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Microbiologically influenced corrosion (MIC) - monitoring and prevention

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Microbiologically influenced corrosion is the destruction (corrosion) of various metals, concrete structures and other structural materials in the presence of microorganisms. In this type of corrosion, the process takes place directly or indirectly under the influence of the metabolic activity of microorganisms. Corrosion of pipelines, in addition to deteriorating the integrity of the materials, also leads to environmental pollution. For this reason, it is of great importance to find suitable methods for research and protection against corrosion processes.

In this paper, we present different methods for assessment, monitoring and prevention of microbiologically influenced corrosion (MIC). Electrochemical methods are important for MIC assessment and monitoring due to their sensitivity, rapidity, and ability to provide real-time data. Different electrochemical methods are presented: polarization resistance (PR) method, linear sweep voltammetry (LSV) and electrochemical impedance spectroscopy (EIS).

Keywords: microbiologically influenced corrosion (MIC), polarization resistance (PR) method, linear sweep voltammetry (LSV), electrochemical impedance spectroscopy (EIS)

INTRODUCTION

Microbiologically influenced corrosion (MIC) is the destruction of various metals, concrete structures and other structural materials in the presence of microorganisms. In this type of corrosion, the process takes place directly or indirectly under the influence of the metabolic activity of microorganisms. Damage caused by microbiologically influenced corrosion (MIC) leads to a reduction in the tensile strength of structural materials, their breaking point, workability and other important mechanical properties. Wastewater discharged from industrial enterprises and also from households is one of the main corrosive environments that attracts attention for its high toxicity. Corrosion of pipelines, in addition to deteriorating the integrity of the materials, also leads to environmental pollution. For this reason, it is of great importance to find suitable methods for research and protection against corrosion processes. MIC is a major problem facing global sewer structures and is a hotly debated topic. In general, four main causes are at the basis of corrosion processes - formation of hydrogen sulfide in waste steam, radiation and accumulation of gaseous hydrogen sulfide, generation of sulfuric acid and deterioration of the structure of construction materials [1]. Water and sewage pipelines are made of different types of materials, divided into iron pipes (spherical cast iron, cast iron and steel), concrete pipes (reinforced concrete and pressure concrete pipes), ceramic-based pipes (bricks and clay) and plastic pipes (polyvinyl chloride, polyethylene) [2] (Fig.1).

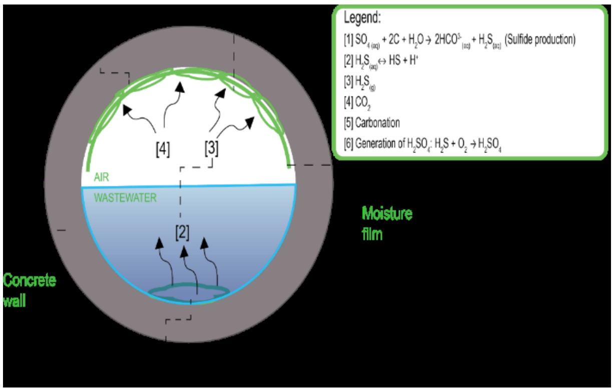

Fig. 1. Diagram of a pipeline and the processes taking place in it.

Appropriate application of electrochemical and surface analytical techniques is required for the detection and monitoring of MICs. This is crucial for

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understanding the biocorrosion mechanisms of various structural metals and their alloys.

In bioelectrochemical systems (BES), in which extracellular electron transfer occurs between specific microorganisms and electrodes by mechanisms similar to those causing MIC in natural conditions, these processes have a positive effect with energy generation and wastewater treatment, but in natural conditions the same processes have a destructive effect on construction materials.

Corrosion in general and MIC in particular are among the most dangerous phenomena accompanying the operation of metal equipment in the field of industry. If a precise analysis is made of the economic losses that corrosion causes, the amount is likely to be in the millions.

Appropriate application of MIC detection and monitoring techniques is critical to understanding interaction mechanisms and selecting appropriate prevention and control techniques. In the present work, various methods are presented that can be successfully used for assessment, monitoring and prevention of MIC.

METHODS FOR ASSESSMENT AND MONITORING OF MIC

Despite the large number of publications on the subject, the evaluation and prevention of MIC are still difficult to realize. Electrochemical methods are a good solution to the problems posed, in view of the fact that they are useful both for laboratory and field studies. Detailed and reliable information on MIC can be obtained when different electrochemical techniques are combined [3].

Open circuit potential (OCP)

OCP involves measuring the natural potential of a metal in a specific environment without applying an external current or voltage. Based on the measurements, changes in the electrochemical environment due to microbial activity can be detected and the initiation of corrosion processes can be monitored.

Corrosion potential (E_{corr})

Corrosion potential variation can be measured by determining the difference in voltage between the metal immersed in liquid medium and a suitable reference electrode [4-6]. Since OCP measurements change over time, it is important to estimate the effect of corrosion on the reaction depolarizers. A plot of potential as a function of time can be used [29]. An increase in OCP means depolarization of the cathode and increased corrosion; a drop in potential is evidence for decreased corrosion [7, 8].

Electrochemical tests to monitor corrosion changes. The disadvantage is that this technique provides little information because it needs a stable reference electrode (RE), but its surface is constantly changing due to microbial adhesion and biofilm formation. (E_{corr}) cannot tell if the corrosion rate is decreasing or increasing. Measuring the polarization resistance (R_p) together with (E_{corr}) can give a more complete estimate of the MIC as it gives information on the changes in the anodic and cathodic partial reactions (they determine the corrosion rate) [3, 9].

Tafel curves

Increasing the applied potential in the noble direction away from the corrosion potential causes the specimen to behave as an anode. The anodic current increases with increasing noble potential, giving rise to the measured anodic curve. In theory, both the cathodic and the anodic curves should be linear when the applied potential, V, is plotted *vs* the logarithm of the current density, i (A/cm^2), and the two curves should intersect at a point representing the corrosion potential and the corrosion current density. The measured log current *vs* potential curves both deviate from linearity in the vicinity of the corrosion potential; nevertheless, both often contain linear segments, sometimes referred to as Tafel regions. Extrapolating the linear segments of either the anodic or cathodic curves back to the corrosion potential yields the corrosion current density [10].

Taking polarization curves in Tafel coordinates is a fast and accurate technique for MIC analysis (Fig. 2) [8].

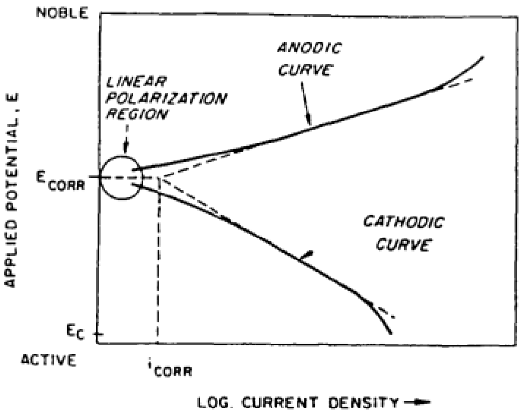

Fig. 2. Idealized polarization curve represented in Tafel coordinates [10]

The technique involves the displacement of the potential in an interval of ±250 mV, respectively, from the OCP to record the current values of the system. The Tafel equation represents a kinetically controlled electrochemical half-reaction (1).

$$i = i_0 e^{\left[\frac{2.303(E-E_0)}{b}\right]} \quad (1)$$

In the presented equation, (i) is the current displayed by the system at an input potential (E). The equilibrium voltage is shown by (E_0) and (b) is the reaction coefficient. The exchange current density is represented by (i_0). The Tafel equation for both the positive and negative regions of the metal sample is combined to give the Stern-Geary equation (2):

$$i_{corr} = \frac{\beta_a \beta_c}{R_p 2.3(\beta_a + \beta_c)} \quad (2)$$

By the logarithm of (i) with (E) two curves are drawn - cathodic and anodic. Extrapolation of the linear region of the cathode and anode segments gives the value of corrosion current (i_{corr}) for the system at their point of intersection. Tafel parameter values are useful in analyzing MICs. Corrosion rate (CR) and polarization resistance (R_p) can be calculated from these parameters using the following equations (3) and (4):

$$CR(mmpy) = \frac{3272 i_{corr} E}{\rho A} \quad (3)$$

$$R_p = \frac{\beta_a \beta_c}{2.3(\beta_a + \beta_c)(i_{corr})} \quad (4)$$

In the above equations, the cathodic and anodic Tafel slopes are represented by (β_a) and (β_c), respectively. The equivalent weight of the corroded metal is represented by (E), (ρ) is density, and the area of the sample is represented by (A).

Each one of the parameters is affected by changes in the corrosion environment and allows predicting the corrosion behavior of the investigated metal. Tafel curves can provide information on the nature of the biofilm in terms of time and rate of corrosion, which can then be used to control MIC [11].

Electrochemical impedance spectroscopy (EIS)

Electrochemical impedance spectroscopy (EIS) is another important technique frequently used in MIC studies to understand microbial degradation processes. EIS has been shown to be a safe technique for studying microbial corrosion, as it does not cause damage to the biofilm and microbial population [11] and at the same time provides information on electrochemical processes at the surface, including the formation and destruction of biofilms and corrosion products.

EIS records impedance data as a function of frequency of an applied signal at a fixed electrode potential. To obtain a complete impedance spectrum, a wide frequency range must be investigated. The small signals required for EIS do not adversely affect the number, viability and activity of microorganisms in the biofilm. The EIS data determine the polarization resistance (R_p) values, which also allow the corrosion rate to be calculated. (R_p) from EIS data is calculated by (5):

$$R_p = \sum\left(R_\Omega + R_p\right) - R_\Omega \quad (5)$$

where (R_Ω) represents the ohmic resistance of the system.

EIS is a technique that provides information about the properties of the formed layer on the electrode surface by analyzing the polarization resistance values, allowing it to be used in MIC evaluation investigations [3].

Polarization resistance method

Polarization resistance method is based on the nature of the linear relationship between changes in the applied potential and the resultant current density, when the applied potentials are within about ± 10 mV of the corrosion potential. The technique is based on the assumption that the interface behaves as a simple resistor, whose magnitude is inversely proportional to the corrosion current [12]. The slope of the potential current curve is approximately linear and has units of resistance [10].

By measuring polarization resistance (R_p), the corrosion rate of any metal can be continuously monitored. The polarization resistance can be determined from (6)

$$R_p = \left(\frac{dE}{di}\right) i = 0 \quad (6)$$

where (R_p) is the slope of the potential (E) versus the current density (i) at (E_{corr}) where i = 0. The corrosion current density (i_{corr}) is calculated from (R_p) as follows (7), (8)

$$i_{corr} = \frac{B}{R_p} \quad (7)$$

where:

$$B = \frac{\beta_a \beta_c}{2.303(\beta_a + \beta_c)} \quad (8)$$

Accurate calculation of (i_{corr}) for a given time requires simultaneous measurements of (R_p) and anodic and cathodic slopes of the Tafel curve (β_a and β_c). Modern instruments are able to determine the exact values of (i_{corr}). A simplification of the polarization resistance technique is the linear polarization technique, where the relationship between (E) and (i) is assumed to be linear in a narrow range around (E_{corr}). Usually, only two points (E, i) are measured and (B) is assumed to have a constant value of about 20 mV. This approach is applicable to field tests and forms the basis of commercial corrosion rate monitoring.

The polarization resistance can also be defined as the DC limit of the EIS (i.e. at the low frequency limit).

Using the Stern-Geary theory (where the corrosion rate is inversely proportional to (R_p) at potentials close to (E_{corr})) is valid for electron transfer-controlled conditions but not for diffusion-controlled systems as is often happening in MIC.

The advantage of the polarization resistance method is the quick and easy interpretation of the results and it shows a good correlation with the gravimetric method which measures the difference in weight before and after corrosion. Its disadvantage is that it is not applicable in cases of localized corrosion. The presence of a biofilm introduces additional electrochemical reactions that complicate the interpretation of linear polarization, thus potentially leading to nonlinear polarization behavior. This uncertainty is the reason for linking this method with other complementary techniques [3].

Cyclic voltammetry (CV)

Cyclic voltammetry (CV) involves cyclically changing the potential of the metal electrode and measuring the resulting current (Fig. 3). This method provides information on reversible and irreversible electrochemical reactions and is suitable for analyzing the redox behavior of microbial metabolites, as well as studying the electrochemical properties of biofilms [8].

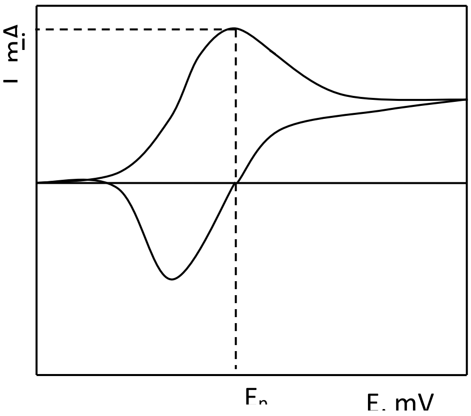

Fig. 3. Typical cyclic voltammetry

Integration with other techniques

Electrodes (working, reference, counter), used in all electrochemical techniques, measure the current and/or voltage in order to estimate the corrosion rate. The electrodes undergo changes due to the presence of microorganisms in the system and the thickness and character of the film formed on the electrode. That is why, for more comprehensive MIC assessment and monitoring, electrochemical methods are often combined by themselves or with other methods, for example with:

Surface analysis methods: Scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDS) and X-ray photoelectron spectroscopy (XPS) to analyze the composition and morphology of biofilms and corrosion products.

SEM can be regarded as an effective method in the analysis of organic and inorganic materials on a nanometer to micrometer (μm) scale. SEM works at a high magnification reaching to 300,000× and even 1,000,000× in producing very precise images of a wide range of materials [13].

Energy dispersive X-ray spectroscopy (EDS) works together with SEM to provide qualitative and semi-quantitative results. X-ray is generated when the electron beam, which is emitted from the gun, penetrates and interacts with the volume beneath the surface of the sample. Electrons entering the coulomb field of a specimen will decelerate and the loss of electron energy emits as a photon. Those photons have energies particular to specimen elements; these provide the SEM the capabilities and are called characteristic X-rays [14]. Both techniques together have the potential to supply fundamental information on material composition of scanned specimens, which could not be provided by common laboratory tests.

X-ray photoelectron spectroscopy is a surface-sensitive analytical technique in which X-rays bombard the surface of a material and the kinetic energy of the emitted electrons is measured. The two major characteristics of this technique that make it powerful as an analytical method are its surface sensitivity and its ability to reveal chemical state information from the elements in the sample [15].

Microbiological analysis methods: DNA sequencing, fluorescence microscopy, and culture-based techniques to identify and quantify the microorganisms involved in MIC.

There are four best known DNA sequencing techniques: the Sanger method, the Maxam and Gilbert method, the pyrosequencing^{TM} method – DNA sequencing in real time by detection of released pyrophosphate (PPi) and single molecule sequencing with exonuclease (exonuclease digestion of a single molecule composed of a single strand of fluorescently labeled deoxynucleotides) [16]. An astounding potential exists for DNA sequencing methods to bring enormous change in genetic and biological research and to enhance our fundamental biological knowledge [17].

Methods of chemical analysis: chromatography and spectroscopy for the detection and quantification of microbial metabolites. Chromatography is based on the principle that molecules in a mixture are applied onto the surface or into the solid, and fluid stationary phase (stable phase) is separating from each other while moving. Nowadays, chromatography is accepted as an extremely sensitive, and effective separation method [18]. There are various chromatographic methods like column chromatography, thin-layer chromatography (TLC), paper chromatography, gas chromatography, ion exchange chromatography, gel permeation chromatography, high-pressure liquid chromatography, and affinity chromatography [19].

Spectroscopy is a method of studying matter in which rays, sounds or particles emitted, absorbed, reflected or otherwise interacted with the object under study, are analyzed. Spectroscopic methods are widely used to identify substances by the spectrum they emit or absorb.

PREVENTION OF MICROBIOLOGICALLY INFLUENCED CORROSION

The assessment and prevention of microbiologically influenced corrosion (MIC) is of critical importance in many industries due to the serious economic consequences that this process can have. MIC causes significant economic losses due to the need for repairs, replacement of damaged parts and interruptions in the production process. MIC assessment helps to detect and reduce these costs early. On the other hand, sudden failures of equipment and structures caused by MIC pose a serious safety risk in various sectors such as oil and gas industry, chemical industry, etc. Regular assessment of MIC is a key factor to preventing accidents and protecting human life.

By monitoring MIC, companies can evaluate the effectiveness of their existing corrosion control systems and optimize them as needed. This includes the use of anti-corrosion coatings, cathodic protection and additives to inhibit microbial growth. Early detection and management of MICs can extend the life cycle of equipment and infrastructure by reducing the need for frequent replacements and repairs, resulting in cost savings.

Systems that are protected from MIC are more reliable and offer better performance. This is especially important in various industrial facilities. Last but not least, MIC can lead to the release of hazardous substances into the environment, which has serious environmental consequences.

MIC prevention helps to avoid such incidents and protect the environment. There are various methods of prevention of MIC [8, 20, 21].

Anti-corrosion coatings create a barrier between the metal surface and the corrosive environment, preventing contact with microorganisms and corrosive agents. Epoxy and polyurethane coatings can be used, which provide excellent chemical resistance; inhibitor coatings contain substances that inhibit corrosion and growth of microorganisms, and others [22].

Another method is cathodic protection [21]. It reduces the corrosion potential of metals by electrochemical methods, making them less susceptible to corrosion. It is possible to use the so-called sacrificial anode – using anodes that are more reactive than the metal being corroded instead of the protected metal or applying an external electric current to suppress corrosion.

It is possible to influence the MIC by affecting the relevant microorganisms. Chemicals such as biocides and inhibitors are used that kill or inhibit the growth of microorganisms and thus prevent corrosion processes [23]. Microorganisms are able to dramatically alter the electrochemical conditions at the metal/solution interface through biofilm formation. These changes can range from inducing or accelerating corrosion to inhibiting corrosion. Any inhibitory action developed by bacteria may be achieved within the diverse and complex interactions between biofilm/corrosion products occurring on a biocontaminated metal surface [24].

The choice of materials is also important, the more corrosion resistant the better. This is a key factor in minimizing the risk of MIC. Well-known materials with high corrosion resistance are titanium [25, 26] and nickel alloys, as well as stainless steels with a high molybdenum content [27].

Regular maintenance and cleaning prevent the build-up of biofilms and corrosion products that contribute to MIC. Mechanical cleaning is used - removal of biofilms and corrosion products by brushing or jet cleaning; chemical cleaning, by using chemicals to dissolve deposits and kill microorganisms, or ultrasonic cleaning using ultrasonic waves to destroy biofilms.

Another important factor that can significantly reduce the risk of MIC is the control of environmental parameters (temperature, oxygen, pH) which can significantly reduce the risk of MIC. An interesting possibility is the use of competitive microorganisms or enzymes (to degrade biofilms) for corrosion control [3, 28].

CONCLUSION

Combining different electrochemical techniques to assess and control MIC leads to comprehensive understanding of MIC processes, which in turn leads to the development of effective prevention and control strategies.

The most effective prevention of microbiologically influenced corrosion is achieved by using a combination of chemical, physical and biological methods. By proper selection and application of these methods, it is possible to significantly reduce the risk of MIC.

The assessment and prevention of microbiologically influenced corrosion is essential to maintain the durability, safety and efficiency of industrial equipment and infrastructure. By applying appropriate monitoring techniques and preventive measures, economic losses can be significantly reduced, the reliability of systems and equipment can be increased, and the environment can be protected.

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