www.czasopisma.pan.pl PAN POLSKA AKADEMIA NAUK www.journals.pan.pl

Arch. Metall. Mater. **67** (2022), 4, 1355-1358

DOI: https://doi.org/10.24425/amm.2022.141062

N.A.A. JAMALUDDIN[1], M. YUSOFF[1], S.K. WEE[1], M.N. MASRI[1]*

# MECHANISMS OF MICROBIOLOGICAL CORROSION EMPLOYING IRON-REDUCING BACTERIA

Iron-reducing bacteria (IRB) seek to unravel iron corrosion for oil and gas steel pipeline failure. IRB continued to be dominating the microbiological corrosion of iron structures in steel by deteriorating steel surface via Fe(III) reduction. The mechanisms by IRB mediate Fe(III) reduction into Fe(II) for bacterial respiration to contribute to iron steel corrosion. However, the complexity of corrosion is not fully comprehended. It remains controversial due to the corrosion mechanisms proposed by IRB that may induce or inhibit corrosion when engaged with microbial biofilm. In this brief review, understanding microbiological corrosion mechanisms associated with IRB interactions may better understand microbiological corrosion and derive corrosion control.

*Keywords:* Microbiological Corrosion; Iron-Reducing Bacteria

## 1. Introduction

Microbiological corrosion has been a severe effect of the pipeline's failure in the transmission of oil and gas. Recently, microbiological corrosion accounts for more than 20% of corrosion cost, which is around US$2.5 trillion a year [1]. This economic crisis has received the most attention among researchers and corrosion engineers; however, the complexity of the corrosion process influenced by bacteria has become a matter of debate. They could either be inducing or inhibiting corrosion [2-8].

Microbiological corrosion refers to the biodeterioration of a wide range of metallic materials with bacteria's influence [9]. It involves an electrochemical process by which bacteria mediate iron reduction via electron transfer, causing an atom to lose an electron and become ions under favourable environments [10]. At high corrosion rates conditions, iron steel corrosion is followed by forming small holes on the steel surface in the form of localized corrosion referred to as pitting corrosion, thus inducing steel damage for a time.

Corrosion in steel pipelines is influence by bacteria, primarily caused by aqueous medium and the by-products formed via bacterial activities. The presence of bacteria in the system is a prerequisite for microbiological corrosion to occur. Further requirements such as an energy source, a carbon source, an electron donor, an electron acceptor in an aqueous medium facilitate microbiological corrosion with the generating microbial biofilm [11]. The interaction between those components are believed to cause steel pipeline leaks with varying concentration of ions within the biofilm and lead to the electrons to flow.

A preliminary study has discovered the type of bacteria associated with steel pipeline failure referred to as iron-reducing bacteria (IRB). Presently, IRB continues to dominate microbiological corrosion as they evolved extracellular electron transfer (EET) strategies to perform Fe(III) reduction, either direct or indirect actions. Some notable IRB, including *Shewanella oneidensis* and *Geobacter sulfurreducens*, are the most comprehensively studied model bacteria used in the present microbiological corrosion studies that potentially induce corrosion microbial EET strategies [12]. Therefore, this review introduces the fundamental knowledge of microbiological corrosion mechanisms employed by IRB via Fe(III) reduction and its relevant effects. It is either induced or inhibited corrosion in steel pipelines.

## 2. Iron-reducing bacteria

Iron-reducing bacteria (IRB) is a group of facultative anaerobes with such versatile Fe(III)-reducing components in their electron transport systems. IRB related strain, *Shewanella oneidensis* MR-1, has provided insight into its respiratory capabilities to utilize oxygen under aerobic conditions and switch into anaerobic to respire a variety of terminal electron acceptors, including amorphous Fe(III) oxide, Fe(III) citrate,

---

[1] UNIVERSITI MALAYSIA KELANTAN, FACULTY OF BIOENGINEERING AND TECHNOLOGY, 17600 JELI KELANTAN, MALAYSIA

* Corresponding author: najmi.m@umk.edu.my

hematite, goethite, magnetite, nitrate, nitrite and fumarate [13]. In microbiological corrosion, *S. oneidensis* MR-1 is often found on corroded iron structures attributed to mainly their ability to reduce the insoluble Fe(III) forms to soluble Fe(II) forms using ferric ion ($Fe^{+3}$) as electron acceptor under anaerobic conditions, which can either induce or inhibit corrosion [14,15].

## 3. Microbial extracellular electron transfer strategies

Microbial extracellular electron transfer (EET) is a relevant mechanism postulated to induce corrosion of iron structures in steel pipelines employing IRB since IRB cannot incorporate solid materials such as solid iron metal into their cells due to a unique physiological problem, to find alternative pathways to respire anaerobically on largely solid forms of Fe(III) compounds as terminal electron acceptors that presumably unable to contact across their inner membrane of electron transport systems [12,16].

Three modes of EET mechanisms are proposed, as illustrated in Fig. 1. The first mode is the enzymatic reduction of solid Fe(III) compounds by which IRB are directly attached to the metallic surface and transferring electrons via outer membrane redox proteins (Fig. 1A) [12]. The second mode is the direct pathway by transferring electrons via electrically conductive nanowires. The nanowires (50-150 nm in diameter and 10 nm in length) may facilitate electron transfer from the IRB cell surface to directly external Fe(III) compounds without any contact to the metallic surface (Fig. 1B) [17]. The third mode indirectly forms an electron shuttle to transfer an electron to the target metallic surface (Fig. 1C). The variety of potential electron shuttle compounds, including phenazines, flavin derivatives, naturally occurring humic acids, and artificial quinone compounds, are known to work as electron-shuttling by IRB to reduce extracellular Fe(III) compounds [18-20].

## 4. Mechanisms of microbial corrosion induction

There are different mechanisms postulated on how IRB induce corrosion. In this case, IRB derives benefits by reducing the amorphous Fe(III) oxide to soluble Fe(II) under anaerobic conditions, leading to the removal of a thin protective layer of Fe(III) oxide film such as hematite, goethite and magnetite that are formed on the exposed steel surface. The increasing concentration of cells will accelerate the corrosion with a further attack by microbial cells on the steel surface [21].

Furthermore, the capability of IRB that utilize oxygen under aerobic conditions also makes severe localized corrosion in steel pipelines by creating a corrosive environment where oxygen is available. The direct consumption of oxygen by IRB will lead to corrosive surroundings with a higher concentration of oxygen in which can quicken the reduction of steel pipeline [22]. Fig. 2

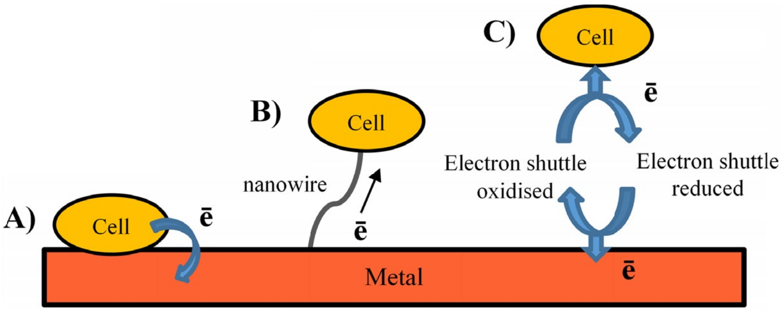

Fig. 1. Illustrated diagram of A) direct attachment of IRB cell to metallic surface via enzymatic reduction B) direct EET by nanowires and C) indirect EET via electron-shuttling compounds

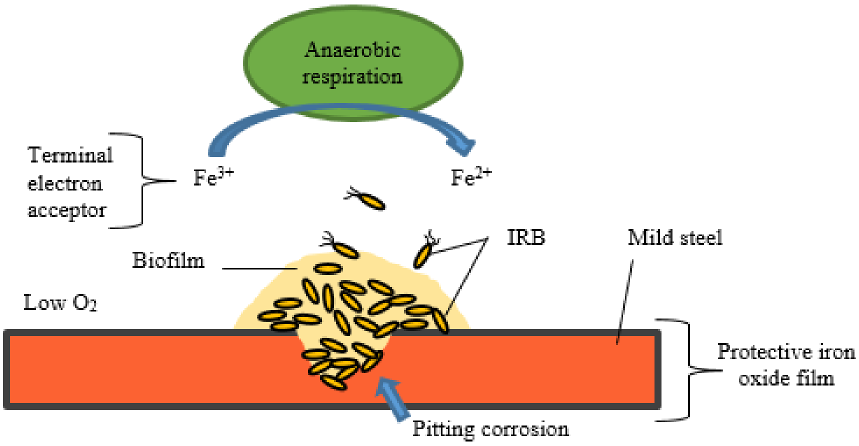

Fig. 2. Schematic diagram of Fe(III) reduction on mild steel pipeline corrosion employed by IRB under anaerobic conditions

summarizes the overall microbiological corrosion mechanisms in the schematic diagram yet to be the most relevant employed by IRB to induce corrosion.

In recent evidence, Salgar-Chapparo et al. [23] conducted an experiment using IRB isolate *Shewanella chilikensis*, which triggered pitting corrosion by producing nitrite via nitrate reduction. The accumulation of nitrite at a higher concentration in a system could induce corrosion rate on the corroded steel surface by increasing the ionic conductivity in the aqueous medium thus, accelerating corrosion [24].

## 5. Biofilm and its relevance to microbial corrosion inhibition

In microbiological corrosion, the corrosion begins with the formation of microbial biofilm on steel surface. Biofilm is multispecies of microbial communities that perform combined processes by which an individual microbe cannot. Biofilm is mainly composed of 95% of water in the form of gel and containing a suspension of microbial cells held together by a thick slime known as extracellular polymeric substance (EPS) [25].

The production of EPS embedded in biofilm is enclosed in a self-produced extracellular polymeric matrix. The EPS matrix helps to improve the microbial adhesion on steel by forming cohesive, three-dimensional polymeric networks that interconnected and transiently immobilized microbial cells [26]. The major components of EPS consist of polysaccharides, lipids and proteins containing functional groups, including carboxylic and amino acids groups, to provide mechanical stability of dynamic structural in biofilms.

Generally, when steel is submerged in aqueous medium, bacteria get attached to the steel surface before forming a strong adhesion of biofilm. The accumulation of inorganic ions and organic compounds embedded in EPS encourage further bacterial growth on steel by generating biofilm consisting sequence of steps, including direct attachment of microbial cells on steel surface, the immobilization of microbial cells to grow, and reproduce by consuming nutrients from their surroundings, and to produce EPS matrix to form biofilm. Finally, the biofilm will grow to a certain size, and some microbes are detached in clumps or "seeding dispersal" to form new areas (Fig. 3).

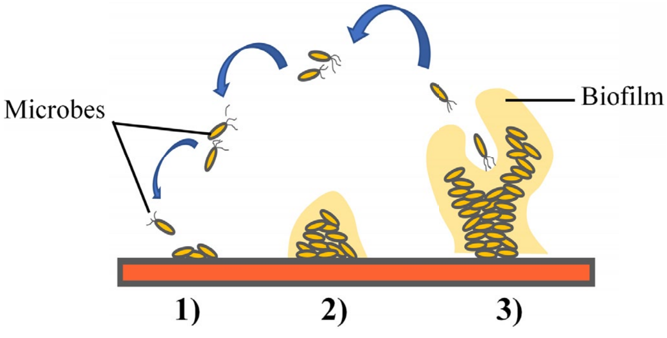

Fig. 3. Sequence of steps in biofilm formation 1) attachment 2) maturation 3) dispersion on steel surface

In time progress, the subject regarding IRB against corrosion engaged with biofilm is still further discussed among researchers. However, several biofilm inhibition mechanisms have been proposed, including synergistic microbial actions in mixed cultures. In the study of Lee et al. [27], IRB inhibits corrosion with the presence of SRB (sulphate-reducing bacteria), a corrosion-inducing bacterium. In mixed culture coexists two bacterial species, *Shewanella oneidensis* MR-1, an iron reducer, and Desulfovibrio desulfuricans G20, a sulphate reducer were able to couple the oxidation of lactate as the electron donor to the reduction of Fe(III) (hydr)oxides and sulphate, respectively, as explained in equations (1) and (2). From these two equations, the mixed culture IRB-SRB inhibited steel corrosion by destroying the corrosive sulphide film produced by SRB within the biofilm. In this case, IRB served as a corrosion agent in corrosion due to $Fe^{3+}$ reduction [28].

$$\frac{1}{4}CH^3CHOHCOO^- + Fe(OH)_3 + \\ + 2H^+ \rightarrow \frac{1}{4}CO^2 + \frac{1}{4}\,H_2O \tag{1}$$

$$2CH_3CHOHCOOO^- + SO_4^{2-} + \\ + 2H^+ \rightarrow 2CH^3COO^- + 2CO^2 + HS^- + 2H_2O \tag{2}$$

Several biofilm-forming *Bacillus sp.* such as *Bacillus subtilis* and *Bacillus brevis* have been reported to secrete types of antimicrobials, polymyxins and gramicidin S in their microbial biofilms [29]. These antimicrobials act as physical barriers by breaking up the bacterial cytoplasmic membrane of corrosive sulphate-reducing bacteria (SRB) in mixed culture. Meanwhile, *Bacillus licheniformis* was significantly reduced the corrosion rate by 90% of aluminium 2024 through secretion of corrosion inhibiting polymer, γ-polyglutamate at medium pH attributed to its unique biofilm [30]. The γ-polyglutamate is a homopolymer of glutamic acid bonded with amide linkages between glutamate γ-carboxyl and α-amino groups. It is found that γ-polyglutamate has a great metal-binding affinity to $Fe^{3+}$ thus, inhibiting the corrosion process in aluminium 2024.

The formation of microbial biofilm at the metal interface is correspondingly changing the metal's chemical and electrochemical environment, such as concentrations of ions, oxygen, and pH, resulting in a change in the electrochemical behaviour of the steel [31-32]. Moreover, the role of EPS capability to bind to the metallic ions via electrochemical reactions will affect the overall electrochemical process of the metal interface, which contributes to the corrosion process.

## 6. Conclusion

This review deals with microbiological corrosion mechanisms employing iron-reducing bacteria (IRB) for their roles in corrosion induction and inhibition. Some IRB species, including *S. oneidensis* MR-1, *S. chilikensis* and *G. sulfurreducens*, are known to be involved in microbiological corrosion due to

Fe(III)-reducing properties in their electron transport chain-linked metal reduction to generate energy, causing the severity of pitting corrosion in steel. On the contrary, when exposed to an anaerobic environment, *Bacillus sp.* derive benefits with their unique biofilm-forming features when lacking nutrients in harsh environments. The benefits of biofilms lead to many significant metal surface changes in an aqueous environment and result in the change of electrochemical behaviour, thus inhibiting corrosion in steel. However, the mechanisms of corrosion inhibition associated with IRB when engaged with microbial biofilm remained unclear. Hence, further investigation is recommended to unravel corrosion with IRB interactions in the future.

### Acknowledgement

The authors would like to express heart-felt gratuity to Universiti Malaysia Kelantan for UMK Raising Star Scheme in financial supported.

## REFERENCES

[1] J. Bhandari, F. Khan, A. Rouzbeh, V. Garaniya, R. Ojeda, J. Loss Prev. Process Ind. **37**, 39-62 (2015).

[2] D. Enning, J. Garrelfs J, Appl. Environ. Microbiol. **80** (4), 1226-1236 (2014).

[3] L.K. Herrara, H.A. Videla, Int. Biodeterior. Biodegradation. **63** (7), 891-895 (2009).

[4] S.R.A. Saupi, M.A. Sulaiman, M.N. Masri, Journal of Tropical Resources And Sustainable Science. **3**, 14-18.

[5] S.R. Ahmad Saupi, N.A.H. Abdul Haris, M.N. Masri, M.A. Sulaiman, Materials Science Forum. **840**, 309-314 (2016).

[6] M.N. Masri, M.F. Samsudin, M.A. Sulaiman, M. Mohamed, M.F. Mohd Amin, Key Engineering Materials. **694**, 172-176 (2016).

[7] S.R.A. Saupi, N.A.H.A. Haris, M.N. Masri, M.A. Sulaiman, M.B.A. Bakar, Mater. Sci. Forum. **840**, 309-3 (2016).

[8] M.N. Masri, A. Hamid, M. Mohamed, M. Mohamad, S.A. Sobri, IOP Conference Series: Earth and Environmental Science. **765** (1), 012088.

[9] D. Blackwood, Corros. Mater. Degrad. **1** (1), 59-76 (2018).

[10] N.A.H.A. Haris, A.R.S. Fatimah, M.A. Sulaiman, M.N. Masri, J. Trop. Resour. Sustain. Sci. **3**(1), 29-33 (2015).

[11] R. Javaherdashti, Eng. Mater. Processes. Springer, Cham. (2017)

[12] S. Kato, Microb. Biotechnol. **9** (2), 141-148 (2016).

[13] T. Martial, J.S. Beckler, E. Carey, J.L. Burns, C.M. Fennessey, T.J. DiChristina. J. Inorg. Biochem. **101** (11-12), 1760-67 (2007).

[14] J. Philips, N. Van den Driessche, K. De Paepe, A. Prévoteau, J.A. Gralnick, J.B.A. Arends, K. Rabaey. Appl. Environ. Microbiol. **84** (20), 1-19 (2018).

[15] A. Ibrahim, K. Hawboldt, C. Bottaro, F. Khan, Corros. Eng. Sci. Technol. **53** (8), 549-563 (2018).

[16] T.J. DiChristina, J.K. Fredrickson, J.M. Zachara, Mol. Geomicrobiol. **59**, 27-52 (2005).

[17] S. Pirbadian, S.E. Barchinger, K.M. Leung, H.S. Byun, Y. Jangir, R.A. Bouhenni, et al. Proc Natl Acad Sci USA. **111**, 12883-12888 (2014).

[18] E.E Roden, A. Kappler, I. Bauer, J. Jiang, A. Paul, R. Stoesser, H. Konishi, H.F. Xu, Nat. Geosci. **3**, 417-421 (2010).

[19] M.E. Hernandez, A. Kappler, D.K. Newman, Appl. Environ. Microbiol. **70**, 921-928 (2004).

[20] K. Richter, M. Schicklberger, J. Gescher, Appl. Environ. Microbiol. **78**, 913-921 (2012).

[21] J. Starosvetsky, R. Kamari, Y. Farber, D. Bilanović, R. Armon, Corros. Sci. **102**, 446-454 (2016).

[22] C. Cote, O. Rosas, R. Basseguy, Corros. Sci. **94**, 104-113 (2015).

[23] S.J. Salgar-Chaparro, A. Darwin, A.H. Kaksonen, L.L. Machuca. Sci. Rep. **10** (1), 1-15 (2020).

[24] L.D. Young, W.C. Kim, J.G Kim, Corros. Sci. **64**, 105-14 (2012).

[25] J. Lin, R. Ballim, Afr. J. Biotechnol. **11** (91), 15736-15747 (2012).

[26] H.C. Flemming, Colloids Surf. B. **86**, 251-259 (2011).

[27] A.K. Lee, M.G. Buehler, D.K. Newman. Corros. Sci. **48** (1), 165-78 (2006).

[28] E. Valencia-Cantero, Eduardo, J.J. Peña-Cabriales. J. Microbiol. Biotechnol. **24** (2), 280-86 (2014).

[29] U. Eduok, M. Khaled, A. Khalil, R. Suleiman, B. El Ali, RSC Adv. **6** (22), 18246-18256 (2016).

[30] D. Örnek, A. Jayaraman, B. Syrett, C.H. Hsu, F. Mansfeld, T. Wood, Appl. Microbiol. Biotechnol. **58** (5), 651-657 (2002).

[31] R. Zuo, Appl. Microbiol. Biotechnol. **76** (6), 1245-1253 (2007).

[32] N. Jamlus, M.N. Masri, S.K. Wee, N.F. Shoparwe, IOP Conference Series: Earth and Environmental Science. **765** (1), 012115 (2021).