



Contents lists available at ScienceDirect

Journal of Materials Science & Technology

journal homepage: www.jmst.org



Anaerobic microbiologically influenced corrosion mechanisms interpreted using bioenergetics and bioelectrochemistry: A review

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ARTICLE INFO

Article history:

Received 30 December 2017

Received in revised form 13 February 2018

Accepted 13 February 2018

Available online xxx

Keywords:

Microbiologically influenced corrosion

Bioenergetics

Biofilm

Bioelectrochemistry

MIC classification

Extracellular electron transfer (EET)

ABSTRACT

Microbiologically influenced corrosion (MIC) is a major cause of corrosion damages, facility failures, and financial losses, making MIC an important research topic. Due to complex microbiological activities and a lack of deep understanding of the interactions between biofilms and metal surfaces, MIC occurrences and mechanisms are difficult to predict and interpret. Many theories and mechanisms have been proposed to explain MIC. In this review, the mechanisms of MIC are discussed using bioenergetics, microbial respiration types, and biofilm extracellular electron transfer (EET). Two main MIC types, namely EET-MIC and metabolite MIC (M-MIC), are discussed. This brief review provides a state of the art insight into MIC mechanisms and it helps the diagnosis and prediction of occurrences of MIC under anaerobic conditions in the oil and gas industry.

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Contents

| | |
|------------------------------|----|
| 1. Introduction..... | 00 |
| 2. Bioenergetics of MIC..... | 00 |
| 3. EET in MIC..... | 00 |
| 4. MIC classification..... | 00 |
| 5. Conclusion..... | 00 |
| Acknowledgements..... | 00 |
| References..... | 00 |

1. Introduction

Corrosion causes an annual financial loss of US\$4 trillion globally, half of which is due to corrosion damages while the other half are costs for corrosion protection measures [1,2]. Microbes are ubiquitous in industrial systems. Microbiologically influenced corrosion (MIC), i.e. corrosion resulting from the activities of microorganisms, is a challenging problem in the oil and gas industry and is said to be behind of more than 20% of pipeline corrosion [3–5]. Pipeline leakages and facility failures due to MIC have

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<https://doi.org/10.1016/j.jmst.2018.02.023>

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been common occurrences with environmental damages over the past two decades [6–8]. Research activities on biocides, biocide enhancers, antibacterial stainless steels, and antibacterial coatings have been conducted to mitigate MIC [9–12]. MIC problems are more prevalent nowadays due to enhanced oil recovery that relies on seawater injection, which can lead to MIC and reservoir souring [13,14]. Furthermore, the increased awareness of MIC leads to more MIC problems identified.

Microbial contamination also causes biofouling and corrosion to equipment and infrastructure in other industrial settings including underground storage tanks [15], water distribution systems [16], rail systems [17], cooling water systems [18,19], ships [20], medical devices [21], and nuclear waste storage facilities [22]. MIC plays a considerable role in the corrosion and degradation of different materials, including but not limited to carbon steel [23], aluminum alloy [22], stainless steel (SS) [24], duplex SS (DSS) [11,25–28], hyper duplex SS (HDSS) [29], super austenitic SS (SASS) [30], high nitrogen SS (HNS) [31], magnesium [32], and even concrete [33]. Furthermore, MIC is not merely a type of corrosion by itself. It synergistically interacts with other corrosion processes, for instance, stress corrosion cracking (SCC) [34], crevice corrosion [35], fatigue-crack tip embrittlement [36], and under-deposit corrosion [37]. MIC is a persistent issue for corrosion engineers and scientists in various fields.

Many microorganisms are capable of MIC including bacteria, archaea, and fungi. Sulfate-reducing bacteria (SRB) and sulfate-reducing archaea (SRA) have been extensively investigated as the major causative microorganisms in MIC for decades because sulfate is widely distributed in many systems such as seawater, brackish water and agricultural runoff water [9,38]. SRB and SRA are isolated frequently from oil and gas fields with MIC problems [4,39]. A positive correlation among pitting corrosion, sulfide generation, and sulfate consumption is often observed in the presence of SRB [40]. In addition, nitrate-reducing bacteria (NRB) [41], methanogens [40,42], iron-oxidizing bacteria (IOB) [43], manganese-oxidizing bacteria (MOB) [44], and diverse fungal species [45] have also been linked to MIC.

In the natural environment, microorganisms often exist in a community called a biofilm, which is central to the occurrences of biofouling, biodegradation, and biocorrosion. A biofilm consists of extracellular polymeric substances (EPS) and embedded sessile cells. EPS play an important role in biofilm formation, maturation and also maintenance [46,47]. EPS compounds include polysaccharides, proteins, lipids, and nucleic acids, which sometimes form a gel-like slime [48].

Under field conditions, mixed-culture biofilms with a rich microbial diversity are difficult to mitigate [9,49]. Synergistic interactions of different microorganisms in biofilm consortia can cause severe MIC because of nutrient and energy sharing. The symbiotic proliferation of SRB and sulfide-oxidizing bacteria (SOB) was hypothesized to explain severe MIC on 2205 DSS [50]. Fig. 1 shows an example of C1018 carbon steel pitting corrosion by an oilfield biofilm consortium in 7 days in a lab test [49].

It is inaccurate to believe that all biofilms degrade the integrity of metals. *Pseudomonas aeruginosa* biofilms increased the corrosion rate of a nickel–copper alloy but protected a nickel–zinc alloy [51]. *Escherichia coli* and *Geobacter sulfurreducens* biofilms formed a protective barrier on a SS surface enhancing its corrosion resistance [52,53]. Aerobic biofilms can serve as an oxygen barrier slowing down oxygen permeation and thus possibly retarding the corrosion. Biofilms at each stage affect a corrosion process differently. A biofilm sample isolated from a drinking water system accelerated corrosion during the initial 7-day incubation but it offered protection to the pipe after incubating for 30 days [54]. Therefore, a clear link should be established between the microbial community and its influence on the corrosion behavior of different materials.

Table 1
Redox potential^a (E°).

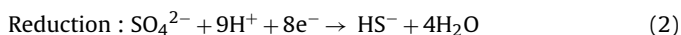
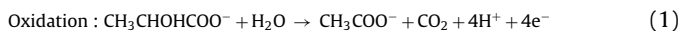
| Redox couple | E° (mV) |
|--|------------------|
| Fe ²⁺ /Fe ⁰ | –447 |
| CO ₂ + acetate/lactate | –430 |
| CO ₂ /formate | –432 |
| CO ₂ /methanol | –370 |
| SO ₄ ^{2–} /HS [–] | –217 |
| CO ₂ /CH ₄ | –244 |
| NO ₂ [–] /NH ₃ | +330 |
| NO ₃ [–] /NH ₃ | +360 |
| 2NO ₃ [–] /N ₂ | +760 |

^a Data from [41,65]. “o” in bioelectrochemistry indicates the condition with 1 M solutes (1 bar gases) except for H⁺, 25 °C and pH 7.

Various mechanisms have been proposed to explain MIC mechanisms. In the classical cathodic depolarization theory (CDT), SRB cells use hydrogenase enzymes to lower the activation energy of the H atom desorption process [55]. This is regarded as the rate-limiting step for MIC by SRB. The CDT can only explain MIC caused by hydrogenase-positive SRB, but it is not applicable to SRB lacking the enzyme. Many MIC researchers embraced this early theory [56–59]. However, the understanding of MIC is hampered by the absence of a clear explanation of the bioelectrochemical processes occurring at the interface between biofilm and metal matrix. To make a step ahead, the mechanism of metal MIC is elucidated from a multidisciplinary perspective in this review. The reasons regarding why and how MIC occurs are explained based on bioenergetics and extracellular electron transfer (EET). Thus, this review provides useful information for corrosion management and risk assessment.

2. Bioenergetics of MIC

Microorganisms require the following principal components to provide energy for their metabolism: an electron donor (energy source) and an electron acceptor [60]. Hydrocarbons and fatty acids (e.g., formate, pyruvate, acetate, methanol and lactate) usually serve as organic carbons for SRB growth [61]. They provide energy and carbon for growth. For hydrogenase-positive SRB, hydrogen gas is an alternative electron donor. SRB usually use sulfate as the terminal electron acceptor, reducing it finally to HS[–] [62,63]. In addition to sulfate, some SRB can also use sulfite, thiosulfate, and elemental sulfur. In addition, some SRB strains may switch to nitrate or nitrite as the terminal electron acceptor [64,65]. The oxidation and reduction reactions for SRB metabolism in the presence of carbon source (using lactate as an example) and sulfate are listed below [65].



Using the redox potentials shown in Table 1, the reaction combining the two reactions above yields a change in the Gibbs free energy (ΔG°) of –164 kJ/mol of sulfate under standard condition. Therefore, sulfate reduction using lactate is a thermodynamically favorable process producing energy for microbial growth.

The E° value of the couple Fe²⁺/Fe⁰ is close to that of the couple CO₂ + acetate/lactate. Consequently, the coupling of iron oxidation with sulfate reduction is thermodynamically favorable. Thus, elemental iron is an electron donor (i.e., energy source) for SRB metabolism.

In 2009, Gu et al. [66] proposed the biocatalytic cathodic sulfate reduction (BCSR) theory, which is the first theory that utilizes bioenergetics to explain the motive behind SRB MIC against carbon steel. The BCSR theory assumes that the electrons released by iron oxidation are transported across the SRB cell wall and finally uti-

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