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Many techniques have been described for diagnosing, measuring and monitoring microbiologically influenced corrosion (MIC), however none has been accepted as an industry standard. Diagnosing MIC requires a combination of microbiological, metallurgical and chemical analyses. Electrochemical techniques can be used to measure and monitor MIC. The major limitation for MIC monitoring programs is the inability to relate microbiology to corrosion in real time. Some techniques can detect a specific modification in the system due to the presence and activities of microorganisms (e.g., heat transfer resistance, fluid friction resistance, galvanic current) and assume something about the corrosion. Other techniques measure some electrochemical parameter (e.g., polarization resistance, electrochemical noise) and assume something about the microbiology. With experience and knowledge of a particular operating system either can be an effective monitoring tool, especially for evaluating a treatment regime (biocides or corrosion inhibitors).

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DIAGNOSING, MEASURING AND MONITORING MICROBIOLOGICALLY INFLUENCED CORROSION (MIC)

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Summary: Many techniques have been described for diagnosing, measuring and monitoring microbiologically influenced corrosion (MIC), however none has been accepted as an industry standard. Diagnosing MIC requires a combination of microbiological, metallurgical and chemical analyses. Electrochemical techniques can be used to measure and monitor MIC. The major limitation for MIC monitoring programs is the inability to relate microbiology to corrosion in real time. Some techniques can detect a specific modification in the system due to the presence and activities of microorganisms (e.g., heat transfer resistance, fluid friction resistance, galvanic current) and assume something about the corrosion. Other techniques measure some electrochemical parameter (e.g., polarization resistance, electrochemical noise) and assume something about the microbiology. With experience and knowledge of a particular operating system either can be an effective monitoring tool, especially for evaluating a treatment regime (biocides or corrosion inhibitors).

1. DIAGNOSING

The following are required for an accurate diagnosis of MIC: 1) a sample of the corrosion product or affected surface that has not been altered by collection or storage, 2) identification of a corrosion mechanism, 3) identification of microorganisms capable of growth and maintenance of the corrosion mechanism in the particular environment, and 4) demonstration of an association of the microorganisms with the observed corrosion.

The list of microorganisms involved in MIC and the resulting mechanisms are continuously growing. Causative microorganisms are from all three main branches of evolutionary descent, i.e., bacteria, archaea and eukaryotes. For many years the first step in identifying corrosion as MIC was to determine the presence of specific groups of bacteria in the bulk medium (planktonic cells) or associated with corrosion products (sessile cells). There are four approaches: culture the organisms on solid or in liquid media, extract and quantify a particular cell constituent, demonstrate/measure some activity, or demonstrate a spatial relationship between microbial cells and corrosion products using microscopy.

1.1 Culture Techniques

The method most often used for detecting and enumerating groups of bacteria is the serial dilution to extinction method using selective liquid or solid culture media. To culture microorganisms, a small amount of the sample of interest as a liquid or a suspension of a solid (the inoculum) is added to a solution or solid that contains nutrients (culture medium). There are three considerations when growing microorganisms: type of culture medium, incubation temperature, and length of incubation. The distinct advantage of culturing techniques to detect specific microorganisms is that low numbers of cells grow to easily detectable higher numbers in the proper culture medium. However, there are numerous limitations for the detection and enumeration of cells by culturing techniques. Under all circumstances culture techniques underestimate the organisms in a natural population. Kaeberlein *et al.* (2002) suggest that 99 percent of microorganisms from the environment resist cultivation in the laboratory. Viable microorganisms can enter into a non-culturable state. Another problem is that culture media cannot approximate the complexity of a natural environment. Growth media tend to be strain-specific. For example, lactate-based media sustain the growth of lactate-oxidizers, but not acetate-oxidizing bacteria. Incubating at one temperature is further selective. The type of medium used to culture microorganisms determines to a large extent the numbers and types of microorganisms that grow. Zhu *et al.* (2005) demonstrated dramatic changes in the microbial population from a gas pipeline after samples were introduced into liquid culture media. Similarly, Romero *et al.* (2005) found that some bacteria present in small amounts in the original waters were enriched in the culture process.

1.2 Biochemical Assays

Biochemical assays have been developed for the detection of specific microorganisms associated with MIC. Unlike culturing techniques, biochemical assays for detecting and quantifying bacteria do not require growth of the bacteria. Instead, biochemical assays measure constitutive properties including adenosine triphosphate (ATP) (Littmann1977), phospholipid fatty acids (Franklin and White1991), cell-bound antibodies (Pope1986) and DNA (Romero et al. 2005). Adenosine-5'-phosphosulfate reductase (Tatnall et al. 1988) and hydrogenase (Boivin et al. 1990) have been used to estimate SRB populations.

1.3 Physiological Activity

Phelps *et al.* (1991) used a variety of ^{14}C-labelled compounds to quantify catabolic and anabolic bacterial activities associated with corrosion tubercles in steel natural gas transmission pipelines. They demonstrated that organic acid was produced from hydrogen and carbon dioxide in natural gas by acetogenic bacteria, and that acidification could lead to enhanced corrosion of the steel. Mittelman *et al.* (1990) used measurement of lipid biosynthesis from ^{14}C-acetate, in conjunction with measurements of microbial biomass and extracellular polymer, to study effects of differential fluid shear on physiology and metabolism of *Alteromonas* (formerly *Pseudomonas*) *atlantica*. Increasing shear force increased the rate of total lipid biosynthesis, but decreased per cell biosynthesis. Increasing fluid shear also increased cellular biomass and greatly increased the ratio of extracellular polymer to cellular protein. Maxwell (1986) developed a radiorespirometric technique for measuring SRB activity on metal surfaces.

1.4 Molecular Techniques

Molecular techniques have been used to identify and quantify microbial populations in natural environments. These techniques involve amplification of 16S rRNA gene sequences by polymerase chain reaction (PCR) amplification of extracted and purified nucleic acids. The PCR products can be evaluated using community fingerprinting techniques such as denaturing gradient gel electrophoresis (DGGE). Each DGGE band is representative of a specific bacterial population and the number of distinctive bands is indicative of microbial diversity. The PCR products can also be sequenced, and the sequences are compared to the sequences in the Genbank database, which allows the identity of the species within an environmental sample. Horn *et al.* (2003) identified the constituents of the microbial community within a proposed nuclear waste repository using two techniques: 1) isolation of DNA from growth culture and subsequent identification by 16S ribosomal rRNA genes, and 2) isolation of DNA directly from environmental samples followed by subsequent identification of the amplified 16S rRNA genes. Comparison of the data from the two techniques demonstrates that culture dependent approaches underestimated the complexity of microbial communities. Zhu *et al.* (2003, 2004) used quantitative PCR and functional genes, i.e., dissimilatory sulfite reductase for SRB, nitrite reductase gene for denitrifying bacteria and methyl-coenzyme M reductase gene for methanogens, to characterize the types and abundance of bacterial species in gas pipeline samples. They found that methanogens were more abundant in most pipeline samples than denitrifying bacteria and that SRB were the least abundant bacteria. Lutterbach et al. (2011) used a real-time quantitative PCR technique to quantify SRB in bottom water from fuel tanks. The technique, requiring 1 day, produced results comparable to 28-day culture techniques. Fluorescent in situ hybridization (FISH) uses the specific fluorescent dye-labeled oligonucleotide probes to selectively identify and visualize SRB both in established and developing multispecies biofilms. Takai and Horikoshi (2000) report that quantitative nucleic acid hybridization and FISH with archaeal rRNA-targeted nucleotide probes and competitive quantitative PCR could be used to detect and quantify archaea in a microbial community. Restrictive fragment length polymorphism (RFLP) is a technique in which microorganisms can be differentiated by analysis of patterns derived from cleavage of their DNA. RFLP has been used to characterize bacterial communities in biofilms on copper pipes (Reyes 2008 et al.) and in concretions on the USS Arizona (McNamara et al. 2009). The conclusion in both studies was that the bacterial community played a role in corrosion.

1.5 Microscopy

Using light microscopy and periodic acid-Schiff stain to detect polysaccharides in biofilms Chamberlain *et al.* (1988) demonstrated a relationship between an unusual variety of copper pitting corrosion and biofilms. Epifluorescence microscopy techniques have been developed for the identification of specific bacteria in biofilms Epifluorescence cell surface antibody methods are based on the binding between cell-specific antibodies and subsequent detection with a secondary antibody. Antigenic structures of marine and terrestrial strains are distinctly different and therefore antibodies to either strain do not react with the other. Confocal laser scanning microscopy (CLSM) permits one to create three-dimensional images, determine surface contour in minute detail, and accurately measure critical dimensions by mechanically scanning the object with laser light. A sharply focused image of a single horizontal plane within a specimen is formed while light from out of focus areas is repressed from view. The process is repeated again and again at precise intervals on horizontal planes and the visual data from all images are compiled to create a single, multidimensional view of the subject. Geesey *et al.* (1994) used CLSM to produce three-dimensional images of bacteria within scratches, milling lines and grain boundaries. Atomic force microscopy (AFM) uses a microprobe mounted on a flexible cantilever to detect surface topography by scanning at a sub nanometer scale. Repulsion by electrons overlapping at the tip of the microprobe cause deflections of the cantilever that can be detected by a laser beam. The signal is read by a feedback loop to maintain a constant tip displacement by varying voltage to a piezoelectric control. The variations in the voltage mimic the topography

of the sample and together with the movement of the microprobe in the horizontal plane are converted to an image. Telegdi *et al.* (1998) used AFM to image biofilm formation, extracellular polymer production and subsequent corrosion.

Many of the conclusions about biofilm development, composition, distribution and relationship to substratum/corrosion products have been derived from traditional scanning electron microscopy (SEM) and transmission electron microscopy (TEM). Environmental electron microscopy includes both scanning (ESEM) and transmission (ETEM) techniques for the examination of biological materials with a minimum of manipulation, i.e., fixation and dehydration. Little *et al.* (1991) used ESEM to study marine biofilms on stainless steel surfaces. They observed a gelatinous layer in which bacteria and microalgae were embedded. Traditional SEM images of the same areas demonstrated a loss of cellular and extracellular material. Ray and Little (2003) used ESEM to demonstrate sulfide encrusted SRB in corrosion layers on copper alloys and iron-depositing bacteria in tubercles on galvanized steel. Ray and Little (2003) used ETEM to image *Pseudomonas putida* on corroding iron filings and to demonstrate that the organisms were not directly in contact with the metal. Instead, the cells were attached to the substratum with extracellular material. There are fundamental problems in attempting to diagnose MIC by establishing a spatial relationship between numbers and types of microorganisms in the bulk medium or those associated with corrosion products using any of the techniques previously described. Because microorganisms are ubiquitous, the presence of bacteria or other microorganisms does not necessarily indicate a causal relationship with corrosion.

1.6 Pit Morphology

Chung and Thomas (1999) compared MIC pit morphology with non-MIC chloride-induced pitting in 304/304L and E308 stainless steel base metals and welds. A faceted appearance was common to both types of pits in 304 and 304L base metal. Facets were located in the dendritic skeletons in MIC and non-MIC cavities of E308 weld metal. They concluded that there were no unique morphological characteristics for MIC pits in these materials. The problem that has resulted from the assumption that pits can be independently interpreted as MIC is that MIC is often misdiagnosed. For example, Welz and Tverberg (1998) reported leaks at welds in 316L stainless steel hot water system in a brewery after six weeks in operation were due to MIC. The original diagnosis was based on the circumstantial evidence of attack at welds and the pitting morphology of scalloped pits within pits. MIC was subsequently dismissed as the cause of localized corrosion. The hemispherical pits had been produced when CO_2 was liberated and low pH bubbles nucleated at surface discontinuities. More recently several investigators have demonstrated that during the initial stages of pit formation due to certain types of bacteria, pits do have unique characteristics. Geiser *et al.* (2001) found that pits in 316L stainless steel due to the manganese-oxidizing bacterium *Leptothrix discophora* had different morphologies than pits initiated by anodic polarization. The similarity between the dimensions of the bacterial cells attached to the surface and the dimensions of corrosion pits indicate a possibility that the pits were initiated at the sites where the microorganisms were attached. Eckert et al. 2003) used API 5L steel to demonstrate micro-morphological characteristics that could be used to identify MIC initiation. Coupons were installed at various points in a pipeline system and were examined by SEM at 1,000 and 2,000 times. They demonstrated that pit initiation and bacterial colonization were correlated and that pit locations physically matched the locations of cells. Telegdi *et al.* (1998) demonstrated that pits produced by *Thiobacillus intermedius* had the same shape as the bacteria. None of these investigators claims that these unique features can be detected with the unaided eye or that the features will be preserved as pits grow, propagate and merge.

1.7 Corrosion Product Composition

1.7.1 Elemental Composition

Elements in corrosion deposits can provide information as to the cause of corrosion. Energy dispersive x-ray analysis (EDS) coupled with SEM can be used to determine the elemental composition of corrosion deposits. Because all living organisms contain ATP, a phosphorus peak in an energy dispersive x-ray analysis spectrum can be related to cells associated with the corrosion products. Other sources of phosphorus, e.g., phosphate water treatments, must be eliminated. The activities of SRB and manganese oxidizing bacteria produce surface bound sulfur and manganese, respectively. Chloride is typically found in crevices and pits and cannot be directly related to MIC. There are several limitations for EDS surface chemical analyses. Samples for EDS cannot be evaluated after heavy metal coating, so that EDS spectra must be collected prior to examination by SEM making it difficult or impossible to match spectra with exact locations on images. This is not a problem with the ESEM because non-conducting samples can be imaged directly, meaning that EDS spectra can be collected of the area that is being imaged by ESEM. Little *et al.* (1991) documented the changes in surface chemistry as a result of solvent extraction of water, a requirement for SEM. Other shortcomings of SEM/EDS include peak overlap. Peaks for sulfur overlap peaks for molyhdenum and the characteristic peak for manganese coincides with the secondary peak for chromium. Wavelength dispersive spectroscopy can be used to resolve overlapping EDS peaks. Peak heights cannot be used to determine the concentration of elements. It is also impossible to determine the valence state of an element with EDS.

1.7.2 Mineralogical Fingerprints

McNeil *et al.* (1991) used mineralogical data determined by x-ray crystallography, thermodynamic stability diagrams (Pourbaix) and the simplexity principle for precipitation reactions to evaluate corrosion product mineralogy. They concluded that many sulfides under near surface natural environmental conditions could only be produced by microbiological action on specific precursor metals. They reported that copper sulfides, djurleite, spionkopite and the high temperature polymorph of chalcocite, were mineralogical fingerprints for the SRB induced corrosion of copper-nickel alloys. They also reported that the stability or tenacity of sulfide corrosion products determined their influence on corrosion. Jack *et al.* (1996) reported that the mineralogy of corrosion products on pipelines could provide insight into the conditions under which the corrosion took place.

1.7.3 Isotope Fractionation

The stable isotopes of sulfur (^{32}S and ^{34}S), naturally present in any sulfate source, are selectively metabolized during sulfate reduction by SRB and the resulting sulfide is enriched in ^{32}S. Little *et al.* (1993) demonstrated sulfur isotope fractionation in sulfide corrosion deposits resulting from activities of SRB within biofilms on copper surfaces. Accumulation of the lighter isotope was related to surface derivatization or corrosion as measured by weight loss. Use of this technique to identify SRB-related corrosion requires sophisticated laboratory procedures.

2. MEASURING AND MONITORING

Electrochemical techniques used to measure and monitor MIC include those in which no external signal is applied (e.g., measurement of redox potential (E_{redox}) or corrosion potential (E_{corr}) and electrochemical noise analysis (ENA)), those in which only a small potential or current perturbation is applied (e.g., polarization resistance (R_p) and electrochemical impedance spectroscopy (EIS), and those in which the potential is scanned over a wide range (e.g., anodic and cathodic polarization curves, pitting scans). The terms used to describe monitoring tools are real-time, on-line, in-line and side-stream. Real-time refers to the measurements that are available at the actual time of collection and are usually continuous, or nearly continuous. On-line monitors are installed to provide real-time measurements and in-line defines a measurement made in the bulk medium of a process stream. Side stream devices are installed in parallel to the main system, taking a portion of the flow under identical operating conditions. The major limitation for MIC monitoring programs is the inability to relate microbiology to corrosion in real time.

2.1 Techniques Requiring No External Signal

2.1.1. Galvanic Couples

Zero resistance ammeter (ZRA) measurements of galvanic current have been used for many years to measure and monitor the electrochemical impact of microorganisms on metal surfaces in laboratory experiments and in field conditions using several designs, including concentric ring electrodes, dual cells and occluded cells mimicking small crevices. Galvanic current cannot be directly related to corrosion current. The previously described techniques do not provide a means to calculate corrosion rates, but rather changes due to the presence of a biofilm.

Angell *et al.* (1995) used a concentric ring 304 stainless steel electrode to demonstrate that a consortium of SRB and a *Vibrio* sp. maintained a galvanic current between the anode and cathode. The anode (0.031 cm^2) was concentric to, and separated from, the cathode (4.87 cm^2) by a polytetrafluoroethylene spacer. Current was applied for seventy-two hours either during or after microbial colonization. Once the applied current was removed the resultant galvanic current flowing between the anode and the cathode was monitored by ZRA. They found that a current was maintained in the presence of a microbial consortium. No current was measured in a sterile control. The authors state that the concentric ring electrode provides a technique by which MIC can be studied and is not intended to represent any natural situation.

Licina and Nekoksa (1995) developed a probe consisting of ten 316 stainless steel concentric rings separated by epoxy. A potential (which varies according to experimental conditions) was imposed for 1 hour each day between the electrodes so that the electrodes are alternately anodes and cathodes. The metal discs were polarized to produce an environment "conducive to biofilm formation." The applied current, required to achieve a pre-set potential between electrodes, remained stable until a biofilm formed. Once a biofilm was established, applied current increased. The emergence of generated current (galvanic current that continued to flow between the electrodes after the external polarization had been removed) was another indication of biofilm development. In the absence of a biofilm the generated current was zero. The probe is intended to provide information about an operating system (such as a flowing cooling water piping) that can be used to make decisions about cleaning or treatment, not to investigate localized corrosion mechanisms. The device has been used in fire protection systems, emergency service water stands and equipment cooling water systems in nuclear power plants. The device provides a warning when the biofilm maintains a certain current so that the system can be cleaned or biocides can be added. This technique only indicates a corrosion risk. It does not measure any specific properties of biofilms or any parameter related to corrosion.

Uchida *et al.* (1997) developed an electrochemical device for simulating a single pit consisting of an artificial anode and a carbon steel tube acting as the cathode coupled to a ZRA. The monitoring device was evaluated at a refinery plant-cooling tower. Pitting associated with biofilms had been observed on some heat exchangers during maintenance shut downs. The goal was to improve the cooling water treatment program by reducing total maintenance costs. The authors reported that the galvanic current measurement was a sensitive indicator of biofilm formation and biocide effectiveness for real-time monitoring. Iimura *et al.* (1996) reported that they had succeeded in predicting the penetration rate of carbon steel tubes of heat exchangers with a growth model of pitting corrosion and a similar device.

2.1.2 Open-Circuit or Corrosion Potential, E_{corr}

E_{corr} measurements require a stable reference electrode - usually assumed to be unaffected by biofilm formation - and a high-impedance voltmeter. E_{corr} values are difficult to interpret, especially when related to MIC. Despite this limitation, no other phenomenon has fascinated those studying MIC more than ennoblement, i.e., the increase of E_{corr} due to formation of a biofilm on a metal surface. Although ennoblement has been observed for metals exposed to both fresh water (rivers and estuaries) and natural seawater, the mechanisms may be different. Little and Mansfeld (1994) categorized the proposed mechanisms for ennoblement in marine environments into three categories: thermodynamic, kinetic, and alteration of the nature of the reduction reaction itself. It is not possible to determine the cause of ennoblement from E_{corr} vs. time curves.

2.1.3 Electrochemical Noise Analysis (ENA)

Electrochemical noise (EN) data can be obtained as fluctuations of potential and/or current. In laboratory studies, it is possible to measure potential and current fluctuations (EPN and ECN, respectively) simultaneously. In this approach two electrodes of the same material are coupled through a ZRA. Current fluctuations are measured with the ZRA, while the potential fluctuations are measured with a high-impedance voltmeter between the two coupled electrodes and a reference electrode which could be a stable reference electrode such as a saturated calomel electrode (SCE) or a third electrode of the same material as the two test electrodes. The main application of EN data has been in corrosion monitoring. King *et* (1986) interpreted noise measurements for steel pipes in environments containing SRB as being indicative of film formation and breakdown. Higher noise levels and greater fluctuations indicated localized corrosion. The magnitude of noise fluctuations depends on the total impedance of the system. A corroding metal undergoing uniform corrosion with fairly high corrosion rates might be less noisy than a passive metal showing occasional bursts of noise due to localized breakdown of the film followed by rapid repassivation. Since that early work several investigators have suggested the potential for EN in MIC studies. In laboratory testing for corrosion in fresh water-cooled heat exchangers it was suggested that a reproducible electrochemical noise response was an MIC signature (Brennenstuhl et al, 1994). Bullard *et al.* (2002) recommended that the EN sensors be evaluated in gas transmission pipelines.

2.2 Techniques Requiring a Small External Signal

2.2.1 Polarization Resistance Technique

Polarization resistance (R_p) techniques can be used to continuously monitor the instantaneous corrosion rate of a metal (Mansfeld 1976). A simplification of the polarization resistance technique is the linear polarization resistance (LPR) technique in which it is assumed that the relationship between E and i is linear in a narrow range (+/- 20 mV) around E_{corr}. This approach is used in field tests and forms the basis of commercial corrosion rate monitors. Mansfeld *et al.* (1991) used the LPR technique to determine R_p for mild steel sensors embedded in concrete exposed to a sewer environment for about nine months. R_p data are meaningful for general or uniform corrosion but less so for localized corrosion, including MIC. Additionally, the use of Stern-Geary theory where corrosion rate is inversely proportional to R_p at potentials close to E_{corr} is valid for conditions controlled by electron transfer, but not for diffusion-controlled systems as frequently found in MIC.

2.2.2 Electrochemical Impedance Spectroscopy (EIS)

EIS techniques record impedance data as a function of the frequency of an applied signal at a fixed potential. A large frequency range (65 kHz-1 mHz) must be investigated to obtain a complete impedance spectrum. Dowling *et al.* (1988) demonstrated that the small signals required for EIS do not adversely affect the numbers, viability, and activity of microorganisms within a biofilm. EIS data may be used to determine R_p, the inverse of corrosion rate. EIS is commonly used for steady state conditions (uniform corrosion), however sophisticated models have been developed for localized corrosion. Several reports have been published in which EIS has been used to study the role of SRB in corrosion of buried pipes Kasahara and Kajiyama (1991) and reinforced concrete (Moosavi et al. 1986). Ferrante and Feron (1991) used EIS data to conclude that the material composition of steels was more important for MIC resistance than bacterial population, incubation time, sulfide content, and other products of bacterial growth. A disadvantage of EIS is the inability to quantify electrochemical parameters, such as R_p, from impedance spectra when MIC is the identified corrosion mechanism. Quantification requires a model electrical circuit for impedance analysis. Mansfeld and Little (1992) state "this type of analysis is qualitative and no models for the impedance behavior have been presented for complicated systems encountered in MIC."

3. LARGE SIGNAL POLARIZATION

Recording polarization curves provides an overview of reactions for a given corrosion system-charge transfer or diffusion controlled reactions, passivity, transpassivity and localized corrosion phenomena. Large signal polarization techniques require potential scans ranging from several hundred mV to several V. Large signal polarization is applied to obtain potentiostatic or potentiodynamic polarization curves as well as pitting scans. Polarization curves can be used to determine i_{corr} by Tafel extrapolation, while mass-transport-related phenomena can be evaluated based on the limiting current density (i_{lim}). Mechanistic information can be obtained from experimental values of b_a and b_c. Pitting scans are used to determine pitting and protection potentials (E_{pit} and E_{prot}, respectively).

Numerous investigators have used polarization curves to determine the effects of microorganisms on the electrochemical properties of metal surfaces and the resulting corrosion behavior. In most of these studies comparisons have been made between polarization curves in sterile media with those obtained in the presence of bacteria and fungi (Schmitt 1997; Deshmukh *et al.* 1980). Disadvantages of large-signal polarizations are irreversible changes to surface properties of the metal and changes to biofilm structure and character.

4. MULTIPLE DEVICE MONITORS

Several investigators have used a combination of techniques to monitor MIC. Stokes *et al.* (1994) described an on-line, real-time fouling and corrosion monitoring system that consisted of a miniature side stream heat exchanger with an arrangement of corrosion sensors, flow and heat controllers and a data collection device. Either heat transfer rate or wall temperature could be controlled. If the heat transfer rate was controlled, the wall temperature increased as the surface fouled to maintain the set heat rate. If the wall temperature was set, the heating rate decreased to maintain the set wall temperature as the resistance to heat transfer increased. Changes in heat transfer resistance from that of a clean surface were used as a measure of biofilm formation. Corrosion was monitored using four electrochemical techniques: ZRA, ECN, EPN and LPR. The unit was used for one year on a cooling water system that used river water makeup to the cooling towers and had suffered severe under-deposit corrosion. Before cleaning the value of ECN and ZRA were always near full scale (no units). The trace of EPN showed transients typical of pit initiation. After cleaning, EPN was featureless and the ECN and ZRA values dropped by two and one orders of magnitude, respectively. By contrast the LPR output indicated a larger active area of apparently increased corrosion. During the field trial, corrosion rates as high as 100 mpy due to underdeposit corrosion were indicated. Metallography confirmed extensive localized corrosion. The authors did not analyze fouling deposits, but based on the use of a natural water they assumed biofilm formation.

Enzien and Yang (2001) described a differential flow cell method for monitoring localized corrosion in an industrial water. In this technique, a combination of LPR and ZRA measurements were used to obtain the rate of localized corrosion for carbon steel in aqueous solutions. The measurements were carried out in an electrolytic flow cell with a large cathode placed in faster flow conditions and two small anodes placed in a slower flow condition. The anodes and cathode were electrically connected together via a ZRA. The technique was used in a pilot cooling water test focused on optimizing a scale and corrosion treatment program specifically for localized corrosion. They reported that monitoring planktonic bacteria was not effective at predicting microbial fouling or MIC. Additionally, general corrosion rates were low throughout experiments; therefore linear polarization resistance measurements did not accurately predict a localized corrosion problem.

Videla *et al.* (1994) described a monitoring program in an oilfield for assessing biodeterioration on mild steel and stainless steel in recirculating cooling water systems. The program was based on 1) water quality control; 2) corrosion monitoring in the field (weight loss and LPR); 3) laboratory corrosion tests (polarization techniques and E_{corr} vs. time measurements); and 4) use of a side stream sampling device for monitoring sessile populations, biofilms, corrosion morphology and intensity, and biological and inorganic deposits analysis. Comparison of the corrosive attack on carbon steel coupons maintained with and without biocide indicated that there was little metal attack in the biocide-treated cooling system.
Brossia and Yang (2003) developed a multielectrode array sensor system (MASS) to monitor corrosion in both laboratory tests and industrial processes. The probe was used to conduct a series of biotic and abiotic tests to determine if the probe could detect MIC. The MASS probe consists of multiple miniature electrodes made of metals to be studied. The miniature electrodes were coupled together by connecting each of them to a common joint through independent resistors, with each electrode simulating an area of corroding metal. The standard deviation of the currents from the different miniature electrodes was used as an indicator for localized corrosion. Using carbon steel (UNS G10100) electrodes they were able to demonstrate that corrosion rates increased by an order of magnitude in the presence of SRB compared to sterile controls. For comparative purposes, several test cells were constructed using flat coupons and monitored using LPR to determine corrosion rates under similar conditions to those in the MASS probes. The corrosion rates obtained using the probe were much higher than those determined using LPR. The probe, however, cannot distinguish between biotic and abiotic pitting.

5. CONCLUSIONS

It is essential in diagnosing MIC to demonstrate a spatial relationship between the causative microorganisms and the corrosion phenomena. However, that relationship cannot be independently interpreted as MIC. Pitting due to MIC can

initiate as small pits that have the same size and charaeteristics of the causative organisms. These features are not obvious to the unaided eye and are most often observed with an electron or atomic force mieroscope. MIC does not produce a macroscopic unique metallographic feature. Metallurgical features previously thought to be unique to MIC, e.g., hemispherical pits in 300 series stainless steel localized at weld or tunneling in carbon steel, are consistent with some mechanisms for MIC, but cannot be interpreted independently. Bacteria do produee corrosion products that could not be produced abiotically in near surface environments, resulting in isotope fractionation and mineralogical fingerprints. The electrochemical techniques described in this chapter for measuring and monitoring MIC are useful for specific applications. All of the techniques are based on assumptions that can only be validated by a thorough understanding of the system that one is attempting to monitor.

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