MICROBES PLAY A CONSIDERABLE ROLE IN CORROSION

Reports from industrial, academic, and government laboratories provided an International Conference on Microbiologically Induced Corrosion with persuasive evidence that microorganisms are of considerable importance in establishing corrosion on a wide variety of structures in a number of industries. Held at NBS, the conference was co-sponsored by the Research Committee, National Association of Corrosion Engineers, and NBS under the chairmanship of Dr. Stephen C. Dexter of the University of Delaware at Lewes. It was the second of its kind to be held internationally, the first being held at the National Physical Laboratory, Teddington, England in March 1983.

Approximately 125 persons, representing 13 countries and 26 of the 50 states in the U.S., attended the three day conference. Thirty-nine papers on microbial corrosion were presented. They dealt with historical perspectives and current problems, case histories, mechanisms, experimental methods, and control procedures.

In his welcoming address, Raymond Kammer, of NBS, said a good portion of the cost of corrosion in the United States, estimated to be $167 billion in 1985, was biologically induced. He spoke of the long history of NBS involvement in underground corrosion, a significant portion of which is probably biologicaly induced.

HISTORICAL PERSPECTIVES AND CURRENT PROBLEMS

R. Starky, formerly of Rutgers University, New Brunswick, NJ, and for many years the foremost investigator in the U.S. on biological corrosion (primarily anearobic corrosion caused by sulfate-reducing bacteria (SRB)) examined the contributing corrosion factors, including sulfide and iron-sulfide. He stated the need for a critical reexamination of all of these factors which contribute to anaerobic corrosion.

The European research investigations directed toward an understanding of the mechanisms of microbial corrosion were summarized by K. Tiller of the National Corrosion Service, National Physical Laboratory, Teddington, England. Tiller, who for many years has headed the foremost biological corrosion research group outside the U.S., also discussed the advances made in assessing the corrosivity of a wide range of environments as well as some of the problems in the offshore oil and gas industry.

A recently published literature review on microbiologically influenced corrosion (MIC) was prepared for the Materials Technology Institute of the chemical process industries in cooperation with an interdisciplinary group of scientists at Rensselaer Polytechnic Institute. D. Pope summarized the conclusions of this review, which included current corrosion problems in the chemical process industries and recommendations made by the group regarding research priorities.

CASE HISTORIES

Reports of MIC in a number of processes and industries as well as of various ferrous and nonferrous alloys were presented. In many cases, SRB were associated with the corrosion process. An unusual case of welded mild steel and 304 stainless corrosion by blue-green and red algae, however, was described by C. R. Das, Ravenshaw College, Cuttack, India. C. R. Schmitt, Bechtel National Inc., Oak Ridge, TN reported on a case which he believed to be due to microbiological pitting of an aluminum heat exchanger exposed to potable water.

Cases of MIC found to be associated with SRB included those in oil production systems, reported by P. F. Sanders, University of Aberdeen, Scotland; cooling water systems in alcohol distillation plants, reported by J. O. Silva, Aquatec Commercial Ltda, Sao Paulo, Brazil; the power industry, reported by M. Bibb, ESCOM, Johannesburg, South Africa; and cathodically protected offshore structures, reported by G. Eidsa, Central Institute for Industrial Research, Oslo, Norway.

MIC of mechanically superior spun ductile iron pipe, used to replace spun grey iron pipe in the U.K. water industry in the 1960's as a result of SRB activity, was investigated by R. A. King and co-workers, University of Manchester Institute of Science and Technology, Manchester, England. King reported that the biological processes were similar on both materials; the corrosion performance of the new spun ductile iron pipes not being as good as was expected. R. Patenaude, of the Wisconsin Division of Highways, Madison, reported that field observations and tests indicated that nearly one-half of the corrosion of steel culvert pipe in Wisconsin was related to the activity of SRB. Perforation of underground brass pipes of low zinc content (91.6% Cu; 8.22% Zn) in less than two years of use was explained by N. De Cristofaro, Instituto Nacional de Technologia Industrial, San Martin, Argentina, as being due to the metabolic products of SRB.

MECHANISMS

MIC has been attributed to one or several of the following mechanisms: 1) removal of hydrogen (electrons) from the surface of a metal (cathodic depolarization) through the activities of the bacterial enzyme, hydrogenase; 2) creation of oxygen or chemical concentration cells; 3) formation of corrosive metabolic products; 4) destruction of passive or protective films; and 5) inactivation or destruction of microbiological or corrosion inhibitors.

The session on mechanisms was introduced by R. E. Ricker, University of Notre Dame, South Bend, IN, who described the possible and probable electrochemical mechanisms by which microorganisms initiate or enhance corrosion reactions. Special emphasis was devoted to the concepts of "depolarization" and "depassivation."

Enhanced production of hydrogenase, the enzyme critical to the cathodic depolarization mechanisms, by SRB in the presence of high surface clays, silicas, and several modified silicas, was reported by R. E. Williams, National Research Council, Ottawa, Canada.

F. A. Tomei, Harvard University, Cambridge, MA, employed a non-electrochemical technique to demonstrate the cathodic depolarization effect by the SRB hydrogenase system. Fumarate, instead of sulfate, was utilized as an electron acceptor, being reduced to succinate, the appearance of which could be measured. Thus the formation of succinate or the disappearance of furmarate could be used as an indirect measure of hydrogen uptake from the metal surface and thereby a measurement of the corrosion rate could be afforded. The highest corrosion rate determined, using this system was 33 milligrams per square decimeter per day, but this was still lower than the corrosion rates observed in the field.

Several papers were concerned with formation of concentration cells by mixed populations of bacteria or consortia, appearing as biofilms on metal surfaces, which create oxygen depeleted conditions for the development of SRB. W. A. Hamilton, University of Aberdeen, Scotland reported on the development of a (^{35}S) radiorespirometric method to determine the activity of SRB within the biofilm on metal test coupons. Results obtained by this technique are compared with the amount of marine fouling and corrosion occurring. The technique would appear to have considerable value for monitoring corrosion in the field and evaluating the efficacy of corrosion-protection methods. The use of this technique within the ballast legs of large concrete oil production platforms in the north sea off Scotland was described by S. Maxwell, Corrosion Specialists (North Sea) Ltd., Aberdeen, Scotland. The rate of sulphate reduction on mild steel coupons exposed in the entrained seawater was found to be very high on the metal's surface but below detection in bulk phase samples.

The formation and ecology of surface colonization on metals which may result in corrosion was graphically illustrated by J. W. Costerton, University of Calgary, Canada. Within complex microbial consortia, local differences in protons and other cations, substantially different from those of the general biofilm, are produced, which Costerton stated, form local electrochemical corrosion cells. SRB are found in most of these cells, but need not be, to induce corrosion.

D. C. White, Florida State University at Tallahassee, outlined the physical (Fourier transform infrared spectroscopy) and chemical methods which he used to analyse surface biofilms on the surface of metals on a scale approaching the size of microcolonies of bacteria. He reported his findings on the accelerated corrosion of 304 stainless steel in seawater by an aerobic marine pseudomonad and its polysaccharide exopolymer, as well as by two Vibrio species with exopolymers of unknown composition.

Studies on the comparison of abiotic vs. biotic oxygen concentration cells in MIC were presented by B. Little, Naval Oceanographic Research and Development Agency, Mississippi and S. Dexter, University of Delaware at Lewes. Studies, using nickel 201 and thermophilic bacteria, according to Little, indicated that the bacteria did not increase the corrosion current over abiotic oxygen concentration (differential aeration) cells in the presence of the acidic metabolites, isovaleric and isobutyric acids. Dexter, in a study of crevice corrosion initiation, found that oxygen was depleted within a 304 stainless steel cell, containing sterile sea water, much more effectively (150:1) than in a nonmetallic (teflon) nonsterile cell with natural seawater.

Two studies on metal deterioration by metabolic products were reported. In a study of hydrogen producing bacteria, M. Walch, Harvard University, Cambridge, MA, reported that small amounts of hydrogen were absorbed by metals beneath films of these bacteria. Hydrogen uptake by some metals can initiate hydrogen embrittlement of these metals. W. Iverson, NBS, indicated that some SRB produce a volatile, phosphorus compound which is highly corrosive to mild steel. This compound can also be produced by the action of hydrogen sulfide on certain phosphorus compounds. Anaerobic corrosion may be initiated when a film of iron sulfide, produced by SRB generated hydrogen sulfide, breaks down and permits the phosphorus compound to come in contact with the steel surface. Iverson suggested that the breakdown of this iron sulfide film may be detected by an electrochemical noise technique.

Destruction of passive or protective films, the fourth mechanism previously mentioned, was the subject of two papers, one by D. W. S. Westlake, University of Alberta, Edmonton, Canada and the other by H. Videla, INIFTA, La Plata, Argentina. Westlake reported on the corrosive effect of certain pseudomonas species on the interior of oil pipelines in Alberta which have the capacity to reduce ferric iron to ferrous iron, as well as the ability to reduce sulfite, thiosulfate and sulfur (but not sulfate) to sulfide. The corrosive effect, he stated, was due to the ability of these organisms to remove or prevent the formation of a protective film of ferric iron by reducing this insoluble film to soluble ferrous iron. Videla described his work on the electrochemical behavior of prepassivated SAE 1020 steel in the presence of SRB. He stated that the corrosion process was initiated by the replacement of the passive film on the steel by a poorly protective film or iron sulfide (mackinawite), which was followed by pitting at these sites.

Combination of the described mechanisms undoubtedly play a part in many corrosion processes. Such a role was described by Videla in another study on the corrosion of aluminum by the fungus *Cladosporium resinae*, using electrochemical techniques (potentiostatic) together with SEM-EDAX analysis. From these studies, he concluded that the localized corrosion of metal was due to: 1) a local increase in the hydrogen ion concentration due to organic acid production; 2) a decrease in the stability of the passive film by metabolic substances; and 3) a decrease in the concentration of corrosion inhibitors due to their utilization by the organisms.

EXPERIMENTAL METHODS

R. Tatnall, E. I. duPont de Nemours & Co., Wilmington, DE, introduced the session on experimental methods by outlining a general, recommended program to study MIC. He stated that many methods used in other fields are not applicable to biocorrosion phenomena.

A more accurate simulation of environmental conditions for microbiological corrosion testing was stressed by R. G. J. Edyvean, University of Sheffield, England. He stated that two methods, artifical seawater or a sodium chloride solution saturated with hydrogen sulfide, are used to test steels (for offshore use) for corrosion fatigue cracking. The hydrogen sulfide concentration in saturated seawater (3150 ppm) is far more aggressive than typical concentrations found under marine fouling conditions (~ 100 ppm). New experimental methods were described.

The use of mixed cultures of bacteria, which more accurately reflect environmental conditions, in studying anaerobic corrosion, was reported by C. Gaylarde, City of London Polytechnic, England. Testing the effect of three bacterial cultures, including one SRB, on the corrosion of mild steel coupons singly and in combination, various inhibitory and enhancement effects were noted.

F. Kajiyama, Tokyo Gas Company, Japan, reported on his successful laboratory attempt to simulate the high rate of corrosion of ductile iron in anaerobic soils. High rates of corrosion, 2 millimeters per year were reproduced by establishing a test cell between two soils with different SRB activities (cell numbers). Both anode and cathode were of the same material, the anode being of smaller surface area than the cathode (ratio:1 to 1000). The SRB activity in the vicinity of the anode, according to Kajiyama, played a vital role in the corrosion process.

AC impedance and electrochemical noise techniques were found useful by A. N. Moosavi, University of Aberdeen, Scotland, in monitoring the corrosion rate and in studying the type of corrosion process in reinforcing steel. The sulfide produced by SRB was found to have an adverse affect on the durability of the bond between the reinforcing steel and concrete.

Several techniques to rapidly detect and identify organisms which may be involved in MIC were described by Pope. These techniques involve indirect labelled antibody techniques. Secondary antibodies coupled to biotin and fluorescently labeled Avidin, permit cells reacting to the primary antibody to be observed, using a fluorescence microscope. A similar technique permits use of the light microscope by coupling the Avidin to an enzyme which with an appropriate substrate produces a colored product. These enzyme-secondary antibody reagents have been used to develop macroscopic color tests with rapid and semi-quantitative estimation of specific organism which may be present in the corrosion products.

CONTROL PROCEDURES

The University of Manchester's King described various measures to control microbial corrosion, external and internal, in long, large capacity, subsea pipelines. These include bacterial monitoring, biocide treatment, and cathodic protection by sacrifical anodes.

A routine procedure for external corrosion protection of pipelines has been to apply cathodic protection, polarizing the pipe to a standard-850 mV with respect to a saturated $Cu/CuSO_4$. In areas where there is a lot of activity due to SRB, this potential is not sufficient. Potentials of −950 mV have been recommended. R. G. Worthingham, NOVA/Husky Research Corporation Ltd., Calgary, Canada, stated that bacterial corrosion occurred beneath disbonded plastic tape coatings even when the cathodic protection potentials were well above −1000 mV. Laboratory studies by NOVA to determine the cathodic protection criteria to control anaerobic bacterial corrosion were described by T. R. Jack, also of NOVA/Husky.

An overview of MIC in industry was presented by J. G. Stoecker, Monsanto Co., St. Louis, MO. He reviewed the progress made toward understanding this type of corrosion as well as the future needs of corrosion engineering to present or minimize the potential of MIC still further.

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