced Corrosion (MIC) researchers from universities, government agencies, and industrial companies, were asked to select and to present issues they felt were vital to understanding MIC. The discussion took place during the MIC symposium at the NACE 2002 Conference in Denver. The notes presented in this paper are commentary from this discussion.

Keywords: microbiologically influenced corrosion, MIC, biocorrosion, biofouling, biodeterioration.

INTRODUCTION

As more and more researchers from various disciplines, and with diverse backgrounds, identify components of their professional pursuits as MIC research, a pressing need exists to establish a set of acceptable definitions that enhance the exchange of ideas among these researchers. Recognizing the importance of establishing a common ground for information exchange, the basic premises for the panel discussion were: (1) to clarify the existing definitions related to MIC, (2) to define the domain of the MIC research, and (3) to identify the directions of future research needed to advance the understanding of MIC. Toward a global perspective of MIC related research, the participants were invited from the continents of North America, South America, Europe, Asia, and Africa. To reflect coordinated international activities related to MIC, chair-persons of two international programs dedicated to MIC were invited: (1) European Cooperation in the Field of Scientific and Technical Research (COST) Action #511: Interactions of Microbial Systems with Industrial Materials, and COST Action# 520: Impact of Biofilm and Biofouling on Materials and Processes, and (2) International Water Association IWA, Specialist Group on Biofouling and Biocorrosion.

During the discussion, the participants presented the topics of their choice, within the framework determined by the basic premises for the discussion. The final document was generated from the notes taken during the discussion (special thanks are due to Dr. Cloete for taking the notes, and for preparing the first draft of this document). During the months following the discussion, the participants received the draft of the document, and they were asked for comments clarifying their positions, and amending the notes with additional statements they felt were relevant, but which due to time constraints they were unable to present during the discussion. The intended outcome of this effort is a document that clarifies the definitions, presents the basic concepts of MIC, and identifies vital areas of future MIC research.

WHAT IS MIC?

A comprehensive definition of corrosion needs to address the degradation of both metallic and non-metallic materials. For the purpose of the present discussion, however, we have limited our definition to the corrosion of metals and alloys, and to MIC of metals and alloys. Within these limits, we agreed that MIC is taking place whenever the reactants or products of the microbial metabolic reactions interact with the reactants or products of the electrochemical reactions occurring between the metal surface and the environment in such way that these interferences affect the thermodynamics and/or kinetics of anodic dissolution of the metal.

MIC vs. BIOCORROSION

The panelists acknowledged that the term biocorrosion is often used interchangeably with the term Microbiologically Influenced Corrosion (MIC), and that both terms bear similar meanings. However, an interesting argument was raised demonstrating that these terms are not synonyms. More specifically, the argument was referring to the metalworking processes, like milling, grinding, and tapping, which momentarily expose a nascent metal surface (usually iron) and make it amenable to corrosion attack. One of the functions of the water-based metalworking fluids used in metalworking processes is to provide corrosion protection. The three major groups of these fluids are 1) passive inhibitors (nitrites, borates, molybdates) 2) polar organic (amines, amides, fatty acids) and 3) barrier layer (essentially soluble oils i.e. o/w emulsions), and they all protect the new metal surface. However, all three are subject to biodegradation, which diminishes their protective qualities, and results in corrosion. Additionally, the 3rd group loses protective ability when the effects of microbial growth cause the splitting of the o/w emulsion with the loss of the protective barrier. These events are better described as MIC than as biocorrosion because the resulting corrosion attack is facilitated by microbial destruction of corrosion protection rather than by the microbially stimulated modifications of cathodic and anodic reactions.

The above example implicates that the term MIC should be preferred when biological agents indirectly affect corrosion processes, e.g. by biodegrading corrosion inhibitors, while the term biocorrosion should be preferred when biological agents directly affect the anodic and/or cathodic reactions, e.g. by depolarizing one of these reactions. However, such distinction between these two terms, although easy to understand and internally consistent, in practice may not be very useful because in most cases the exact mechanism by which microbes affect the corrosion processes remains unknown or hypothetical at best, and without knowing the exact mechanism a corrosion process could not be qualified as MIC or biocorrosion. Therefore, the possible distinction between MIC and biocorrosion is reported here as an item for further discussion, and it does not affect the terminology used throughout this report, which uses the term MIC when referring to corrosion processes that are directly and/or indirectly affected by microbial processes.

MIC vs. BIODETERIORATION

Often in the literature of non-metallic materials, the term MIC is wrongly used as a synonym of biodeterioration. Biodeterioration can be defined as "loss of value, function or utility due to biological activity." Therefore, the meanings of these terms overlap partially; MIC is always a form of biodeterioration but biodeterioration does not have to be a form of biocorrosion. Although the term biodeterioration is rightfully used as a synonym of MIC when the damaged substratum is either a metal or alloy, the term biodeterioration applies to a wide range of natural materials such as wood, stone, refined and processed materials such as fuels, lubricants, and paints, and also structures such as buildings, transport systems and vehicles. In many of these cases the nature of the material decay is not electrochemical, even though the role of the microorganisms is equally relevant. Thus the term MIC would be preferentially used to denote the electrochemical process of metal dissolution initiated or accelerated by microorganisms.

MIC MECHANISMS

When a biofilm accumulates on a metal surface, the metabolically induced changes in near-surface water chemistry can interact with electrochemical processes occurring at the interface between the metal and its environment. All microbial process affecting the anodic or cathodic reactions are regarded as MIC. Structural and physiological heterogeneities of biofilms together with heterogeneity of metal surface chemistry cause the mechanisms, the extent, and rates of these metabolic and corrosion reactions to vary from one location in the biofilm to another.

Traditionally, the microorganisms involved in corrosion processes have been classified into four distinct groups: (1) sulfate-reducing bacteria (SRB), (2) "slime-forming" bacteria, (3) iron- and manganese-metabolizing bacteria (or metal-depositing bacteria), and (4) a miscellaneous group containing sulfur-oxidizing bacteria, acid producing bacteria, fungi and algae. However, recent research suggested that many more organisms are involved in MIC processes: e.g. metal-reducing bacteria, hydrogen-consuming bacteria such as methanogens and also hydrogen-producing bacteria. For example, one of the microorganisms receiving increased attention, is *Shewanella putrefaciens*, which is able to reduce solid Fe^{3+}-oxides to soluble Fe^{2+} ions; and which in addition to iron-reduction and hydrogenase activity, is able to reduce various sulfur compounds to produce sulfide. In practice, MIC is probably not the result of a single organism acting via a single mechanism, but rather is a result of a consortium of microorganisms acting by several mechanisms. It should be emphasized that the biofilm community is a primary reason why pure-culture laboratory tests often do not adequately reflect the real world situation, and why such tests often fail to accurately reproduce MIC.

Anaerobic corrosion of steel has been linked particularly to SRB, i.e. by cathodic depolarization via the hydrogenase enzyme or by sulfide production. Other anaerobic reactions that consume hydrogen may also depolarize the cathode of mild steel. These reactions include reduction of thiosulfate, sulfite, sulfur, fumarate and nitrate, as well as methanogenesis and acetogenesis. Numerous possible corrosion mechanisms have been described. SRB are also involved in the corrosion of stainless steels, although the number of reported cases is smaller than that for mild steel.

In the case of bacteria, such as the sulfate-reducing and iron and manganese-oxidizing microbes, MIC depends on the nature of the precipitated manganese oxides, iron oxides or iron sulfides at the metal surface. It was demonstrated by using several electrochemical techniques that biogenic surface deposits of manganese dioxide led to an increase of the stainless steel potential (E_{corr}). These precipitates, acting alone or in concert with physical effects such as differential aeration or biological factors such as the presence of SRB, can modify the electrochemical processes occurring at the steel-solution interface and increase the risk of localized corrosion of the stainless steel. Sulfide production at the stainless steel surface can indeed decrease the pitting (E_p) or repassivation (E_{rp}) potential of steel underneath the biofilm, which allows localized corrosion to proceed. The iron- and manganese-depositing bacteria constitute a special case because of their direct involvement in metal transformations and subsequent key role in the etiology of MIC. Activity of these metal-depositing bacteria provides a unique microhabitat for a corrosive consortium of bacteria (e.g. together with SRB). The deposition of iron and manganese oxides yields large localized masses of exopolymer-bound cells and minerals that limit diffusion of oxygen and nutrients in and out of the developing tubercle. Oxygen that does penetrate is consumed, either abiotically or biotically, by oxidation of ferrous ions. The electroactivity of iron, manganese, and sulfide rich deposits in conjunction with consequent oxygen concentration cells, probably represents one of the major mechanisms of biocorrosive action, however the effect on mild steel surfaces is frequently masked by the action of the anaerobic community within the tubercle.

Since microorganisms within biofilms are capable of maintaining unique environments that differ from that of the bulk liquid, MIC can produce compounds different from those expected by thermodynamic analysis of the bulkwater chemistry. Some of the bacterial products created in these microenvironments may function as corrosion inhibitors, e.g. by raising the pitting and repassivation potentials of the underlying metals. Ideally, analytical identification of the compounds created within the biofilm microenvironment would allow signatures of MIC to be established. In practice, the fact that different mechanisms can occur simultaneously and/or successively, resulting in a mixture of reactions and end products makes it difficult to elucidate which mechanism is causing and/or influencing corrosion. The physical presence of microbial cells on the surface, in addition to their metabolic activities, modifies electrochemical processes. Chemical methods, however, often fail to detect properly the mechanisms of corrosion, because some compounds may be subject to a metabolic turnover (organic acids, nitrogen compounds, etc.). The following key questions require answers in any attempt to describe mechanisms underlying microbial corrosion:

- Are microorganisms involved in the creation of an electrochemical cell, or in its continued functioning over a prolonged period?
- Do they affect principally the anodic or cathodic reaction?
- Is the mechanism direct or indirect?
- What is the identity of the cathodic electron acceptor, particularly under anoxic conditions?
- Is the influence of biofilm growth primarily metabolic through the combined action of organisms present as a consortium, or physical through the development of diffusion gradients and microenvironments?
- Can pitting corrosion be the consequence of colonial growth or development of a patchy biofilm?
- Do the corrosion products themselves have an influence on the nature and extent of any further corrosion?

SURFACE CHARACTERISTICS AND MICROBIAL COLONIZATION

There are a number of factors that promote the adhesion of microorganisms to surfaces. Surface roughness and composition play a major role in the early stages of biofilm formation and may influence the rate of cell accumulation and cell distribution. Another key factor in microbial adhesion is hydrodynamic shear stress. The following observations indicate the processes related to microbial colonization of metal surfaces that may lead to MIC.

Bacterial adhesion at welds and heat-affected zones

The heat-affected zones (HAZ) of stainless steel weldments are most susceptible to MIC-associated pitting corrosion due to "sensitization" by chromium carbide formation in these regions. Materials in the HAZ may also be susceptible to MIC if the heat tint from welding is not removed by pickling or as a result of distortions in the size and shape of the metal grains caused by uneven postweld cooling process (this latter effect is usually minor).

There seems to be a correlation between MIC and the sensitization state of austenitic stainless steels, or more exactly with the chromium depleted zones and carbide precipitations at the grain boundaries or in the austenite-ferrite interfaces. In turn, the structural and physiological heterogeneities in the biofilm may locally increase corrosivity. It was acknowledged, however, that both the heat tint and sensitization effects are not unique to MIC. Those effects also make the alloy highly susceptible to localized attack in chemical (abiotic) environments.

Bacterial adhesion at inclusions and grain boundaries

Heterogeneous attachment, proliferation and/or aggregation of bacteria is determined by proximity to metallurgical features such as inclusions. Even the composition and morphology of these inclusions may influence MIC. It has been reported that biofilm-forming bacteria selectively colonize grain boundaries. Selective colonization at these boundaries may reflect high surface energy or electrochemical activity of the surface oxide films that promote attachment and colonization by some bacteria. This may lead to long-term patchiness in surface coverage by the surface-associated bacteria; offering ample opportunity for the initiation of localized corrosion that might evolve from such biological heterogeneity.

Bacterial adhesion at crevices

A final area of significant controversy relating to heterogeneous MIC is the involvement of microorganisms in crevice corrosion. Some results indicate that the presence of a biofilm on cathodic areas produces an increase of the corrosion rate by about two orders of magnitude by depolarization of oxygen reduction or by the introduction of new cathodic reactions. Efficient cathodic processes under biofilms near crevices may help initiate and support crevice corrosion by diminishing solution IR drops that otherwise limits attack.

INTERFACE BETWEEN BIOFILM AND METAL

It was recognized that intensive work has to be done in analyzing the interface between the adhered microorganisms and underlying materials (including the effects of EPS). In particular, the processes occurring within the space between the microbial cells and the underlying material, filled with EPS containing possibly oxidants like iron (III) ions and/or electroactive exoenzymes, deserves full attention in future research. Understanding these processes will give better insights into the nature of MIC and, hence, lead to optimized materials and countermeasures for MIC. This finding/conclusion also arose in the course of the final evaluation of the EU COST action 520: ..."Emphasis should be put on research at the interface between biofilm and material's surface".

Investigation of microbial parameters, such as the identity of the microorganisms and their spatial distribution, e.g. using fluorescently labelled 16S rRNA probes, is a promising approach to understanding microbial heterogeneity. Data on microbial activity and chemical conditions within the biofilm (investigated via micro-electrodes) also has vital relevance towards understanding heterogeneity. This information needs to be quantified and related to electrochemical phenomena occurring at the interface between the biofilm and metal to provide a comprehensive understanding of the relations between biofilm structure and MIC.

Recent findings demonstrate that some manganese oxidizing bacteria change morphology and chemistry of passive films on stainless steels, which may initiate pitting corrosion, indicating a possibility that some microorganisms are more directly involved in the corrosion processes than previously suspected. The nature of this involvement can only be determined by studying the chemistry of the interface between the adhered microorganisms and the underlying metals.

CORROSION INHIBITION BY MICROORGANISMS

There have been an increasing number of reports in recent years that microorganisms in aqueous environments, especially those forming biofilms, may decrease the corrosion rate of various metals, or even protect them from corrosion. While this is an exciting possibility that warrants further investigation, there also is a need to proceed with some caution. Most of the research to date demonstrating this microbial inhibitory action has been conducted in a laboratory setting, where more or less axenic biofilms and simulated media containing added nutrients were used. Certain nutritional supplements present in yeast extract or trypticase soy (amines and nitrates) and minerals, such as phosphates, commonly introduced into microbiological media are chemical corrosion inhibitors that can affect results. More recent experiments, in both laboratory and field studies, have begun to investigate corrosion inhibition under more realistic conditions, trying to determine whether a bacterial inoculation (a single strain or a bacterial consortium) can reduce corrosion rates in the presence of microorganisms living in environmental or industrial waters. The answer that is beginning to emerge is that they can, although optimization of the effect is still being studied. Bacteria can protect metals by several different processes: (1) passive sulfide film formation by SRB, (2) the presence of a uniform layer of living aerobic bacteria whose respiration decreases oxygen concentrations, (3) formation of a diffusion barrier, of corrosion products for example, as a result of exopolymers produced by attached bacteria, 4) production of antimicrobial compounds or corrosion inhibitors, and 5) by other not yet recognized mechanisms. Because the microbiological component of corrosion is very complex and therefore seldom identified as a single organism or a unique mechanism, future research needs to be conducted to elucidate the influence of natural consortia of bacteria on corrosion processes. However, in order to have a representative situation, natural waters with their naturally occurring consortia should be used for those experiments.

ANTIMICROBIAL METALS

The possible use of bactericide releasing materials, and more particularly bactericidal stainless steels was discussed. In fact, there are several possibilities of alloying elements with possible bactericidal effects: mercury, silver and copper are well-known examples. Also molybdenum is found to affect biofilm development, possibly due in part to its reported inhibitory action on the growth of SRB.

There are, however, several concerns regarding the efficacy of antibacterial alloy technology, including environmental safety. Firstly, bacteria may develop resistance to silver and other metals, which would limit the efficacy of these bactericide-releasing materials. Results also indicated that colonization could only be delayed, but ultimately not prevented. This may, nevertheless, be of some value in making intermittent biocide dosages more effective. A further limiting factor may be the cost of such biocide releasing materials, as well as the rate of leaching of the oligodynamic metals resulting in protection against MIC for only a limited period of time.

ENVIRONMANTALLY FRIENDLY MITIGATION STRATEGIES

Biocides used to treat industrial water are eventually released into the environment. Ideally, the biocide should affect only the target microorganisms against which its use was intended. Most microbicidal chemicals, however, exhibit some effect on non-target plant and animal life. It is generally assumed that dilution and natural degradation will inactivate any biocide, and laboratory investigations have confirmed that the commercially available biocides can be biodegraded. However, such findings do not necessarily imply that biodegradation will take place equally readily in all environments. If industry is to continue to use biocides for the control of biofouling, additional questions of '*in situ*' biocide effectiveness, resistance, biodegradability and environmental impact will have to be answered. These answers require co-operation between biocide manufacturers, operators, chemists, biochemists, microbiologists, aquatic biologists and legislative authorities. A number of new biocides with limited environmental impact may help in this regard. Included in this group are electrochemically activated water and stabilized bromine, in addition to the more known technologies like ozone and UV irradiation.

An alternative, environmentally benign method to control MIC entails disarming rather than destroying the microorganisms. This approach would include manipulating the biofilm ecology and/or microbial phenotype to inhibit MIC. Methods to control many of the dominant classes of MIC microorganisms using this approach can be envisioned. As an example, small molecule gene-repression of extracellular slime production could reduce the binding matrix that enables mineral deposits, oxygen concentration cells, and biological metabolites to accumulate and exert their corrosive effects. Adjustment of pH may be used to alter microbial ecology and promote the dominance of less aggressive microorganisms, eg by promoting fungal over bacterial colonization. Inhibitors that interfere with the polymer activities responsible for manganese biodeposition have been reported, and it may be possible to use such inhibitors to reduce or eliminate this cause of stainless steel corrosion. The use of nitrate and nitrite to control oil well souring is also widely acknowledged. The technology makes nitrate available as an alternate electron acceptor to inhibit SRB growth as well as to oxidize cathodic iron-sulfide deposits that have formed.

THE CONTRIBUTION OF MIC TO THE OVERALL CORROSION PROCESS

Despite significant efforts, no comprehensive theory of MIC has been established. Microorganisms are generally acknowledged not to mediate a new corrosion mechanism, but rather (directly or indirectly) to accelerate electrochemical processes that cause corrosion. Due to the complexity of the metal-biofilm system and lack of advanced MIC monitoring techniques, it is not possible at this time to determine the contribution of MIC to the overall process of corrosion with any certainty. In any specific instance of corrosion, the influence of microorganisms may range from none to 100%

MIC MONITORING

Many techniques that have proven useful for elucidating fundamental electrochemical properties of MIC under laboratory conditions have proven much less useful under field conditions. This apparent luck of success in monitoring MIC is, in part at least, due to the lack of comprehensive theory of MIC and the resulting difficulties in separating the MIC component from the overall corrosion processes. Detection of specific and/or generic groups of microorganisms and their unique metabolic products represent indirect evidence for MIC but their presence alone does not necessarily substantiate MIC. New devices conceived to quantify MIC and biofilm effects in real time are needed.

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