Microbiologically Influenced Corrosion Testing

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Foreword

The symposium on Microbiologically Influenced Corrosion Testing was presented at Miami, Florida on 16–17 Nov. 1992. ASTM Committee G-1 on Corrosion of Metals sponsored the symposium. Jeffery R. Kearns, Allegheny Ludlum Corporation, and Brenda J. Little, Naval Research Laboratory, served as co-chairs for the symposium and were co-editors of the resulting publication.

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Overview

ASTM Committee G-1 on Corrosion of Metals began the development of standards on Microbiologically Influenced Corrosion (MIC) Testing in 1991. There were several challenges. The first was to organize an interdisciplinary task group with expertise in the use of electrochemical, metallurgical, surface analytical, microbiological, and biotechnological techniques. This was a particularly difficult problem because of limited communication between the different disciplines. Microbiologists had the skills necessary to manipulate and characterize microbial behavior and, consequently, their contributions tended to dominate the field. In addition, many practicing corrosion engineers were skeptical of claims made about the unique characteristics of MIC, since most of the observed corrosion could be accounted for by traditional concepts of localized and underdeposit corrosion.

The second challenge in developing standardized MIC tests was that much of the information on the performance and testing of materials in microbiologically active environments consisted of anecdotal evidence and descriptive case histories. There was virtually no consensus on how to conduct corrosion tests in microbiologically active environments or how to interpret test results. Exaggerated claims about the possible corrosive effects of microbial activity alarmed many people, but the lack of reliable, quantitative test data prevented the inclusion of microbiological factors in engineering designs. Although significant progress was made in solving industrial problems related to MIC and in developing analytical tools for studying biofilms, important issues related to materials testing, such as reproducibility and bias, were all but ignored. Field test results were considered to be site specific and the population dynamics of microbial consortia in natural waters were considered to be too complex to reproduce in the laboratory. Few considered the essential question of "What factor actually accelerates corrosion in a microbiologically active system?"

Faced with this situation, people with important materials selection decisions to make devised testing strategies based on the assumption that the factors that caused MIC are essentially the same chemical and physical factors that are well known to cause severe pitting and crevice corrosion in tests that do not intentionally involve microbes (abiotic tests). The controversy over a representative test and how to conduct it has persisted for over a decade.

MIC demands attention primarily because of the growing number of rather spectacular failures associated with the presence and activity of microbes in environments that would otherwise have been considered to be rather benign. All over the world, process and natural waters are becoming more corrosive for several reasons. Traditional methods of mitigation through cleaning and water treatment are becoming less effective because of high maintenance costs and more restrictive legislation on the chemical contents of process water effluents. Industrial waters are recycled more often, which tends to concentrate corrosive elements. MIC has resulted in premature failures of system components, increased downtime of equipment for repairs and maintenance, and increased operating costs associated with mitigation measures. MIC has forced premature replacement of tanks, heat exchangers, and piping systems with a severe detrimental effect on plant production. Cases of MIC have been reported in nuclear and fossil-fueled power plants, oil production, chemical processing industries, pulp and paper, transportation, and water distribution networks. If materials change-out and up-grade options are to be used for new and existing plants and vessels, reliable accelerated test methods have to be developed. MIC testing should be regarded as an essential part of the mitigation and control of corrosion in natural waters.

As a first step toward developing consensus on technical issues and toward creating a multidisciplinary task group that would develop standards on MIC within the ASTM G-1 Committee, a symposium on MIC Testing was organized. The participants in the symposium were from Argentina, Canada, England, France, Germany, Italy, Japan, New Zealand, and the United States and represented the multiple disciplines and industries engaged in MIC testing.

This ASTM Special Technical Publication (STP) resulted from the First International Symposium on Microbiologically Influenced Corrosion (MIC) Testing held in Miami during November of 1992. The STP consists of a Keynote Address and twenty-one papers arranged in six topical sessions: Electrochemical Methods, On-Line Monitoring Methods, Surface Analysis Techniques, SRB Characterization, Non-Metallic Materials, and Service Water Systems. The reader is advised that several papers deserve to be under two or more of these headings. Two papers are reviews of the state-of-the-art on electrochemical and surface analytical techniques for the study of MIC, and a third review addresses the effects of marine biofilms on corrosion of stainless steels.

The Keynote Address describes the evolution of the study of MIC from phenomenological case histories toward a mature multidisciplinary science. The most advanced technologies for determining cellular constituents within biofilms and for identifying and measuring MIC are described. Emphasis is given to recent developments in image analysis systems, electron, atomic and laser microscopy that have made it possible to image biological materials in hydrated states. New insights into complex interactions between biofilms and metal surfaces have lead to important findings, such as the absence of a correlation between the numbers and types of microbial cells and the occurrence of localized corrosion.

Electrochemical Methods

The development of an accelerated test for assessing the susceptibility of materials to MIC is very difficult because the usual methods of accelerating corrosion, such as increasing the temperature and concentration of aggressive chemical species, can alter the microbiological activity in the system, and hence bias test results. New methods of acceleration and detection are proposed.

Three types of electrochemical techniques are recommended since they do not perturb the microbiologically active system during the measurement: electrochemical noise measurement (ENM), electrochemical impedance spectroscopy (EIS), and zero resistance ammetery (ZRA). Measurements made in the field were combined with laboratory studies. For example, ENM was used to detect and monitor the ingress of oxygen into a biofouled test vessel at an Ontario Hydro nuclear power plant. Laboratory studies were conducted when it was necessary to explore specific issues or when more control of key test variables, such as temperature and oxygen content, were required. Successes in producing MIC in the laboratory and in identifying the crucial factors that accelerate corrosion are described. Inorganic analogs for simulating these factors in laboratory tests are also proposed.

The advantage of field tests over laboratory tests in microbiologically active systems is that the data generated are more directly applicable to the system of interest. However, field testing has three main limitations: (1) corrosion can take a long time to occur since no critical factor is accelerated, (2) natural fluctuations in the environment can mask significant changes in localized corrosion behavior, and (3) individual parameters are difficult to discriminate. A combination of failure analyses, laboratory studies, and field simulations is recommended to determine the mechanism of corrosion.

A biofilm limits oxygen diffusion to the surface of a metal or alloy and affects the pH at the biofilm/alloy interface. In addition, the biofilm may also contain electrically conductive (or semiconductive) phases, such as pyrroles. Factors such as these can catalyze oxidation-reduction reactions and thereby accelerate localized corrosion. The pH at the biofilm/alloy interface was measured by two different techniques. In one case, a sophisticated micro-electrode apparatus was used to achieve outstanding spatial resolution, and in the other case various alloys in the form of wire mesh electrodes are monitored while cathodically polarized in natural and artificial seawater.

On-Line Monitoring Methods

Four different experiences with on-line monitoring methods for MIC and biofouling in industrial cooling water systems, service water systems, and secondary oil recovery water injection systems are documented in this section. Conventional monitoring methods tend to be too slow or are of insufficient sensitivity to permit reliable process control and water treatment in microbiologically active systems. This limitation means that mitigation activities are often costly, both environmentally and in terms of the direct costs of the anti-microbial chemicals. The papers in this section present proven alternatives to conventional methods of monitoring. The papers describe monitoring systems for heat exchangers and water distribution pipelines where the objective is to maintain heat transfer efficiency or flow. This is done by controlling the formation of biological deposits, while not compromising the effectiveness of corrosion inhibitors or promoting scale formation. The capabilities and test parameters for the on-line monitoring systems were developed in the laboratory and the effectiveness of the system was demonstrated at sites such as the Amoco Chemical Company Chocolate Bayou petrochemical plant and the Tennessee Valley Authority Browns Ferry nuclear plant. Electrochemical monitoring methods were the primary tool used in three of the four papers. However, as described in the second paper of this section, it was necessary to monitor water microbiology and chemistry at Husky Oil Operations Limited's Wainwright waterflood operation in order to improve the water treatment practice.

Surface Analysis Techniques

Surface analytical techniques provide powerful tools for understanding MIC. X-ray Photoelectron Spectroscopy (XPS) was shown to provide detailed information about the oxidation and reduction of metals as transformed by microbial metabolism. More specifically, XPS was used to determine quantitative chemical information on the interaction of *Desulfovibrio sp.* with the corrosion products from stainless steels (Fe, Cr, Ni and Mo ions) under anoxic conditions. Microbial sulfate reduction produced multiple reduced sulfur species (SO_3^{2-}, elemental S and S^{2-}), as well as reduced molybdate and ferric ions.

The utilization of conventional surface analytical techniques in failure analysis and laboratory studies is reviewed in the second paper of the section. Surface analysis techniques were utilized for elucidating the processes involved with MIC and for establishing causal relationships between microbial activity and corrosion.

SRB Characterization

The traditional microbiological methods as well as the latest genetic techniques for the characterization of SRB (Sulfate-Reducing Bacteria) are described in two of the three papers in this section. A thermodynamic analysis of SRB behavior is presented in the first paper. Efforts to characterize SRB contribute to the identification of "fingerprints" for the presence and activity of SRB that can be unequivocally linked to corrosion.

For many years all SRB were cultured on standard media using lactate as the electron donor and carbon source. Two modern alternatives are presented: Sulfur Isotope Fractionation is presented as a definitive tool for identifying MIC by SRB, and, the molecular biological technique of reverse sample genome probing (RSGP) is demonstrated to be of practical industrial value in solving a biofouling/MIC problem in the heavy oil operations of the Wainwright and Wildmere fields in Alberta, Canada.

Non-Metallic Materials

Although the majority of work on MIC is concerned with metals and alloys, in this section, three novel papers on the MIC of polymers, concrete, and natural sandstone are presented. A unique test system developed in Germany is to simulate the combined effects of atmospheric gaseous pollutants (SO_2 and NO_x) and nitrifying bacteria (biogenic nitric acid) on natural sandstone and calcium alginate mortars. This system revealed that gaseous pollutants (SO_2) remove microbiologically produced nitrite and nitrate which effectively reduces the rate of corrosion. It is rather ironic that the reduction of sulfur dioxide in the atmosphere increases the risk of damage to historical buildings by biogenic nitric acid corrosion.

From historical buildings to ships: a US Navy field test program evaluated the seawater corrosion resistance of several conductive caulks and sealants that are used to protect ship antenna arrays. Environmental scanning electron microscopy was used as a non-destructive means of observing the activity of biofilms on the caulks. A nickel-based conductive caulk with a corrosion inhibitor resisted degradation well in all of the field and accelerated laboratory tests over a period of 15 months. Consequently, this material was recommended for this application.

Results from chemical tests can be misleading when it comes to predicting the behavior of materials in natural environments because the influence of bacteria on the corrosion process is not well represented. For example, calcium aluminate cement has performed well in sewage systems for many years, although the results of conventional chemical tests indicate that it was inadequate for this application. To obtain more reliable test results, a simulation chamber for biogenic sulfuric acid corrosion was created at the University of Hamburg. By optimizing the growth conditions for microbes in the simulation chamber, the aggressive conditions in the Hamburg sewer system were created within a year. The city of Hamburg now requires this test to qualify new materials for the sewage system.

Service Water Systems

Nearly 60 years ago, Wolzogen and Van der Vlugt considered the influence of SRB on corrosion of cast iron pipe in soil. The second paper of this section reconsidered this topic with one of the newest electrochemical monitoring techniques—Electrochemical Impedance Spectroscopy (EIS). The strong correlation between EIS data and weight loss data recommend this method for accelerated testing and monitoring.

Effective measures for mitigating MIC often have to be developed, substantiated and introduced into practice to protect existing installations even though the mechanism for MIC is not known. Two examples of such cases are presented in regard to the potable water distribution systems in several European hospitals. First, the corrosion was confirmed to be MIC by the presence of solid corrosion products mixed with a gelatinous film consisting of polysaccharides, polysilicates, lactate and pyruvate. Then the factors related to operating conditions were discriminated from those related to piping system design. This was done by means of test rigs installed at various locations within a hospital. A combination of ultraviolet radiation and bicarbonate additions mitigated the corrosion of the copper piping in cold water supply, while maintaining the water above 55°C solved the corrosion problem in hot water supply. The likelihood of MIC increased drastically after an induction period. Consequently, accelerated, short term tests were devised to simulate the induction period. In order to further accelerate the processes that lead to corrosion and overcome seasonal changes in microbial activity, the test rigs were inoculated with bacteria from corroding sites.

Laboratory tests for service water systems are often criticized for not being representative of actual field situations because pure strains of bacteria are grown on enriched media then exposed to alloys under stagnant flow conditions. These limitations are addressed in an accelerated test system built at the Center for Environmental Biotechnology which simulates the ecological, physiological and nutritional requirements for the various species of bacteria found in the sediments, slime, tubercles, and corrosion products at an operating plant. Test solutions were prepared to simulate field conditions with nutritional supplements to stimulate the growth of microbes. Electrochemical techniques were used to monitor corrosion of mild steel without perturbing the biofilm. The system provided a means to simulate and accelerate MIC of mild steel.

Summary

The combined offerings of the contributors to this STP will provide the reader with a review of the state-of-the-art of MIC testing in the early 1990s. Many industrial needs in the area of MIC testing are identified in these papers along with latest laboratory and field testing techniques. Strategies to monitor and control corrosion and biofouling in water distribution systems, underground pipelines, buildings, and marine vessels are discussed. From this a consensus emerges on how to evaluate and reliably simulate microbiological factors in real systems and laboratory tests. It is hoped that some of the proposed test methods and guidelines presented in this STP will gain wider acceptance and eventually lead to the development of new ASTM standards.

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