Chapter 4
Microbiologically Influenced Corrosion (MIC)

Abstract In this chapter essential elements of Microbiologically influenced corrosion that are required to know by both researchers and engineers are discussed.

Keywords Importance of MIC · Bacterial characterisation features and its engineering importance · Biofilm formation and its dynamic structure · SCC and the role of bacteria in it · SRB and their contribution to MIC · Dual role of IRB in MIC · Possible role of magnetotactic bacteria in corrosion · Role of Clostridia in MIC

4.1 Introduction

One type of corrosion that can be very harmful to almost all engineering materials is what is called microbiologically influenced corrosion, or briefly, MIC.[1] The term MIC must be misleading into the idea that it is only micro-organisms that are capable of influencing corrosion, in fact, biofouling which is a more general term can be used to study both the microbiological and macrobiological growths that happen on surfaces and can show both the enhancing or inhibiting effects.[2]

MIC and the way it affects corrosion has always been a matter of debate. For example, while acid production by bacteria is presumed to be one of the ways by

---

[1] In 1990, NACE officially accepted the term "Microbiologically Influenced Corrosion" to address this type of corrosion (see: Materials Performance (MP), September 199, p 45). This type of corrosion is also called "microbiologically induced corrosion", microbial corrosion or biocorrosion. In this book, all of these terminologies will be used interchangeably.

[2] Little BJ, Lee J, Ray R (2007) How marine condition affect severity of MIC of steels. In: MIC—an international perspective symposium. Extrin Corrosion Consultants-Curtin University, Perth-Australia, 14–15 Feb 2007.

R. Javaherdashti, *Microbiologically Influenced Corrosion*,
Engineering Materials and Processes, DOI 10.1007/978-3-319-44306-5_4

which corrosion can be enhanced, some researchers[3] in their experience with aerobic *Pseudomonas* sp. have reported that acid production was not a major cause of corrosion and some[4] have pointed out that the presence of bacteria was not "an important factor in the deterioration of steels". It seems that it is not easy all the time to come up with a clear, once-forever-true explanation of the impact of bacteria on corrosion. As a matter of fact, such relatively confusing outcomes have helped to show MIC as a puzzle to some and to others as an "industrial joke" that is used when there is no other explanation for the failure.

This chapter will deal with MIC, its definition and importance and how historically both our understanding of and research methods for the study of MIC have evolved. We will then have a look at the parameters that can be used for categorising bacteria, and also the steps involved in biofilm formation. After discussing the ways by which biofilms can both accelerate and decelerate corrosion, at the end of the chapter, we will look at three examples of bacteria that are involved in corrosion, the well-known SRB (sulphate-reducing bacteria), the rather "shy", infamous IRB (iron-reducing bacteria) and almost unknown magnetic bacteria.

4.2 Definition of MIC

Microbiologically Influenced Corrosion (MIC) has been defined in many ways which more or less are similar to each other. Bearing in mind that the term "micro-organism" actually refers to bacteria, cyanobacteria, algae, lichens and fungi,[5] some of the definitions for MIC are as follows:

---

[3] Franklin MJ, White DC, Isaacs H (1991) Pitting corrosion by bacteria on carbon steel, determined by the scanning vibrating electrode technique. Corr Sci 32(9):945–952. While the authors have ruled out the effect of the acid produced by the bacteria on corrosion acceleration, they have suggested that in the presence of an aerobic heterotrophic bacterium, repassivation of pits does not happen but pit growth continues. They nominate pit propagation in the presence of bacteria as the main mechanism for observing the drop in carbon steel's open circuit potential (OCP) and polarisation resistance.

[4] Sandoval-Jabalera R, Nevarez-Moorillon GV, Chacon-Nava JG, Malo-Tamayo JM, Martinez-Villafane A (2006) Electrochemical behaviuor of 1018, 304 and 800 alloys in synthetic wasterwater. J Mex Chem Soc 50(1):14–18. The researchers have reported, however, that the biofilm formed by the bacteria in their study could have a protecting rather than a deteriorating effect.

[5] Sand W (1997) Microbial mechanisms of deterioration of inorganic substrates—a general mechanistic overview. Int Biodeterior Biodegradation 40(2–4):183–190.

- MIC is an electrochemical process whereby micro-organisms may be able to initiate, facilitate or accelerate corrosion reactions through the interaction of the three components that make up this system: metal, solution and micro-organisms[6]
- MIC refers to the influence of micro-organisms on the kinetics of corrosion processes of metals, caused by micro-organisms adhering to the interfaces (usually called "biofilm"). Prerequisites for MIC are the presence of micro-organisms. If the corrosion is influenced by their activity, further requirements are: (I) an energy source, (II) a carbon source, (III) an electron donator, (IV) an electron acceptor and (V) water.[7]
- MIC is the term used for the phenomenon in which corrosion is initiated and/or accelerated by the activities of micro-organisms.[8]

What can be inferred from the above-mentioned sample definitions are the following:

1. MIC is an electrochemical process,
2. Micro-organisms are capable of affecting both the extent, severity and course of corrosion,
3. In addition to the presence of micro-organisms, an energy source, a carbon source, an electron donator, an electron acceptor and water must be also present to initiate MIC.

We will limit our study in this book to the effect that certain bacteria can have on corrosion. So, in this sense, MIC can be taken as an example of micro-fouling to differentiate it from macro-fouling.[9] However, for the reasons that will be understood towards the end of this chapter, we will define MIC as "an electrochemical type of corrosion in which certain micro-organisms have a role, either enhancing or inhibiting".

---

[6] de Romero MF, Urdaneta S, Barrientos M, Romero G (2004) Correlation between desulfovibrio sessile growth and OCP, hydrogen permeation, corrosion products and morphological attack on iron, Paper No. 04576, CORROSION 2004, NCAE International.

[7] Beech I, Bergel A, Mollica A, Flemming H-C (Task Leader), Scotto V, Sand W, "Simple Methods for The Investigation of the Role of Biofilms in Corrosion", Brite Euram Thematic Network on MIC of Industrial Materials, Task Group 1, Biofilm Fundamentals, Brite Euram Thematic Network No. ERB BRRT-CT98-5084, September 2000. See also footnote 31.

[8] Li SY, Kim YG, Jeon KS, Kho YT, Kang T (2001) Microbiologically influenced corrosion of carbon steel exposed to anaerobic soil. CORROSION 57(9):815–828, Sept 2001.

[9] For more on macro-fouling and its effects on corrosion see, for example, Powell C (2006) Review of splash zone corrosion and biofouling of C70600 sheathed steel during 20 years exposure. In: Proceedings of EuroCorr 2006, 24–28, Sept 2006, Maastricht, the Netherlands, and Little BJ, Lee J, Ray R (2007) How marine condition affect severity of MIC of steels. In: MIC—an international perspective symposium. Extrin Corrosion Consultants-Curtin University, Perth-Australia, 14–15 Feb 2007, also especially; Palraj S, Venkatacahri G (2006) Corrosion and biofouling characteristics of mild steel in mandapam waters. Mater Performance (MP) 45(6): 46–50. In their paper, Palraj and Venkatacahri rank Mandapam first in corrosivity (0.244 mmpy) and third in biofouling. They are also reporting that in their study mild steels exposed to natural seawater for periods of quarterly, semi-annually and annually have undergone uniform corrosion.

4.3 Importance of MIC

MIC can be observed in almost all environments such as soil, fresh water, seawater and all industries such as oil, power generation and marine industries.[10]

MIC is believed to account for 20 % of the damage caused by corrosion.[11] On the basis of Gross National Product (GNP), annual MIC-related industrial loss in Australia, for instance, is estimated to be AUD$6b[12] (about US$5b). A 1954 estimate of MIC loss in buried pipelines, for instance, puts a figure between 0.5 and 2.0 billion US dollars a year, a figure that can only have increased since then.[13] It has been suggested that[14] overall loss to the oil and gas industry could be over US $100 million per annum.

Biocorrosion has been estimated to be responsible of 10 % of corrosion cases in the UK.[15] MIC has caused a lifetime reduction of flow lines in Western Australia from the designed +20 years to less than 3 years.[16] Also, microbial corrosion has been addressed as one of the major causes of corrosion problems of underground pipelines.[17]

Sulphate-reducing bacteria (SRB), a notorious corrosion-enhancing bacteria, has been reported to be responsible for extensive corrosion of drilling and pumping machinery and storage tanks (see footnote 13).[18] SRB have also been reported to contaminate the crude oil resulting in increasing the sulphur level of fuels. These bacteria are important in secondary oil recovery processes, where bacterial growth in injection waters can plug machinery used in these processes. It has also been

---

[10] Javaherdashti R (1999) A review of some characteristics of MIC caused by sulphate-reducing bacteria: past, present and future. Anti-Corr Methods Mater 46(3):173–180.

[11] Flemming H-C (1996) Economical and technical overview. In: Heitz E, Flemming H-C, Sand W (eds) Microbially influenced corrosion of materials. Springer-Verlag Berlin, Heidelberg.

[12] Javaherdashti R, Singh Raman RK (2001) Microbiologically Influenced corrosion of stainless steels in marine environments: a materials engineering approach. In: Proceedings of engineering materials 2001, the institute of materials engineering, Australia, 23–26 Sept 2001.

[13] Singleton R (1993) The sulfate-reducing bacteria: an overview. In: The sulfate-reducing bacteria: contemporary perspectives. Springer-Verlag New York Inc.

[14] Maxwell S, Devine C, Rooney F, Spark I (2004) Monitoring and control of bacterial biofilms in oilfield water handling systems, Paper No. 04752, CORROSION 2004, NCAE International, 2004. Tributsch et al. quote a work by WK Choi and AE Torma where in the US industry, an annual loss of about US$200 billion is attributed to MIC, see Tributsch H, Rojas-Chapana JA, Bartels CC, Ennaoui A, Hofmann W (1998) Role of transient iron sulfide films in microbial corrosion of steels. CORROSION 54(3):216–227, March 1998.

[15] de Romero M, Duque Z, de Rincon O, Perez O, Araujo I, Martinez A (2000) Online monitoring systems of microbiologically influenced corrosion on Cu-10 % Ni alloy in chlorinated, brackish water. CORROSION 55(8):867–876.

[16] Cord-Ruwisch R (1996) MIC in hydrocarbon transportation systems. CorrosionAustralasia 21 (1):8–12, Feb 1996.

[17] See footnote 25.

[18] Javaherdashti R, Sarioglu F, Aksoz N (1997) Corrosion of drilling pipe steel in an environment containing sulphate-reducing bacteria. Intl J Pres Ves Piping 73:127–131.

suggested that these micro-organisms may play a role in biogenesis of oil hydrocarbons (see footnote 13).

MIC failures could have ecological impacts as well such as loss of tritiated D_2O (Deuterium Oxide or Heavy Water) to the environment.[19] Sulphate-reducing bacteria have been responsible for massive fish kills, killing of sewer workers by development of "poisonous dawn fogs", and killing of rice crops in paddies via oxygen depleting (see footnote 13).

Another interesting application of MIC is in military where genetically engineered corrosion-enhancing bacteria could be used to corrode the opposite forces machinery and facilities so that the logistics of the enemy forces would be paralysed. This aspect, known as "anti-material weaponry", has been discussed in length elsewhere.[20]

4.4 Historical Profile of Advances in Understanding MIC

The role of micro-organisms in corrosion was not investigated till the late nineteenth century. In fact, several reports of corrosion resembling MIC have been found that date back to the mid-1800s.[21] We refer to this era as "historical", Fig. 4.1. During the contemporary era (from the 20s to the 60s) MIC had been identified and studied. In 1910, Gains considered MIC to explain very high sulphur content of corrosion products from the Castgill aqueduct in the USA, in fact as early as those years, the role of SRB in MIC had been identified.[22]

More detailed investigations on MIC started as early as 1923 with R. Stumper's report, to be followed in about 1940 by R.L. Starkey and K.L. Wight who indicated that oxidation-reduction (redox) potential was the most reliable indicator of MIC.[23]

---

[19] Angell P, Urbanic K (2000) Sulphate-reducing bacterial activity as a parameter to predict localized corrosion of stainless alloys. Corr Sci 42:897–912.

[20] Javaherdashti R (2004) On the role of MIC in non-lethal biological war techniques. In: Proceedings of weapons, webs and warfighters, land warfare conference 2004, 27–30 Sept 2004, Melbourne, Australia.

[21] Walsh D, Pope D, Danford M, Huff T (1993) The effect of microstructure on microbiologically influenced corrosion. J Mater (JOM) 45(9):22–30, Sept 1993. In this paper, it is reported that in 1891 the role of acids of microbial origin on the corrosion of lead-sheathed cable had been suggested.

[22] Stott JFD (1993) What progress in the understanding of microbially induced corrosion has been made in the last 25 years? a personal viewpoint. Corr Sci 35(1–4): 667–673.

[23] Fitzgerald III JH (1993) Evaluating soil corrosivity—then and now. Mater Performance (MP) 32 (10):17–19, Oct 1993. It is also interesting to note that Hadley in early 1940s and Wanklyn and Spruit in early 1950s were among the first who used open circuit potentials as a function of time for the steel specimens put inside a culture of SRB, see, McKubre MCH, Syrett BC (1986) Harmonic impedance spectroscopy for the determination of corrosion rates in cathodically protected systems. Corrosion Monitoring in Industrial Plants Using Nondestructive Testing and Electrochemical Methods, ASTM STP 908, Moran GC, Labine P (eds) American Society for Testing and Materials, Philadelphia.

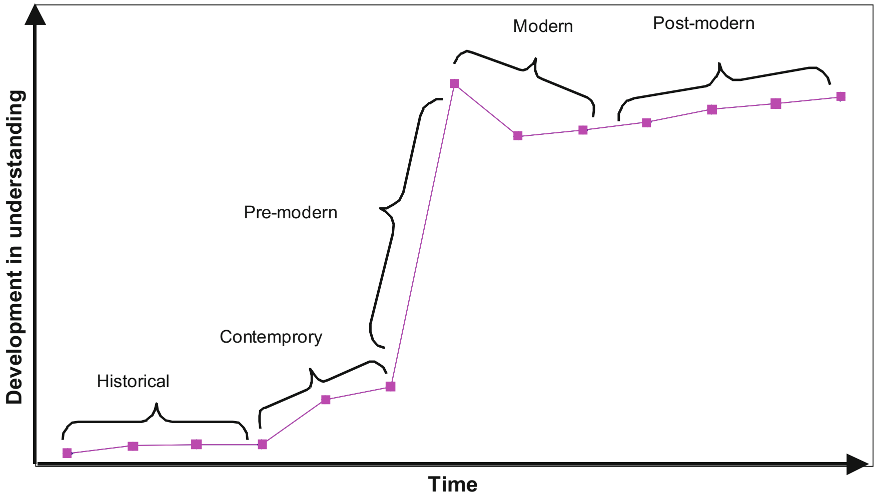


Fig. 4.1 Milestones in time to mark development of ideas and techniques for studying MIC

About three years after the discovery of the enzyme hydrogenase[24] in 1931 (see footnote 22), the first MIC case of failure of underground pipelines was identified.[25] The same year, 1934, was the year in which the first electrochemical interpretation of MIC, proposed by Von Wolzogen Kuhr and Van der Vlugt, provided significant evidence that anaerobic corrosion was caused by the activity of SRB. The two scientists suggested a theory that was named "cathodic depolarisation theory" or briefly CDT, this theory is also known as the "classical theory".[26]

The years following the CDT time were spent on challenging the theory. As Videla[27] put it "during the 1960s and the beginning of the 1970s, the research on MIC was devoted either to objecting or to validating" corrosion by SRB as formulated by CDT. It was during these years when electrochemical techniques such

---

[24] Hydrogenase is an enzyme that catalyses the reversible oxidation of molecular hydrogen and it is present in many anaerobes but it is particularly active in some SRB.

[25] Li SY, Kim YG, Kho YT (2003) Corrosion behavior of carbon steel influenced by sulfate-reducing bacteria in soil environments, Paper No. 03549, CORROSION 2003, NACE International.

[26] Stott JFD, Skerry BS, King RA (1988) Laboratory evaluation of materials for resistance to anaerobic corrosion caused by sulphate reducing bacteria: philosophy and practical design. In: Francis PE, Lee TS (eds) The use of synthetic environments for corrosion testing, ASTM STP 970, pp 98–111, ASTM, 1988. Also see footnote 10 and the references given there.

[27] Videla HA (2007) Mechanisms of MIC: Yestrday, Today and Tomorrow. In: MIC—an international perspective symposium. Extrin Corrosion Consultants-Curtin University, Perth-Australia, 14–15 February 2007.

as polarisation measurements were applied for the first time in MIC-related studies. While Booth and Tiller produced evidence for CDT (see footnote 25) in the early 1960s, King and Miller minimised the role of SRB in corrosion by putting more emphasis on the corrosion product iron sulphide in 1971 (see footnote 26). The mid-1970s is marked with Costello's work who introduced an alternative reaction of reduction of biogenic hydrogen sulphide,[28] Castello basically kept Miller and King's theory but instead of hydrogen evolution as the cathodic reaction, he involved hydrogen sulphide produced by the bacteria (see footnotes 26, 27).

Premodern times, the 80s, may be considered as to be a real "boom" in MIC studies. By 1980s the impact of stagnant hydrotest conditions on inducing MIC (or more accurately, microbially assisted chloride pitting corrosion) into stainless steel at chloride ion concentrations as low as 200 mg per litre was quite well known (see footnote 26). The 80s also produced the opportunity for more effective communication among almost all disciplines involved in MIC studies ranging from metallurgy and materials science to microbiology and chemistry. This was enhanced by an increase in the number and quality of experimental studies carried out on MIC. Videla has done a valuable review on this matter (see footnote 27).

The postmodern era covers the 90s and beyond. Some of the characteristic activities of this era are such as application of rather sophisticated devices such as atomic force microscope (AFM) in addition to scanning electron microscope (SEM) and techniques such as energy dispersive X-ray analysis (EDXA)[29] and X-ray diffraction (XRD) (see footnote 29),[30] and electron microprobe analysis in MIC investigations and studies.

In principle, the postmodern era can be said to have the following characteristics (see footnote 27):

- Development of new methods for laboratory and field assessment of MIC,
- Use of micro-sensors for chemical analysis within biofilm,
- Application of fibre optic microprobes for finding the location of the biofilm/bulk water interface,
- Use of scanning vibrating microscope (SVM) for mapping of electric fields,
- Application of advanced microbiological techniques such as DNA probes,

---

[28] King RA (2007) Microbiologically induecd corrosion and biofilm Interactions. In: MIC—an international perspective symposium. Extrin Corrosion Consultants-Curtin University, Perth-Australia, 14–15 Feb 2007.

[29] EDXA technique detects elements, whereas XRD can be used for crystalline compounds.

[30] Ibid footnote 26.

- Application of environmental scanning electron microscope (ESEM), confocal laser microscope (CSL), AFM such that the biofilm and its interactions can be observed in real time, allowing to profile oxygen concentration within biofilms.

The author would like to also add that in the 90s (especially second half of it and early years of the twenty-first century) researchers have seemingly freed themselves from the paradigm of taking SRB as the most important bacteria in MIC, in contrast to a trend that was predominant during the 80s. In their iconoclast paper[31] in late 1990s, Little and Wagner correctly named such beliefs as “myth”. Nowadays, a reasonable amount of work has been generated to consider the effects that bacteria other than SRB can have on corrosion. Examples of such bacteria will be discussed in this chapter with a particular interest in iron-reducing bacteria.

4.5 Categorising Bacteria

Microbiologists use some “features” to differentiate various types of bacteria from each other. Some of these categorising factors are[32]

Shape and appearance:

(1) Vibrio: comma-shaped cells.
(2) Bacillus: rod-shaped cells.
(3) Coccus: round-shaped cells.
(4) Myces for filamentous fungi-like cells, etc.

Temperature:

(1) Mesophile: the bacteria that grow best at 20–35 °C.
(2) Thermophile: the bacteria that show activity at temperatures above 40 °C.

Oxygen consumption:

(1) Strict or obligate anaerobes, which will not function in the presence of oxygen.
(2) Aerobes which require oxygen in their metabolism.
(3) Facultative anaerobes which can function either in the absence or presence of oxygen.
(4) Micro-aerophiles, which use low levels of oxygen.

---

[31] Little BJ, Wagner P (1997) Myths related to microbiologically influenced corrosion. Mater Performance (MP)36(6):40–44, June 1997.

[32] Geesey GG (1993) Biofilm formation. In: A practical manual on microbiologically-influenced corrosion. In: Kobrin G (ed), NACE, Houston, TX, USA.

Fig. 4.2 Culture development according to oxygen consumption, *1*. the zone of strictly anaerobic (Obligate anaerobic), *2*. micro-aerophile band, *3*. Aerobic band and *4*. the facultative anaerobic zone

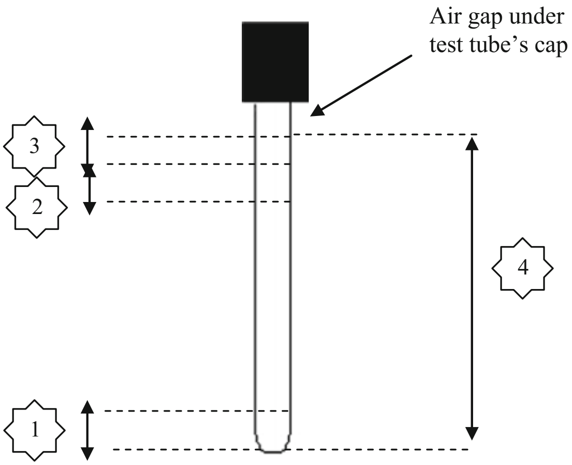
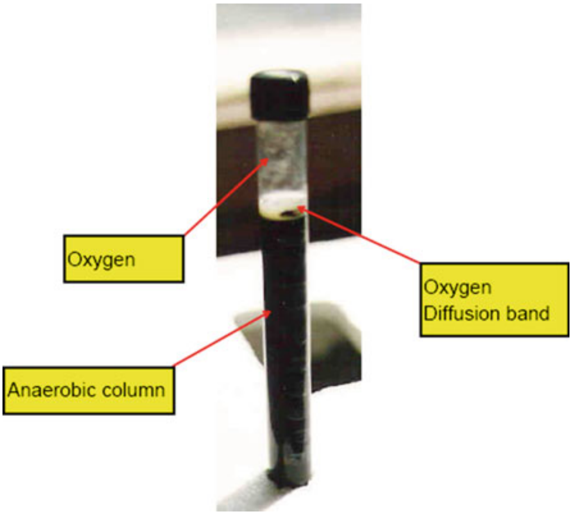


Fig. 4.3 SRB culture developed in a solid environment (Agar) within a test tube. A portion of the *top* section of the sample was taken for transfer purposes. During the culture transfer, oxygen was introduced and diffused into the solid culture. Oxygen did not have a chance to diffuse down furthermore. Note that the bacteria within the oxygen diffusion band are not active as they are not capable of reducing sulphate and producing the *black-coloured* iron sulphide



(5) Aero-tolerants, which are anaerobes that are not affected by the presence of oxygen. This means that if these anaerobic micro-organisms are exposed to oxygen, their metabolism will not be, literally, destroyed by oxygen and they can still be functional.

Figure 4.2 presents the oxygen consumption regimes in a test tube schematically.

Sulphate-reducing bacteria are examples of anaerobic bacteria whereas sulphur-oxidising bacteria are examples of aerobic bacteria, Fig. 4.3.

Table 4.1 Categorising bacteria in accordance with the energy and carbon sources and electrochemical reactants

If the …	…is provided by	… then the growth type is called:
Energy Source	Light	Phototrophic
	Chemical Substances	Chemotrophic
Carbon Source	CO_2	Autotrophic
	Organic Substances	Heterotrophic
Electron donor (that is oxidised)	Inorganic Substances	Lithotrophic
	Organic Substances	Organotrophic
Electron acceptor (that is reduced)	Oxygen	Aerobic
	NO_2^-, NO_3^-	Anoxic
	SO_4^{2-}, CO_2	Anaerobic

Diversity in Metabolism:

(1) The compounds from which the bacteria obtain their carbon for growth and reproduction, these can be alternatively called "nutrients".
(2) The chemistry by which they obtain energy or recharge the oxidative capacity of the cell, i.e. fermentation or respiration, and the terminal electron acceptors used.
(3) The compounds they produce as a result of these processes, e.g. organic acids, reduced metal ions, etc.

Some facultative anaerobic iron-reducing bacteria can not only reduce ferric ions to ferrous, but can also reduce SO_3^{2-}, $S_2O_3^{2-}$ and S^0 to S^{2-}.[33] Many of the recently described iron reducers are capable of using a variety of electron acceptors including nitrate and oxygen in addition to manganese and ferric ions (Mn^{+4} and Fe^{+3}).[34]

---

[33] Obuekwe CO, Westlake DW, Plambeck JA, Cook FD (1981) Corrosion of mild steel in cultures of ferric iron reducing bacterium isolated from crude oil, polarisation characteristics. CORROSION 37(8):461–467.

[34] Little BJ, Wagner P, Hart K, Ray R, Lavoie D, Nealson K, Aguilar C (1997) The role of metal reducing bacteria in microbiologically influenced corrosion, Paper No. 215, CORROSION/97, Houston, TX: NACE, USA.

With regard to the energy source, carbon source and electrochemical reactants, further categorising of the bacterial species is possible. An example of such categorisation (see footnote 7) can be seen in Table 4.1.

4.6 Biofilm Formation and Its Stages

When bacteria attach themselves onto metallic surfaces, they start to form a thin film known as “biofilm” (see footnote 32) that consists of cells immobilised at a substratum, frequently embedded in an organic polymer matrix of microbial origin.[35] Biofilms are believed to typically contain about 95 % water.[36] Figure 4.4 shows the steps of biofilm formation.

Gradual formation of biofilms can change chemical concentrations at the surface of the metal substrate significantly because the physical presence of biofilm exerts a passive effect in the form of restriction on oxygen and nutrients diffusion to the metal surface.

While a biofilm with a thickness of 100 μm may prevent the diffusion of nutrients to the base of a biofilm, a thickness of just 12 μm can make a local spot anaerobic enough for SRB activity in an aerobic system.[37] Active metabolism of the micro-organisms, on the other hand, consumes oxygen and produces metabolites. The net result of biofilm formation is that it usually creates concentration gradients of chemical species across the thickness of the biofilm.[38]

Biofilm formation may take minutes to hours—according to the aqueous environment where the metal is immersed (see footnote 27). The first stage of biofilm formation, that is the formation of the so-called “conditioning film”, is due to electrostatic arrangement of a wide variety of proteins and other organic compounds combined with the water’s chemistry to be followed by the attachment of the bacteria through the EPS to “minimize energy demand from a redundant appendage” (see footnote 28). At this stage, the bacteria are referred to as “sessile bacteria” as opposed to their “floating around” or “planktonic” state before attachment to the conditioning film. It has been reported that the presence of sessile SRB on the metal surface results in a higher corrosion rate than that caused by planktonic bacteria alone.[39]

---

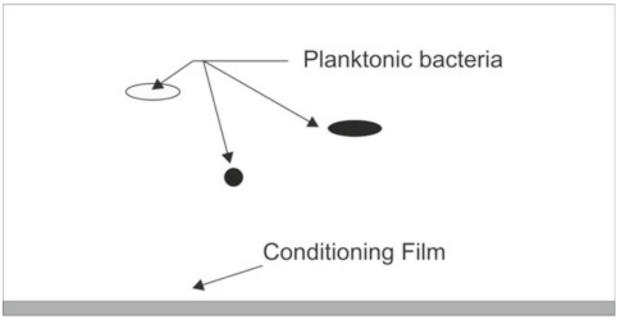
[35] Dexter SC, LaFontain JP (1998) Effect of natural marine biofilms on galvanic corrosion. CORROSION 54(11):851–861.

[36] Guiamet PS, Gomez de Saravia SG, Videla HA (1999) An innovative method for preventing biocorrosion through microbial adhesion inhibition. Int Biodeterior Biodegradation 43:31–35.

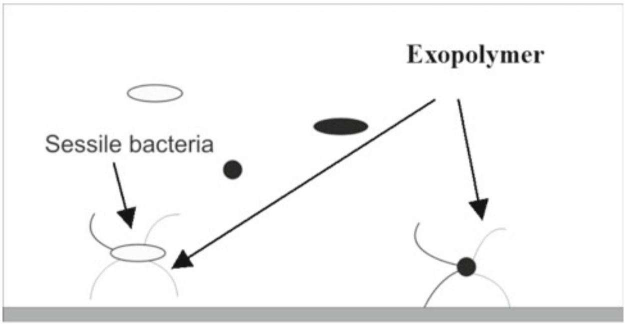
[37] Al-Hashem A, Carew J, Al-Borno A (2004) Screening test for six dual biocide regimes against planktonic and sessile populations of bacteria, Paper No. 04748, CORROSION 2004, NACE International.

[38] Xu K, Dexter SC, Luther GW (1998) Voltametric microelectrodes for biocorrosion studies. CORROSION 54(10):814–823.

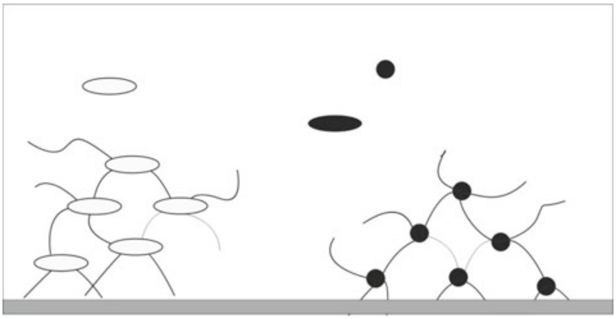
[39] Liu H, Xu L, Zeng J (2000) Role of corrosion products in biofilms in microbiologically induced corrosion of carbon steel. Br Corros J 35(2):131–135.



Stage 1: Conditioning film accumulates on submerged surface.

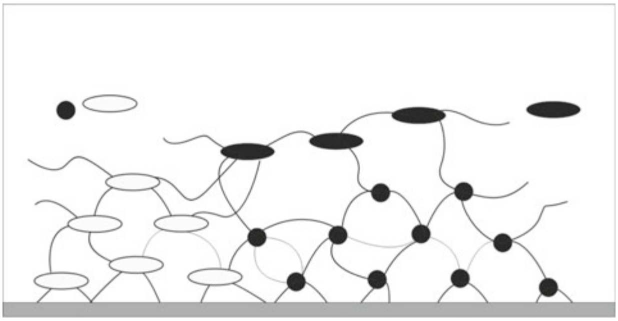


Stage 2: Planktonic bacteria from the bulk water form colonies on the surface and become sessile by excreting exopolysaccharidic substances (EPS). that anchors the cells to the surface.

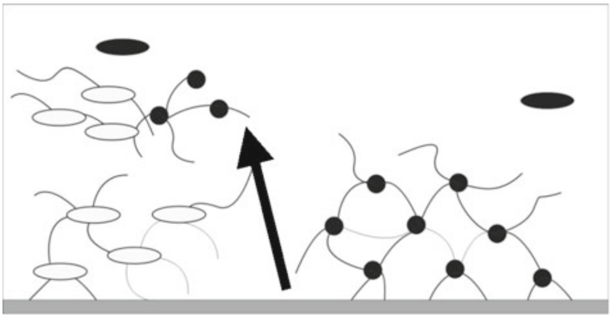


Stage 3: Different species of sessile bacteria replicate on the metal surface.

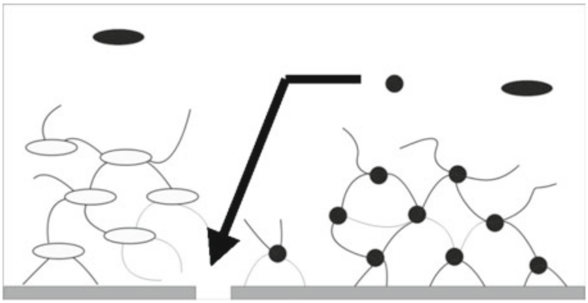
Fig. 4.4 Stages of biofilm development (see footnote 32)



Stage 4: Micro-colonies of different species continue to grow and eventually establish close relationship with each other on the surface. The biofilm increases in thickness and the electrochemical conditions beneath the biofilm begin to vary in comparison with the bulk of the environment.



Stage 5: Portions of the biofilm slough away from the surface.



Stage 6: The exposed areas of the surface are recolonised by planktonic bacteria or sessile bacteria adjacent to the exposed areas.

Fig. 4.4 (continued)

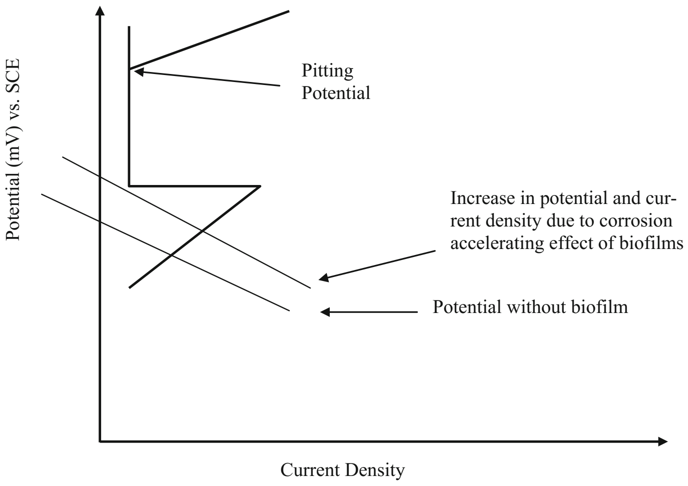


Fig. 4.5 Schematic of the effect of biofilm on the ennoblement of carbon steel in the presence of a microbial culture containing corrosion-enhancing bacteria

When the biofilm is formed and developed, that is stages 1–3 in Fig. 4.2, the outer cells will start to consume the nutrient available to them more rapidly than the cells located deeper within the biofilm so that the activity and growth rate of the latter are considerably reduced (see footnote 39). Therefore, while the outer cells increase in number, the biofilm starts to act like a "net" to trap more and more particles, organic or inorganic. This will increase the thickness of the biofilm even furthermore.

It is believed that formation of exopolysaccharidic substances (EPS) could help the fragile bacteria as a survival technique to protect themselves from external factors that could be life threatening to them (see footnote 28) and, perhaps, increasing their capacity to absorb more food by expanding their surface area through the EPS. The role of the EPS material in enhancing corrosion has been emphasised.[40]

Under biofilm, factors such as pH, dissolved oxygen, etc. may be drastically different from those in the bulk solution resulting in a phenomenon called ennoblement which has been documented for a range of metals and alloys, for example, stainless steel, at various salinities (see footnotes 32 and 35).[41]

---

[40] Taheri RA, Nouhi A, Hamedi J, Javaherdashti R (2005) Comparison of corrosion rates of some steels in batch and semi-continuous cultures of sulfate-reducing bacteria. Asian J Microbiol Biotech Env Sci 7(1):5–8.

[41] Dickinson WH, Lewandowski Z, Geer RD (1996) Evidence for surface changes during ennoblement of type 316L stainless steel: dissolved oxidant and capacitance measurements. CORROSION 52(12):910–920.

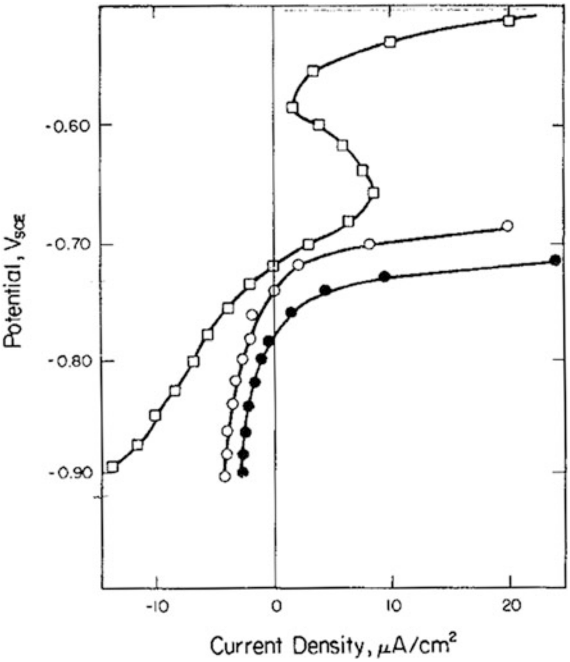


Fig. 4.6 How ennoblement increases susceptibility to pitting, Potentiostatic polarisation curves for AISI 1020 steel in anaerobic artificial seawater(pH = 8)(□), in artificial seawater contaminated by SRB (total sulphide 10^{-3} M, pH = 7.8, redox potential –510 mV) (○), and in artificial seawater with the addition of 10^{-3} M Na_2S (pH = 8.0) (●)(Reprinted, with permission, from STP 908 Corrosion Monitoring in Industrial Plants Using Nondestructive Testing and Electrochemical Methods, copyright ASTM International, 100 Barr Harbour Drive, West Conshohocken, PA 19428,. Also see Salvarezza RC, Videla HA (1980) CORROSION 36:550–554). It is seen that the presence of SRB has caused a positive shift (*dragging down*) the potential thus facilitating pitting in "lower" potentials

Ennoblement can be described as a displacement of the corrosion potential towards more positive potentials[42] that result in increasing susceptibility to pitting, as shown in Fig. 4.6. Videla (see footnote 42) reports that ennoblement involves a change in the cathodic reaction on the metal, caused by the microbial activity within biofilms at the metal/surrounding interface. This phenomenon may serve to clearly justify the effects that biofilm formation can have on changing the electrochemistry of the biofilm-metal system. Despite that there are still debates about the exact mechanism(s) of ennoblement (see footnote 2), Dexter has listed the followings as the proposed mechanisms[43]:

---

[42] Videla HA (1996) Manual of biocorrosion. Chap. 4, CRC press, Inc.

[43] Dexter SC, Chandrasekaran P (2000) Direct measurement of pH within marine biofilms on passive metals. Biofouling 15(4):313–325, 2000. In addition to these mechanisms, there is a mentioning of "enzymatic mechanism" where hydrogen peroxide (produced as a result of

(1) Effect of low pH
(2) Combination of pH with peroxide and low oxygen
(3) Influence of heavy metals
(4) Formation of (Passivating) Siderophores
(5) Manganese dioxide contribution

Little et al. (see footnote 2) have pointed out that ennoblement in fresh and brackish water is related to the microbial deposition of manganese whereas in seawater, this phenomenon may be ascribed to depolarisation of the oxygen reduction reaction that may occur, in effect, due to some of the proposed mechanisms mentioned above such as mechanisms 1, 2 and 4. For example, it is well known that the oxygen reduction potential shifts positive (about 60 mV) for each decrease in pH unit and such a decrease produces a noble shift of 35–40 mV on stainless steel electrodes in seawater (see footnote 43).[44] Figure 4.5 shows how the increase in potential due to biofilm formation can endanger the material to pitting (Fig. 4.6).

Corrosion resistance of stainless steels results from formation of a passive oxide film which is stable in an oxidising environment. Any physico-chemical instability of this oxide film either as a result of change in the chemistry of the environment or formation of cracks and/or scratches on the metal surface provides conditions for formation of an oxygen concentration cell which can result in localised corrosion. An example of chemical change of the environment leading into oxide film instability mentioned above is the effect of chloride ions. Chloride ions can locally damage the protective film on stainless steels.[45]

Steel surfaces can develop biofilms that may form chemical concentration or differential aeration cells resulting in localised corrosion. In addition, if chloride ions are present, the pH of the electrolyte under tubercles (discrete hemispherical mounds (see footnote 32) may further decrease, enhancing localised corrosion. In the presence of certain bacteria such as iron-oxidising bacteria (IOB),[46] under tubercle conditions may become very acidic as Cl^- ions combine with the ferric ions produced by IOB to form very corrosive acidic ferric chloride solution inside the tubercle (see footnote 32).

In summary, the bacteria will initiate localised corrosion cells on the inside surface of the tubercles and the corrosion will progress as a result of the

---

(Footnote 43 continued)

oxidation of glucose) can cause ennoblement of stainless steel, for more details see Landoulsi J, Pulvin S, Richard C, Sabot K (2006) Biocorrosion of stainless steel in artificial fresh water: role of enzymatic reactions. In: Proceedings of EuroCorr 2006, 24–28 Sept 2006, Maastricht, the Netherlands.

[44] Scotto V, Mollica A, A guide to laboratory techniques for the assessment of mic risk due to the presence of biofilms, See footnote 7.

[45] Kovach CW, Redmond JD (1997) High performance stainless steels and microbiologically influenced corrosion, www.avestasheffield.com, acom 1-1997.

[46] Ibid footnote 34.

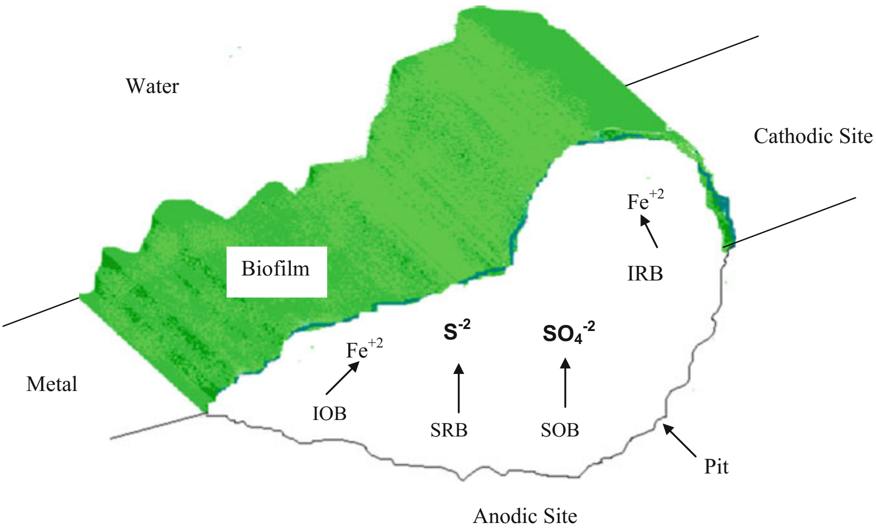


Fig. 4.7 Schematic diagram of possible processes that may occur during pitting of steel resulting from biological activity

concentration of chlorides induced by bacteria and the low pH generated at the base of the pits,[47,48,49] Fig. 4.7 shows schematically how bacterial action can induce anodic and cathodic sites leading into pitting. It must be noted that while different types of bacteria are shown in this figure, and in nature it is possible to have different types of micro-organisms living together, it may not be possible for all the bacterial species shown in the figure to coexist simultaneously.

4.7 How Biofilms Demonstrate Their Effects on Corrosion

Biofilms are contributing to corrosion not only by enhancing the electrochemical conditions and increasing corrosion, but also sometimes by slowing it down. This dual role of biofilms can be puzzling as it is expected that when bacteria are present in a system, they will form biofilms under which the pits thus produced can be contributing to initiation and/or enhancing of different types of corrosion, for example stress corrosion cracking (SCC), where local stresses could be built up well above of the material's yield point at pits acting as stress concentration sites.

---

[47] Pope DH, Morris III EA (1995) Some experiences with microbiologically- influenced corrosion. Mater Performance (MP) 34(5):23–28.

[48] Borenstein SW, Lindsay PB (1987) MIC failure analyses, Paper No. 381, Corrosion/87, Houston, TX: NACE.

[49] Metals Handbook vol 13, Corrosion, 9th edn, ASM, Metals Park, USA, p 122.

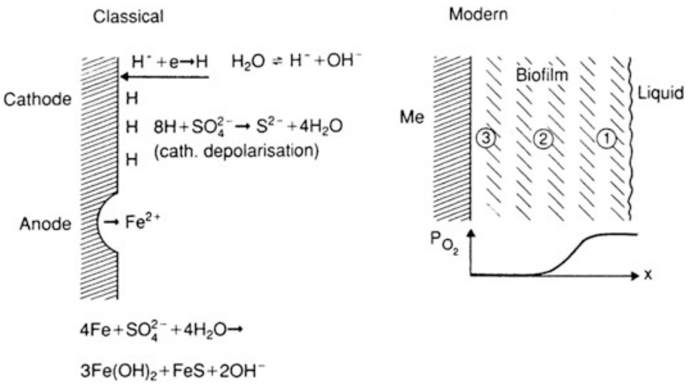


Fig. 4.8 Comparison of classic and modern models of biofilm to explain sulphate reduction ("A Working Party Report on Microbiological Degradation of Materials—And Methods of Pretection", Sect. 4.3.3, European Federation of Corrosion Publications, Number 9, The Institute of Materials, London, England, 1992.)

4.7.1 Enhancing Corrosion

To understand how biofilms can accelerate or decelerate corrosion, an understanding of the structure of biofilms is necessary. In order to explain biofilms structures, some models have been purposed. We will very briefly describe such models below.

4.7.1.1 Biofilm Models

Although MIC and biofilms have been studied for many years, neither the exact mechanisms nor the structure of biofilms are still fully understood. Figure 4.8 compares two conceptual models of sulphate reduction for SRB.

According to the classic model of biofilm, due to depolarisation that occurs as a result of sulphate reduction, the anodic reaction becomes more activated whose net result is the production of "rust" in the form of iron sulphide and creation of anodic site on the metal substrate. However, new theories have recognised that due to the biofilm build-up regions nearby the metal (region 3 in Fig. 4.8) are formed that in comparison with regions 2 and 1, are more anaerobic. This may give a good chance for the establishment of oxygen gradient from outside of biofilm thickness towards inside.[50] Figure 4.9 presents schematically a conceptual biofilm model.

As the model presented in Fig. 4.9 shows, the biofilm is a negatively charged, open structure under which localised corrosion can happen. Models describing

---

[50] Wilderer PA, Characklis WG (1989) Structure and function of biofilms. In: Characklis WG, Wilderer PA (eds) Structure and function of biofilms. John Wiley and Sons, New York, NY, pp 5–17.

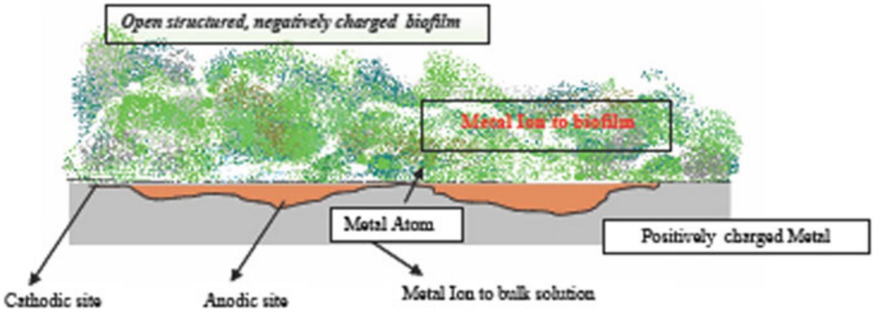


Fig. 4.9 A conceptual model for an open, patchy biofilm structure and its regions

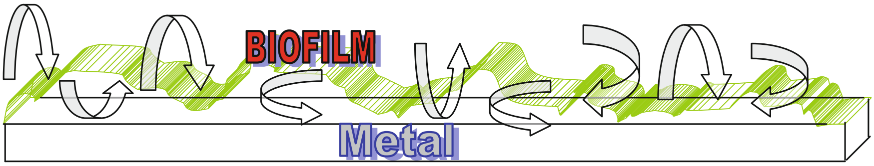


Fig. 4.10 An impression of latest conceptual model of biofilms formed in biotic environments. The arrows present entrance and exits of gases (such as oxygen) and chemical species through the "open" structure of the biofilm

structure and functions of biofilms have been continuously improving. Some researchers,[51,52,53] even believe that cell-free biofilms with exopolymers and function groups, formed within the biofilm, create an environment whose local pH is low enough to favour corrosion.

The more recent model of biofilm assumes a completely open, non-uniform structure where due to non-uniform structure, establishment of gradients is highly possible.[54] Figure 4.10 presents schematically a cross section of one of such new models.

The model in Fig. 4.10 shows biofilms as an open system where transport of gases and particles including chemical species into and out of it is quite possible. In such

---

[51] Ibid footnote 41.

[52] Roe FL, Lewandowski Z, Funk T (1996) Simulating microbiologically influenced corrosion by depositing extracellular biopolymers on mild steel. CORROSION 52(10):744–752, Oct 1996.

[53] Lewandowski Z, Funk T, Roe FL, Little BJ (1994) Spatial distribution of ph at mild steel surfaces using an iridium oxide microelectrode. In: Microbiologically influenced Corrosion Testing", (Continued from footnote 53) Kearns JR, Little BJ (eds) STP 1232, ASTM, 1994, USA. See also Chan G, Kagwade SV, French GE, Ford TE, Mitchell R, Clayton CR (1996) Metal Ion and exopolymer interaction: a surface analytical study. CORROSION 42(12):891–899.

[54] Lewandowski Z, Stoodley P, Altobelli S (1995) Experimental and conceptual studies on mass transport in biofilms. Water Sci Technol 31:153–162.

structures, the easy flow of mater and gas transport across the biofilm allows for establishment of "spots" with high and low concentration of these chemicals or gases.

When these spots have been formed, differential aeration cells and/or differential concentration cells may be formed. The net results of formation of such cells are anodic and cathodic sites where anodic sites will manifest themselves as pits. Although this model also allows for transport of gases and materials like the model presented in Fig. 4.8, it emphasises more on the biofilm as to be a quite open system rather than layers being laid upon each other with different and distinguishable characteristics. Figure 4.11a, b show two examples of biofilms formed by sulphate-reducing bacteria and iron-reducing bacteria on carbon steel. They also compare the abundance of elements that have been traced within these biofilms, probably giving rise to the formation and establishment of electrochemical cells such as concentration cells. The patchy fabric of biofilms may result in the formation of differential aeration cells.

4.7.2 Corrosion Deceleration Effect of Biofilms

Micro-organisms may not always enhance corrosion. The same bacterial species may show both corrosive and protective effects. For example, Hernandez et al.[55] reported the corrosive effects of two microbial species, one of which was *Pseudomonas* sp. By changing certain conditions, the very same micro-organisms were showing protective effects and slowing down corrosion. The same researchers also reported that in the presence of bacteria like aerobic *pseudomonades* sp. and facultative anaerobic *serratia marcescens* in synthetic seawater, corrosion of mild steel is inhibited. The effect seemed to disappear with time in natural seawater. Jack et al.[56] report about monocultures of an aerobic *Bacillus* sp. that induced greater corrosion than that of abiotic environment, but the rate of this corrosion decreased to that of a sterile control after 17 days.

Iron-reducing bacteria (IRB) are a good example of the bacteria that can both accelerate and retard corrosion. These bacteria act by reduction of the generally insoluble Fe^{+3} compounds to the soluble Fe^{+2}, exposing the metal beneath a ferric oxide protective layer to the corrosive environment.[57,58]

---

[55] Hernandez G, Kucera V, Thierry D, Pedersen A, Hermansson M (1994) Corrosion inhibition of steel by bacteria. CORROSION 50(8): 603–608.

[56] Jack RF, Ringelberg DB, White DC (1992) Differential corrosion rates of carbon Steel by combinations of Bacillus sp., *Hania Alvei* and *Desulfovibrio gigas* established by phospholipid analysis of electrode biofilm. Corro Sci 33(12):1843–1853.

[57] Graff WJ (1981) Introduction to offshore structures, Chap. 12, Gulf Pub. Co., Huston, TX, USA.

[58] Obuekwe CO, Westlake DWS, Cook FD, Costerton JW (1981) Surface changes in mild steel coupons from the action of corrosion-causing bacteria. Appl Environ Microbiol 41(3):766–774, March 1981.

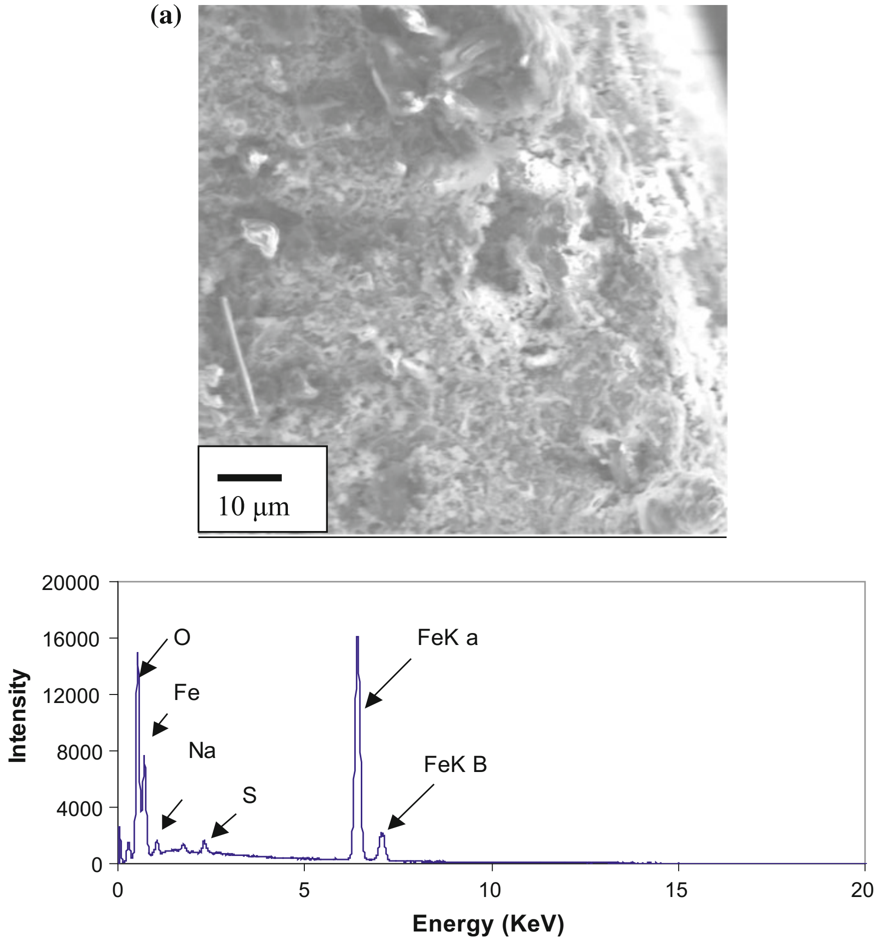


Fig. 4.11 Comparison of biofilms formed by **a** SRB and **b** IRB (from: Javaherdasht R (2006) Making sense out of chaos: general patterns of MIC of carbon steel and bio-degradation of concrete. In: Proceedings of corrosion and prevention 2006 (CAP06), 19–22 Nov 2006, Hobart, Australia. **a** A biofilm formed by SRB (sulphate-reducing bacteria) on carbon steel along with the results of EDXA analysis of the elements found in it. **b** A biofilm formed by IRB (iron-reducing bacteria) on carbon steel along with the results of EDXA analysis of the elements found in it

Pseudomonas spp. are IRB species reported to have corrosive effects.[59,60] However, there is an increasing body of evidence that IRB could actually slow down corrosion.

---

[59] Borenstein SW (1988) Microbiologically influenced corrosion failures of austenitic stainless steel welds. Mater Performance (MP) 27(8):62–66.

[60] Stoecker JG (1993) Penetration of stainless steel following Hydrostatic test. In: G. Kobrin (ed) A practical manual on microbiologically-influenced corrosion. NACE, Houston, TX, USA.

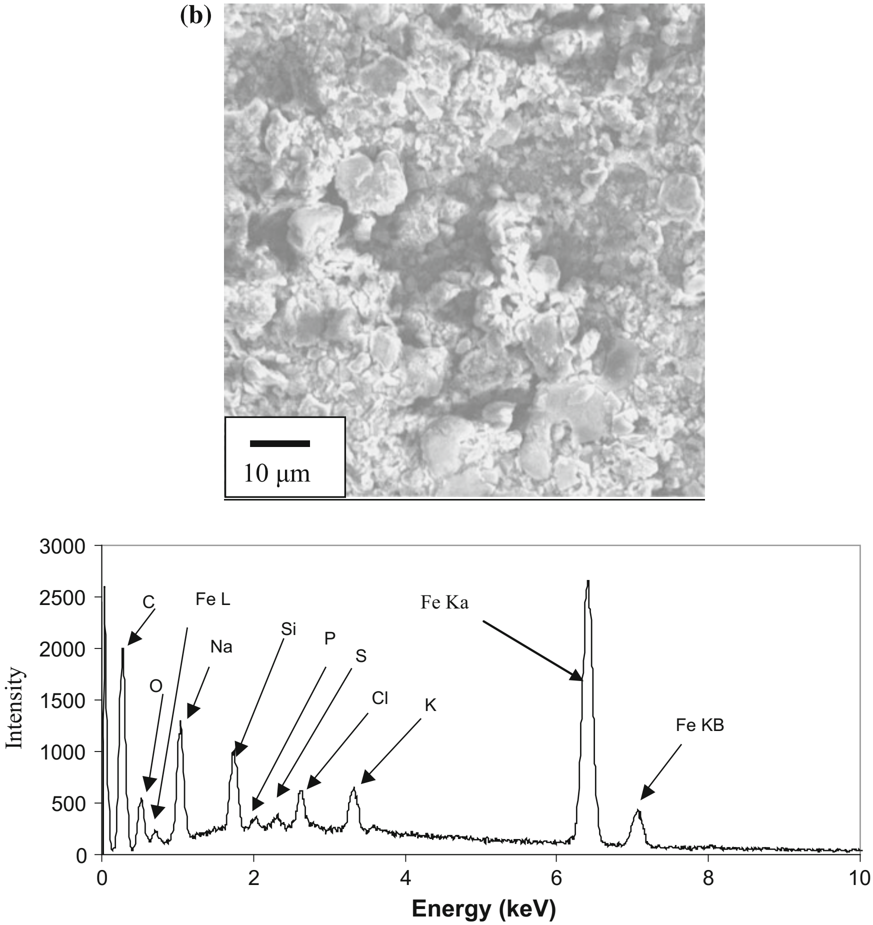


Fig. 4.11 (continued)

Experimental work of Ornek et al.[61] has also shown that with biofilm producing bacteria which can also produce corrosion inhibitors, pitting corrosion of some aluminium alloys could be controlled. It has been reported[62] that two strains of IRB, called S*hewanella algae* and S*hewanella ana,* were able to significantly reduce corrosion of mild steel and brass. The work postulates that the bacterial strains are capable of reducing the rate of both the oxygen reduction and anodic reactions.

---

[61] Ornek D, Wood TK, Hsu CH, Sun Z, Mansfeld F (2002) Pitting corrosion control of aluminum 2024 using protective biofilms that secrete corrosion inhibitors. CORROSION 58(9):761–767.

[62] Nagiub A, Mansfeld F (2002) Microbiologically influenced corrosion inhibition observed in the presence of shewanella micro-organisms. In: Proceedings of 15th international corrosion Council, Spain, Sept 2002.

A recent research on MIC of mild steel by iron-reducing bacteria[63] has also suggested that this type of bacteria may decrease rather than accelerate corrosion of steel due to reduction of ferric ions to ferrous ions and increased consumption of oxygen. The ferrous ions produced by the bacteria prevent oxygen from attacking the steel surface.

Although Obuekwe had demonstrated the corrosivity of IRB, mainly on mild steel (see footnote 57),[64,65] other researchers (see footnotes 51 and 52) found out that some strains of pure IRB such as *Shewanella* could actually slow down the corrosion process.

The effect of certain conditions has been proposed by some researchers (see footnote 62).[66] These "conditions" are schematically shown in Fig. 4.12.

The core idea here is that (see footnote 62) pure IRB can contribute to decelerating corrosion as the ferrous ions produced by the bacteria form a "reducing shield" that blocks oxygen from attacking the steel surface and acts like a protective coating. It seems that this mechanism can happen if the bacterial growth results in biofilm formation on the metal surface. As oxygen is eliminated for instance by combining with more ferrous ions produced by the bacteria, differential aeration cells are removed. Lee and Newman (see footnote 67) also discuss that the facultative IRB switch to using ferric iron as the primary electron acceptor. In the authors' ideas, this in turn will lead into accumulation of ferrous ions in solution that creates a reducing environment and rapidly scavenges residual oxygen.

Videla has extensively reviewed probable mechanisms by which corrosion can be slowed down or inhibited by bacteria.[67] In this respect, he addresses three main mechanisms that can be summarised as the following:

1. Neutralising the action of corrosive substances present in the environment.
2. Forming protective films or stabilising a preexisting protective film on a metal.
3. Inducing a decrease in the medium corrosiveness.

Therefore corrosion deceleration could be the result of either one or a combination of these mechanisms. These three mechanisms can successfully explain most of the cases mentioned here. Therefore, by considering the possibility of having one or more of these mechanisms in place, it seems, the bacteria can play a different role in corrosion.

---

[63] Dubiel M, Hsu CH, Chien CC, Mansfeld F, Newman DK (2002) Microbial iron respiration can protect steel from corrosion. Appl Environ Microbiol 68(3):1440–1445, March 2002.

[64] Ibid footnote 33.

[65] Obuekwe CO, Westlake DWS, Cook FD (1981) Effect of nitrate on reduction of ferric iron by a bacterium isolated from crude oil. Can J Microbiol 27:692–697.

[66] Lee AK, Newman DK (2003) Microbial iron respiration: impacts on corrosion processes, on line, Appl Environ Microbiol, 7 May 2003.

[67] Ibid footnote 42, pp 74–120 and 193–196.

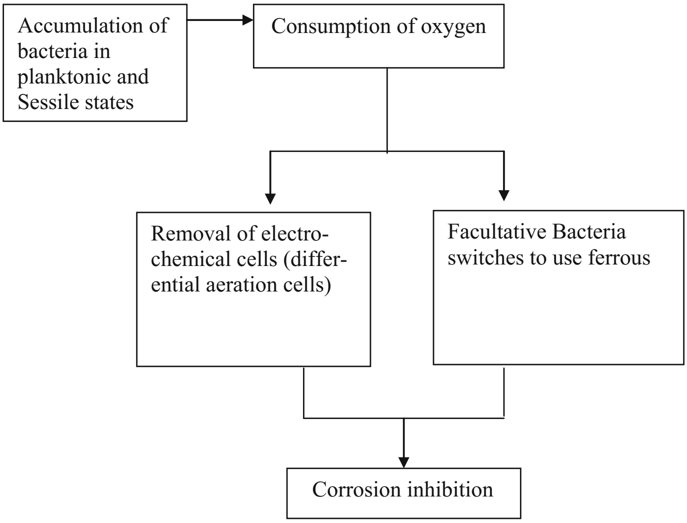


Fig. 4.12 The mechanisms occurring in batch systems to inhibit corrosion

The works by researchers on slowing down of corrosion by IRB cultures (see footnote 51),[68] postulate that for batch culture of IRB there is a chance for corrosion deceleration instead of acceleration due to increased number of ferrous ions thus produced because of the reduction of ferric ions by these bacteria. These ferrous ions can also combine with oxygen to form more ferric ions and meanwhile depleting oxygen. This can assist in abolishing differential aeration cells and thus decreasing corrosion.

4.8 The Bacteria Involved in MIC

One of the “myths” of MIC, as B.J. Little and P. Wagner call it (see footnote 31), is the importance of sulphate-reducing bacteria. This is indeed a misleading issue to reduce all MIC problems to SRB by saying “in oil and gas production, the primary source of problems is *Desulfovibrio desulfuricans*, commonly known as SRB”.[69]

---

[68] Newman RC, Rumash K, Webster BJ (1992) The effect of pre-corrosion on the corrosion rate of steel in natural solutions containing sulphide: relevance to microbially influenced corrosion. Corros Sci 33(12):1877–1884.

[69] Byars HG (1999) Corrosion control in petroleum production, Chap. 2, 2nd edn. TPC Publicatiosn 5, NACE international. It must be noted that the term SRB can not exclusively be applied to address D. desulfuricans only, there are other types of SRB as well. However, *Desulfovibrio* is the most important genera of SRB in salt solutions above 2 % (quoted from Archer ED, Brook R, Edyvean RGJ, Videla HA (2001) Selection of steels for use in SRB environments, Paper No. 01261, Corrosion 2001, NACE International, 2001).

Quoting Sanches del Junco et al.[70] it seems that the source of this "SRB myth" has been started with W. A. Hamilton's work addressing MIC being "most commonly associated with sulphate-reducing bacteria". For sure, SRB's role has been exaggerated.

Chamritski et al. have found that MIC of stainless steel 304 in low-chloride (less than 100 ppm) waters could be caused by bacteria such as iron-oxidising bacteria (reduction of the pitting potential), manganese-oxidising bacteria (ennoblement impact) and sulphate-reducing bacteria (pit stabilisation effects).

Critchley and Javaherdashti,[71] I. Beech et al. (see footnote 7) and, more completely, D. A. Jones and P. S. Amy[72] give a detailed list of the bacteria that could be involved in corrosion where SRB are just one of these bacterial groups.

In fact, in nature there is no such a thing as a pure culture of this or that bacteria (see footnote 5) and it is quite possible to have a rather complex picture of all possible microbial reactions that may happen simultaneously or consequently. Figure 4.13a shows a typical biomass formed on a steel pile being exposed to sea water conditions. Such a mass can easily harbour various types of corrosion-related bacteria. Figure 4.13b gives a schematic presentation of possible bacterial types and their interactions within a typical biofilm.

In this section two examples of the wide spectrum of the bacteria involved in biocorrosion will be given. These examples will be the well-known SRB and the relatively infamous iron-reducing bacteria.

4.8.1 Sulphate-Reducing Bacteria (SRB)

Sulphate-reducing bacteria (SRB) derive their energy from organic nutrients, they are anaerobic; in other words, they do not require oxygen for growth and activity, so as an alternative to oxygen, these bacteria use sulphate with the consequent production of sulphide (see footnote 10).

---

[70] Sanchez del Junco A, Moreno DA, Ranninger C, Ortega-Calvo JJ, Saiz-Jimenez C (1992) Microbial induced corrosion of metallic antiquities and works of art: a crtical review. Int Biodeterior Biodegradation 29:367–375.

[71] Critchley MR (2005) Javaherdashti Materials, micro-organisms and microbial corrosion— a review. Corros Mater 30(3):8–11. June 2005.

[72] Jones DA, Amy PS (2002) A thermodynamic Interpretation of microbiologically influenced corrosion. CORROSION 58(8):638–645, August 2002. Also see "Jack TR (2002) Biological corrosion failures. ASM International, March 2002; Blackburn FE (2004) Non-bioassy techniques for monitoring MIC. Corrosion 2004, paper 04580, NACE International, 2004; and Marconnet C, Dagbert C, Roy M, Feron D (2006) Micxrobially influenced corrosion of stainless steels in the Seine River. In: Proceedings of EuroCorr 2006, 24–28 Sept 2006, Maastricht, the Netherlands.

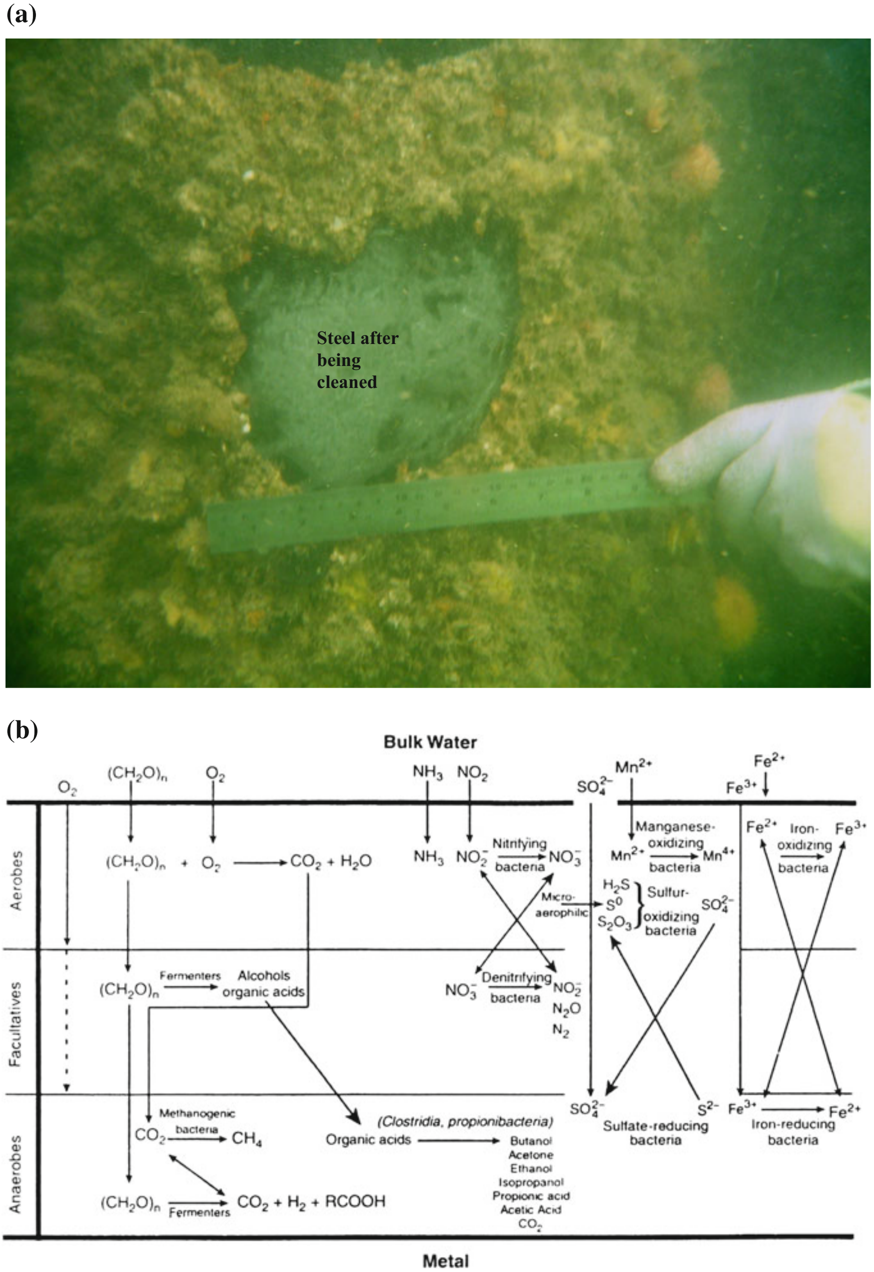


Fig. 4.13 **a** The Biomass formed on a steel pile being exposed to seawater at a depth of 3 m. Note the thickness around the sampling area (Courtesy of Extrin Consultants). **b** Complex environment of a typical aquatic biofilm (see footnote 31)

SRB will grow in the pH range between 4 and 9.5.[73] It has been reported that sulphate-reducing bacteria can tolerate pressures of up to 500 atmospheres.[74] R. King (see footnote 28) reports Butlin and Postgate's estimation of sulphide tolerance of sulphate-reducing bacteria to be a concentration of 3000 ppm, however, in his another work,[75] he mentions that the maximum sulphide produced by SRB is not above 600 ppm where the sulphide concentration in sediments and water floods rarely exceeds 500 ppm. SRB can be found everywhere, from more than 70 m deep in clay[76] to sea water.[77] It is believed that[78] the black colour of the Black Sea could be the result of the activity of these bacteria. SRB can also be found in the human body such as the mouth[79,80] and bowel.[81] By 1997, seven cases of SRB-influenced diseases, two of which occurring in Australia, had been diagnosed (see footnote 77) and it seems that this number is increasing since then.[82] SRB have been reported to

---

[73] Barton LL, Tomei FA (1995) Characteristics and activities of sulfate-reducing bacteria. In: Barton LL (ed) Sulfate-reducing bacteria, Biotechnology Handbooks, vol 8, Plenum Press, New York, USA.

[74] Stott JFD (1988) Assesment and control of microbially-induced corrosion, Met Mater 224–229, April 1988.

[75] King RA (2007) Trends and developments in microbiologically induced corrosion in the oil and gas industry. In: MIC—an international perspective symposium. Extrin Corrosion Consultants-Curtin University, Perth-Australia, 14–15 February 2007.

[76] Miller JDA, Tiller AK (1970) Microbial aspects of Metallurgy. In: Miller JDA (ed), American Elsevier Publishing Co. Inc., NY, USA.

[77] Ibid footnote 56.

[78] "The Role of Bacteria in the Corrosion of Oilfield Equipment", TPC.3, NACE International, 1982.

[79] Willis CL, Gibson GR, Holt J, Allison C (1999) Negative correlation between oral malodour and numbers and activities of sulphate-reducing bacteria in the human mouth. Arch Oral Biol 44:665–670.

[80] Langendijk PS, Hagemann J, Van der Hoeven JS (1999) Sulfate-reducing Bacteria in Periodontal Pockets and in Healthy Oral Sites. J Clin Periodonotl 26:596–599. Apart from whether or not the SRB are the cause of the mouth malodour, can their existence in the mouth and their known corrosive effects on most engineering materials be a factor in accelerating corrosion of dental fillings?

[81] McDougall R, Robson J, Paterson D, Tee W (1997) Bacteremia caused by a recently described novel desulfovibrio species. J Clin Microbiol 1805–1808, July 1997. It has also been reported that 50 % of healthy individuals have significant populations of SRB in faeces compared to the 96 % of Ulcerative colitis (an acute and chronic inflammatory disease of the large bowel) sufferers especially the *Desulfovibrio* genus, see: Lfill C, "The isolation and Purification of Sulphate-reducing Bacteria from the Colon of Patients Suffering from Ulcerative Colitis", B.Sc. (Hons) School of Pharmacy and Biomedical Sciences, University of Portsmouth, UK, June 1999.

[82] Private communication with Dr. R. McDougal, 18/January/2007.

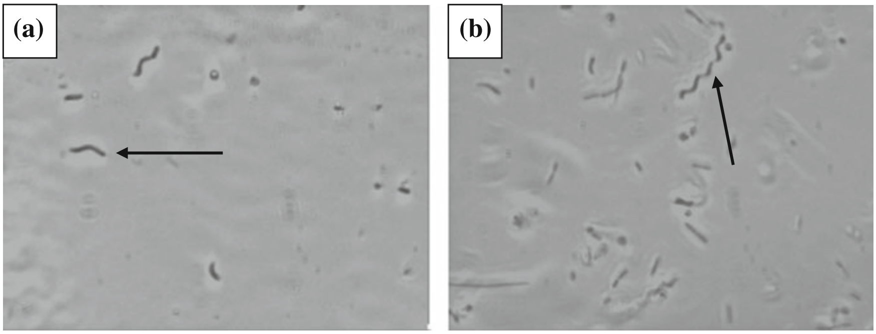


Fig. 4.14 Two morphologies of the SRB found in the mixed culture shown by arrows **a** vibrio **b** spiral

be responsible for environmental impacts such as massive fish kills, killing of sewer workers, development of "poisonous dawn fogs" and wastage of rice crops in paddies.[83] Figure 4.14a, b show two different morphologies of SRB.[84]

4.8.1.1 Mechanisms of MIC by SRB

In 1934 Holland, VonWolzogen Kuhr and Van der Vlugt provided significant evidence that anaerobic corrosion was caused by the activity of SRB. The two scientists suggested a theory that was named the "cathodic depolarisation theory" or "classical theory". From that time on, modifications to which we collectively refer as "alternative theories", have been made to this original theory.

The Classical Theory, Its Rise and Fall

The mechanism postulated by Kuhr and Vlugt attempts to explain the corrosion problem in terms of the involvement of SRB. According to this explanation (see footnote 26), the bacteria use the cathodic hydrogen through consumption by an enzyme called hydrogenase. It has been postulated that main probable effect of SRB on corroding metal is the removal of hydrogen from the metal surface by means of hydrogenase and catalysing the reversible activation of hydrogen.

---

[83] Singleton Jr R (1993) The sulfate-reducing bacteria: an overview, Chap. 1. In: Odom JM, Singleton Jr R (eds) The sulfate-reducing bacteria: contemporary perspectives. Springer-Verlag, New York Inc., 1993. One must however note that SRB could also have some benefits ranging from assistance in the Evolution (see footnote 82, pp. 17–19) to contribution to nitrogen-fixing capacity of the soil and killing nematodes which infest the rice plant roots by sulphide toxicity (see footnote 82, Chap. 8, pp. 205–206).

[84] Javaherdashti R (2005) Microbiologically influenced corrosion and cracking of mild and stainless steels. PhD Thesis, Monash University, 2005, Australia.

Sequences of reactions of the classical theory can be divided into three categories; metal, solution and micro-organism as follows:

METAL: Anodic reaction: $4Fe \longrightarrow 4Fe^{2+} + 8e^-$ Electrochemical cell

SOLUTION: Cathodic reaction: $8H^+ + 8e^- \longrightarrow 8H_{ad}$

Cathodic reaction $8H_2O \longrightarrow 8H^+ + 8OH^-$ Electrolyte

MICRO-ORGANISM $SO^{2-}_4 + 8H_{ad.} \longrightarrow S^{2-} + 4H_2O$ Microbial depolarisation

$Fe^{2+} + S^{2-} \longrightarrow FeS$ Corrosion products

$3Fe^{2+} + 6OH^- \longrightarrow 3Fe(OH)_2$ Corrosion Products

$4Fe + 4H_2O + SO^{2-}_4 \longrightarrow 3Fe(OH)_2 + FeS + 2OH^-$ Overall reaction

In the absence of oxygen, the cathodic areas of a metal surface quickly become polarised by atomic hydrogen. In anaerobic conditions, the alternative cathodic reaction to hydrogen evolution, such as oxidation by gaseous or dissolved oxygen, is not available either. These conditions will result in the dissociation of water as to become the main cathodic reaction with the hydrogen ions thus produced both adsorbed on the metallic surface (polarisation) and consumed by the hydrogenase enzyme. Figure 4.15 schematically summarises the classical theory.

Although the classical theory could explain MIC by SRB for the first time on the basis of electrochemistry, it suffered from serious flaws, some of which are as follows:

1. Research has confirmed that it is impossible for hydrogenase to contribute to the depolarisation of a cathode by removal of atomic hydrogen as "hydrogenase cannot work on atomic hydrogen at all" (see footnote 22).
2. According to this theory, the ratio of corroded iron to iron sulphide must be 4:1, however, in practice this ratio varies from 0.9 to 1.[85]

---

[85] Tiller AK (1983) Electrochemical aspects of microbial corrosion: an overview. In: Proceedings of microbial corrosion, 8–10 March 1983, The Metals Society, London, UK.

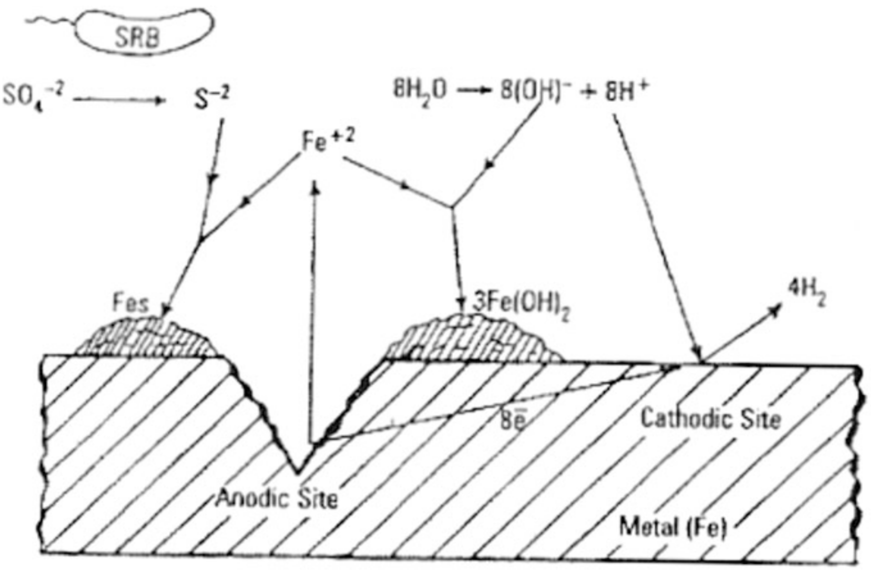


Fig. 4.15 Schematic of the cathodic depolarisation "classical" theory of SRB activity (see footnote 10)

3. In a recent study,[86] a culture of nitrate-reducing SRB that could grow and consume hydrogen faster and more efficiently was used. When sulphate was replaced by nitrate, these nitrate-reducing bacteria proved to efficiently oxidise the cathodic hydrogen from the metal, but unlike sulphate-reducing bacteria cultures, failed to stimulate corrosion. So this study showed that MIC by SRB could not just be attributed to the uptake of cathodic hydrogen.

Alternative Theories to the Cathodic Depolarisation Theory

Discovering such shortcomings as mentioned in Sect. 6.1.1.1, helped shift the paradigm of involvement of SRB in the corrosion to that which collectively can be called as "Alternative theories". These theories cover a wide range of research whose main common point is that they try to explain MIC by SRB although not directly involving the bacteria itself.

As Stott reports (see footnote 22), as early as 1923, Stumper had shown that the metal sulphides themselves can act like cathodes to the underlying steel, thus generating a galvanic cell and increasing corrosion rate, even in the absence of hydrogen sulphide. When in 1971, Miller and King attributed the corrosive effect to both hydrogenase and the iron/iron sulphide galvanic cell (see footnote 22), in other

---

[86] Ibid footnote 16.

words, they proposed iron sulphide as the absorber of molecular hydrogen,[87] this was in fact the first step towards minimising the role of the bacteria in cathodic depolarisation (see footnote 27). A modification to Miller and King's proposal was made in mid 1970s by Costello who replaced iron sulphide with hydrogen sulphide as the cathodic reactant as shown in the reaction below:

$$2H_2S + 2e^- \rightarrow 2HS^- H_2$$

In addition to these theories, Iverson proposed a hypothesis about the existence of a corrosive phosphorous metabolite leading to observed high corrosion.[88]

New theories put more emphasise on the anodic breakage of iron sulphide films and the galvanic cell formation in anodic spots and zones that have an enhanced SRB population (see footnote 6). Videla summarises the new picture of the SRB-induced MIC mechanisms as the following[89]:

- In saline media, at high Fe^{2+} concentrations, the steel is dissolved, resulting in the formation of a hydrated ferrous hydroxide film where the thickness and protective characteristics of this film depend on factors such as the concentration of Fe^{2+} and the solution's acidity (pH),
- The anion adsorption processes that are occurring at the metal/solution interface will be competing with each other, so that the outcome of these competitions could either be enhancing or inhibiting corrosion,
- The physico-chemical properties of the iron sulphide film can control the impact of sulphides on the steel dissolution, whereas these impacts and effects themselves are dependent on the ferrous ion/sulphide anions ratio, the presence of SRB and how the biofilm has covered the metal surface.[90]

---

[87] Rainha VL, Fonseca ITE (1997) Kinetics studies on the SRB influenced corrosion of steel: a first approach. Corro Sci 39(4):807–813.

[88] Iverson WP (1998) Possible source of a phosphorus compound produced by sulfate-reducing bacteria that cause anaerobic corrosion of iron. Mater Performance (MP) 37(5):46–49, May 1998.

[89] Videla HA, Herrera LK, Edyvean RG (2005) An updated overview of SRB induced corrosion and protection of carbon steel, Paper No. 05488, Corrosion 2005, NACE International, 2005.

[90] It may be worth of noticing that researchers such as Smith and Miller in their review of the corrosive effects of sulphides on ferrous metals have reported that in the media with high ferrous ion concentration, most of the corrosion of mild steel in biotic (bacterial) cultures can be attributed to the ferrous sulphide produced by the bacteria. In other words, it seems that when SRB are present, the iron sulphide produced by their interactions could be more corrosive than chemically (no bacteria) prepared iron sulphide. See Smith JS, Miller JDA (1975) Nature of sulphides and their corrosive effect on ferrous metals: a review. Br Corros J 10(3):136–143, 1975. (The Author would like to appreciate Dr. Peter Farinha's remarks regarding this paper and his kindness for providing the author with this paper).

As seen in all of these new theories, apart from all of their similarity and dissimilarities, the role of the bacteria in corrosion becomes less and less important. Recently some research by D.T. Hang[91] has come up with very interesting results. In this research, SRB were directly enriched with metallic iron and sulphate as the only growth substrate in carbon dioxide/bicarbonate-buffered medium. The rod-shaped SRB isolated from the culture has been shown to be genetically very closely related to *Desulfobacterium catecholicum,* however, physiologically significantly different from them! This new species has been given the name *Desulfobacterium corrodens.* But this is not the whole story; the bacterial strains use only iron, lactate and pyruvate for the reduction of sulphate. In the presence of iron, the strain reduces sulphate more rapidly than *Desulfovibrio,* whereas in the presence of hydrogen or lactate, sulphate reduction becomes remarkably slower than for the *Desulfovibrio* species. This work also reports another new species of *Desulfovibrio* (named *Desulfovibrio ferrophilus*) that, in the presence of iron, could reduce sulphate at a higher rate than other *Desulfovibrio* species but slower than *Desulfobacterium corrodens.*

In this study, D. T. Hang, F. Widdel and H. Cypionka model anaerobic corrosion of iron without the involvement of hydrogen. They are postulating that the SRB that grow in very close contact with the iron surface, can take electrons directly from the metal surface, that we call this step as "electron pick-up", and transfer these electrons to the sulphate-reducing system (SRS). While this proposed mechanism by Hang is certainly a breakthrough, there are still serious questions to be answered. For example, it is unknown how the electron pickup step works and what mechanisms are involved there. As we will see later (see footnote 116) Little et al. have also demonstrated that for another group of bacteria which are important in corrosion, that is, *Shewanella purefaciens* which are iron-reducing bacteria, the reduction of metal requires contact between the cell and the surface where the reduction rate is directly related to the surface area. The same researchers have also found that the location of pits induced by these bacteria on carbon steel coincided with sites of bacterial colonisation.

One can not help but think that if Hang's approach is correct, then all the alternative theories that so far have tried to minimise the role of SRB in MIC would have to be seriously reconsidered.

4.8.1.2 Examples of Corrosion by SRB

Almost all types of engineering materials have been reported to experience MIC by SRB; copper, nickel, zinc, aluminium, titanium and their

---

[91] Hang DT (1991) Microbiological study of the anaerobic corrosion of iron, PhD Dissertation, University of Bremen, Bremen, Germany, 2003.

alloys[92,93,94] mild steel[95,96,97] and stainless steels (see footnotes 26, 68 and 74)[98] are just some examples. Among duplex stainless steels SAF 2205 has been reported for its vulnerability to MIC.[99,100,101] According to these studies, SAF 2205 can corrode and have pitting initiated due to the presence of SRB after immersion into seawater for more than one year (18 months) (see footnote 100). Corrosion rates of 10 mm/year (see footnote 6) in oil treatment plants and 0.7–7.4 mm/y due to the action of SRB and/or acid producing bacteria in soil environments (see footnote 8) have been reported.

4.8.1.3 SCC[102] and SRB

Gradual formation of biofilms can change chemical concentrations at the surface of metal substrata significantly: The physical presence of a biofilm exerts a passive effect in the form of restriction on oxygen diffusion to the metal surface. Active metabolism of the micro-organisms, on the other hand, consumes oxygen and produces metabolites. The net result of biofilm formation is that it usually creates concentration gradients of chemical species across its thickness which is typically between 10 μm to ~400 μm (see footnote 38).

If chlorides are present, the pH of the electrolyte under the biofilm may further decrease leading to more severe corrosion. In the presence of certain bacteria, such as iron-oxidising bacteria (IOB),[103] under tubercule conditions may become very

---

[92] Scott PJB, Goldie J (1991) Ranking alloys for susceptibility to MIC-a preliminiary report on high-Mo alloys. Mater Performance (MP) 30(1):55–57, January 1991.

[93] Schutz RW (1991) A case for Titanium's resistance to microbiologically influenced corrosion. Mater Performance (MP) 30(1):58–61, January 1991.

[94] Wagner P, Little BJ (1993) Impact of alloying on microbiologically influenced corrosion a review. Mater Performance (MP) 32(9):65–68, September 1993.

[95] Hamilton WA (1985) Sulphate-reducing bacteria and anaerobic corrosion. Annu Rev Microbiol 39:195–217.

[96] Hardy JA, Brown JL (1984) The corrosion of mild steel by biogenic sulfide films exposed to air. CORROSION 40(12):650–654, December 1984.

[97] Lee W, Characklis WG (1993) Corrosion of mild steel under anaerobic biofilm. CORROSION 49(3):186–198, March 1993.

[98] Tiller AK (1983) Is stainless steel susceptible to microbial corrosion?" proceedings of microbial corrosion, 8–10 March 1983, The Metals Society, London, UK, 1983.

[99] Ibid footnote 45.

[100] Neville A, Hodgkiess T (1998) Comparative study of stainless steel and related alloy corrosion in natural sea water. Br Corros J 33(2):111–119.

[101] Johnsen R, Bardal E (1985) Cathodic properties of different stainless steels in natural seawater. CORROSION 41(5):296–302, May 1985.

[102] SCC is the abbreviation for "stress corrosion cracking". It is a type of corrosion that is caused by simultaneous action and effect of both tensile stresses to a vulnerable material in a corrosive medium.

[103] Ibid footnote 34.

acidic due to combining of the chloride ions with the ferric ions that are produced by the bacteria to form acidic ferric chloride solution inside the tubercule (or biofilm) that is highly corrosive (see footnote 32). Pitting is the predominant morphology of MIC.[104,105,106]

On the other hand, pitting can act as an SCC initiator; because the "root" of pits acts as "stress magnifiers", so that the applied stress becomes multiplied several times resulting in stresses far in excess of the tensile yield strength, thus, producing failure.[107]

Among investigations addressing the effect of SRB and other bacteria such as iron-reducing bacteria (IRB) on enhancing corrosion of steels (carbon steel, stainless steel 316 and duplex stainless steel SAF2205), Javaherdashti et al. have produced a series of papers.[108,109,110,111,112] In these studies, mixed (containing SRB, IRB and other unidentified micro-organisms) and pure cultures of SRB (only SRB) and IRB (only IRB) and their impacts on both electrochemical and mechanical properties of the above-mentioned steels were investigated. The test cell used for conducting SCC by slow strain rate testing (SSRT) for the steel samples had been designed in such a way that it could sustain the environment anaerobic enough for the SRB. For this reason, the test chamber was designed such that it could reveal blackening as a sign of growth, Fig. 4.16a. The SRB biofilm could easily be observed, Fig. 4.16b.

It is interesting to see how mixed and pure cultures of SRB can affect the severity of SCC of carbon steel and duplex stainless steel by decreasing the time of

---

[104] Ibid footnote 18.

[105] Ibid footnote 47.

[106] Linhardt P (1996) Failure of chromium-nickel steel in a hydroelectric power plant by manganese-oxidising bacteria. In: Heitz E, Flemming WS (eds) Microbially influenced corrosion of Materials, Springer-Verlag Berlin, Heidelberg 1996.

[107] "Stainless Steel Selection Guide", Central States Industrial Equipment & Service, Inc., http://www.al6xn.com/litreq.htm, USA, 2002.

[108] Javaherdashti R, Raman Singh RK, Panter C, Pereloma EV (2006) Microbiologically assisted stress corrosion cracking of carbon steel in mixed and pure cultures of sulfate reducing bacteria. Int Biodeterior Biodegradation 58(1):27–35, July 2006.

[109] Javaherdashti R, Raman Singh RK, Panter C, Pereloma EV (2005) Role of microbiological environment in chloride stress corrosion cracking of steels. Mater Sci Technol 21(9):1094–1098.

[110] Javaherdashti R, Raman Singh RK, Panter C, Pereloma EV (2004) Stress corrosion cracking of duplex stainless steel in mixed marine cultures containing sulphate reducing bacteria. In: Proceedings of corrosion and prevention 2004 (CAP04), 21–24 November 2004, Perth, Australia.

[111] Singh Raman RK, Javaherdashti R, Panter C, Cherry BW, Pereloma EV (2003) Microbiological environment assisted stress corrosion cracking of mild steel. In: Proceedings of corrosion control and NDT, 23–26 November 2003, Melbourne, Australia.

[112] Ibid footnote 12.

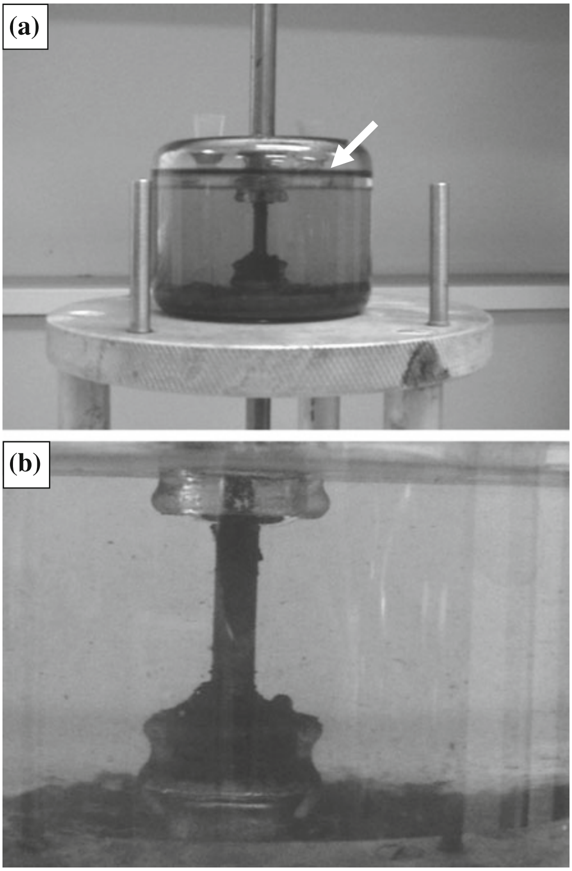


Fig. 4.16 **a** SSRT of a carbon steel sample in the anaerobic chamber inoculated with SRB. Note the oil layer (*arrow*) to prevent oxygen ingress (see footnote 108). **b** Close up of Fig. 4.16a showing thick, *black* biofilm formed on the exposed section of the mild steel SSRT sample (see footnote 111)

failure. In other words, when SRB is present, the material is likely to fail in a relatively shorter time than an abiotic (no bacteria present) environment, Figs. 4.17 and 4.18a, b.

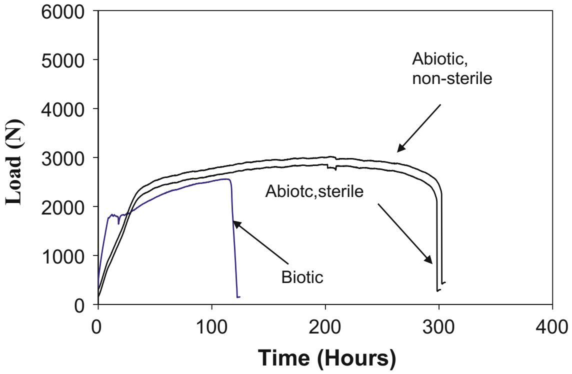
4.8.2 *Iron-Reducing Bacteria*

There are other micro-organisms in addition to SRB which are also important in corrosion. For example, the MIC of stainless steel 304 in low-chloride natural water can involve the combination of some or all of the following factors[113]:

---

[113] Chamritski IG, Burns GR, Webster BJ, Laycock NJ (2004) Effect of iron-oxidizing bacteria on pitting od stainless steels. CORROSION 60(7) July 2004.

Fig. 4.17 Typical load versus time curves generated by SSRT tests of mild steel in the environments consisting of a mixed SRB culture, abiotic non-sterile containing 3.5 % sodium chloride solution alone, whereas the abiotic sterile environment contained modified Postgate B medium along with some chemicals to keep it sterile (see footnote 108)



- Ennoblement of potential, possibly caused by manganese-oxidising bacteria,
- Reduction of the pitting potential because of either (1) the crevice-like action of surface deposits produced by iron-oxidising bacteria, or (2) the activating effect of sulphide or thiosulphate produced by SRB, or (3) simply the effect of silicate in the water.

Iron-reducing bacteria (IRB) are also another group of micro-organisms which are of interest in MIC. However it seems that their importance in corrosion has been overshadowed by the iron bacteria (IB), or more precisely, iron-oxidising bacteria (IOB). For example, ASTM D 932-85 defines iron bacteria as a general classification for micro-organisms that utilise ferrous iron Fe^{+2} as a source of energy, and are characterised by the deposition of ferric Fe^{+3} hydroxide.[114] A common example of IOB is the *Gallionella* sp. Fig. 4.19 shows two examples of Ferrooxidans which are examples of IOB.

The reducing effects of IRB on metals such as copper, nickel, gold and silver have been known for nearly 50 years.[115] As the name implies, IRB act by reduction of the generally insoluble Fe^{+3} compounds to the soluble Fe^{+2}, exposing the metal beneath a ferric oxide protective layer to the corrosive environment (see footnotes 57, 63 and 64).

It is important to understand how iron-reducing bacteria can reduce iron, or more precisely, ferric iron ion. The reason is that while the bacteria can reduce iron in some way or another, it is one of these methods that may be of more importance with regard to its contribution to corrosion. In the following section, possible reasons and mechanisms for microbial iron reduction are discussed.

---

[114] "Standard test method for iron bacteria in water & water-formed deposits", ASTM D932-85 (Reapproved 1997), ASTM annual book, ASTM, USA, 1997.

[115] Simpson WJ (1999) Isolation and characterisation of thermophilic anaerobies from bass strait oil production waters, M App Sci Thesis, School of Applied Sciences, Monash University.

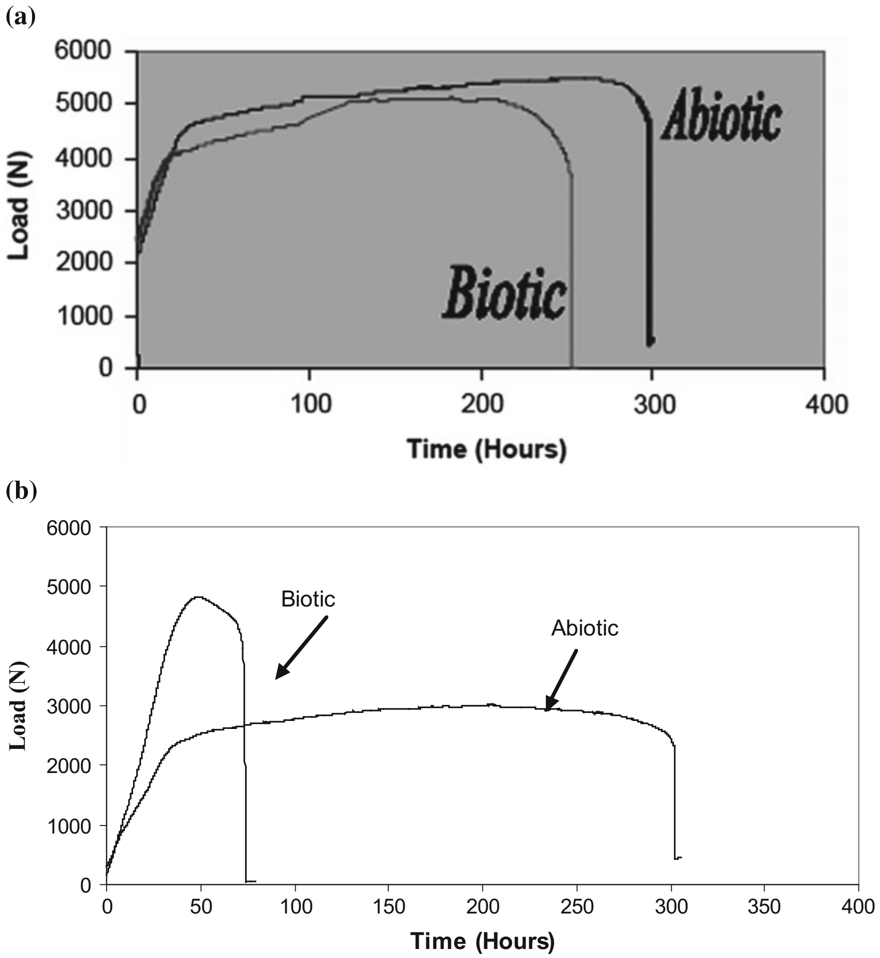


Fig. 4.18 **a** Typical load versus time curves generated by SSRT tests of duplex stainless steel SAF2205 in abiotic and biotic (mixed culture of SRB) environment (see footnote 110). **b** Typical load versus time curves generated by SSRT tests of mild steel in a 3.5 % chloride solution, with and without pure SRB culture, termed, respectively, as biotic and abiotic conditions (see footnote 108)

4.8.2.1 Why Is Microbial Reduction of Iron Important?

Some of the possible reasons why iron reduction by bacteria is important can be as follows:

1. Availability of iron: iron is not very soluble but if it is reduced to ferrous iron (which is soluble) so that the organic compounds can stabilise iron by chelation

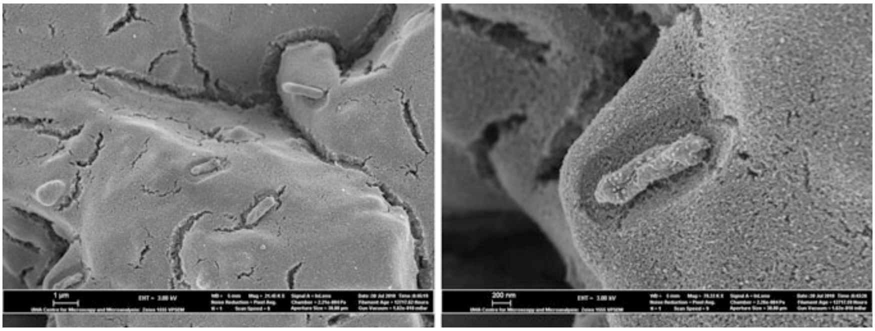


Fig. 4.19 Two examples of iron-oxidising bacteria (Ferrooxidans) grown on chalcopyrite, (This author wishes to thank Dr. Kayley Usher for her permission to use these images. We also wish to thank the Australian Microscopy and Microanalysis Research Facility at the Centre for Microscopy, Characterisation and Analysis, the University of Western Australia, a facility funded by the University, State and Commonwealth Government)

where, later on, that iron can "liberate" itself from the organic matter and precipitate as iron.[116,117]

2. IRB are a very important part of the soil microbial community, as most of the IRB are facultative anaerobes, thus if oxygen is available, they will prefer it for their growth whilst maintaining also their capability of growth under anaerobic conditions too. It is estimated that in the surface layer of soil, on the average, the number of IRB could be as 10^6 cells per gram of soil.[118] It must be reminded that as IRB are both chemoheterothrophic (organic compounds are the source of energy for them) and facultative anaerobes, their numbers within the soil's surface layer is higher than deeper levels especially if the soil is rich in organic matter at the surface level (see footnote 117). As a result, in case their numbers in soil are reported, the depth of sampling for the organic carbon content must also be recorded.
3. Incorporation (assimilation) of iron into proteins containing heme or iron-sulphur (see footnote 67).
4. IRB are capable of making the environment suitable for SRB. In a mixed population of micro-organisms in a biofilm, as oxygen is consumed, the redox potential starts to decrease so that nitrate, then manganic and ferric ion and the sulphate are reduced (see footnote 117), this consequence can be seen in Table 4.2.

---

[116] Ibid footnote 34.

[117] Panter C (2007) Ecology and characteristics of iron reducing bacteria-suspected agents in corrosion of steels. In: MIC—an international perspective symposium. Extrin Corrosion Consultants-Curtin University, Perth-Australia, 14–15 February 2007.

[118] Panter C (1968) Iron reducing bacteria of soil, MSc thesis, Dept of Soil Science, University of Alberta, Canada.

Table 4.2 Sequence of reduction in redox potential (E_h) under anaerobic conditions

….	… is reduced to	Comments	E_h
NO_3^-	N_2	Through first reduction of NO_3^- into NO_2^- and then into N_2O	<400 mV
NO_3^-	NH_4^+	By first reduction of NO_3^- into NO_2^-	
Mn^{4+}	Mn^{2+}		<400 mV
Fe^{3+}	Fe^{2+}		<300 mV
SO_4^{2-}	H_2S		<100 mV
Organic C	H_2, CO_2		<−100 mV
$H_2 + CO_2$	CH_4		<−300 mV

"A Working Party Report on Microbiological Degradation of Materials—And Methods of Pretection", Sect. 4.3.3, European Federation of Corrosion Publications, Number 9, The Institute of Materials, London, England, 1992

Most of the IRB are fermentators under anaerobic conditions, however there are a few that actually need ferric iron under anaerobic conditions (see footnote 117), to add more into the complex picture, some of the IRB can use nitrate for anaerobic respiration (see footnote 117). Little et al. (see footnote 116) have reported that IRB such as *Shewanella purefaciens* can use oxygen, Fe(III), Mn(IV), NO_3^-, NO_2^-, $S_2O_3^2$, SO_3^{2-} and others. The same researchers also report that *S. purefaciens* under aerobic and anaerobic conditions may or may not use the same material (e.g. acetate that can be used aerobically but not anaerobically). Perhaps C. Panter is right in his recommendation that "oxygen content [for IRB] is more important in determination [of their] numbers than available ferric ion content" (see footnote 117).

In soil environments, most IRB that can be isolated are fermentators and for the IRB that carry out dissimilatory reduction of ferric ion by anaerobic respiration, isolation may not be "as regular", however, the latter can more easily be isolated from freshwater streams, lakes and marine waters (see footnote 117). Javaherdashti (see footnote 84) isolated a *Bacillus* sp. that could grow in nutrient broth under aerobic conditions. The bacterium was also motile in Postgate B medium modified with 35 g/l NaCl. This isolate was from a muddy sample taken from the depth of 14 m of the Estuary of Merimbula river, New South Wales, Australia; Fig. 4.20 shows such a bacterium.

In fact, the mechanisms of microbial iron reduction can be grouped into two (see footnote 67):

- Assimilation
- Dissimilation

Assimilation, as mentioned above, is unlikely to have an effect on corrosion as trace amounts of iron are required for it to occur, whereas dissimilatory iron reduction involves electron transfer to iron as part of both anaerobic fermentation or anaerobic respiration (see footnote 67). The impact of fermentor iron reducers has not been studied in details maybe because they do not reduce ferric iron as rapidly or extensively as anaerobic respiratory IRB (see footnote 117). However, C. Panter

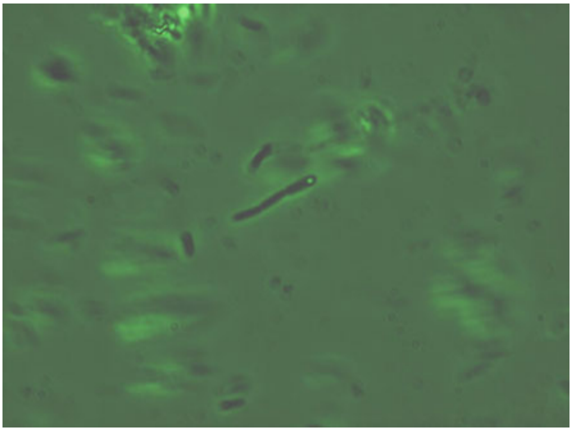


Fig. 4.20 Iron-reducing bacterium culture; the terminal bright spot is an endospore (1000×) (see footnote 113)

reports (see footnote 117) that fermentative IRB in submerged environments are encountered more frequently than the IRB that use ferric ion in anaerobic respiration. None the less, as mentioned earlier, it is not yet known if the fermentative IRB could have a great contribution to corrosion. Most probably, then, the only remaining nominee for having an impact on corrosion would be the respiratory iron reducers.

IRB are very interesting when considered for their effects on corrosion. Next section considers their impact on the corrosion severity.

4.8.2.2 Contradicting Impacts of IRB on Corrosion

Most engineers and even scientists who are familiar with MIC, would not believe that some times the bacteria can actually retard corrosion and protect the metal. In fact, there is a growing body of evidence that IRB could, under some circumstance, enhance corrosion and, under other circumstance, could inhibit corrosion.

In the following sections, examples of corrosion enhancement by IRB will be presented. The next section, will overview some possible reasons for the IRB to inhibit corrosion.

Corrosion Enhancement by IRB

Obuekwe et al. in a series of papers on IRB (*Pseudomonas* sp.) reported corrosion effects of the bacteria under the micro-aerobic (which contains trace amounts of oxygen) conditions (see footnotes 57, 63 and 64). These works included polarisation studies of mild steel in the media with and without yeast extract. These researchers reported that the IRB may contribute to corrosion of mild steel by anodic depolarisation due to their ability of reducing and removing the protective film of ferric compound.

Obuekwe's pioneering work on characterising corrosion effect of IRB by using polarisation method has been debateable, as a potentiodynamic approach over a range of 0.4 V has been used to examine corrosivity and this may affect and alter the "natural" behaviour of microbial communities.

The examples below suggest how "opposite" results may be obtained by applying voltage:

- A report on the CP effects on steel pipes against MIC[119] suggests that under laboratory conditions applying voltages more negative than $-0.98V_{Cu-CuSO4}$ may decrease the number and/or the activity of iron bacteria as a result of environmental changes caused by cathodic protection process. Although in this report, the type of the bacteria (IOB or IRB) has not been specified, from general recognition of iron bacteria (see footnote 114), it may be anticipated that it was iron-oxidising bacteria whose number had been adversely affected by applying voltage. The report, thus, demonstrates the negative effect of applying voltage on micro-organisms and their numbers.
- It has been recommended practice to apply a voltage of about $-0.98V_{Cu-CuSO4}$ in order to suppress bacterial effects by cathodic protection, resulting in decreasing extent and severity of corrosion. In this way, the localised pH is increased and the environment becomes too alkaline for the micro-organisms to comfortably withstand, thus decreasing the corrosion rate. However, in one particular case of cathodic protection, it has been reported that applying voltages up to—$1.1V_{Cu-CuSO4}$ not only failed to prevent the growth of bacteria on the metal surfaces, it rather prompted the growth of certain microbial species and the rate of corrosion.[120] The possible effects of CP on MIC will be discussed in more details later in Chap. 10 of this book.

The same debatable effects might have also affected the results in the work by Obuekwe. It seems that applying a voltage to the medium (as was done in Obuekwe's works on corrosion of mild steel by IRB) may not resemble MIC properly because there is no way to know how the microbial activity has been affected by the applied voltage and how this would affect the outcome of the experiments.

On the other hand, Little et al. (see footnote 116) who did not use polarisation methods but instead one of the safest electrochemical methods, electrochemical noise analysis (to be discussed later in Chap. 6), for their investigations, reported the corrosion-enhancing effects of another type of IRB, *Shewanella purefaciens.*

Javaherdashti (see footnote 84) in his investigation regarding the mechanical and electrochemical behaviour of mild steel, stainless steel 316L and duplex stainless

---

[119] Kajiyama F, Okamura K (1999) Evaluating cathodic protection reliability on steel pipes in microbially active soils. CORROSION 55(1):74–80.

[120] Pope DH, Zintel TP, Aldrich H, Duquette D (1990) Efficacy of biocides and corrosion inhibition in the control of microbiologically influenced corrosion. Mater Performance (MP) 29 (12):49–55.

steel SAF2205, found out that when mild steel is exposed to a culture of IRB, in comparison with an abiotic environment it shows lesser times of failure, therefore implying that IRB could actually enhance corrosion. Figure 4.21 represents typical slow strain rate SCC behaviour of mils steel in a culture of IRB.

The above-mentioned points may suggest that IRB are indeed important in increasing corrosion rate. If you have a mixed culture of SRB and IRB, for example, the carbon steel sample in the mixed culture will fail earlier with respect to an abiotic environment, Fig. 4.17. A possible explanation for premature failure of mild steel in such a mixed culture could schematically be shown as in Fig. 4.22.

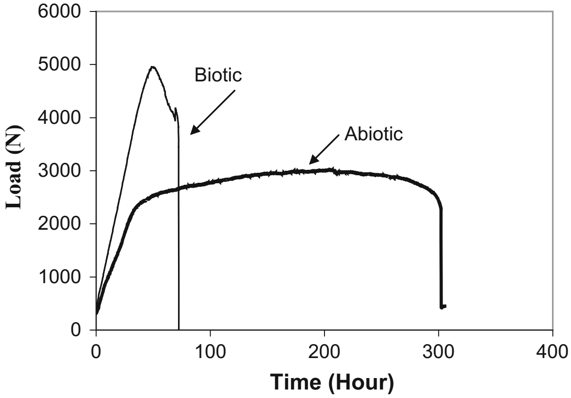


Fig. 4.21 Typical load versus time curves for mild steel in IRB culture comparing it with slow strain rate behaviour of mild steel in abiotic synthetic seawater media

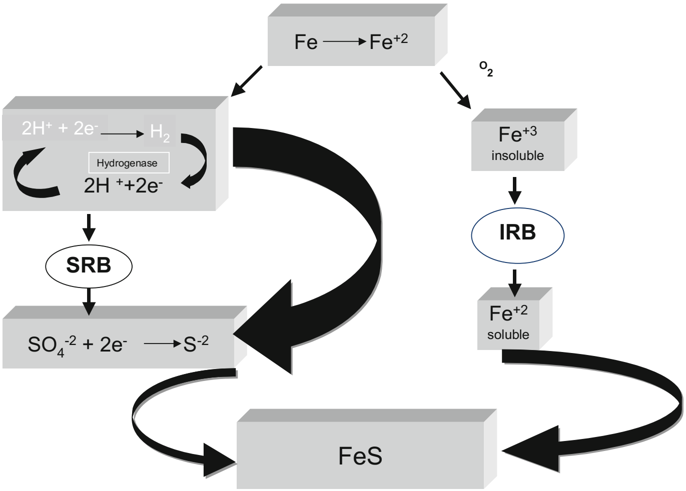


Fig. 4.22 Possible interaction between SRB and IRB

However, IRB still have the power to surprise us!, Lee et al.[121] have reported that a mixed culture (biofilm) containing IRB (*Shewanella oneidensis*[122]) and SRB (*Desulfovibrio desulfuricans*) that had been formed on mild steel, could provide a short-term (4 days) protection to the steel. As the authors put it, "[t]he fact that an iron-reducing bacterium can inhibit corrosion when a corrosion-enhancing bacterium is present warrants future study with respect to its potential applicability to the design of biological corrosion-control measures". Such reports can lead us into another aspect of IRB: a corrosion inhibiting bacteria! This matter has been discussed previously (See the section entitled "Corrosion deceleration effect of biofilms" of this Chapter) and will not be repeated again.

4.8.3 Magnetic Bacteria

Magnetic bacteria have the ability of synthesising intracellular nano-sized fine magnetic particles.[123] Each of these magnetic particles, called a magnetosome, is about 50 nm in width.[124] Figure 4.23 shows a schematic presentation of *Aquaspirillum magnetotacticum* where magnetosomes can be clearly seen as a string. Note that the total magnetic energy of the magnetosome string is the sum of the individual magnetic moments of the beads, so magnetic energy of the cell being calculated as to be in the order of 10^{-19} J/G, is adequate to align the bacterium in the 0.5 G geomagnetic field (see footnote 124).

First discovered in 1975 by Blakemore, the magnetotactic bacteria are bottom-dwelling micro-organisms which are either anaerobic or microaerophilic.[125] It seems that the tendency of the bacteria for migrating downwards along the component of the magnetic field is an evolutionary tactic that the anaerobic bacteria use to avoid the toxic effect of oxygen available in the surface water (see footnote 125).[126] These bacteria could be very important for the biogeochemical cycling of metals as when the bacteria die, sedimentation of fine magnetic particles will occur

---

[121] Lee AK, Buehler MG, Newman DK (2006) Influence of a dual-species biofilm on the corrosion of mild steel. Corros Sci 48(1):165–178.

[122] *Shewanella oneidensis* is a facultative anaerobe that can use oxygen or ferric ion as its terminal electron acceptor. See footnote 62.

[123] Sakaguchi T, Tsujimura N, Matsunaga T (1996) A novel method for isolation of magnetic bacteria without magnetic collection using magnetotaxis. J Microbiol Methods 26:139–145.

[124] Hughes MN, Poole PK (1989) Metals and micro-organisms, Sect. 5.9, Chapman and Hall, NewYork, 1989. Note that the earth's magnetic field has a strength of the order of 1 G, see footnote 125.

[125] Blakemore RP, Frankel RB (1981) Magnetic navigation in bacteria. Sci Am 245, pp 42–49, December 1981.

[126] Bean CP (1990) Magnetism and life. In: Halliday D, Resnick R (eds) Fundamentals of physics, Section E 14-1, 3rd edn, 1974, c1990.

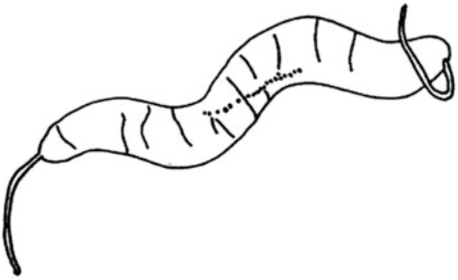


Fig. 4.23 Schematic presentation of a magnetotactic bacterium (*Aquaspirillum magnetotacticum)* where the magnetosomes can be seen as black beads (Javaherdashti R (1997) Magnetic bacteria against MIC, Paper No. 419, CORROSION 97, NACE International, 1997.)

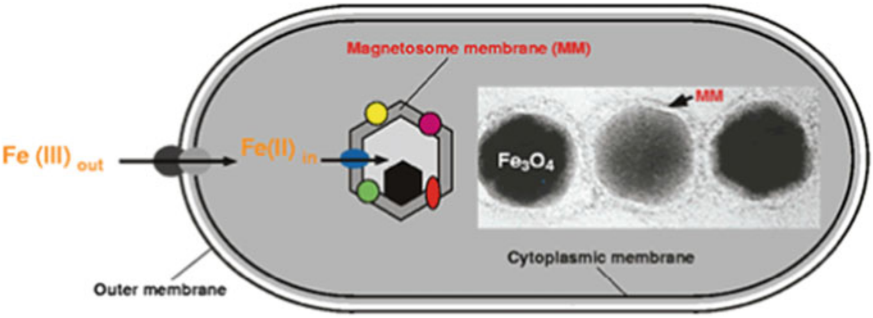


Fig. 4.24 Possible mechanism of formation of magnetite within magnetosomes (see footnote 128)

(see footnote 124), also, these bacteria have been reported to be useful for their potential capability of removing metals from contaminated soils.[127]

But what does all this have to do with corrosion and MIC? There are some indirect and direct evidence here: magnetotactic cells can accumulate iron approximately 20,000–40,000 fold over its extracellular concentration (see footnote 124). Between 14 and 79 % by weight of the magnetosome is magnetite (Fe_3O_4), where "the existence of … other oxides of iron or… iron sulphides in certain magnetotactic bacteria cannot be ruled out" (see footnote 124). If these bacteria need this much iron, from where can they get it?

Proposed model for magnetite biomineralization in *Magnetospirillum* species is that Fe(III) is actively taken up by the cell, possibly via a reductive step, and then, it is thought to be re-oxidised, resulting in magnetite production within the magnetosome, as seen in Fig. 4.24.[128]

---

[127] "Magnetic Bacteria may Remove metals from contaminated Soils" Chemical News, Materials Performance (MP) 36(1):47, January 1997.

[128] The Magneto-Lab, Dr. Dirk Schüler, Junior Group at the MPI for Marine Microbiology, Bremen, http://magnum.mpi-bremen.de/magneto/research/index.html.

Could magnetosome formation mechanisms contribute to corrosion in the way that iron-reducing bacteria do by consuming ferric iron ions?. While this is yet not known about magnetic bacteria, there is indirect evidence showing that the bacteria with magnetic properties could be indeed very important in MIC.

In an investigation, Bahaj et al.[129] used *Gallionella ferruginea* that are known to form tubercles and MIC (see footnote 74), and accumulate iron hydroxide in their bodies. If these bacteria are present in an iron rich medium, they pick up iron, and due to the increase of iron concentration in their bodies, their magnetic susceptibility and tendency for the attachment to magnetic surfaces such as iron also increase. This in turn will increase the likelihood of biofilm formation and hence further enhancement of corrosion. As these investigators put it, the "interaction" between the iron "in" the micro-organism and the iron "out" of the micro-organism, that is the metallic substrate, could result from factors such as (see footnote 129).

- Existence of a magnetic substrate (steel surface for instance),
- Magnetic features of corrosion products, including various iron oxides such as magnetite,
- Formation of a wide range of (ferromagnetic) sulphides during MIC,
- Induction of magnetic fields due to factors such as application of CP systems (especially impressed current), use of electric welding facilities and transportation means such as electric trains or trams.

Bahaj et al. could establish a way of explaining, at least theoretically, how magnetic fields may be effective in encouraging biofilm formation and MIC. Javaherdashti (1997) proposed using magnetotactic bacteria to, literally, corral corrosion-enhancing bacteria at a suitable corner of a system and then expose them to MIC chemical (biocide application) or physical (filtration) mitigation methods.

Certainly, there are still many puzzles in dealing with magnetic bacteria, however, using these bacteria in mitigation programs may prove to be more efficient than other MIC control methods, if research in this very new and exotic area of MIC is supported in the way it deserves.

4.8.4 Clostridia

In the literature of MIC, one often sees APB (acid producing bacteria). This alone can give no information at all as APB can either be aerobic (like sulphur-oxidising

---

[129] Bahaj AS, Campbell SA, Walsh FC, Stott JFD (1992) The importance of environmental factors in microbially-influenced corrosion: Part 2., magnetic field effects in Microbial Corrosion. In: Sequeira CAC, Tillere AK (eds) Proceedings of the 2nd EFC workshop, Portugal 1991, European Federation of Corrosion Publications, Number 8, The institute of Materials.

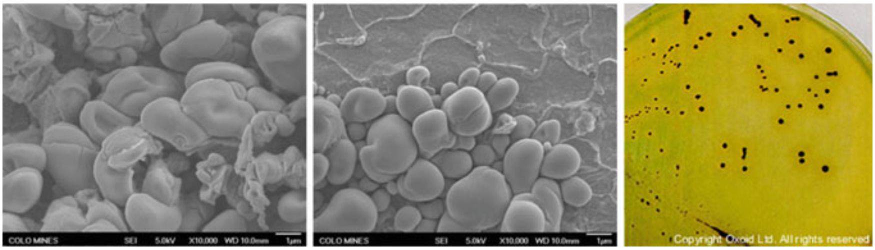


Fig. 4.25 (*Left*) Clostridium Sp. on API X52 steel and (*right*) on API X70 steel. Both Magnifications are 10,000× (see footnote 125). © NACE International 2013. (*Far right*) how Clostridia colonies (*black dots*) may look like in a culture (Dr. Reza Javaherdashti's Courtesy with sincere thanks to S. Moayedi Rad and A. Dermanaki)

bacteria or anaerobic ones such as Clostridia. Therefore in the same way that "underdeposit corrosion" is a useless terminology (because it just shows where corrosion is occurring and says nothing about the mechanism), APB is of no particular use either as, without specifically mentioning if it is aerobic or anaerobic APB, it is of no use at all.

Amongst CRB perhaps the most important one can be Clostridia. In this author's opinion the highest level of awareness about MIC will only be attained if Clostridia, in addition to other CRB, are also included in any case of corrosion susceptible to be MIC-related. There are three reasons for this.

1. Like SRB, these bacteria are also anaerobic.
2. There are contradicting reports about these bacteria and their impact on corrosion.
3. They can cause very serious diseases.

Figure 4.25 shows two examples of Clostridia as established on two types of steel.

Amongst CRB perhaps the most important one can be Clostridia. In this author's opinion the highest level of awareness about MIC will only be attained if Clostridia, in addition to other CRB, are also included in any case of corrosion susceptible to be MIC-related. The mechanism by which MIC can be facilitated by Clostridia is by generation of mainly organic acids as metabolic by-products In this regard, Clostridia can be shown as an example: these bacteria produce organic acids that by lowering the pH can assist in inducing corrosive conditions. It has also been suggested (see footnote 126) that perhaps one of the reasons for the lack of link between the number of SRB and corrosion rate is the contribution of Clostridia to MIC.

These bacteria are known to us from 1880 (see footnote 127). They have been reported (see footnotes 127 and 128) to contain more than 83 species and this number is still increasing. Clostridia are indeed so diverse a species: some have been reported of having the ability of generating hydrogen sulphide gas (see footnote 129) or, like *Clostridium Butyricum* which are butyric acid producing species even capable of iron reducing.[130]

There are four criteria that can be used to differentiate Clostridia from other types of bacteria, including SRB. It must be noted that all these four criteria must be taken together and not individually. These criteria are (see footnote 127).

1. Clostridia can produce endospores (under the laboratory culture conditions, though, some of Clostridia species may not appear as to be forming endospores), this feature will give them resistance to dryness, heat and aerobic environments. Temperature resistance due to their spores results in psychrophilic, mesophilic and thermophilic species,
2. Clostridia are anaerobic, however they can exist in aerobic environments as endospores and then when the environment becomes anaerobic, they will become reactive,
3. Clostridia cannot carry out dissimilatory sulphate reduction. This will not only separate them from SRB (and especially *Desulfotomaculum* sp which are also spore-formers) but also will explain why metal sulphide corrosion products are not found where these bacteria exist.

Clostridia can produce hydrogen, in fact this production of hydrogen gas is so effective that they have been used in bioreactors to generate hydrogen artificially[131] and some of Clostridia isolates have been found to be able to produce hydrogen sulphide as well.[130] Features of *Clostridia* can give it a notorious “disguised serial killer” fame: these bacteria are like SRB anaerobes but not necessarily producing indicative footprints such as sulphides. They are capable of applying at least three mechanisms that, potentially, will enhance corrosion: enhancing anodic reactions by producing acids, facilitating hydrogen-induced cracking (HIC) via hydrogen generation and constant availability of freshly corroding steel surface by ferric iron reduction, similar to IRB. In addition to the above, Clostridium sp. have been reported to be resistant to high temperatures.[130]

These bacteria have been quoted to have caused corrosion in systems such as subsea carbon steel pipe lines[131] natural gas pipelines (see footnote 125), injection systems using produced brine to displace oil from the reservoir (see footnote 126) as well as a potential problem in closed water systems that could form anaerobic environments.[132] Figure 4.26 shows two examples of pitting induced by the corrosive effect of Clostridia sp. on carbon steel pipe line coupons.

---

[130] Alabbas FM, Kakpovbia A, Mishra B, Williamson C, Spear JR, Olson DL (2013) Corrosion of linepipe carbon steel (X52) influenced by A SRB consortium isolated from a sour oil well, Paper No. 2275, CORROSION 2013, Houston, TX.

[131] Dias C, Bromel MC, Beulah ND (1990) Microbially induced organic acid under deposit attack in a gas pipeline. Mater Performance 29(4):53–56.

[132] Roberge PR (2000) Handbook of corrosion engineering. McGraw- Hill Companies Inc.

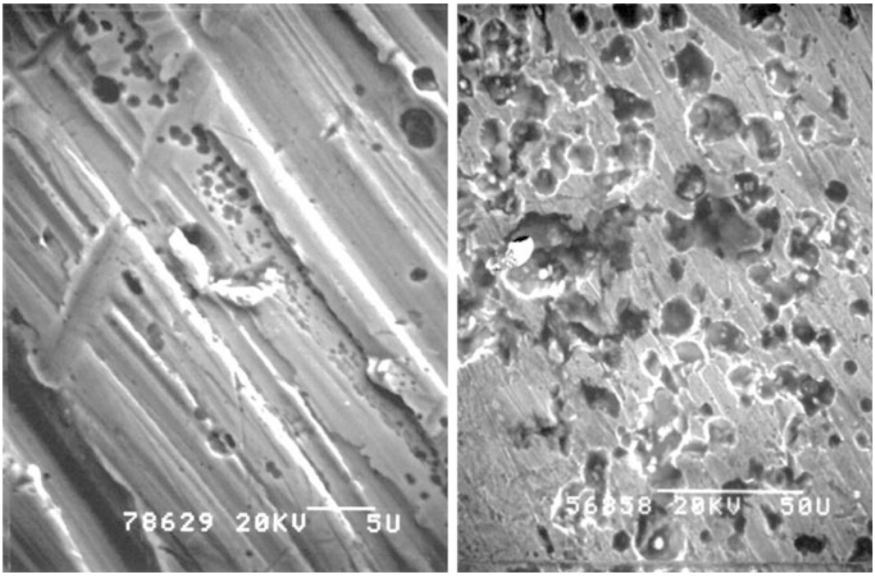


Fig. 4.26 SEM of a coupon made of pipeline steel exposed to a mixed culture containing SRB as well as Clostridium after (*left*) 2 h and (*right*) 1 month (see footnote 126) © NACE International 2004

Fig. 4.27 An example of gangrene caused by Clostridia (Clostridium perfringens bacteria)[135]

Apart from corrosion, Clostridia are also significant from a hygienic point of view: the spores by Clostridia in addition to being resistant to heat, can also be resistant to chlorination at levels that are normally used to treat water.[133] The resistance of spores within Clostridia is a serious matter and must be treated with high level of care.[134] Clostridia have been responsible for a very tragic type of "Gas gangrene" that can even cause amputation of the affected member, as shown in Fig. 4.27.

4.9 Summary and Conclusions

Microbiologically influenced corrosion (MIC) is a subdivision of biocorrosion that deals with the role of micro-organisms such as bacteria in initiation and increasing both the intensity and extent of corrosion.

MIC is so important that its industrial, economical and even public health-related impact can not be overlooked. MIC-related expenses can account for a certain fraction of GNP (about 0.8 % GNP calculated) and the domain of its effects can be as far reaching as agriculture and even some diseases.

MIC is electrochemical in essence, however it does not have a straight forward electrochemistry. It has been more than seven decades that researchers have been trying to explain MIC by electrochemistry, but it seems that the bacteria have more surprises in store for us: while the Classic Theory proposed in mid-1930s put all the blame on SRB, the alternative, new theories tried to sequester the bacteria as much as possible. Recently, however, it has been suggested that perhaps the bacteria itself are engaged in picking up the required electrons directly from the metallic surface. However, these new finds still need to be refined more as to enable them to elaborate the complexities encountered in practice more efficiently.

SRB are not the only bacteria, or even the most important bacteria, involved in MIC. There are many bacteria that could be much more interesting than SRB. While SRB and their corrosive effects and, especially for the first time, their impact on stress corrosion cracking were discussed, another example of the bacteria involved in corrosion was also presented. This was a group of bacteria collectively named as the iron-reducing bacteria (IRB).

---

[133] Indian Standard Packaged natural mineral water specification (Second Revision), Annex C (Clause 6.1.4) detection and enumeration of the spores of sulphite-reducing anaerobes (clostridia) bureau of Indian standards Newdelhi, India, First Reprint DECEMBER 2006.

[134] Maillard J-Y (2010) Innate resistance to sporicides and potential failure to decontaminate. J Hosp Infect 1–6. doi: 10.1016/j.jhin.2010.06.028.

[135] Schröpfer E, Rauthe S, Meyer T (2008) Diagnosis and misdiagnosis of necrotizing soft tissue infections: three case reports. Cases J 1:252. doi:10.1186/1757-1626-1-252, CC BY 2.0, https://commons.wikimedia.org/w/index.php?curid=6886224.

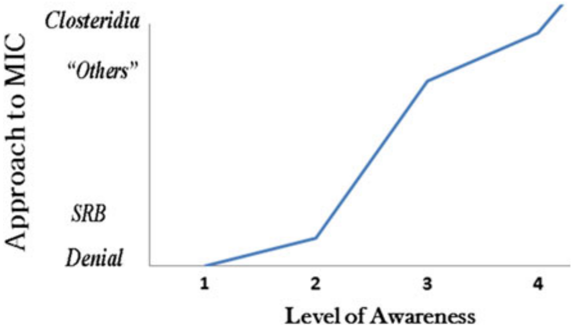


Fig. 4.28 Schematic categorised levels of awareness (LoA) against one's knowledge and appreciation of MIC. Relative distance between each level presents the effort it can take to arrive at that particular level. It starts with total denial of MIC and ends with appreciation that not only the role of SRB in corrosion is undeniable, but also "other" types of CRB such as IRB, IOB, SOB and the like do exist and perhaps the most important CRB is Clostridia

IRB are interesting not only because of their possible corrosivity and, again for the first time, their impact on accelerating of stress corrosion cracking processes, but also because of their possible protective and inhibitive features on corrosion.

We tried to also briefly introduce Clostridia and its contribution to corrosion as well as general health. In this author's opinion, if one can show the level of awareness about MIC, there can be four levels as shown in Fig. 4.28.

Clostridia are anaerobic, capable of producing low pH environments as well as inducing HIC. Clostridia do induce localised corrosion manifested as pitting in the absence of SRB, a feature that some researchers (see footnote 126) have hypothesised it as the reason why there has been no link between the number of SRB and the observed corrosion rate.

This author would like to propose another possibility here: what if the pitting which is observed is being induced by a mixed community of both SRB and Clostridia, where conventional methods for identification of microbial communities (such as Field rapid tests) only detect SRB and not Clostridia? Thus, the measured corrosion rate which is originally coming from two communities (SRB and Clostridia, such as *Clostridium acetobutylicum*) is measured just based on one community (SRB) alone. This is certainly a possibility that needs to be tested but if it is true, then we can explain why there has been no linked between levels of SRB and corrosion rates.

Despite what we know about micro-organisms and their role in corrosion, we must be humble and honest to say that these tiny little living things do have the power of puzzling us. Comparing what we know about them with what we do not know is like comparing a single grain of sand with the beach.

On the other hand, it is very crucial to know more about MIC and how it affects our industrial systems, obviously because of the risks involved, either economical or environmental. Logically, in order to know more, much better conditions of research and development are required and in order to achieve this, more funds are essential. To attract more funds, apart from considering economical and environmental risks, industry needs to know how systems can be become vulnerable to MIC, as prevention is much better than mitigation.

The next chapter deals with expressing the general guide lines to find out how industrial systems, let it be a heat exchanger, or a gas pipeline or a ballast tank, could be in danger of being attacked by MIC.

Selected References

Alabbas FM, Kakpovbia A, Mishra B, Williamson C, Spear JR, Olson DL (2013) Corrosion of linepipe carbon steel (X52) influenced by A SRB consortium isolated from a sour oil well, Paper No. 2275, CORROSION 2013, Houston, TX

Dias C, Bromel MC, Beulah ND (1990) Microbially induced organic acid under deposit attack in a gas pipeline. Mater Performance 29(4):53–56

Indian Standard Packaged natural mineral water specification *(Second Revision)*, Annex C *(Clause 6.1.4)* detection and enumeration of the spores of sulphite-reducing anaerobes (clostridia) bureau of Indian standards Newdelhi, India, First Reprint DECEMBER 2006

Maillard J-Y (2010) Innate resistance to sporicides and potential failure to decontaminate. J Hosp Infect 1–6. doi:10.1016/j.jhin.2010.06.028

Roberge PR (2000) Handbook of corrosion engineering. McGraw- Hill Companies Inc.

Schröpfer E, Rauthe S, Meyer T (2008) Diagnosis and misdiagnosis of necrotizing soft tissue infections: three case reports. Cases J 1:252. doi:10.1186/1757-1626-1-252, CC BY 2.0, https://commons.wikimedia.org/w/index.php?curid=6886224

Further Reading

Duan J, Wu S, Zhang X, Huangb G, Du M, Hou B (2008) Corrosion of carbon steel influenced by (Jang YS, Woo HM, Im JA, Kim IH, Lee SY (2013) Metabolic engineering of Clostridium acetobutylicum for enhanced production of butyric acid. Appl Microbiol Biotechnol 97:9355–9363) anaerobic biofilm in natural seawater, Electrochimica Acta 54 (2008) 22–28)

Eckert R, Aldrich H, Pound BG (2004) Biotic pit initiation on pipeline steel in the presence of sulphate reducing bacteria, Paper No. 04590, CORROSION 2004, NACE, USA

Kane DR, Jain LA, Williamson C, Spear JR, Olson DL, Mishra B (2013) Microbiologically influenced corrosion of linepipe steels in ethanol and acetic acid solutions, Paper No.2250, CORROSION 2013, Houston, TX, USA

Lutey RW (1996) The occurrence and influence of anaerobic bacteria in cooling water systems, Paper G-06, pp 705–724, Proceedings of the 7th middle east corrosion conference, vol 2, Manama-Bahrain, 26–28 February 1996)

Mead GC (1992) Principles involved in the detection and enumeration of Clostridia in foods. Int J Food Microbiol 17:135–143

Mendez BS, Pettinari MJ, Ivanier SE, Ramos CA, Sineriz F (1991) Clostridium therrnopapyrolyticum sp. nov., a cellulolytic thermophile. Int J Syst Bacteriol 41(2):281–283

Zhang H, Bruns MA, Logan BE (2006) Biological hydrogen production by Clostridium acetobutylicum in an unsaturated flow reactor. Water Res 40:728–734