

Engineering Materials and Processes

Reza Javaherdashti

Microbiologically Influenced Corrosion

An Engineering Insight

Second Edition

 Springer

Engineering Materials and Processes

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Reza Javaherdashti
Perth, Western Australia
Australia

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Preface to the Second Edition

When I was writing the first edition of this book, what I had in mind were two ideal goals. One was to reach to a wider audience, both academics at research facilities and field engineers and professionals. It was an enthusiastic target but now, after the first edition of this book has been one of the best sellers in its category, I am glad that I have achieved my enthusiastic goal. In all MIC workshops that I have designed and run for various industries around the world, I have advised this book as the main course material and the very positive feedback that I received after more than 4000 h of teaching microbial corrosion to industry and academia has ensured me that this book has achieved the first goal I originally had in mind.

Microbiologically influenced corrosion (MIC), despite its relatively short life (initial academic research about MIC started in 1930s), has proved to become one of the most significant sources of confusion for both industry and academia. It is so complicated that in many cases it is mixed up with other corrosion phenomena and therefore wrongly reported and treated. In addition to “self-proclaimed” MIC experts that make the already blurred waters of research and treatment about MIC even more muddled, misunderstanding about MIC still exists, even among professionals. For example, it is still believed that MIC should be studied as a subject within the general topic of “internal corrosion”. I would like to see how defenders of such classifications would define external corrosion of pipelines due to corrosion or ALWC (Accelerated Low Water Corrosion) induced MIC as examples of “internal corrosion”?!

The second goal that I had in mind and I am glad that my readers did appreciate was that I had decided to write my book in a language which is quite precise but simple and in a tone that would only pick up the essential elements of the topic without too much details about it. This new edition will still with both of these goals: reaching a wider audience with a simple yet precise and right-to-the-point language.

This edition has some features that will put it a head and shoulder above its first edition. I have added, as much as I could, the following:

- A discussion about a relatively unknown corrosion-related bacteria, that is, Clostridia,
- A full chapter about mathematical modelling of MIC, in particular fuzzy logic,
- A comparison of culture-independent methods with culture-dependent methods and also a quick reference in comparing pros and cons of various culture-independent methods with each other,
- Further practical strategies for dealing with MIC in terms of combination of CKM and CM in the context of MIC,
- A brief introduction to natural biocides and especially neem tree.

My reasons for feeling the need to add the above topics were basically the following:

- Corrosion professionals must hear more about what had been hidden within pure academic research papers and discussions, particularly with regard to mathematical modelling by using fuzzy logic and calculations because the possibility of applying mathematical thinking into the prediction of MIC is certainly an important issue: this is a feature absent from corrosion prediction models so far—or at least the famous ones this author knows,
- while SRB and its possible impact on corrosion is yesterday’s news to many corrosion professionals, knowing about “the sometimes contradicting corrosion features” of Clostridia is certainly a must that so far has been largely overlooked by many field engineering practices.
- Culture-dependent methods seem to be slowly replaced by culture-independent methods thanks to recent advances in molecular biology. Using culture-independent methods are still far from being totally ideal but even now they are much superior to culture-dependent methods for diagnosing MIC.
- As one of my main target audiences has always been field engineers, I have tried to give much more practical clues about how to deal with microbial corrosion. I have applied this in two areas: first by talking about the “diplomacy: of dealing with MIC by redefining what I introduced as corrosion knowledge management (CKM), and second, having everyday growing conscience and concerns about what we are doing to mother Earth, I through a brief introduction into “Natural biocides”, I mean those biocides that are both green (eco-friendly) and natural (*Directe a Natura*).

When I was writing the first edition of this book, I had wished that my elder daughter, Helya, who was 2 years old then, would become interested in this topic. I think my wish has been granted. Now I wish that her sister, Hannah, would also become interested in understanding what daddy is doing too!

I would like to thank all those who have supported me, directly or indirectly, by their comments, contributions and encouragements I also would like to thank Springer for giving me the chance of preparing the first edition of this book and supporting me for the second edition.

I have tried to “blow soul to the body” of this book to make it even much better than what it was and what may be available in the market today as its counterparts. I hope that I have succeeded!

I would like to dedicate this edition to the memory of Tesla, someone who showed with his life that dreams may come true...

Perth, Australia
March 2016

Reza Javaherdashti

Preface to the First Edition

A Few Words About the Structure of This Book

Let me be honest with you: I rarely read the prefaces of books! It is, I guess, because I think that I am interested only in the context of the book, not what the author wants to teach me about how to read the book. I have found very few books whose “introduction” has been interesting to me. But for this book, I strongly recommend that readers study this preface to understand why I chose the structure used in placing the chapters.

I have always wanted to write a book about microbial corrosion (there are some alternative names to address this type of corrosion; they’re given in Chapter 4) that would have a rather wide audience, ranging from academics (lecturers, researchers, postgraduate students) to industry specialists (field engineers, design engineers, industry managers). This goal may seem very enthusiastic, to put it politely. There has always been an unseen, undefined gap between different disciplines of science (Videla has touched on this very meaningfully, and his paper is quoted in later chapters of this book), let alone between industry and research/university environments.

Despite these obstacles, I have tried to be fair to both of my target audiences, university/research and industry. In addition, I have tried to focus on a very important aspect of corrosion mitigation: the human management factor. With this in mind, readers must understand the structure of this book to gain the maximum advantage of reading a book with such a wide potential audience.

We will start our microbial corrosion journey by reviewing some basic corrosion – to put it more precisely, electrochemical corrosion, in Chapter 1. In this chapter, some basic facts regarding electrochemical corrosion are reviewed to a limited extent that may be useful to understand the logic behind using methods and techniques such as cathodic protection, coating and use of inhibitors which are explained in Chapter 2 in the section “Technical Mitigation of Corrosion”. This much can be found in almost every book written on corrosion or microbial corrosion, where basic information regarding corrosion and its mitigation is given.

However, a very important part of mitigation methods against corrosion (and, therefore, against microbial corrosion) is the factor of human management; no matter how good the techniques are that we use in combating microbial corrosion, if there is poor communication between the technical staff (engineers, technicians, foremen, *etc.*) and the management, the resultant practice will have very limited impact on upgrading the performance of the system. If management cannot understand the importance of microbial corrosion, even the best corrosion engineer cannot justify the expense of microbial corrosion recognition and treatment. This may not be a serious matter for academic researchers, but it certainly is important for both industry researchers and field engineers. Chapter 3 deals with a very genuine and innovative concept called “corrosion knowledge management (CKM)” to differentiate it from what is normally known as “corrosion management”. While the later refers to the technicalities involved in corrosion treatment (such as the best design and practice of cathodic protection, the choice of inhibitors and coatings and the like), corrosion knowledge management concentrates more on managerial aspects. Therefore, although a manager may not know what a reference electrode is for, or what the difference between an inhibitor and a non-oxidising biocide is, this manager will need to know how, economically and environmentally, microbial corrosion in particular and corrosion in general could be dangerous. A manager also needs to have a managerial system in place so that an organisational chart can be defined. Chapter 3 introduces the basics of such managerial needs.

Chapter 4 may be described as the heart of this book. It begins with a historical profile of microbial corrosion and definitions, followed by topics such as the “paradoxical” effect of biofilms on corrosion. The text continues with a review of some types of bacteria which are of interest in the microbial corrosion literature. Some of these bacteria, such as the sulphate-reducing bacteria (SRB) have been long known to researchers and industry. Some, like the iron-reducing bacteria (IRB) are not that well known, and I have dubbed them as “shy” as they seem not to get the attention of researchers the way SRB do. The possible role of magnetic bacteria in corrosion is stated for the first time in the literature of microbial corrosion, to the best of my knowledge. Magnetic bacteria are very interesting, and they form an “exotic” realm for further research. Chapter 4 also includes some important concepts regarding the possible impacts and effects of SRB and IRB on enhancing stress corrosion cracking.

Before closing this summary of Chapter 4, I want to add a few words about SRB. I do agree with Brenda Little and Patricia Wagner in calling the importance of SRB a “myth” of microbial corrosion research and practice. But, readers may wonder, if the importance of these bacteria has been naively exaggerated, why I am allocating so many pages to explain them? The answer is easy: the stronger a wrong belief is, the more you have to explain it to make it clear. I have tried to explain that although SRB are important, they are not so important as to cause us to forget other types of bacteria involved in microbial corrosion.

Chapter 5 considers what and how factors must come together to put a system in danger of microbial corrosion. This chapter studies the effect of water quality and velocity, oxygen, hydrotesting and other relevant factors in the initiation of

microbial corrosion in *any* system that has the potential. It does not matter which industry the system may belong to. As long as the required factors are in place, the system will become vulnerable.

Chapter 6 studies the parameters required for “recognition” of microbial corrosion, factors such as the shape of the pits, mineralogical “fingerprints”, and the appearance of corrosion products. This chapter ends with a review of “detection” techniques which are basically microbiological and electrochemical. Thus, for example, culturing, molecular biological methods, and rapid check tests and their pros and cons are among the topics that are. An important part of this chapter for researchers is the review of electrochemical methods and their importance in microbial corrosion investigations.

In Chapter 7, I try to show that microbial corrosion can have more or less similar patterns despite different systems in which it is occurring. This chapter shows how microbial corrosion in fire water lines could be similar to that happening within the legs of a submersible off-shore platform, and how buried pipelines and steel piles of a jetty could experience almost the same scenarios of microbial attack.

Almost no engineering material is safe from or immune to microbial corrosion. In Chapter 8 the vulnerability and susceptibility of copper and cupronickels, duplex stainless steels and concrete will be discussed in a brief and informative manner. I had my reasons for picking these materials: copper and its alloys have the reputation of being poisonous to micro-organisms, duplex stainless steels are known for their high resistance to corrosion thanks to their duplex microstructures of ferrite and austenite, and concrete is widely used in both the marine and water industries because of its good performance and cost effectiveness.

Having said so much about microbial corrosion, in Chapter 9 I address a logical expectation: how is this type of corrosion treated? I go through only the physical/mechanical, chemical, biological, and electrochemical (including cathodic protection) means and factors that have been used thus far to treat and mitigate microbial corrosion. An interesting point, among others, could be the possible explanation of why cathodic protection could be effective (or sometimes ineffective) on microbial corrosion. Although principles of CKM are also applicable here, for reasons that I discussed briefly in the footnote of the opening page of Chapter 9, I did not include the principles in the contents of the chapter.

I have been careful to use language which is very precise, technically sound, and accurate, yet somewhat casual and not too technical. I believe that if there is a truth, it can be explained with accurate yet simple words.

These have been my aims and dreams, and I do hope that my readers will share them with me!

Acknowledgement (First Edition)

I would like to thank many people who have helped me through my years spending on research, consulting and teaching microbial corrosion. I would like to thank my dear friends Prof. Hector A. Videla (University of La Plata, Argentina), Prof. Dr. Filiz Sarioglu (Middle East Technical University, Turkey), Dr. M. Setareh (Arak University of Medical Sciences, Iran), Mr. R.A. Taheri (University of Tehran, Iran), and Dr. M.M. Vargas (Monash University, Australia) for their sincere friendship, kindness and scientific generosity. Supports of Dr. Elena Pereloma, Dr. Raman Singh and Prof. Brian Cherry (Monash University, Clayton Campus) are highly appreciated for my research on microbial corrosion at Monash University. In this regard, I should also highly thank my good friend, Mr. Chris Panter (Monash University, Gippsland Campus) for his priceless assistance, support and contributions. I would like to appreciate my friends and colleagues, Dr. M.S. Parvizi (Principal Technology Engineer, Foster Wheeler Energy Ltd., UK), the recipient of NACE 2007 Technical Achievement Award, Dr. B. Kermani (KeyTech, UK) and also Dr. A. Morshed (Principal Corrosion Engineer, Production Services Network, UK) for reading some parts of this book and their useful comments. I am indeed very thankful to a great friend and mentor, Dr. Peter Farinha, Director and Principal Engineer of Extrin Corrosion Consultants (Perth-Australia). I am thankful to him because he believed in me and gave me the opportunity to develop my vision. Also, he was very kind in proofreading the manuscript and giving suggestions for its improvement. Mrs. Maria Farinha (Director, Extrin) was very kind in proofreading some of the chapters of this book as manuscript. There are also many other professionals and friends to whom I am sincerely thankful but there is no enough space here to either write their names or express my great feelings and thanks for them.

My parents and my sister are the ones who believed in me not just as a son and a brother but someone who can make a change. Margie and David Mills are among the beloved ones to whom I want to present my sincere thanks and love. I also hope that my little daughter, Helya, will find this book useful too, someday in the future, perhaps!

There is no doubt that there are many nameless “soldiers” who, both as “white collars” and “blue collars”, are fighting globally against corrosion to make life easier for all of us. I would like to dedicate this book to all the scientists and engineers, researchers and technicians, academics and students, managers and administrators who, directly or indirectly, work to fight against a silent serial killer called *Corrosion!*

Perth, Australia
July 2007

Reza Javaherdashti

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Introduction

A Few Words About the Structure of This Book

Let me be honest with you: I rarely read the introduction section of books! It is, I guess, because I think that I am interested in the context of the book not what the author wants to teach me about how to read the book. I have found very few books whose “introduction” has been interesting to me. But for this book, I strongly recommend to the reader to study this introduction because of the structure I have used in placing the chapters.

I have always wanted to write a book about microbial corrosion (there are some alternative names to address this type of corrosion, we will name them in Chap. 4) that would have a rather wide range of audience, ranging from academics (lecturers, researchers, postgraduate students) to industry specialists (field engineers, design engineers, industry managers). This dream may seem to be a very enthusiastic target, to put it politely. It has always been an unseen, undefined gap between different disciplines of science (Videla has touched this very delicately and meaningfully, we will quote his paper in later chapters of this book), let alone between industry and research/university environments.

Despite all these, I have tried to be fair to both of my target audiences, university/research and industry. In addition, I have tried to focus on a very important aspect of corrosion mitigation: the human management factor. To achieve this goal, the structure of this book must be understood to enable the reader to gain the main advantage of reading a book with such a wide range of potential audience.

We will start our journey to microbial corrosion by reviewing some basic corrosion, to put it more precisely, electrochemical corrosion, in Chap. 1. In this chapter, some basic facts regarding electrochemical corrosion are reviewed to a limited extent that may be useful to understand the logics behind using some methods and techniques such as cathodic protection, coating and use of inhibitors which are explained in Chap. 2 under the title “Technical Mitigation of Corrosion”. This much can be found in almost every book written on corrosion or microbial corrosion, where some basic information regarding corrosion and its mitigation are

given. However, a very important part of mitigation methods against corrosion (and, therefore, against microbial corrosion), is the factor of human management; no matter how good the techniques are that we use in combating against microbial corrosion, if there is a poor communication between the technical staff (engineers, technicians, foremen, etc.) with the management, the resultant practice will have very limited impact on upgrading the performance of the system. If management can not understand the importance of microbial corrosion, even the best corrosion engineer cannot justify the expenses of microbial corrosion recognition and treatment. This may not be a serious matter for academic researchers but for both industry researchers and field engineers, it is. The next chapter, Chap. 3, deals with a very genuine and innovative concept called “corrosion knowledge management”, or briefly, CKM, to differentiate it from what is normally known as “corrosion management”. While the later refers to the technicality involved in corrosion treatment (such as the best design and practice of cathodic protection, the choice of inhibitors and coatings and the like), corrosion knowledge management concentrates more on managerial aspects. Therefore, although a manager may not know what a reference electrode is for, or what is the difference between an inhibitor and a non-oxidising biocide, this manager will need to know how, economically and environmentally, microbial corrosion in particular, and corrosion, in general, could be dangerous. A manager also needs to have a managerial system in place so that a certain organisational chart can be defined. Chapter 3 introduces the basics of such managerial needs.

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Before closing this descriptive section on Chap. 4, I want to add a few words about SRB. I do agree with Brenda Little and Patricia Wagner in calling the importance of SRB as a “myth” of microbial corrosion research and practice. But, the reader may wonder, if the importance of these bacteria is so naively exaggerated, why I am allocating so many pages to explain them? The answer is easy: the stronger a wrong belief is, the more you have to explain it to make it clear. I have tried to explain that although SRB are important, they are not so important as to cause us to forget other types of bacteria involved in microbial corrosion.

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quality and velocity, oxygen, hydrotesting and other relevant factors in initiation of microbial corrosion in *any* system that has the potential. It does not matter which industry the system may belong to. As long as the required factors are in place, the system will become vulnerable.

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In Chap. 7, we will try to show that microbial corrosion can have more or less similar patterns despite different systems in which it is occurring. This chapter shows how microbial corrosion in fire water lines could be similar to that happening within the legs of a submersible off-shore platform or how buried pipelines and steel piles of a jetty could experience almost the same scenarios of microbial attack.

Almost no engineering material is safe and immune to microbial corrosion. To select some of them, in Chap. 8 the vulnerability and susceptibility of copper and cupronickels, duplex stainless steels and concrete will be discussed in a brief and informative manner. I had my reasons for picking these materials: copper and its alloys have the reputation of being poisonous to micro-organisms, duplex stainless steels are known for their high resistance to corrosion thanks to their duplex microstructures of ferrite and austenite and concrete is so widely used in both marine and water industry because of its good performance and cost effectiveness.

Having said so much about microbial corrosion, Chap. 9 answers a logical expectation: how this type of corrosion is treated? I will go through only the physical-mechanical, chemical, biological and electrochemical (including cathodic protection) means and factors that have been used so far to treat and mitigate microbial corrosion. An interesting point, among others, could be the possible explanation to show why cathodic protection could be effective (or sometimes ineffective) on microbial corrosion. Although principles of CKM are also applicable here, for reasons that I have briefly discussed at the footnote of the opening page of Chap. 9, I will not include them into the contents of the chapter.

I have been careful to use a language which is very delicate, technically sound, and accurate yet somewhat “witty” and not too technical. I believe that if there is a truth, it can be explained with simple, yet accurate words.

These have been my aims and dreams and I do hope that my readers will also share them with me!

Chapter 1

A Short Journey to the Realm of Corrosion

Abstract In this chapter, we will review some important, basic concepts of corrosion. This chapter and the next chapter about technical treatment of corrosion will make the necessary electrochemical corrosion understanding of MIC.

Keywords Standard definition of corrosion · Anodic/cathodic reaction · Thermodynamics of corrosion · Kinetics of corrosion · Pourbaix diagram · Polarisation diagram

1.1 Introduction

The main idea of this chapter is to deal with the principles and basics of corrosion, to an extent that will be necessary for understanding microbial corrosion, or whatever you call it!¹

1.2 Definition of Corrosion

Corrosion, according to ISO 8044 standard, is defined as² “Physicochemical interaction (usually of an electrochemical nature) between a metal and its environment which results in changes in the properties of the metal and which may often lead to impairment of the function of the metal, the environment, or the technical system of which these form a part”. In a sense, corrosion can be viewed as “the chemical reversion of a refined metal to its most stable energy state”.³ During extractive processes to obtain metals out of their ores or mineral compounds, reductive processes are applied. In these processes, by giving more electrons to

¹See Chap. 4 for alternative names.

²Mattson E (1989) Basic corrosion technology for scientists and Engineers, Chap 3. Ellis Horwood Publishers.

³Videla HA (1996) Manual of biocorrosion, Chap. 4. CRC Press, Inc.

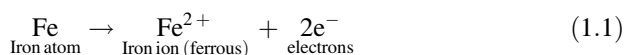
metallic compounds in the ore, thermodynamically stable metal in the ore is brought into thermodynamically instable state by reducing processes of extractive metallurgy. In other words, by investing energy to convert the ore to metal, chemical bonds are broken; oxygen, water and other anions are removed and the pure metal is arranged in an ordered lattice whose formation requires certain amount of excess energy, different for each metal, to be stored. It is the dissipation of this stored energy that drives the corrosion reaction. As a result, metals always are expected to reach a stable energy level by giving off additional electrons they have received during extractive metallurgical processes. This builds up the thermodynamic basis of oxidation, or more generally termed, corrosion, in metals.

The main components of electrochemical corrosion are the Anode (where anodic reactions occur), the Cathode (where cathodic reactions of receiving electrons from the anodic reactions happen) and the aqueous solution, or Electrolyte, which contains positively and negatively charged ions and is a conductor.

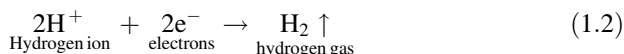
As all of the corrosive processes related to micro-organisms occur electrochemically, i.e. in aqueous environments, this chapter will just focus on the mechanisms of this type of corrosion and will not explain other types of corrosion such as high temperature corrosion.

1.3 Electrochemical Corrosion: A Brief Introduction

Definitions of the anode and the cathode are among basic definitions in electrochemical corrosion. The area of the metal surface that corrodes/the metal dissolves and goes into solution, is called the anode. The cathode is the area of the metal surface that does not dissolve. In the literature of electrochemistry, reduction and oxidation reactions are defined as when metals lose electrons (i.e. oxidation) or gain electrons (reduction):



Reaction (1.1) is an example of an oxidation reaction, the oxidation of iron. As it is seen, this reaction gives off electron into the solution. Such reactions are also called anodic reactions.



Reaction (1.2) is an example of a reduction reaction. Reduction reactions are also called cathodic reactions. So, alternatively, one can define corrosion as anodic reactions that are occurring at the anode. Thus, three main components of any electrochemical corrosive reaction are the anode, the cathode and the solution in which corrosion occurs. This solution is called the electrolyte and always water is an integral part of it. One may show these components as three corners of an “electrochemical triangle”:

The “electrochemical triangle” implies that for *corrosion to happen, all the three components must be available and interactive*. It follows that any method to be implemented to solve a corrosion problem must try to remove at least one of the sides of the triangle. This point will be discussed in more detail later (Fig. 1.1).

Some important points about corrosion are:

- As it is evident from definitions of anodic and cathodic reactions, there is exchange of electrons either as liberated (anodic reaction) or gained (cathodic reaction). This means that one can actually talk about flow of electrons, or, the current. On the other hand, if a certain area “A” of the anode loses (or, as cathode, gains) “n” electrons, it follows that an area of “2A” will give (or, again as cathode, will gain) “2n” electrons. So, it is possible to talk about current density instead of current. Defining the current density as total current (in Ampere) passing through an electrolyte per unit area of an electrode, it is shown as A/m^2 . A very important point is that, by applying Faraday’s laws and noticing that as for many metals of engineering interest the ratio of the relative molar mass (equivalent weight) to the density is roughly constant, then:

$$A/m^2 = mm/yr$$

The relation states that the corrosion rate of metal, expressed in millimetre per year (mm/yr) is numerically equal to the current density expressed in Ampere per unit area (A/m^2).⁴

- Most of the time, there is only one anodic reaction. For instance, in the “Galvanic cells” where there are two dissimilar metals such as iron and copper, the anodic reaction is always dissolution of the metal with higher tendency to corrode. However, there could be more than one cathodic reaction. Some of important cathodic reactions are as follows:

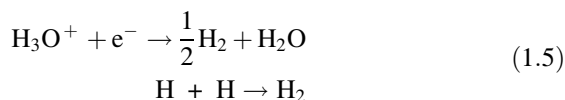
1. Reduction of oxygen in neutral/alkaline solutions:



2. Reduction of hydrogen that in anaerobic (oxygen-free) or acid electrolytes switches to

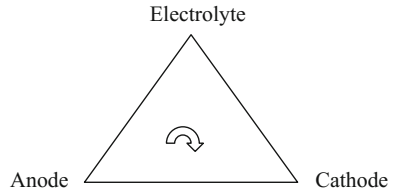


Or



⁴West JM (1986) Basic corrosion and oxidation, Chap. 6. Ellis Horwood Publishers.

Fig. 1.1 main components of an electrochemical triangle



This much slower reaction (except in acid conditions) explains why corrosion is hardly seen in anaerobic environments (except with passive/active metals such as stainless steels and in the presence of the micro-organisms) (see footnote 3).

1.3.1 When Corrosion Happens?

It will be of interest to anticipate under what conditions corrosion can actually occur. Every electrochemical reaction has a specific voltage that can be used with respect to a reference point or standard called “reference potential” to compare the voltages. In this way, one is able to say which reaction is more “noble” (not easy to take place) and which one is more “active” (thermodynamically easier to happen). Reference reactions are defined as to have the following characteristics:

- All of the substances taking part in the electrode reactions must have unit activity (activity = 1).
- Temperature must be 25 °C.
- Hydrogen pressure in the reference electrode must be one atmosphere.

By ranking and rating the electrode reactions according to the values of the standard potential, the *electrochemical series* is obtained. With respect to hydrogen voltage (accepted as zero), the potential required for reduction of Cu^{2+} to Cu is +0.34 volts and the potential of reduction of Fe^{+2} to Fe is -0.41 volts on the standard hydrogen electrode (SHE) scale. As reduction of copper ion to copper requires less energy (in terms of potential) than reduction of ferrous, then Cu^{2+} to Cu takes place easier and sooner. The net effect is cathodic reaction of copper and ANODIC reaction of iron to ferrous resulting in corrosion of iron in copper sulphate solution, in other words, galvanic corrosion of iron by copper cathode ($\text{Fe} + \text{CuSO}_4 \rightarrow \text{FeSO}_4 + \text{Cu}$).

Although using the electrochemical series seem to be very useful, it does have very serious limitations such as (see footnote 2):

- Electrochemical series applies only to oxide-free metal surfaces and at the activities (concentrations), for which the standard potentials are valid. However, in actual practice, oxide films often cover the metal surfaces.

- The activities can deviate considerably from 1, especially when the metal ions are associated with other constituents in the so-called complex ions. It is not always possible to maintain standard temperatures and pressures.

Such conditions can result in the measured potentials having a completely different order than that given in the electrochemical series. That is why metals are exposed to a given electrolyte, say, seawater, and then arranged according to the measured electrode potential. What is then produced is called a *galvanic series* in a given environment at a given temperature. The potentials, however, are only valid for the electrolyte in which the measurements have been made. In seawater at 25 °C, stainless steel (18/8) in the passive state has a potential of 0.19 V (measured with respect to hydrogen scale) which will make it more noble to galvanised steel that has a voltage value of -0.81 V (also with respect to hydrogen scale).

1.3.2 Corrosion Forecast

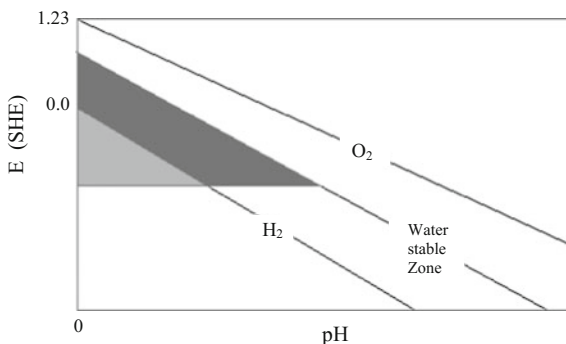
Pourbaix diagrams:

Thermodynamically, one may forecast or predict if certain reactions can occur, however, this does not mean that the reaction in question *will* occur. Thermodynamics can tell us about the “tendency” of corrosion to happen and it is by use of Pourbaix diagrams that one can thermodynamically predict if certain reactions will occur.

Pourbaix diagrams use potential (in Volts) versus pH. A more simplified Pourbaix diagram is seen from Fig. 1.2.

As it is seen from Fig. 1.2, two lines designated by O_2 and H_2 , upper and lower, define the domains for oxygen and hydrogen stability: above the upper line water is oxidised to O_2 , so oxygen is evolved above the upper line. Below the lower line, water decomposes to H_2 and thus, hydrogen will be liberated below the hydrogen line. Hence, the domain with dark colour represents where corrosion occurs solely

Fig. 1.2 A simplified Pourbaix diagram



by oxygen reduction and the domain with lighter colour represents where hydrogen evolution can also take place.

These diagrams can be used to follow the consequences of environmental changes upon corrosion behaviour. Pourbaix diagrams are useful guides as to “what should occur” but what determines “what actually does occur in practice” are the rates of the processes and reactions. To understand kinetics of corrosion, or in other words, to understand how fast corrosion takes place, one may use another tool that is known as polarisation curves. To understand polarisation curves, it is necessary to understand the two components of them, that is, anodic and cathodic polarisations.

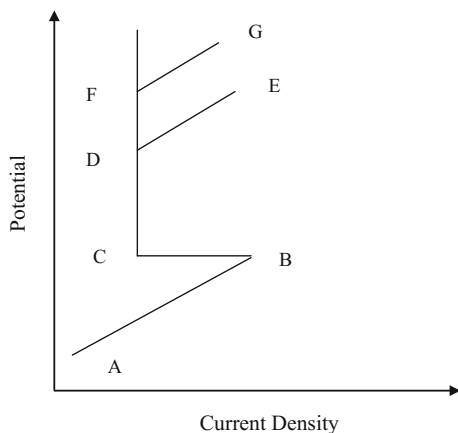
1.3.2.1 Anodic Polarisation (Anodic Polarisation Reaction)

An example of such polarisation curves is given in Fig. 1.3:

Such curves are observed (a) in solutions with very low pH (sufficiently acidic) and (b) if the metal is capable of forming films. In this type of curves, three regions can be differentiated

- The first region is where anodic current, and hence, the dissolution rate, will increase as the anode potential is made more positive (high dissolution)..... (A → B)
- The second region is where film formation and passivation of the metal beneath happen. Formation of the film will act as a barrier to further dissolution so that the current (i.e., corrosion rate) will fall.....(B → C)
- The third region is where the rise in potential (passive state) occurs.....(C → D)
- At very high potentials (point D) three possibilities, depending on the conductivity of the corrosion products film, can occur:

Fig. 1.3 A typical anodic polarisation curve



- (a) If the film has a good electrical conductivity, it may be oxidised to soluble species and thus dissolution starts again along ($D \rightarrow E$), where the metal transfers into the “trans-passive” state. This behaviour may be observed where continued dissolution of the passive film on chromium, Cr_2O_3 [Cr(III)], to chromate, CrO_4^{2-} [Cr(VI)], takes place.
- (b) An alternative is if the film is a good electronic conductor, oxygen evolution may occur along ($F \rightarrow G$).
However, if the film is a poor electronic conductor, then high anodic potentials may be reached along ($F \rightarrow H$) with a constant, high current density. This may facilitate “anodising” which is commercially used as a process for protecting aluminium.

It must be said that the presence of ions such as chloride ions, may prevent or delay passivation. Furthermore, passive films—especially in stainless steels—will tend to break down in the presence of such ions.

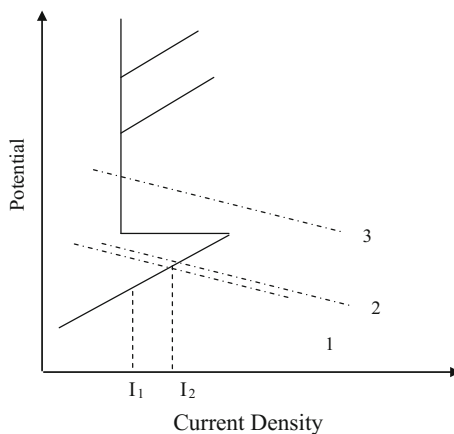
1.3.2.2 Cathodic Polarisation (Cathodic Polarisation Reaction)

Examples of such polarisation curves are shown in Fig. 1.4 as dashed lines:

In Fig. 1.4, the cathodic reaction designated as 2 has a larger corrosion rate than cathodic reaction 1 ($I_2 > I_1$). With a cathodic reaction such as 3, passivation of the metal is reached. As mentioned earlier, there are a number of cathodic reactions such as hydrogen and/or oxygen evolution reactions, reduction of ions such as Fe^{3+} or MnO_4^- or molecular species such as nitric acid. In reality, the cathodic curves are not as straight lines as shown in Fig. 1.4. For example, the shape of the reduction curve of oxygen is rather “curvy” mainly due to the limited solubility of oxygen in aqueous solutions.

When a metal is exposed to an aqueous solution containing ions of that metal, on the surface of the metal, both *oxidation* (changing the metal atoms into the metal

Fig. 1.4 Cathodic polarisation where the *dashed lines* 1, 2 and 3 represent different cathodic reactions that, according to their potentials, can occur



ions, or, *anodic reaction*) and *reduction* (changing the metal ions into the metal atom, or, *cathodic reaction*) can occur. When current is applied to the electrode surface, the electrode potential is changed and it is said that the electrode has been *polarised* and the change in electrode potential is called *polarisation*. *Overpotential* is the difference between the electrode potential of the electrode with applied current and the equilibrium potential for the electrode reaction in question. *Depolarisation* is then defined as the removal of factors diminishing the rate of an electrochemical reaction, for example, cathodic reaction.

1.4 Summary and Conclusions

In this chapter, we very briefly touched on some important theoretical elements of electrochemical corrosion such as how corrosion can be forecast (by using Pourbaix diagrams) and how fast it can happen (by using anodic and cathodic polarisation curves).

Pros and cons of the application of the polarisation methods in studies related to microbial corrosion will be addressed later (Chap. 6). In the next chapter, the implementation of theoretical electrochemistry will be discussed to show how and why some techniques such as inhibitor addition or coating application work in practice.

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Chapter 2

Technical Mitigation of Corrosion: Corrosion Management

Abstract In this chapter we will look at some techniques currently used in industry to mitigate electrochemical corrosion. It is because MIC is in nature an electrochemical corrosion and as such the same measures-at least in principles- must also be applicable to both.

Keywords Coating · Anodic/cathodic protection · Inhibitors

2.1 Introduction

Corrosion can be mitigated by two approaches. One method, that we call “technical approach”, includes all known mitigation techniques such as design and application of cathodic protection, using inhibitors and the like. In the literature of corrosion, this approach has another name: corrosion management. In this chapter, we will discuss “corrosion management”.

2.2 Corrosion Management: A Technical Approach

In this section, some of the technical methods which are frequently used to solve the problem of corrosion and reduce its effects are discussed. These methods, in principle, may include:

- Coatings and linings
- Anodic and cathodic protection
- Use of inhibitors
- Material selection and design improvement

These methods will be discussed in the next sections of this chapter. Care will be taken not to go through all the details of each technique but rather link it with the theoretical aspects of electrochemistry, as covered in Chap. 1.

2.2.1 The Rational of Using Coatings and Linings

The main benefit from using coatings and linings is that they prevent the electrolyte coming into contact with the electrodes. In this way, there will not be an interaction between the anode and the cathode. The “electrochemical triangle”, from Chap. 1, explains how and why, by using coatings and linings, the sides of the triangle are broken and thus no electrochemical corrosion may be expected.

2.2.2 The Rational of Anodic and Cathodic Protection

2.2.2.1 Anodic Protection

Referring to Fig. 1.3 in Chap. 1, the passivation of metal occurs within the passive range (C→D) so that if the potential is kept that high, the metal will anodically be protected. However, anodic protection has some drawbacks such as follows:

- The metallic structure must be of a material of suitable composition for passivation in the particular solution.
- If protection breaks down at any point, corrosion will be extremely rapid at that point because of the low resistance path formed. On the other hand, if the metal potential is made too positive, then the region of passivation may be passed and transpassive corrosion in the form of pitting will occur. To avoid such things happening, extensive monitoring and control facilities are required.
- The passive films will be destroyed if aggressive ions such as chloride ion are present.

Anodic protection is achieved by applying an external cathode and a counter electrode in a manner similar to cathodic protection (next section), except that the current direction is in the opposite sense.

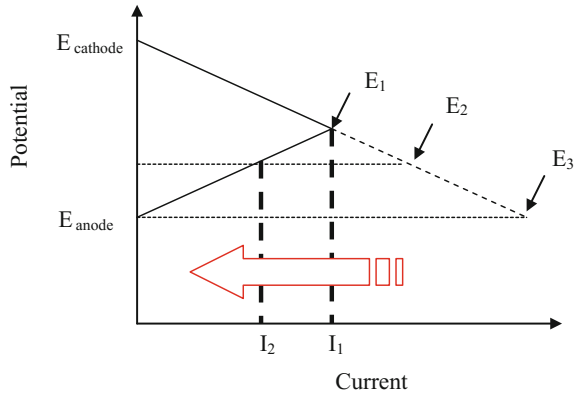
Anodic protection has found some applications in the fertiliser production industry to control corrosion of mild steel in contact with ammonia-ammonium nitrate solutions. It has also been used in vessels containing sulphuric acid.

2.2.2.2 Cathodic Protection (CP)

The corrosion rate of a metal surface in contact with an electrolyte solution is strongly dependent on the electrode potential. In most cases, the corrosion rate can be reduced considerably by shifting the electrode potential to lower values such as those shown in Fig. 2.1.

The main target here is to reduce corrosion by lowering the potential either (1) by connection to an external anode (sacrificial anode) which is a metal more active than the corroding metal or (2) by adjusting the potential of the material by application of an external current (impressed current). Referring to Fig. 2.1, it is

Fig. 2.1 Principle of cathodic protection; at a potential like E_1 , a corrosion current (rate) such as I_1 is reached. By making the potential more negative to E_2 , the corrosion current is reduced to I_2 , as graphically shown by the red arrow



seen that by reducing the potential of the metal from E_1 to E_2 and further down to E_3 , the corrosion current is reduced (note how I_1 is reduced to I_2). It follows that if the potential is further reduced to E_{anode} , then the corrosion current will be zero and the cathodic protection will be completed.

The main concern in CP is that there will be an increase in the alkalinity of the environment produced by the cathodic reaction (see Chap. 1, Eq. (1.3)). This is important because many metals like iron, aluminium and zinc are affected under high pH conditions. If paints have been used with CP system, they must also withstand the alkalinity of the medium. The basic criteria for CP, using a Ag/AgCl seawater reference electrode for the potential measurement, is a negative voltage of at least -0.80 V between the reference electrode and the structure.¹

Some points about sacrificial anodes and impressed current CP systems in offshore structures are² as follows:

- A widely used anode in impressed current CP systems for offshore structures has been lead—6 %, antimony—1 % silver alloy. Other anode materials that have been used with some success are lead—platinum, graphite and a silicon—iron—chromium alloy. The lead—antimony—silver anodes may either be suspended or placed in special holders for rigid attachment to the underwater platform members. Suspended systems are somewhat more susceptible to mechanical damage, but they are simple to instal and relatively easy to maintain. Impressed current systems are capable of long-term protection but are less tolerant of design, installation, and maintenance shortcomings than sacrificial anode systems. Routine comprehensive system monitoring is a must.
- Alloys for offshore platforms may be alloys of magnesium, zinc or aluminium. Different methods may be used to attach the anodes to the structure depending on their type and application but most importantly, a low resistance electrical

¹More on this subject will be explained in Chap. 9.

²Byars HG (1999) Corrosion control in petroleum production. TPC Publication 5, 2nd edn. NACE international, USA.

contact must be maintained throughout the operating life of the anodes. Most sacrificial anode CP systems installed on new structures utilise aluminium alloy anodes. It is easier to design and control the current density with sacrificial anode (galvanic) systems than impressed current systems. Anodes are selected to provide a specific life, often 20–25 years. It is important to note that the total weight of all anodes must be included in the structural design calculations for the platform. Otherwise, practical problems in selecting CP system may arise.

2.2.3 Use of Inhibitors

Inhibitors can be classified as anodic and cathodic. Each of these types of anodes has its own properties depending on the way it affects anodic and cathodic reactions. However, it must be noted that inhibitors are mainly used to affect the electrochemistry of the system and not its microbiology. Below, brief explanation of these types of inhibitors are given.^{3,4,5}

2.2.3.1 Anodic Inhibitors

These types of inhibitors can control the rate of oxidation (anodic) reactions. Anodic inhibitors are of wide variety and include chromates (CrO_4^{2-}) and nitrites (NO_2^-) which are oxidising anions and other compounds such as silicates, phosphates, benzoates and molybdates which are non-oxidising, acting in neutral or alkaline solutions. The mechanism is that the anodic reactions become highly polarised and the mixed corrosion potential of the specimen under such conditions is shifted in the noble direction as shown in Fig. 2.2.

In the presence of air, certain anodic inhibitors such as phosphate and molybdate, form a protective (passivating) oxide layer on the metal surface. If the inhibitor concentration is too low, pores and defects can arise in the oxide layer, where accelerated corrosion can take place. These inhibitors are therefore called “dangerous inhibitors” (see footnote 3).

2.2.3.2 Cathodic Inhibitors

These types of inhibitors can prevent or reduce the rate of reduction (cathodic) reactions. When these inhibitors are used, the mixed potential is lowered and there is again a decrease in corrosion current, Fig. 2.3.

³Mattson E (1989) Basic corrosion technology for scientists and engineers, Chap 3. Ellis Horwood Publishers.

⁴West JM (1986) Basic corrosion and oxidation, Chap 6. Ellis Horwood Publishers.

⁵Mille JDA, Tiller AK (1970) Microbial aspects of metallurgy. In: Miller JDA (ed) American Elsevier Publishing Co., Inc., NY, USA.

Fig. 2.2 Principle of anodic inhibition; when no anodic inhibitor has been added, the corrosion current (rate) is I_1 . When an anodic inhibitor is added, the anodic potential is modified and “rotates up” so that the corrosion rate is reduced (I_2)

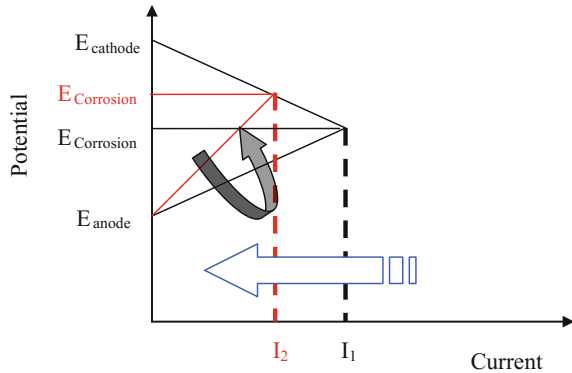
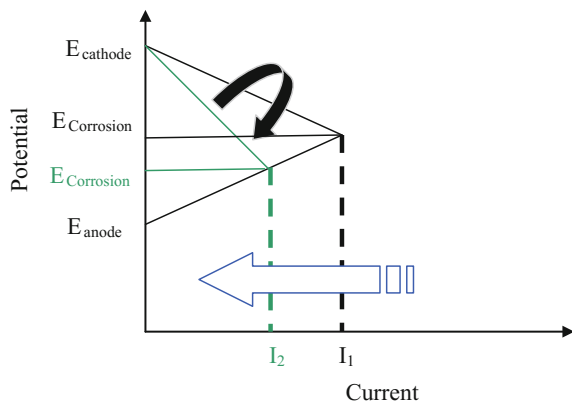


Fig. 2.3 Principle of cathodic inhibition; when no cathodic inhibitor has been added, the corrosion current (rate) is I_1 . When a cathodic inhibitor is added, the cathodic potential is modified and “rotates down” so that the corrosion rate is reduced (I_2)



Examples of cathodic inhibitors are (see footnote 3)

- Zinc salts, e.g. $ZnSO_4$; their action depends on zinc hydroxide being precipitated at the cathode, where the pH increases, thus making the cathode reaction more difficult.
- Polyphosphates, e.g. sodium pyrophosphate ($Na_4P_2O_7$), sodium tripolyphosphate ($Na_5P_3O_{10}$) and sodium hexametaphosphate ($(NaPO_3)_6$) that in the presence of divalent metal ions form a protective coating on the metal surface.
- Phosphonates, which in the presence of two-valent metal ions and preferably in combination with a zinc salt, are effective as inhibitors.

Even with a low concentration, cathodic inhibitors provide some inhibition (in contrast to anodic inhibitors). Therefore, they are not “dangerous” at concentrations which are too low for complete inhibition.

2.2.3.3 Mixed Effect Inhibitors (See Footnote 3)

Some inhibitors function as both anodic and cathodic, influencing both the anode and the cathode reactions to a larger or lesser extent, Fig. 2.4.

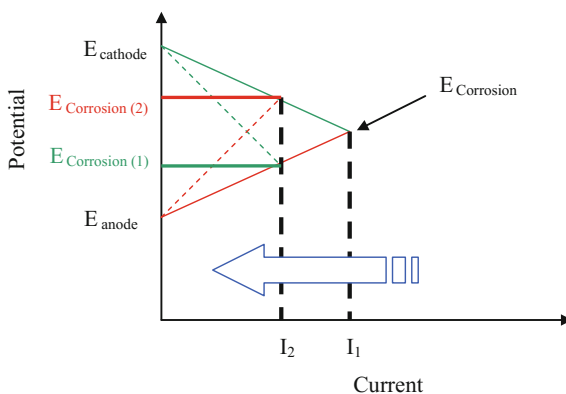
As an example of these types of inhibitors, polyphosphates, phosphates, silicates and benzotriazole can be mentioned. The action of these inhibitors is highly dependent on the environmental factors such as pH and redox potential. Therefore, they are anodic under certain conditions and cathodic otherwise.

2.2.4 Material Selection and Design Improvement

One of important challenges in combating corrosion is replacing available material with an upgraded, more resistant one. Frequently, a material is selected based on its resistance to corrosion but this resistance is not only a result of the physical and chemical features of the material, but also its working conditions. In Chap. 8, we will describe some important materials which are not immune to microbial corrosion despite some myths that have surrounded them regarding their resistance to this type of corrosion.

Most of the time, the upgraded material is not economically compatible with the existing one and the cost of removing old material and replacing it with the new one will also add up more to the question of the feasibility of the program. Therefore, the design engineer must pay attention to a range of factors including the intrinsic resistance/vulnerability of the material to the service conditions as well as the environment in which the material is put into the service and the economy of using a certain material in a given environment. For instance, sometimes, stainless steel 304 can be as vulnerable as carbon steel with regard to microbial corrosion. However, despite all the cost that using corrosion resistant materials may impose on the financial framework of a project by increasing the costs at the design stage, by

Fig. 2.4 The mixed effect of inhibitors, affecting both anodic and cathodic reactions to reduce corrosion



considering the losses (especially economical losses) resulting from corrosion, in the long-term using corrosion resistant materials will be justified and beneficial.

Corrosion prevention by design modification may seem too simple at first glance, but it is not applied in many designs. The following are just some general guide lines for designers to help them avoid corrosion and especially microbial corrosion problems in their designs

- Avoid designs that allow for water or dirt collection/stagnant water and/or moist accumulation. If the system becomes too dirty because of being suitable for dirt and debris collection, the environment may become very receptive to microbial species capable of affecting both the extent and intensity of corrosion. In pipelines, for instance, designs that allow too many ramifications and extra branches and piping can render the pipe quite vulnerable to microbial corrosion.
- Avoid designs that cause turbulence, such designs may indirectly help microbial corrosion by promoting the possibility of erosion–corrosion and thus producing an environment which is already corroding and helping bacteria with the required ferrous ions for example.

In Chap. 5 some important factors contributing to rendering a system vulnerable to microbial corrosion have been explained. Avoiding having such factors in the system can assist in safe-guarding against microbial corrosion. In Chap. 9, treatment of microbial corrosion in more detail will be explained.

2.3 Summary and Conclusions

Corrosion management deals with the study and implementation of techniques and methods such as cathodic protection, coatings and materials selection to mitigate corrosion, and of course, microbial corrosion. In this chapter, the main basics and logics of some of these important techniques were explained. The next chapter deals with a very new concept called corrosion knowledge management which more than concentrating on the technical methods and technologies, relies on team-building and managerial aspects of managing corrosion.

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Chapter 3

Nontechnical Mitigation of Corrosion: Corrosion Knowledge Management

Abstract Treatment of corrosion in general and MIC in particular requires both technical (engineering) and non-technical (management) skills. In this chapter some management skills necessary to control MIC are introduced and discussed.

Keywords Economy and ecology of corrosion losses • Management resources in dealing with corrosion • Corrosion knowledge management (CKM)

3.1 Introduction

Corrosion problems can be approached from different, yet not necessarily opposite, points of view. To solve a corrosion problem as a technical problem, requires applying corrosion mitigation/prevention-related technicalities in the domain of corrosion management, as described briefly in Chap. 2.¹ There is, however, another dimension to this and it is the way that a corrosion engineer has to communicate with the managers who may not have the same level of expertise in corrosion management. Here, the problem is not a technical problem anymore, it is related to using a language which, while corrosion-related, is not that technical. At the same time, this language must be something that will address human relationships and its impact on the management. This is what we may call as “corrosion knowledge management”.

In other words, corrosion engineers can have highly sophisticated knowledge of what is to be involved in mitigation and prevention of corrosion. This will give

¹The author “learnt” to emphasise upon the difference between corrosion management (CM) and corrosion knowledge management (CKM) when he realised that the management-based principles of what he had called as CM were understood by corrosion community as to be not different from technical context of the so-called “corrosion management”. To highlight that this technique is entirely different from the known, so-called corrosion management concept, the author had to make use of the suffix “knowledge management” so that the managerial side of this approach is preserved. However, my rather “early” works still have the label of “corrosion management”. In this context, then, whatever we refer to as corrosion management (CM) must be understood as corrosion knowledge (continued) management (CKM). The author apologises in advance for any confusion and inconvenience thereafter that may be created.

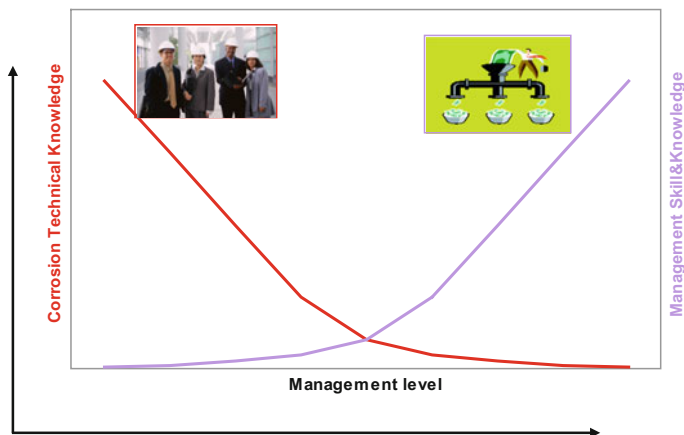


Fig. 3.1 How can corrosion engineers, with high level of corrosion technical knowledge, and managers, who must think of making the industry more profitable, reach a common language?

them a language of their own, a language that is highly technical and may sound like “jargon” to others. On the other hand, the managerial level of a plant/industry has to deal with many issues, one of which being corrosion. This will create a language and “culture” of its own so much out of touch for a technical man that understanding managerial decisions (on either micro- or macro- management levels) may not always make sense, Fig. 3.1.

In this section, we will try to find how such a gap can be filled by a systematic approach towards the problem of corrosion that will use no “corrosion management” language.

3.2 Corrosion (Knowledge) Management: A Managerial Approach

In this section, we will describe some tools by which managers without hands-on experience on corrosion may become confident about the best strategy to be taken against corrosion. The main point here will be advising managers to arrange their resources in a more feasible way to mitigate corrosion. Corrosion Knowledge Management may be defined as the shortest and least expensive way to control corrosion in terms of resource management.

3.2.1 Importance of Defining “Resources” and “Targets”

Among definitions that may be found for management, what one can intuitively recognise is that management is, indeed, an “art & science” of balancing between what you have in hand and what you want to achieve by using the more practical,

the least expensive and the shortest path (route). In other words, a good manager is the one who

- Knows the resources (**R**)
- Understands the targets (**T**)
- Selects the path (**P**) to reach (**T**) via (**R**)

A good manager should also try to find answers for the following questions:

- **W**hat are my resources?
- **W**hy do I choose certain target(s)?
- **H**ow should I get to the target(s) by using the resources?

The above questions may be referred to as “2 W–H” questions. The first **W** deals with what a manager has got in hand, i.e.; **R**. This can include many factors such as human resources, financial resources, etc., but in addition to those, a manager as a professional is also considered as an important resource. For this reason a good manager must have

- Knowledge
and
- Information

Knowledge in this context means the minimum qualifications one has about a topic, in other words, having an academic degree as a minimum. The knowledge gained by getting a degree gives the ability to

- Define the present state of a system
- Predict the future state of the system

However, one has to update one’s knowledge. The continuous process of renewal and updating one’s knowledge can be called “information”. Any processed data entering into the territory of our knowledge to improve it according to existing conditions is called information. To know the resources, a good manager *must* have both knowledge and information about them.

So for a manager, information means a continuous process of being aware of everything related to his/her specific job: if he is a manager of an art museum with a B.Sc. in mechanical engineering, he would definitely have to study more about his particular job and its new developments than one with a degree in art.² Similarly, an engineer who has no degree/skills in corrosion but is committed to manage a plant, has to be more aware of corrosion to be able to take a holistic approach to protect his assets.

Why should a manager make a choice on achieving a particular target? Why should he/she select this, and only this particular one, as the goal to achieve?. There

²It is a fact of life that managers may not always necessarily have been technically trained for their positions.

are many factors that dictate how and why to choose certain things as goals or targets. Some of these factors are:

- Social reasons
- Political reasons
- Economical reasons
- Cultural reasons
- A combination of the above

To make it more clear, an example of building a power plant may be useful: some of the goals (targets) for such a project can be economical (such as solving the problems related to the lack of electricity in the region.), political-economical (winning the elections, to create new jobs and work opportunities...), etc. Therefore, based on which factor becomes more relevant, a certain target may be taken or left.

To answer to the question “HOW” of the 2W–H questions, one has to consider the “work scheduling”, three principals of which are

- Knowing elements of the process/project and their relationships
- Preparing executive time schedule
- Estimation of expenses and required budget

It must be said that of the three principles mentioned above, the first one is the one that makes a project feasible or not. The other two factors are mechanically calculated according to the “complexity” of the project in terms of factors involved. We will see the importance of knowing elements of a project when we are introducing the concepts of CORROSION OF SYSTEM and CORROSION IN SYSTEM.

3.2.2 Why Should We Care About Corrosion?

For a manager, the reason to fight corrosion is to reduce the losses. As corrosion-related losses are very important, we will consider them under a separate section here, however, it must be emphasised that this section is still linked to the topic of the importance of defining targets.

Losses due to corrosion can be divided into three categories³

- (1) Waste of energy and materials
- (2) Economical Loss

2.1 Direct Loss

2.2 Indirect Loss

2.2.1 Shutdown

³Uhlig HH (1971) Corrosion and corrosion control, 2nd edn. John Wiley & Sons. Inc.

- 2.2.2 Loss of efficiency
- 2.2.3 Product contamination
- 2.2.4 Overdesign

(3) Environmental impact/health

We will discuss each of these categories briefly as the followings:

(a) *Waste of energy and materials:*

Internationally, one ton of steel turns into rust every 90 s, on the other hand, the energy required to make one ton of steel is approximately equal to the energy an average family consumes over 3 months.⁴ As another example, take a pipe line of 8-in. diameter and 225 miles (~362 km) long and a wall thickness of 0.322 in.; with adequate corrosion protection wall thickness could have been only 0.250 in. thus saving 3700 tons of steel as well as increasing internal capacity by 5 % (See footnote 3). Of every ton of steel from the world production approximately 50 % is required to replace rusted steel (See footnote 4). Reports show that⁵ the loss of a sea Harrier in the Adriatic in December 1994 and partial structure loss in a 19-year-old Aloha Airlines Boeing 737 in April 1988 can be both attributed to corrosion.

(b) *Economical Loss:*

When economy is mentioned, it can be looked at as both micro-and macro-models. In other words, one can both calculate how corrosion takes away from the pocket of the man on the street and how the national economy is affected by corrosion. The figures here are focused more on national and macroscale economy figures but, as the reader will also appreciate, at the end of the day, it is the man on the street who pays...

Insurance companies have paid out more than US\$91 billion in losses from weather-related natural disasters in the 1990s⁶, whereas direct loss of corrosion in 1994 just in the US industry was US\$300 billion.⁷ The cost of corrosion has been reported from many studies to be of the order of 4 % of the GNP (Gross National Product) of any industrialised country.⁸ In the power industry, it has been estimated that⁹ corrosion losses in utility steam systems amounted to about US\$1.5 billion of the US\$70 billion annual cost of corrosion in the USA in 1978.

⁴New prefabricated joist designs researched. Mater Perform (MP) 36(7):68 (1997).

⁵Hill M, KW Corrosion prevention in the Royal air Force: there is no option. No. 26, Corrosion Management, pp 14–19, Nov/Dec 1998.

⁶Worldwatch News Brief 99-3, “Destructive storms drive insurance losses up”, www.worldwatch.org, 26 March 1999.

⁷Cost of corrosion: \$300 billion a year. Mater Perform (MP) 34(6):5 (1995).

⁸Heitz E (1992) A working party report on microbiological degradation of materials and methods of protection. In: Heitz E, Mercer AD, WS, Tiller AK (eds) The Institute of Materials, England.

⁹Gaona-Tiburcio G, Almeraya-Calderon F, Martinez-Villafane A, Baustista-Margulis R, Stress corrosion cracking behaviour of precipitation hardened stainless steels in high purity water environments. Anti-corros Methods Mater 48(1):37–46.

Figures show that¹⁰ corrosion costs the US electric power industry as much as US\$10 billion dollars each year. New studies on updating US corrosion cost study in year 2000 have shown that¹¹ the total cost of corrosion in 1999 dollars to remediate corrosion-induced structural deficiencies of highway bridges was estimated at approximately US\$30 billion. The same study showed that the current cost of corrosion protection built into new automobiles determined by auto manufacturers and other experts to be US\$150 per vehicle, in fact the percentage of the GNP attributed to motor vehicle corrosion in 1998 was 0.25 %. Other sources report¹² that BP had performed pigging its Prudhoe bay pipelines more than 350 times in 2005. An example of the global “ripple” caused by this disaster was that¹³ when BP said that it would stop the flow of half as much oil in the summer of 2006, the price of oil increased by 3.4 %, skyrocketing to \$US 77.30 a barrel the next day.

(c) *Environmental impact/health:*

Table 3.1 shows some examples of recorded environmental/health impacts of corrosion in different years, countries and places^{14,15}: Recently Shipilov¹⁶ has reviewed economical and environmental impacts of corrosion all around the world. The recent accident at Prudhoe Bay (2006) resulted in an environmental/hazard nightmare: reports indicated that¹⁷ the leaking crude oil has had formed a black layer over an area of grassland about the size of half a football pitch, where, according to BP, the cleanup cost will be over US\$200 million.

Such studies show that the impact of corrosion on the environment and health and safety is so large that ignoring it can cause very serious consequences. Therefore, corrosion and its environmental impacts have the potential of producing a very wide range of hazards and disasters. Rephrasing Shipilov’s words, corrosion is indeed “history’s worst silent serial killer”.

¹⁰Bacteria could help control corrosion at power plants. *Mater Perform (MP)* 37(11):50–51 (1998).

¹¹Cost of corrosion study update: Trends in the automotive industry. *Mater Perform (MP)* 39 (8):104–105 (2000).

¹²Bailey A (2006) BP: Learning from oil spill lessons. *Petroleum News* 11(20), Week of May 14, 2006. <http://www.petroleumnews.com>.

¹³BP Pipeline Failure Follow-Up. *Corros Mater* 32(2):7 (2007).

¹⁴Javaherdashti R (2000b) How corrosion affects industry and life?. *Anticorrosion Methods Mater* 47(1):30–34 (2000).

¹⁵Industrial accidents. *UNEP Ind Environ* 20(3):6 (1997).

¹⁶Shipilov SA (2007) University education in corrosion: a true challenge for the engineering world. In: *Proceedings of the Iranian Corrosion/2007; ICA International Congress, Tehran, Iran, 14–17 May 2007*.

¹⁷THE TIMES, Saturday, 12/August/2006. The author would like to thank Dr. Roger King for providing him with these news. It is “rumoured” that the cause of the failure could be microbial corrosion.

Table 3.1 Some corrosion-related incidents

Year	Place	Accident	Probable reason	Results
1970	North Sea	Platform collapse	Stress corrosion cracking (SCC)	Huge life, material and economic loss
1967	Ohio River (USA)	Collapse of the bridge “silver Bridge”	SCC	Huge life and material loss
1985	Switzerland	Collapse of the 200-Ton concrete ceiling of an indoor swimming pool	SCC in stainless steel bars holding the ceiling, due to existing chlorine ions	12 people died, some others injured
1996	Mexico	Fire and explosion	Petrol leaking from a valve on a 1,300 m ³ storage tank caught fire, causing the tank to explode	Four people died and 16 injured. The Red Cross tended to 960 people and 10,000 were evacuated. It took 2 days to bring the fire under control
1997	Canada	Spill of over 35,000 litres of oil in one night	A leak in a damaged pipeline owned by Mobiloil	Large scale environmental pollution
1997	Russia	Leakage of over 1,200 tons of oil	Leakage from a ruptured pipeline	About 400 tons of oil spilled into the River Volga. A dam was built in a Tributary of the river to prevent further pollution

3.3 Components of Corrosion Knowledge Management as a Managerial Tool

Corrosion Knowledge Management (CKM), in essence, does not differ from other management approaches. CKM requires one to consider “R”, “T” and “P” as well as answering the 2W–H questions in order to decrease unwanted effects of corrosion. CKM in fact summarises what industry can eventually end up with in dealing with corrosion in a more ordered, systematic way.

R (Resources) in CM are

- (a) Capital
- (b) Expert or expert team
- (c) Training
- (d) Research for new anticorrosion materials
- (e) Research for new methods used to control corrosion
- (f) Information

(g) Energy

(h) Time

T (Target) in CKM is

- To control corrosion to lower its costs (Economical-ecological reason)

P (Path) in CKM is, then

- Corrosion Knowledge Management

The above means that to deal with corrosion and decrease its costs efficiently, managers must reconsider their “R”&“T” according to principles of CKM. In other words, if they see there is a corrosion problem in their systems, first they have to check their resources to see if there is enough to mitigate that problem. It should be noted, however, that setting targets (WHY question of the 2W–H questions) would determine which factor is missing in resources or which factor is worth of more consideration and so on.

CKM has four components¹⁸:

1. Modelling
2. Use of information
3. Transparency
4. Corrosion system definition(COFS/CINS)

The first three items have been discussed to some extent in the related literature somewhere else (See footnote 18)^{19,20}. However, it is worth to concentrate more on the last item, i.e.; corrosion system definition.

A very important aspect of solving corrosion problems is understanding the system in which corrosion is taking place. A corrosion system is defined as *a part of universe in which corrosion occurs and is of interest to us*. Corrosion system can be considered as to be consisting of subsystems such as A, B, C, etc.; If corrosion problem of each subsystem “i” is shown as corr(i) and corrosion types observed in each subsystem as a, b, c, ..., one can write

$$\text{Corr}(A) = \{a_1, a_2, a_3, \dots, a_n\}$$

$$\text{Corr}(B) = \{b_1, b_2, b_3, \dots, b_n\}$$

$$\text{Corr}(C) = \{c_1, c_2, c_3, \dots, c_n\}$$

¹⁸Javaherdashti R (2003) Managing Corrosion by Corrosion Management: a guide for industry managers. Corros Rev 21(4):311–325, Summer 2003.

¹⁹Javaherdashti R (2000a) Corrosion Management: CM. www.nrcan.gc.ca/picon/conference2. Natural Resources Canada, 18 Dec 2000.

²⁰Javaherdashti R (2002) How to manage corrosion control without a corrosion background. Mater Perform (MP) 41(3)30–32.

Corrosion of a system, or briefly, *COFS* is then defined as

$$\text{COFS} = \text{Corr}(A) \cup \text{Corr}(B) \cup \text{Corr}(C)$$

Corrosion in a system, or briefly, *CINS*, is then defined as

$$\text{CINS} = \text{Corr}(i) \cap \text{COFS}$$

As an example, take corrosion in an automobile: suppose we define a car as a corrosion system that is to say typical types of corrosion in subsystems of a car. In this case, subsystems can be defined as

$$A = \text{Chassis}, B = \text{Fuel system}, C = \text{brake system}, \dots$$

Corrosion problems in each of the above subsystems, with important mechanisms in parenthesis, can be shown as the following²¹:

$$\text{Corr}(A) = \{ \text{uniform, pitting, (crevice), fretting, stress cracking}, \dots \}$$

$$\text{Corr}(B) = \{ (\text{pitting}), \text{crevice, coating failure} \}$$

$$\text{Corr}(C) = \{ (\text{pitting}), \text{crevice, galvanic, (fretting), (coating failure)} \}$$

So that a project, whose goal is to solve ALL corrosion problems of a car, would have to deal with ALL of the corrosion problems in ALL subsystems, in other words, it would be a COFS approach. In this case, study of the corrosion of just a given subsystem, such as Corr(C), will be a CINS approach.

It is very important to distinguish between CINS and COFS approaches because many problems such as expected time span of the project or required capital for doing the project may largely vary. A practically important alternative definition of a corrosion is a system with “highest risk”. More often than not, a large percentage of the risk (>80 %) is found to be associated with a small percentage of the equipment item (<20 %).²² Once identified, the higher risk equipment becomes the focus of the inspection and maintenance to reduce the risk, while opportunities may be found to reduce inspection and maintenance of the lower risk equipment without significantly increasing risk. In other words, to be on the safe side, it is better to choose the system of concern the one with higher risk and define COFS & CINS according to real, working conditions of the system.

CKM can schematically be represented as in Fig. 3.2:

In dealing with corrosion, a manager needs to check why corrosion mitigation is important (or not important). If he decides to cure corrosion problem, for one or more reasons we mentioned earlier in this section, then he should check his

²¹Corrosion in Automotives. In: Baboian B (ed) Corrosion tests and standards manual: application and interpretation. ASTM manual series: MNL 20, ASTM, 1995.

²²Hovarth RJ (1998) The role of the corrosion Engineer in the development and application of Risk-based inspection for plant equipment. Mater Perform (MP) 37(7):70–75.

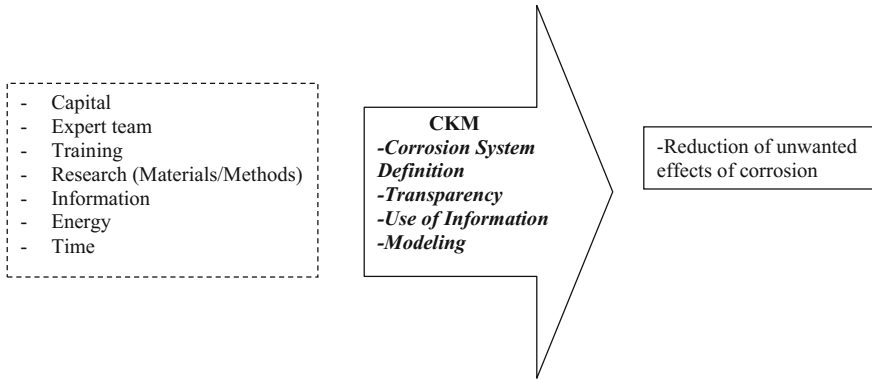


Fig. 3.2 The relationship between the resources, the target and the role of CKM

resources. Some items in the resource box may not be as urgent as the others, for example the manager may not be that concerned about the outcome of research on new and rather “exotic” corrosion resistant materials and/or detection devices as his immediate concern could be solving a problem that has the potential of doing damage and ruining his business. However, this manager must learn to work closely with researchers and research bodies to ensure being updated. In fact, the larger the area of operation in the company the more important the need for paying attention and financial support to research.

Another important item is training. It may be sometimes economical and feasible to train the existing staff with regard to a certain discipline, for example, enrolling them in a cathodic protection system. But sometimes, depending on the severity of the problem, it may be a must to recruit someone(s) to build an expert team to deal with corrosion. Such a team may act in different ways to affect the severity of corrosion. A possible way to do so could be through by a communication network as shown in Fig. 3.3.

Figure 3.3 pictures an imaginary case of corrosion treatment that includes both microbial and nonmicrobial components. As seen from the figure, while an expert team is in direct communication with both the plant operation manager and the consultants for assessing nonmicrobial component of the problem, an advisory team is also involved who would comment on microbial corrosion and the findings by an assigned laboratory. The expert team could be very good at dealing with nonmicrobial cases but as experts, they are prudent to realise that and seek the technical advice from another group of experts who may know microbial corrosion much better.

Figure 3.2 also reveals that a CKM management unit must be supervising the activities requiring a CKM approach. Such a management unit must be able to assess the resources in accordance with CKM principles and prepare the necessary feedback for the management to deal with corrosion more efficiently.

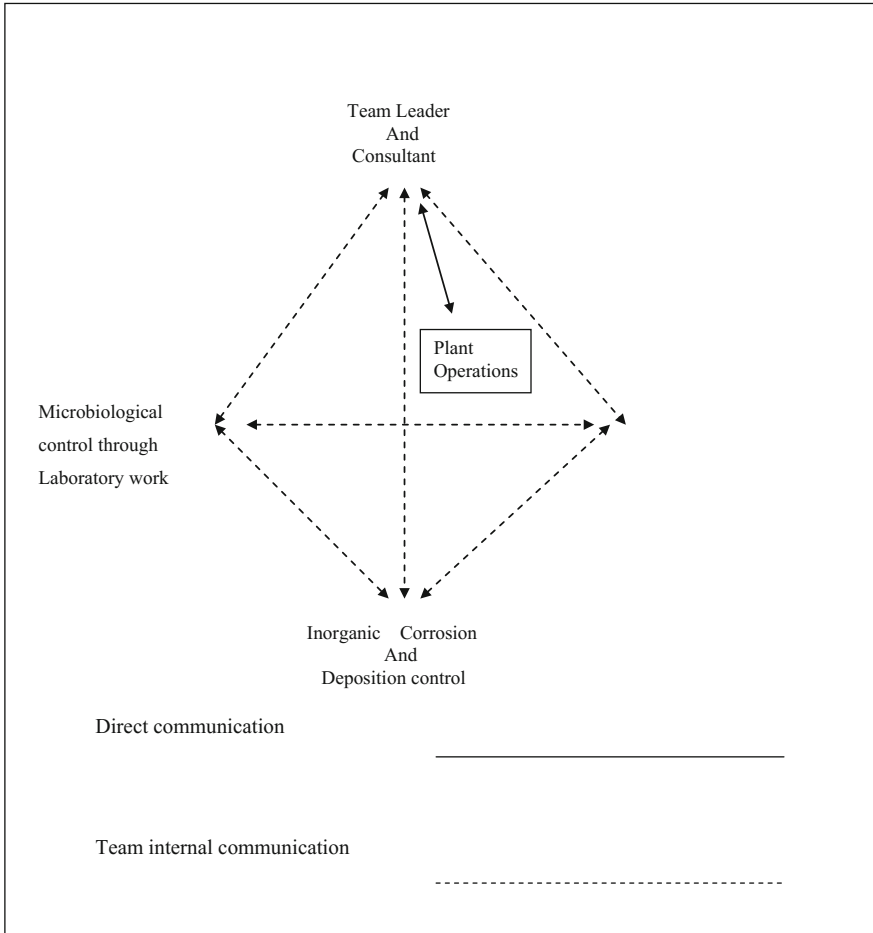


Fig. 3.3 A model for communication between expert teams and consultants to deal with a complex corrosion problem

3.4 Conclusion and Summary

Corrosion knowledge management (CKM) is different from corrosion management. CKM can be regarded as an interface through which managers and engineers can communicate more effectively. This chapter explained briefly the principles of CKM.

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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

¹In 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.

²Little 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.

which corrosion can be enhanced, some researchers³ in their experience with aerobic *Pseudomonas* sp. have reported that acid production was not a major cause of corrosion and some⁴ 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:

³Franklin 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.

⁴Sandoval-Jabalera R, Nevarez-Moorillon GV, Chacon-Nava JG, Malo-Tamayo JM, Martinez-Villafane A (2006) Electrochemical behaviour of 1018, 304 and 800 alloys in synthetic wastewater. *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.

⁵Sand 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-organisms⁶
- 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”.

⁶de 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.

⁷Beech 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.

⁸Li 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.

⁹For 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, Venkatachari G (2006) Corrosion and biofouling characteristics of mild steel in mandapam waters. Mater Performance (MP) 45(6): 46–50. In their paper, Palraj and Venkatachari 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\$6b¹² (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 that¹⁴ 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

¹⁰Javaherdashti 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.

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

¹²Javaherdashti 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*.

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

¹⁴Maxwell 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.

¹⁵de 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.

¹⁶Cord-Ruwisch R (1996) MIC in hydrocarbon transportation systems. *Corrosion Australasia* 21 (1):8–12, Feb 1996.

¹⁷See footnote 25.

¹⁸Javaherdashti 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 as loss of tritiated D₂O (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

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

²⁰Javaherdashti 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.

²¹Walsh 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.

²²Stott 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.

²³Fitzgerald 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.

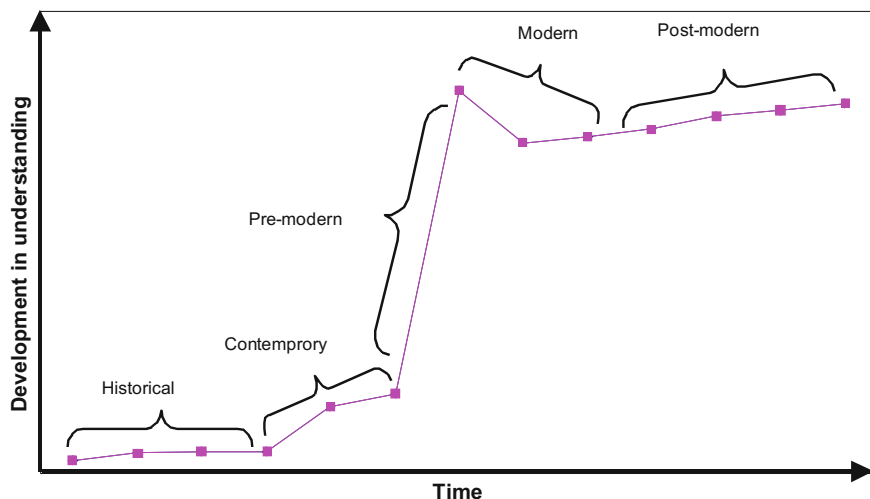


Fig. 4.1 Milestones in time to mark development of ideas and techniques for studying MIC

About three years after the discovery of the enzyme hydrogenase²⁴ 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 Videla²⁷ 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

²⁴Hydrogenase 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.

²⁵Li 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.

²⁶Stott 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.

²⁷Videla HA (2007) Mechanisms of MIC: Yesterday, 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 Costello 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,

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

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

³⁰Ibid 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 paper³¹ 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 are³²

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.

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

³²Geesey 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

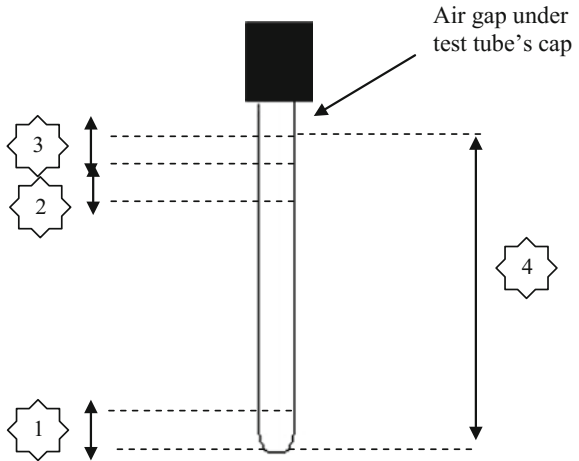
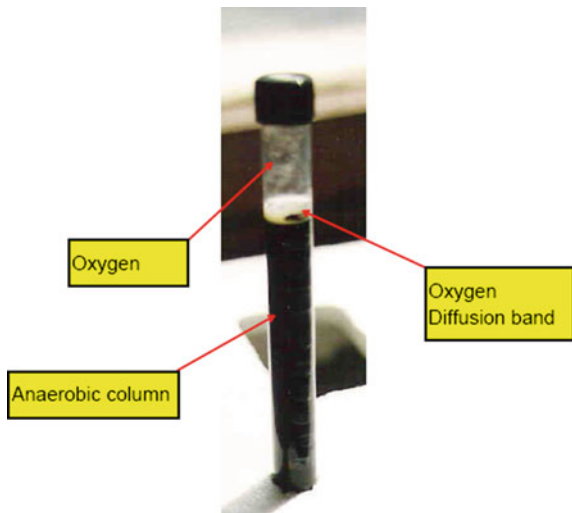


Fig. 4.3 SRB culture developed in a solid environment (Agar) within a test tube. A portion of the top section of the sample was taken for transfer purposes. During the culture transfer, oxygen was introduced and diffused into the solid culture. Oxygen did not have a chance to diffuse down furthermore. 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 theis provided by	... then the growth type is called:
<i>Energy Source</i>	Light	Phototrophic
	Chemical Substances	Chemotrophic
<i>Carbon Source</i>	CO ₂	Autotrophic
	Organic Substances	Heterotrophic
<i>Electron donor (that is oxidised)</i>	Inorganic Substances	Lithotrophic
	Organic Substances	Organotrophic
<i>Electron acceptor (that is reduced)</i>	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 SO₃²⁻, S₂O₃²⁻ and S⁰ to S²⁻.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

³³Obuekwe 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.

³⁴Little BJ, Wagner P, Hart K, Ray R, Lavoie D, Neelson 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

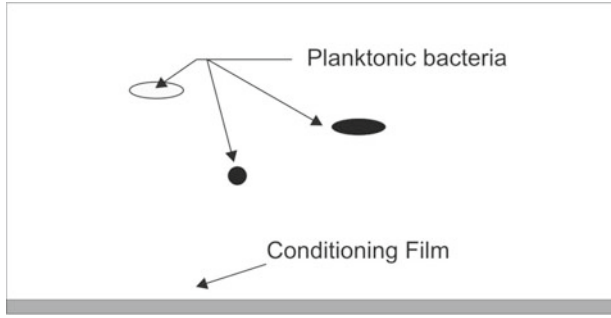
³⁵Dexter SC, LaFontain JP (1998) Effect of natural marine biofilms on galvanic corrosion. *CORROSION* 54(11):851–861.

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

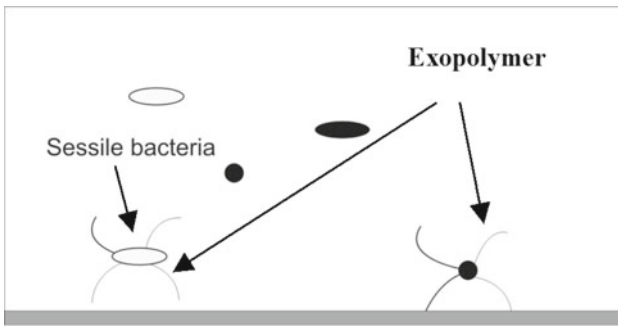
³⁷Al-Hashem A, Carew J, Al-Borno A (2004) Screening test for six dual biocide regimes against planktonic and sessile populations of bacteria, Paper No. 04748, *CORROSION* 2004, NACE International.

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

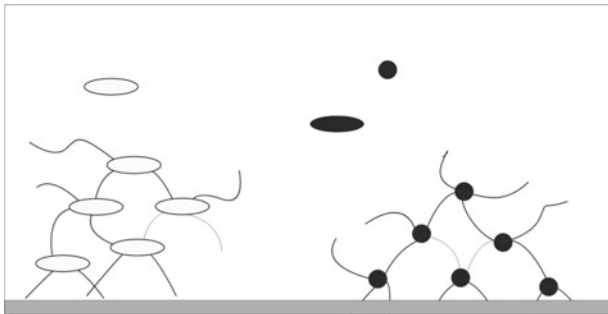
³⁹Liu H, Xu L, Zeng J (2000) Role of corrosion products in biofilms in microbiologically induced corrosion of carbon steel. *Br Corros J* 35(2):131–135.



Stage 1: Conditioning film accumulates on submerged surface.

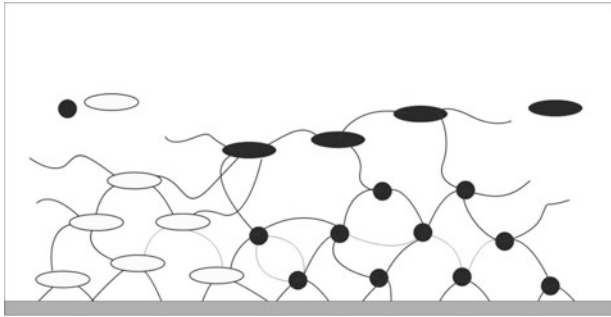


Stage 2: Planktonic bacteria from the bulk water form colonies on the surface and become sessile by excreting exopolysaccharidic substances (EPS) that anchors the cells to the surface.

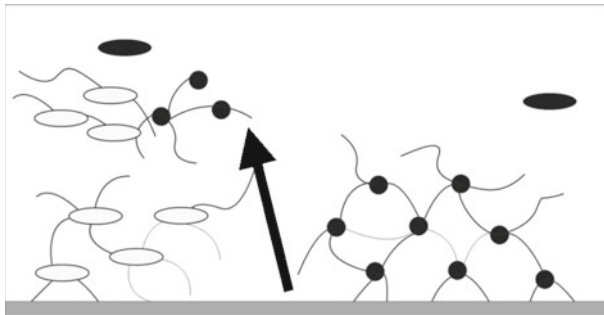


Stage 3: Different species of sessile bacteria replicate on the metal surface.

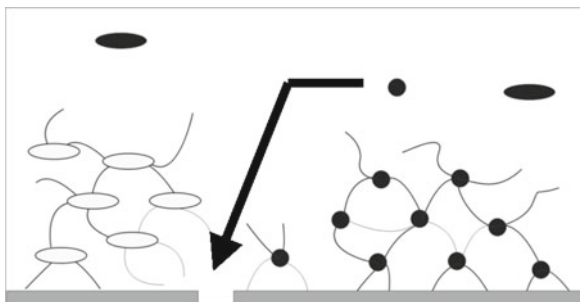
Fig. 4.4 Stages of biofilm development (see footnote 32)



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)

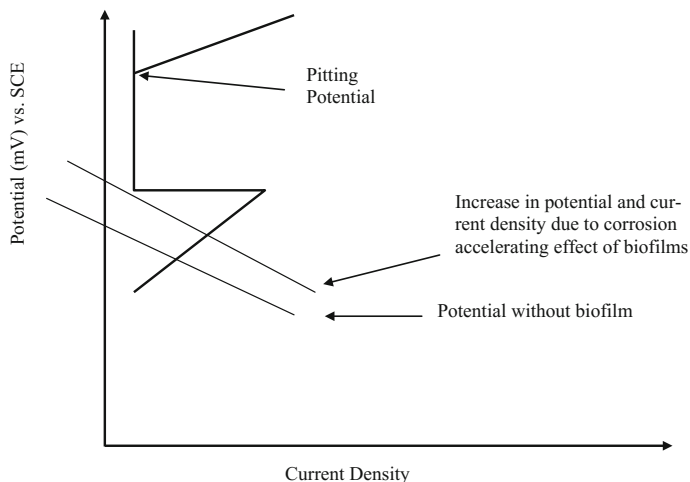


Fig. 4.5 Schematic of the effect of biofilm on the ennoblement of carbon steel in the presence of a microbial culture containing corrosion-enhancing bacteria

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

⁴⁰Taheri RA, Nouhi A, Hamed 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.

⁴¹Dickinson 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.

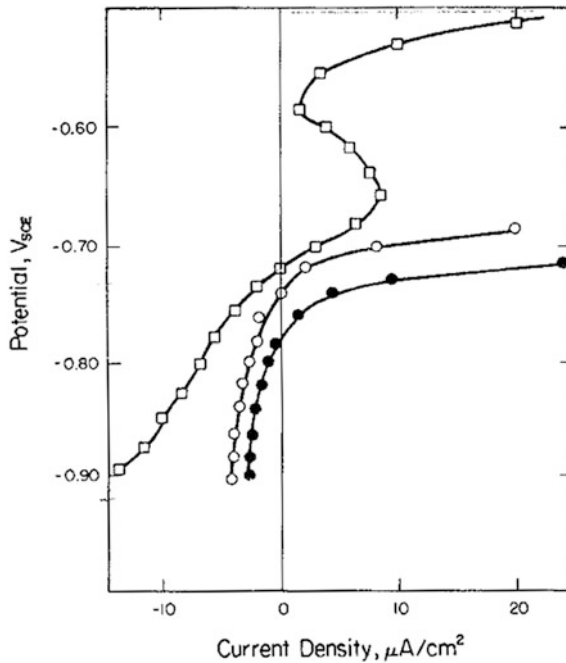


Fig. 4.6 How ennoblement increases susceptibility to pitting, Potentiostatic polarisation curves for AISI 1020 steel in anaerobic artificial seawater (pH = 8) (□), in artificial seawater contaminated by SRB (total sulphide 10^{-3} M, pH = 7.8, redox potential -510 mV) (○), and in artificial seawater 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 potentials⁴² 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 mechanisms⁴³:

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

⁴³Dexter 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.

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

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

⁴⁶Ibid footnote 34.

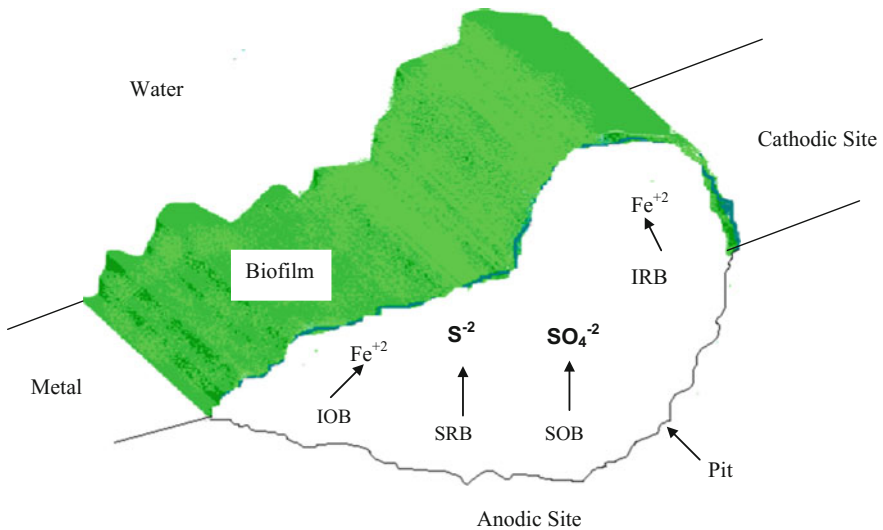


Fig. 4.7 Schematic diagram of possible processes that may occur during pitting of steel resulting from biological activity

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.

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

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

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

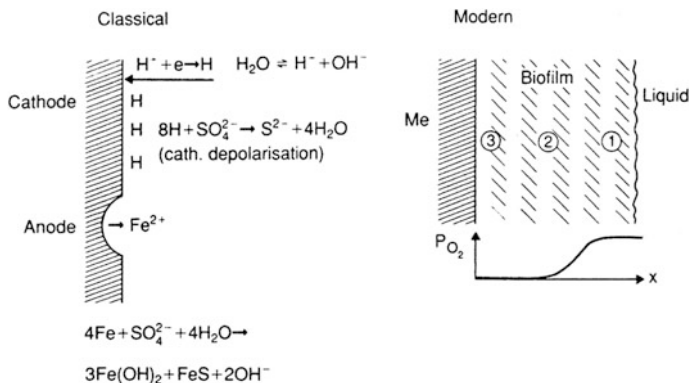


Fig. 4.8 Comparison of classic and modern models of biofilm to explain sulphate reduction (“A Working Party Report on Microbiological Degradation of Materials—And Methods of Protection”, Sect. 4.3.3, European Federation of Corrosion Publications, Number 9, The Institute of Materials, London, England,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

⁵⁰Wilderer 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.

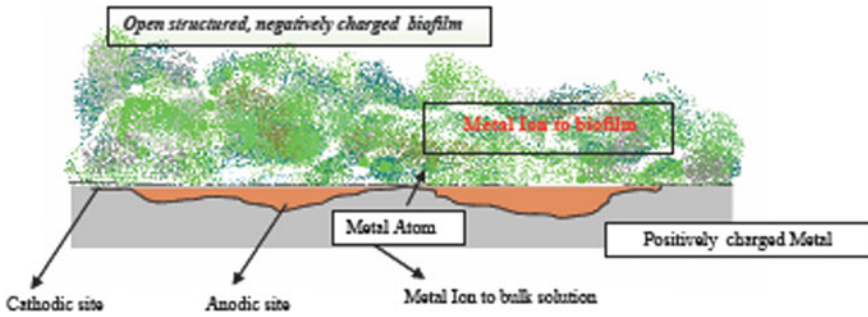


Fig. 4.9 A conceptual model for an open, patchy biofilm structure and its regions

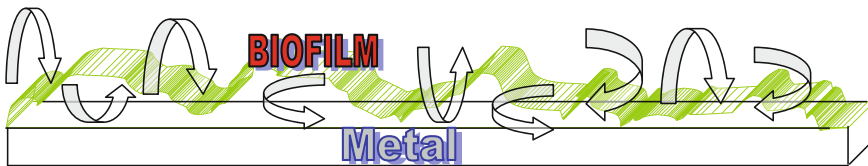


Fig. 4.10 An impression of latest conceptual model of biofilms formed in biotic environments. The arrows present entrance and exits of gases (such as oxygen) and chemical species through the “open” structure of the biofilm

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

⁵¹Ibid footnote 41.

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

⁵³Lewandowski 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.

⁵⁴Lewandowski 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 matter 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}

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

⁵⁶Jack 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.

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

⁵⁸Obuekwe 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.

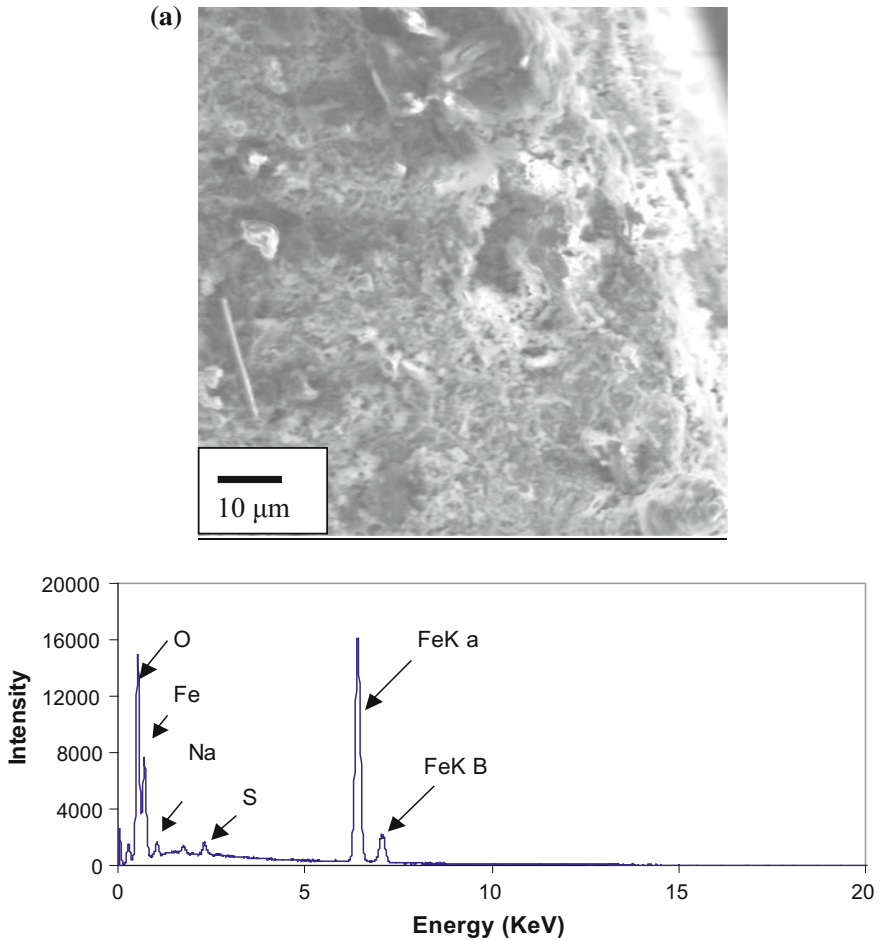


Fig. 4.11 Comparison of biofilms formed by **a** SRB and **b** IRB (from: Javaherdasht R (2006) Making sense out of chaos: general patterns of MIC of carbon steel and bio-degradation of concrete. In: Proceedings of corrosion and prevention 2006 (CAP06), 19–22 Nov 2006, Hobart, Australia. **a** A biofilm 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.

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

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

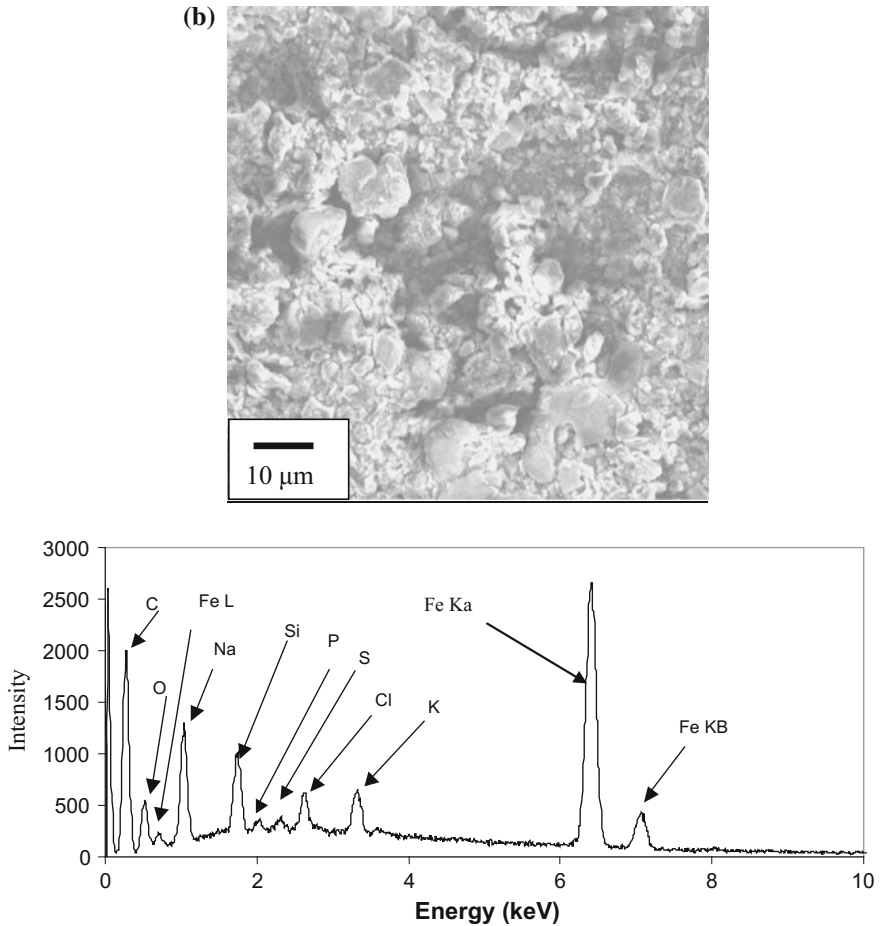


Fig. 4.11 (continued)

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 reported⁶² that two strains of IRB, called *Shewanella algae* and *Shewanella 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.

⁶¹Ornek 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.

⁶²Nagiub 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 bacteria⁶³ 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.

⁶³Dubiel 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.

⁶⁴Ibid footnote 33.

⁶⁵Obuekwe 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.

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

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

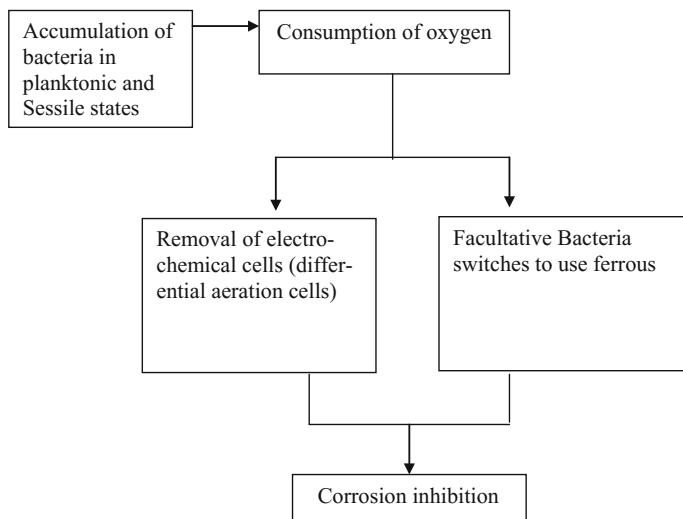


Fig. 4.12 The mechanisms occurring in batch systems to inhibit corrosion

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

⁶⁸Newman 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.

⁶⁹Byars HG (1999) Corrosion control in petroleum production, Chap. 2, 2nd edn. TPC Publications 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. Amy⁷² 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)

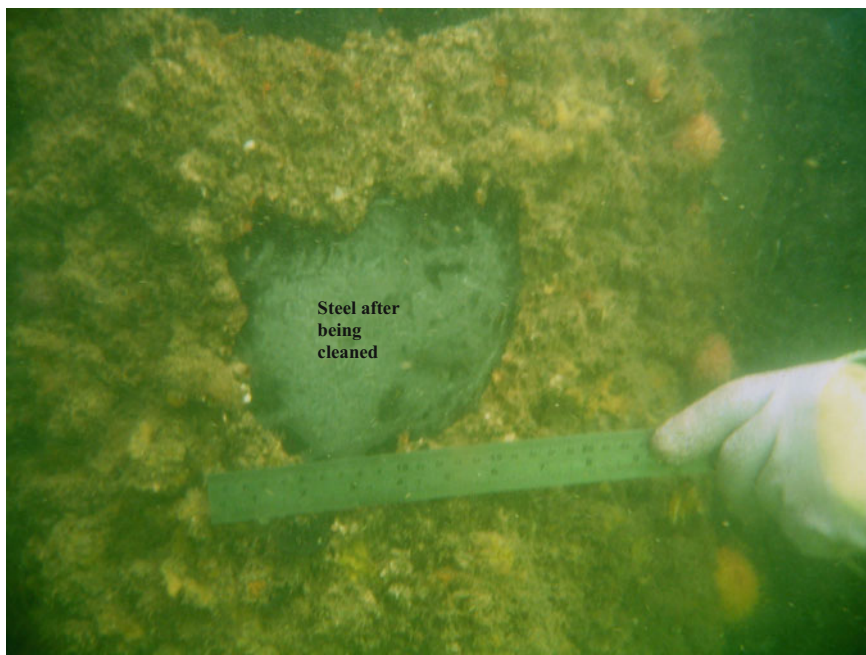
Sulphate-reducing bacteria (SRB) derive their energy from organic nutrients, they are anaerobic; in other words, they do not require oxygen for growth and activity, so as an alternative to oxygen, these bacteria use sulphate with the consequent production of sulphide (see footnote 10).

⁷⁰Sanchez 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 critical review. *Int Biodeterior Biodegradation* 29:367–375.

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

⁷²Jones 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-bioassay techniques for monitoring MIC. Corrosion 2004, paper 04580, NACE International, 2004; and Marconnet C, Dagbert C, Roy M, Feron D (2006) Microbially influenced corrosion of stainless steels in the Seine River. In: Proceedings of EuroCorr 2006, 24–28 Sept 2006, Maastricht, the Netherlands.

(a)



(b)

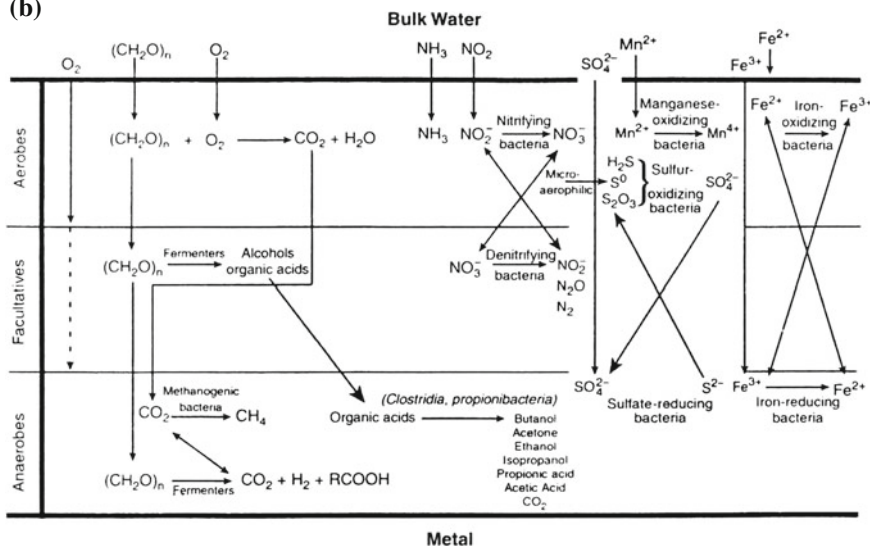


Fig. 4.13 a The Biomass formed on a steel pile being exposed to seawater at a depth of 3 m. Note the thickness around the sampling area (Courtesy of Extrin Consultants). b Complex environment of a typical aquatic biofilm (see footnote 31)

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 clay⁷⁶ to sea water.⁷⁷ It is believed that⁷⁸ 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

⁷³Barton 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.

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

⁷⁵King 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.

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

⁷⁷Ibid footnote 56.

⁷⁸“The Role of Bacteria in the Corrosion of Oilfield Equipment”, TPC.3, NACE International, 1982.

⁷⁹Willis 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.

⁸⁰Langendijk PS, Hagemann J, Van der Hoeven JS (1999) Sulfate-reducing Bacteria in Periodontal Pockets and in Healthy Oral Sites. *J Clin Periodontol* 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?

⁸¹McDougall 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.

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

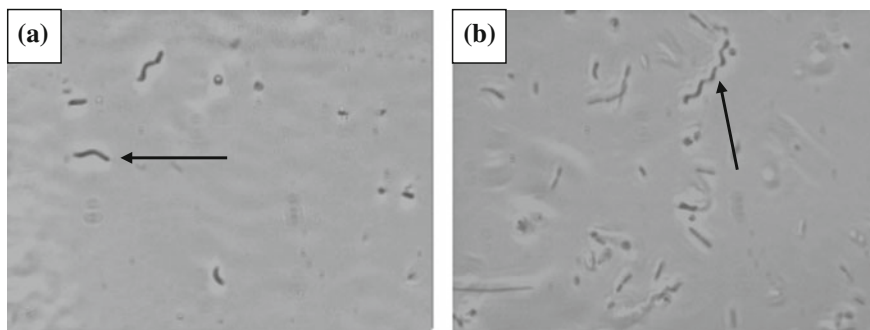


Fig. 4.14 Two morphologies of the SRB found in the mixed culture shown by arrows **a** vibrio **b** spiral

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 Vlught 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.

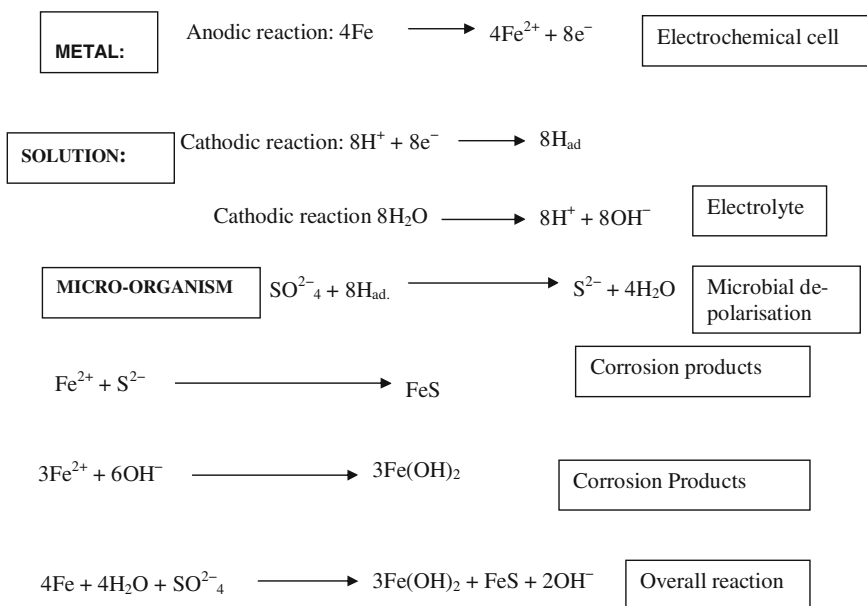
The Classical Theory, Its Rise and Fall

The mechanism postulated by Kuhr and Vlught 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.

⁸³Singleton 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).

⁸⁴Javaherdashti 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:



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

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

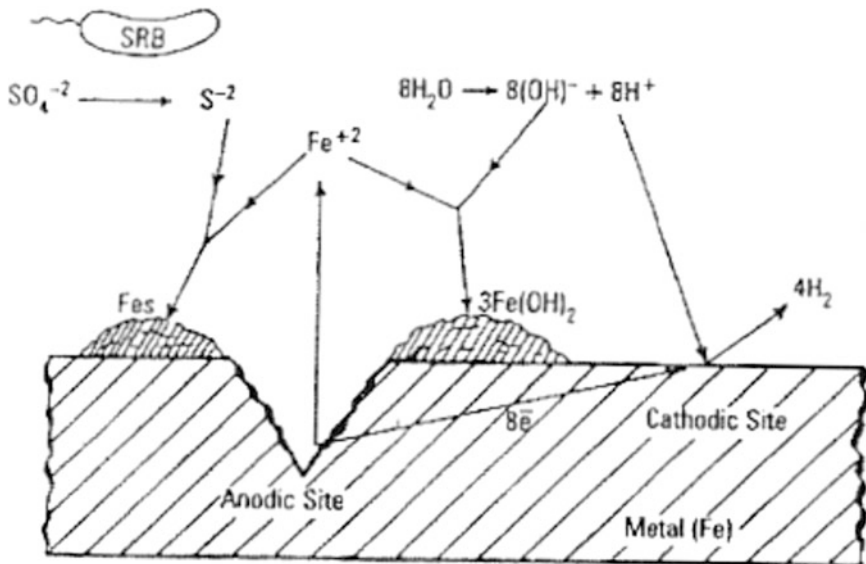


Fig. 4.15 Schematic of the cathodic depolarisation “classical” theory of SRB activity (see footnote 10)

- 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.

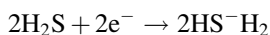
Alternative Theories to the Cathodic Depolarisation Theory

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

⁸⁶Ibid 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:



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 following⁸⁹:

- 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

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

⁸⁸Iverson 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.

⁸⁹Videla 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.

⁹⁰It 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. Hang⁹¹ 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

⁹¹Hang 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 SCC¹⁰² 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 $\sim 400 \mu\text{m}$ (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

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

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

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

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

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

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

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

⁹⁹Ibid footnote 45.

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

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

¹⁰²SCC 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.

¹⁰³Ibid 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

¹⁰⁴Ibid footnote 18.

¹⁰⁵Ibid footnote 47.

¹⁰⁶Linhardt P (1996) Failure of chromium-nickel steel in a hydroelectric power plant by manganese-oxidising bacteria. In: Heitz E, Flemming WS (eds) *Microbiologically 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.

¹⁰⁸Javaherdashti 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.

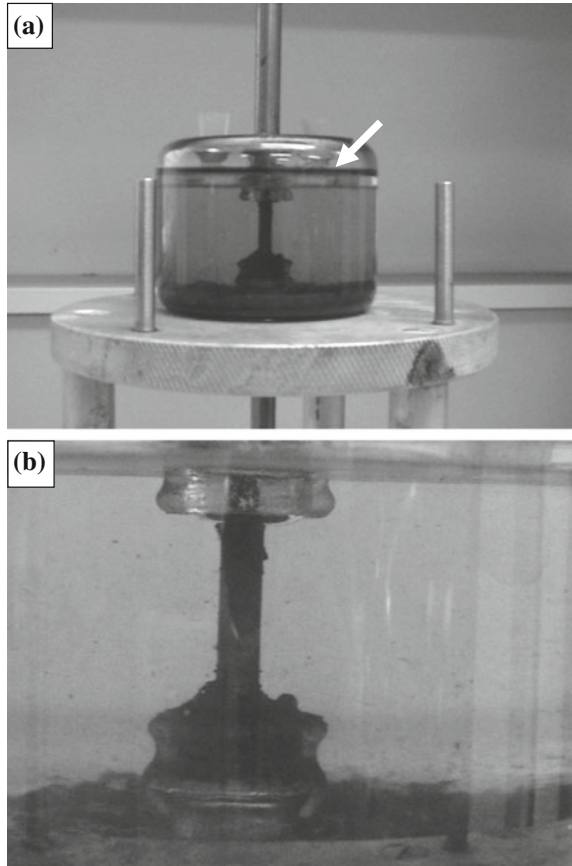
¹⁰⁹Javaherdashti R, Raman Singh RK, Panter C, Pereloma EV (2005) Role of microbiological environment in chloride stress corrosion cracking of steels. *Mater Sci Technol* 21(9):1094–1098.

¹¹⁰Javaherdashti 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.

¹¹¹Singh 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.

¹¹²Ibid 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)



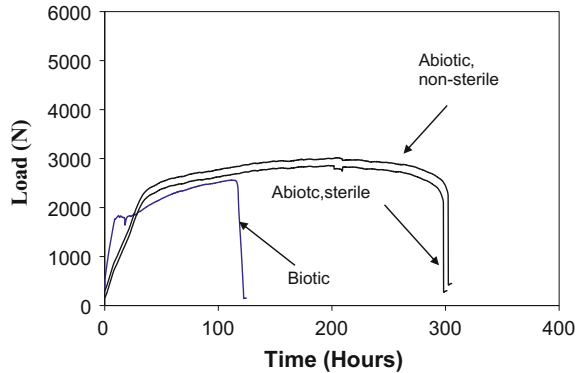
failure. In other words, when SRB is present, the material is likely to fail in a relatively shorter time than an abiotic (no bacteria present) environment, Figs. 4.17 and 4.18a, b.

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 factors¹¹³:

¹¹³Chamritski IG, Burns GR, Webster BJ, Laycock NJ (2004) Effect of iron-oxidizing bacteria on pitting of 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.

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

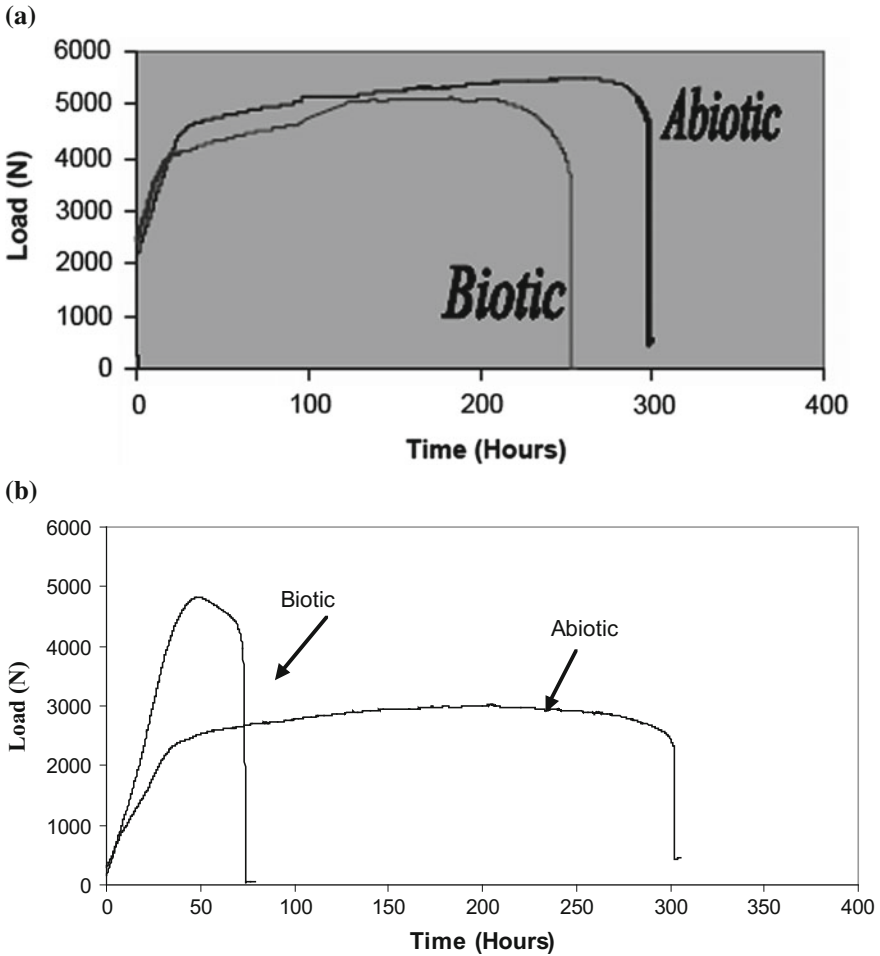


Fig. 4.18 **a** Typical load versus time curves generated by SSRT tests of duplex stainless steel SAF2205 in abiotic and biotic (mixed culture of SRB) environment (see footnote 110). **b** Typical load versus time curves generated by SSRT tests of mild steel in a 3.5 % chloride solution, with and without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

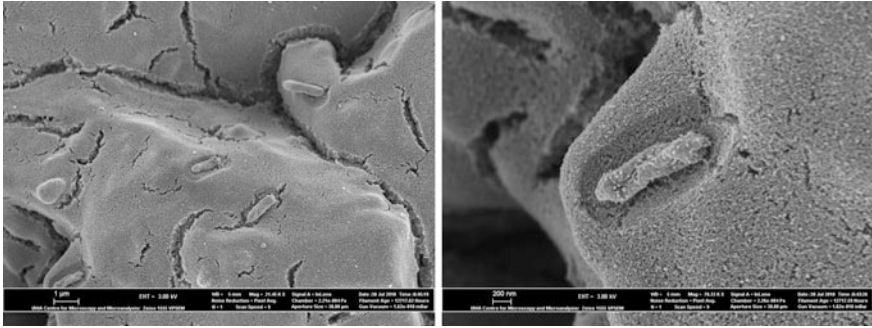


Fig. 4.19 Two examples of iron-oxidising bacteria (Ferrooxidans) grown on chalcopyrite, (This author wishes to thank Dr. Kayley Usher for her permission to use these images. We also wish to thank the Australian Microscopy and Microanalysis Research Facility at the Centre for Microscopy, Characterisation 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 chemoheterotrophic (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.

¹¹⁶Ibid footnote 34.

¹¹⁷Panter 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.

¹¹⁸Panter 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
$\text{H}_2 + \text{CO}_2$	CH_4		<-300 mV

“A Working Party Report on Microbiological Degradation of Materials—And Methods of Protection”, 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^- , $\text{S}_2\text{O}_3^{2-}$, 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).

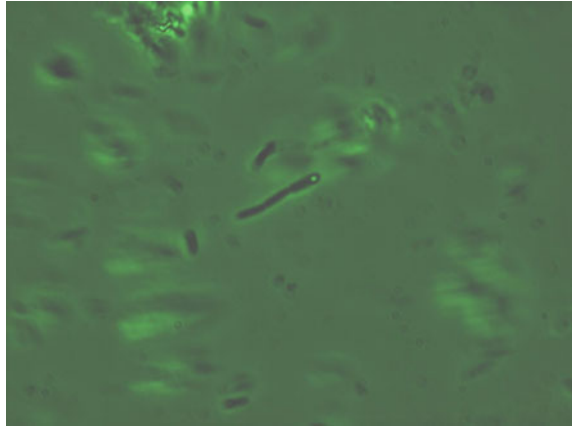
In soil environments, most IRB that can be isolated are fermentators and for the IRB that carry out dissimilatory reduction of ferric iron by anaerobic respiration, isolation may not be “as regular”, however, the latter can more easily be isolated from freshwater streams, lakes and marine waters (see 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 MIC¹¹⁹ suggests that under laboratory conditions applying voltages more negative than $-0.98V_{\text{Cu-CuSO}_4}$ 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 $-0.98V_{\text{Cu-CuSO}_4}$ 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 $-1.1V_{\text{Cu-CuSO}_4}$ 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

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

¹²⁰Pope 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 mild 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.

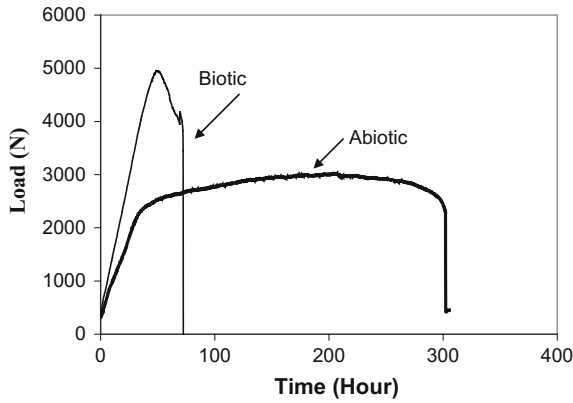


Fig. 4.21 Typical load versus time curves for mild steel in IRB culture comparing it with slow strain rate behaviour of mild steel in abiotic synthetic seawater media

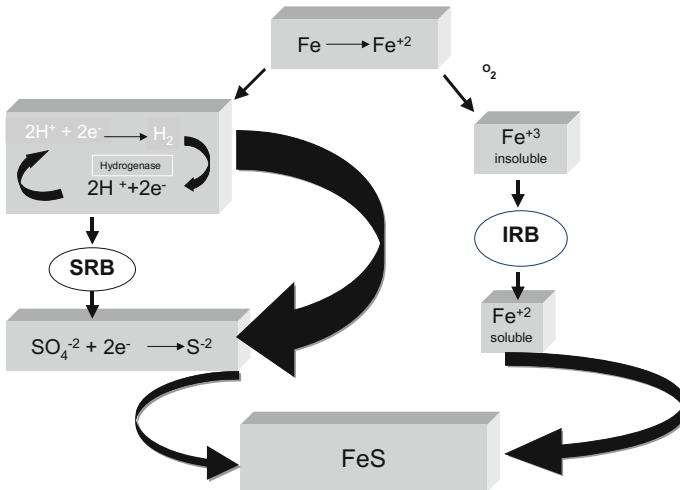


Fig. 4.22 Possible interaction between SRB and IRB

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

¹²¹Lee 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.

¹²³Sakaguchi 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.

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

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

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

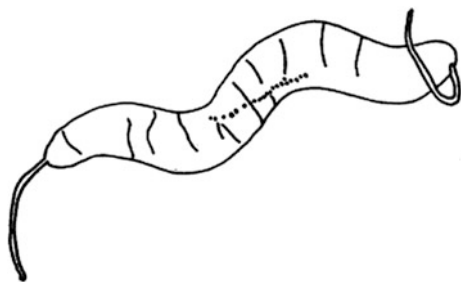


Fig. 4.23 Schematic presentation of a magnetotactic bacterium (*Aquaspirillum magnetotacticum*) where the magnetosomes can be seen as black beads (Javaherdashti R (1997) Magnetic bacteria against MIC, Paper No. 419, CORROSION 97, NACE International, 1997.)

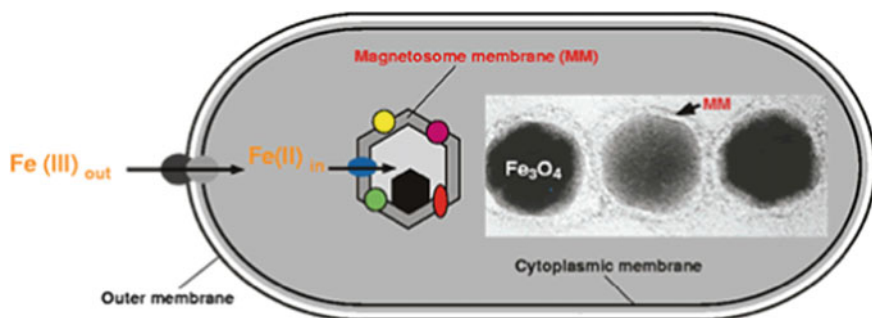


Fig. 4.24 Possible mechanism of formation of magnetite within magnetosomes (see footnote 128)

(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 (Fe₃O₄), 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.

¹²⁸The 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

¹²⁹Bahaj 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.

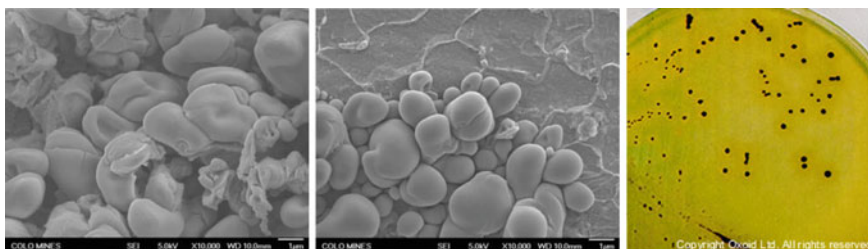


Fig. 4.25 (Left) Clostridium Sp. on API X52 steel and (right) on API X70 steel. Both Magnifications are 10,000 \times (see footnote 125). © NACE International 2013. (Far right) how Clostridia colonies (*black dots*) may look like in a culture (Dr. Reza Javaherdashti's Courtesy with sincere thanks to 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 artificially¹³¹ 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 lines¹³¹ 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.

¹³⁰Alabbas 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.

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

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

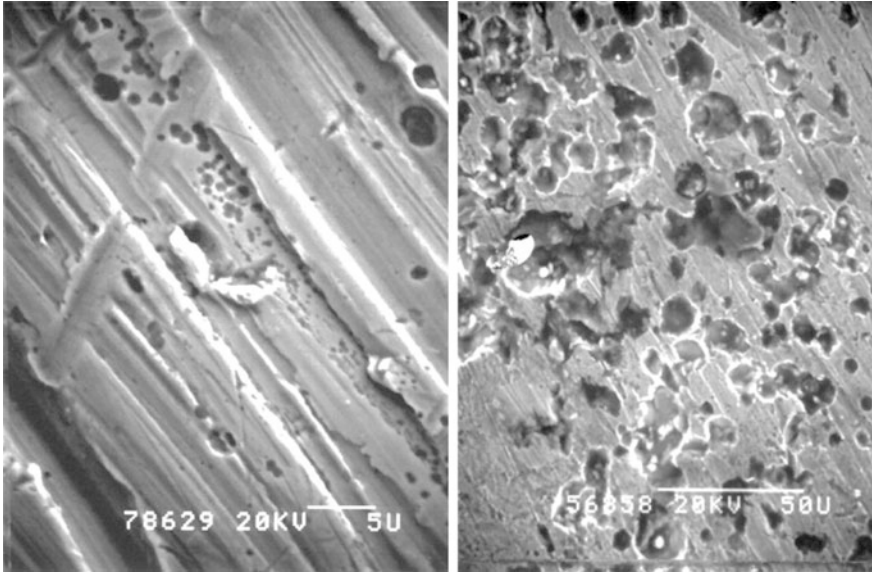


Fig. 4.26 SEM of a coupon made of pipeline steel exposed to a mixed culture containing SRB as well as Clostridium after (left) 2 h and (right) 1 month (see footnote 126) © NACE International 2004



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).

¹³³Indian 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.

¹³⁴Maillard 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](https://doi.org/10.1016/j.jhin.2010.06.028).

¹³⁵Schröpfer 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](https://doi.org/10.1186/1757-1626-1-252), CC BY 2.0, <https://commons.wikimedia.org/w/index.php?curid=6886224>.

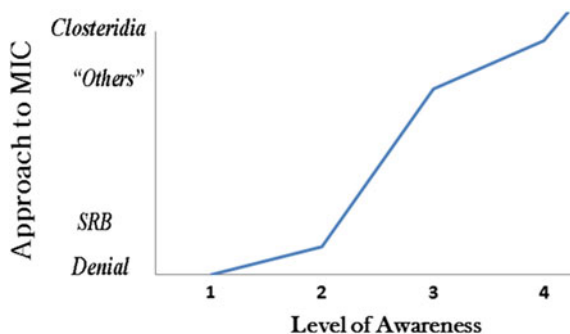


Fig. 4.28 Schematic categorised levels of awareness (LoA) against one's knowledge and appreciation of MIC. Relative distance between each level presents the effort it can take to arrive at that particular level. It starts with total denial of MIC and ends with appreciation that not only the role of SRB 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.

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Chapter 5

How Does a System Become Vulnerable to MIC?

Abstract In this Chapter we will discuss some general important conditions that can be leading into making an industrial system become vulnerable to MIC.

Keywords Water treatment · Welding · Hydrotesting · Alloying elements and material

5.1 Introduction

The late David White has been quoted as saying “*Microbiologically Influenced Corrosion is industrial venereal disease: it’s expensive, everybody has it and nobody wants to talk about it*”. If you ask any one who has been involved in MIC assessment for an industry, for hours he can tell you stories about how he has tried first to convince the industry about (1) The importance of corrosion treatment and (2) The involvement of some “bugs” in corrosion. I personally believe that what happened in Alaska’s Prudhoe Bay must be an alert for all the people who are involved in design, operation and maintenance: *DO NOT UNDERESTIMATE BUGS!*

This chapter will be mainly dealing with the problem of MIC recognition. In other words, we are after knowing what factors could be taken as indicators of MIC, principally independent of the system itself. So, what we are presenting in this chapter can be applied to systems such as pipelines, cooling systems, ballast tanks, hydrants and the like.

5.2 General Points Regarding Vulnerability of Industrial Systems

What we mean by an industrial system? An industrial system is a part of an industry that does a definite job within that industry and due to its working or service conditions, could be vulnerable to MIC. For instance, a pipeline that carries oil or gas is an example of industrial system as much as ballast tank in a ship or

a condenser in a power plant. It is very interesting to see that although industrial systems may be different from each other in shape, design and function, they will be affected by MIC under almost the same operating conditions. This is not only true for different systems, but also for diverse industries ranging from oil industry to power industry, mining, ship industry and even the agricultural industry.

What will be addressed in this chapter regarding the risk of MIC and vulnerability of a system, are just “necessary” and not “enough” conditions, in other words, establishment of the following conditions can just flag the danger of MIC but it does not guarantee its occurrence.

An example of “necessary” but “not enough” factors could be what is known as a ranking table for the estimation and assessment of steel corrosion in marine moods: in late 1970s R. King proposed a “ranking table”, by which through the assessment of some factors such as flow rate, oxygen, heavy metals and nitrogen and phosphorous contents, an index for the corrosivity of the seabed sediments could be produced.¹ Later in early 1980s, P.A. Farinha found this ranking table not adequate enough to explain the marine muds in the UK.² One of the main drawbacks of King’s ranking table is that it is designed for marine sediments, particularly open sea sediments, which are sufficiently different from estuarial or near shore harbour sediments.³ While Farinha’s index can be taken as a modification to King’s method,⁴ among the factors that was added to his ranking table, was the very important factor of sulphate concentration. Farinha’s index has been used successfully in other studies (see footnote 2). However, from an MIC point of view, Farinha’s model just considers the impact of SRB on corrosion and not other corrosion-related microbial species. Perhaps, another ranking method that considers other types of bacteria can also be applied.⁵

Another example is the very useful flow diagram, proposed by Krooneman et al.⁶ for the assessment and reducing the risk of MIC in pipelines. In this simple yet very clever flow diagram, the possibility for different factors leading into the risk of MIC has been addressed. Some of these factors are oxygen content, pH, sulphate content, total organic carbon content, salt concentration and temperature. While the model is certainly a useful tool, it does not consider, for example, the

¹King RA (1979) Prediction of corrosiveness of seabed sediments. Paper 228, CORROSION/79, March 1979, NACE International, Houston, TX, USA.

²Francis R, Byrne G, Campbell HS (1999) The Corrosion of some stainless steels in a marine mud. Paper no. 313, CORROSION/99, NACE International, Houston, TX, USA

³Farinha PA, Javaherdashti R Ranking corrosivity of marine sediments on steel structures as induced by sulphate-reducing bacteria to be published.

⁴Farinha PA (1982) Subsediment corrosion of sheet steel piling in ports and harbours with particular reference to sulphate-reducing bacteria. PhD Thesis, University of Manchester.

⁵Javaherdashti R (2003c) Assessment for buried, coated metallic pipe lines with cathodic protection: proposing an algorithm. In: CORROSION 2003, pipeline integrity symposium, March 2003, USA.

⁶Krooneman J, Appeldoorn P, Tropert R (2006) Detection, prevention and control of microbial corrosion. In: Eurocorr 2006, Maastricht, 2006.

possible effect of thermophilic corrosive bacteria, or the risk of corrosion when the temperature is above 40 °C. This model may not be useful in assessing MIC in, say, geothermal power plants.⁷

The above examples may serve to show that a better understanding of corrosion mechanisms and other involved factors can advance our understanding and power of corrosion prediction tremendously. It can also serve to emphasise that no matter how you do it, there are always factors in your list that may prevent it from being applicable everywhere and anytime. Therefore what will be discussed later in this chapter must be understood within the context of “being-useful-so-far” basis.

As always reminded, it is of great importance to be able to recognise MIC from other types of corrosion and also to find the best remedy for it as, otherwise, the problem will be more enhanced.

5.3 Important System/Working Conditions Leading into MIC

By calling the metallic substrate and the bulk water as “environment”, Fig. 5.1, the following classification can be used.⁸

Water temperature, pH and its chemistry (chlorides, nutrients) are important factors to be reported in addition to factors such as TDS and suspended solids contents.⁹ These factors may have various effects on MIC as well as non-MIC corrosion. In other words, while removing dissolved oxygen can dramatically decrease the likelihood of corrosion (because the cathodic reaction of oxygen will be deleted), in case the system is infested with anaerobic SRB, the very act of

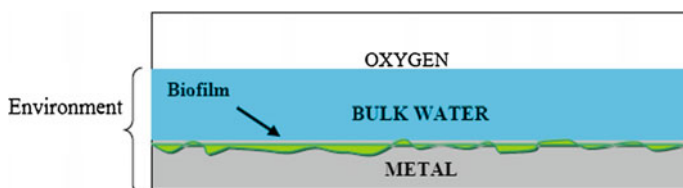


Fig. 5.1 Components of “environment”

⁷Torres-Sanchez R, Garcia-Vagas J, Alfonso-Alonso A, Martinez-Gomez L (2001) Corrosion of AISI 304 stainless steel induced by thermophilic sulphate-reducing bacteria (SRB) from a geothermal power unit. *Mater Corros* 52(8):614–618.

⁸Javaherdashti R (2007) A background fuzzy algorithm for biofilm formation. MIC-An International Perspective Symposium, Extrin Corrosion Consultants-Curtin University, Perth-Australia, 14–15 Feb 2007.

⁹Scott PJB (2004a) Expert consensus on MIC: failure analysis and control Part 2. *Mater Perform (MP)* 43(4):46–50

Table 5.1 The effect of some environmental factors on corrosion and bacteria

Effect of pH	Effect of DO (dissolved oxygen)	Effect of ionic strength
<ul style="list-style-type: none"> • Neutral pH favours bacterial growth • Low pH increases corrosion 	<ul style="list-style-type: none"> • High DO increases corrosion • High DO will support the growth of GAB/APB assists the survival of other bacteria (SRB and GAnB/APB) by symbiosis 	<ul style="list-style-type: none"> • High ionic strength (conductivity), especially chloride, increases corrosion • High salt content slows bacteria growth • Lower salt content favours bacteria growth

GAB General Aerobic Bacteria; GAnB General Anaerobic Bacteria; APB Acid Producing Bacteria
 © NACE International 2015

Olabisi O, Al-Shamari AR, Al-Sulaiman S, Jarragh A, Mathew A (2015) The role of bacteria population density in wet and dry crude asset integrity. CORROSION 2015, Houston, TX

oxygen scavenging would enhance the likelihood of MIC. Table 5.1 summarises the particular impact of some environmental factors on corrosion and bacterial activity associated with corrosion

To report such a diverse range of properties, a distinction can be made as the following: physico-mechanical effects and features of the environment including those of substrate (such as surface energy, roughness, surface temperature, residual stresses, etc.) and those of the bulk water (such as its mean linear velocity, nutrient concentration, temperature, etc.), and chemical effects and features of the environment including those of the substrate metal (such as existence and/or absence of some alloying elements that can encourage growth/attachment of the bacteria,...) and those of the bulk water (such as existing ions, TDS, ...). These two sets of effects are totally arbitrary and interrelated to each other.

5.3.1 Physico-Mechanical Factors and Their Effects on MIC

Figure 5.2 describes schematically the relationship among pH, flow velocity and temperature with regard to the observed corrosion rate. (pH has been considered as a physical—rather than chemical-factor with regard to two other features that contribute to MIC).

What is emphasised in Fig. 5.2 is that microorganisms, like human beings, are capable of living only within a certain range of temperature and pH. If the measured corrosion rate is only high between two temperatures T_1 and T_2 and then it decreases at temperatures below T_1 and above T_2 , then chances are that the type of corrosion could be MIC-related and not, for example, high temperature corrosion, as illustrated in Fig. 5.3.

The same is also true with pH; there is a range of pH that is tolerable for bacteria, and despite that, there may be some violations from this rule, a certain range of pH can always be defined for a certain group of bacteria. For example, the pH range

Fig. 5.2 Schematic relationship between flow velocity (V), pH of the bulk solution and temperature (T) with respect to the observed corrosion rate (R)

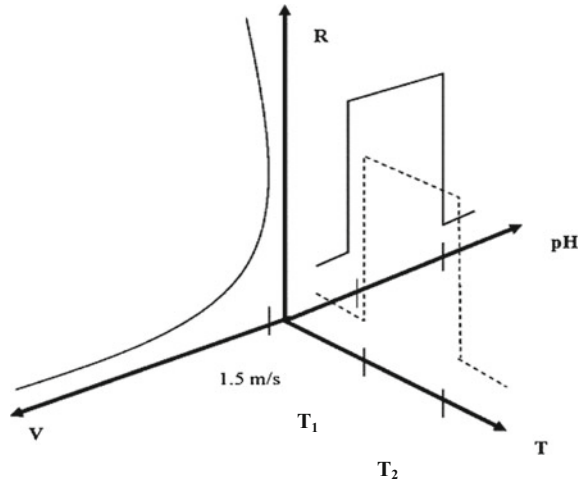
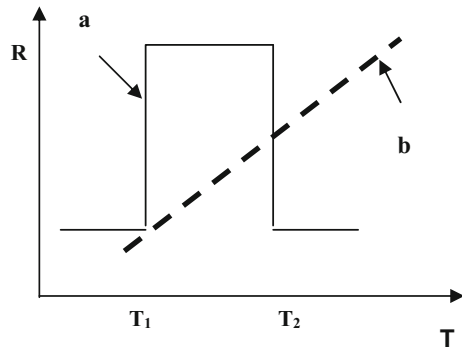


Fig. 5.3 Schematic presentation of corrosion rates that may be observed when the corrosion type is **a** MIC or **b** high temperature corrosion



that is tolerable by acid-loving bacteria is not suitable for SRB. Flow velocity is also an important factor, though this may not always be true. Kobrin¹⁰ has reported that in stainless steel tubes in which the water velocity was higher than normally accepted 1.5 m/s criteria,¹¹ MIC had still been operative. However, it is a trend that by slowing down of the fluid flow velocity, perhaps due to the absence of mechanical shear forces that would otherwise interrupt biofilm formation, the likelihood of MIC also increases.

¹⁰Kobrin G (1994) MIC causes stainless steel tube failures despite high water velocity. Mater Perform (MP) 33(4):62.

¹¹It is generally recommended to keep water flow velocity more than 1.5 m/s, pH above 10–11 and temperature well above 90 °C to lower the risk of MIC. Reader should understand that beyond these seemingly rigid rules and regulations, there are huge uncertainties, making them be understood as a whole not as isolated items. For example, you may try to keep water flowing and still the probability of getting no MIC may not be nil.

5.3.2 Chemical Factors

A very important factor that in a system can lead into MIC is the water quality: if raw, untreated or poorly treated water is being used for an industrial activity such as hydrotesting, one may expect that the risk of MIC will be very high.

What is meant by untreated water is the water on which no certain physical/chemical treatment has been done to remove, mainly, corrosion-related bacteria. This water can be sea, river or well water used for industrial activities.

5.3.2.1 Water Treatment

The water treatment method depends on many variables which includes, but not limited to, availability of alternative methods, economics of replacements, practical limitations related to implementation of physical/chemical treatment.

A crucial aspect of water is its total dissolved solids (TDS). Existence of halophilic (salt loving) SRB in waters with very high TDS (240,000 mg/l) has been reported.¹² Other aspects of water/biocide interaction (such as water activity, TDS content etc.) will be discussed in more details in Chap. 9.

5.3.2.2 Oxygen

Oxygen concentration of water, as bulk fluid, may not always be useful and, in fact, it can even be deceiving. As discussed in Chap. 4, biofilms are capable of forming anaerobic patches in otherwise aerobic bulk solutions. It has been reported that¹¹ a biofilm with a thickness of only 12 μm may be sufficient to create totally anaerobic regions in an anaerobic system where at the base of the biofilm, SRB can be motile and active. Having said that, some researchers believe that by knowing chemical oxygen demand (COD), it may be possible to know the concentration of electron donors available for sulphate or metal reduction so that a low COD would mean a low risk of availability of SRB or other types of “reducers” such as IRB.¹³

5.3.2.3 Nutrients and the Ease of Reaching Them

Availability of nutrients is also a crucial factor, as it may be the principle factor in determining if the prevailing bacterial population will be planktonic or sessile: Enos

¹²Al-Hashem A, Carew J, Al-Borno A (2004) Screening test for six dual biocide regimes against Planktonic and sessile populations of bacteria. Paper 04748, CORROSION 2004, NACE International, Houston, TX, USA.

¹³Scott PJB (2004b) Expert consensus on MIC: prevention and monitoring Part 1. Mater Perform (MP) 43(3):50–54.

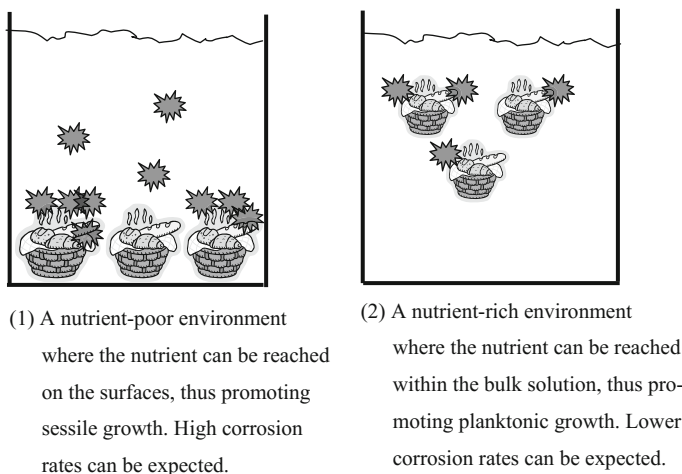


Fig. 5.4 Relationship between nutrient level and bacterial attachment

and Taylor,¹⁴ reported on how the nutrient level could affect the “mode” of bacterial spatial position: when the environment is poor in nutrient, the required nutrients are precipitated onto the surface, therefore the bacteria will settle down on the “food” which is available on the surface. These “seated” bacteria are called the “sessile bacteria”. On the contrary, if the environment is rich in nutrients, the bacteria do not need to go to the surface, so planktonic (floating) growth is favoured. These situations can schematically be presented as Fig. 5.4.

Perhaps one immediate important outcome of such a scenario, as Enos and Taylor have also put it, is how reliable are the microbial laboratory test results (as they are basically run in rich-nutrient culture media) compared to real life experiences (where the nutrient level may not always be that high). In other words, when under laboratory conditions the bacteria have all the required nutrients around, they may be inclined to prefer planktonic growth over sessile conditions whereas a great majority of MIC problems come from sessile bacteria not planktonic ones (this issue will be discussed later in this chapter). While this concern is understandable and quite valid, one should not forget the intrinsic limitations of doing microbial corrosion experimentation, as follows.

Conducting a precisely controlled test that involves all the bacteria and determination the share of each species in evaluating and assessment of corrosion is impractical and almost impossible. It is not practically possible to conduct a test where all the incorporating values and factors are exactly replicas of the natural conditions outside the walls of the laboratory either. The following may illustrate how the real life and the laboratory conditions may be difficult to be compatible:

¹⁴Enos DG, Taylor SR (1996) Influence of sulphate-reducing bacteria on alloy 625 and austenitic stainless steel weldments. CORROSION 52(11):831–842.

Due to practical limits such as difficulty in establishing and running continuous and/or semi-continuous cultures, some MIC experimenters do the tests in batch-type cultures. In these cultures, a certain amount of food (nutrients) are provided to the bacteria and no further change or displacement of the quantity of the nutrients is made. This, then, will be opposing to continuous and/or semi-continuous cultures where the culture/nutrient quantity are frequently or continuously changed.

Although it is true that batch-type experiments may not be able to present the natural habitat of the bacteria as closely as continuous cultures (because in a semi-continuous or continuous test regime the supply and demand of the nutrients more or less is similar to the nature,^{15,16}), it can be argued for batch cultures that they can be the most similar and closest to simulate and mimic what is happening within a stagnant water environment. When one considers a stagnant water environment, one can easily see that due to very slow movement (even almost no movement), no exchange of nutrients into that portion of the system will take place so that the bacteria will have to feed on what is available in that particular environment. Therefore, it follows that the batch cultures may be taken as to be better representatives of some natural conditions than are semi-continuous and continuous test regimes. Yet, the batch cultures are far from the ideal simulation of stagnant environments, obviously due to factors such as the kinetic discrepancies of the two environments.

It, then, can be concluded that the reliability of laboratory test results is not 100 %, they must be accepted and applied with care, having in mind all their advantages and disadvantages.

One of the possible effects of sessile bacteria on the planktonic bacteria is actually addressing the effect that biofilms can have on accelerating biocorrosion. This has been discussed before in Chap. 4 and will not be repeated here.

5.3.2.4 Alloying Elements and Their Impacts

Alloying elements are added to improve mechanical and electrochemical properties of the metal. For example, it is a well-known practice to add up chromium into the steel in order to increase its corrosion resistance. However, alloying elements can sometimes have other impacts as well so that they may affect the way the metal responds to the environment from a microbial corrosion point of view.

¹⁵Stott 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.

¹⁶Scragg AH (1991) Bioreactors in biotechnology: a practical approach, Chap 2. Ellis Horwood. Sections 2.5.10 and 2.5.11 discuss about advantages and disadvantages of continuous cultures over culture methods that could be very instructive.

For instance, it has been reported that¹⁷ by the increasing sulphur content as an alloying element, the likelihood of tubercle formation also increases, or molybdenum can reduce bacterial viability.¹⁸ Lopes et al.¹⁹ investigated the factors that can help adhesion of *Desulfovibrion desulfuricans* on metallic and nonmetallic surfaces. They showed that adhesion of this group of SRB on nickel surfaces is relatively more significant compared to stainless steel 304 or polymethylmetacrylate (PMMA) surfaces, implying that the bacteria did show a powerful tendency for colonisation on nickel surfaces.

The above shows just a few examples of possible enhanced interactions between the bacteria and some alloying elements. It is still not well known what the real mechanism(s) behind such behaviour could be. Whether such behaviour is the result of some sort of chemical response, production of “adhesion proteins” (see footnote 18) or any other mechanisms, the end result is that some alloying elements do have some impact on MIC that will make the use of the material containing those alloying elements a matter of caution where the risk of MIC is involved.

5.3.2.5 Welding

Another important factor that has very crucial impact on rendering a system vulnerable to MIC is welding. For engineering applications, welding is one of the most frequently applied methods that is used for “adhering” metallic parts to each other. However, no matter how useful it is, welding must be regarded as to be equivalent to a wound in body: it always requires highest attention and it can be the best spot for the initiation of problems (infection in the human body and weld decay in welded structures).

According to Kurissery et al.²⁰ the first study reporting weldments as preferred spots for microbial colonisation dates back to 1950. These researchers also quote some references where most of the corrosion failures in cooling water systems made up of “corrosion resistant alloys” is around or within weldments.

When a piece of steel is welded to another, both the temperature and grain boundary energy distribution change along side the welding area, Fig. 5.5.

¹⁷Walsh D, Pope D, Danford M, Huff T (1993) The effect of microstructure on microbiologically influenced corrosion. *J Mater (JOM)* 45:22–30.

¹⁸Percival SL, Knapp JS, Wales DS, Edyvean RGJ (2001) Metal and inorganic ion accumulation in biofilms exposed to flowing and stagnant water. *Br Corros J* 36(2):105–110.

¹⁹Lopes FA, Morin P, Oliveira R, Melo LF (2005) The influence of nickel on the adhesion ability of *Desulfovibrion desulfuricans*. *Colloids and Surf B* 46:127–133.

²⁰Kurissery RS, Nandakumar K, Kikuchi Y (2004) Effect of metal microstructure on bacterial attachment: a contributing factor for preferential MIC attack of welds. Paper No. 04597, CORROSION 2004, NACE International, Houston, TX, USA.

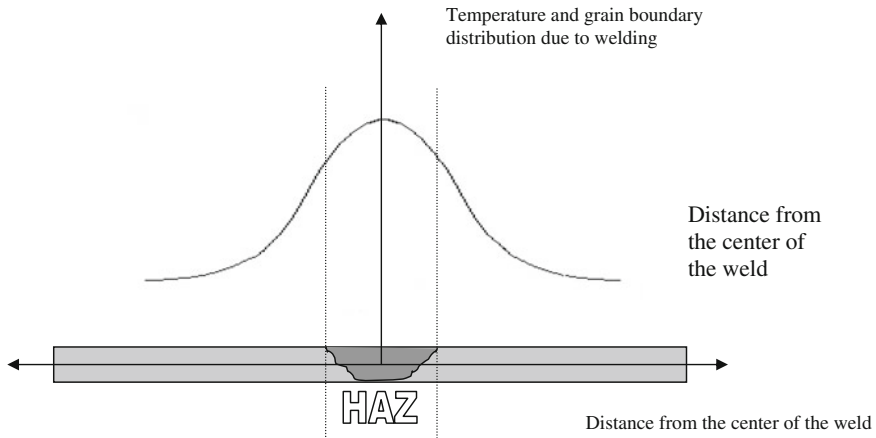


Fig. 5.5 Schematic distribution of temperature due to welding and grain boundary energy in a metallic bar. The *dark area* between the *dashed lines* presents the heat affected zone (HAZ)

As it is seen from Fig. 5.5, at and around the weld zone, both the temperature and energy distribution curves show peaks. This can be interpreted as one of the main features of welding,²¹ introducing zones where thermodynamically the energy is high and the structure has lost its uniform texture. The change in texture and thus surface roughness has been reported as a very important factor in initiation of bacterial attachment (see footnote 19)²² The possible effects of welding on accelerating MIC on metallic surfaces can be short-listed as follows (see footnotes 13, 16, 19 and 20).^{23,24,25}

- Change of the surface roughness so that bacterial colonisation can be facilitated by “hooking” onto the rough surfaces,
- Change of the surface chemistry and microstructure of both the fusion and the HAZ and facilitation of the segregation of alloying elements, therefore making the surface more receptive in terms of bringing the alloying elements from

²¹Kurissery et al. (see footnote 19) quote from two references (see footnotes 23 and 24 in their papers) to explain how grain boundary energy content can affect bacterial attachment. In their reasoning, as bacteria are themselves negatively charged, “chances are more for the cells to be attracted towards the grain boundaries with a high energy level and elemental segregation”.

²²Duddridge JE, Pritchard AM (1983) Factors affecting the adhesion of bacteria to surfaces. In: Proceedings of microbial corrosion, 8–10 March 1983, The Metals Society, London, UK.

²³Borenstein SW (1998) Microbiologically—influenced corrosion failures of austenitic stainless steels welds. Mater Perform (MP) 27(8):62–66.

²⁴Borenstein SW (1991) Microbiologically influenced corrosion of austenitic stainless steel weldments. Mater Perform (MP) 30(1), 52–54.

²⁵Brinkley III DW, Moccari AA (2000) MIC causes pipe weld joint problems. Mater Perform (MP) 39(6):68–70.

within the bulk materials onto the surface, thus letting the microorganisms have a better chance of finding the required nutrients

- Welding can result in generating a heterogeneous surface so that formation of electrochemical cells on the surface may become much easier,
- Introducing/highlighting the impact of factors such as the existence of inclusions, and secondary phases.

As it appears, if post welding treatments (such as stress relief, trimming and finishing the welded area) are ignored, chances are that welding through a series of changes that are introduced into the parent material, will promote the possibility of colonisation by sessile bacteria in terms of biofilm formation and microbial corrosion gets started. *So, treat weldings as you would treat the wounds to your own body.*

5.3.2.6 Impact of Hydrotesting

Another very important factor in initiation of MIC is wrong/incomplete hydrotesting. While pneumatic testing is just leakage test, hydrotesting is both leak and strength testing.²⁶

Hydrotesting is a routine test in industry to assess mainly the strength of weldments in systems that will operate under pressure. The test is done by introducing water into the system and applying internal pressures about 1.1 times the

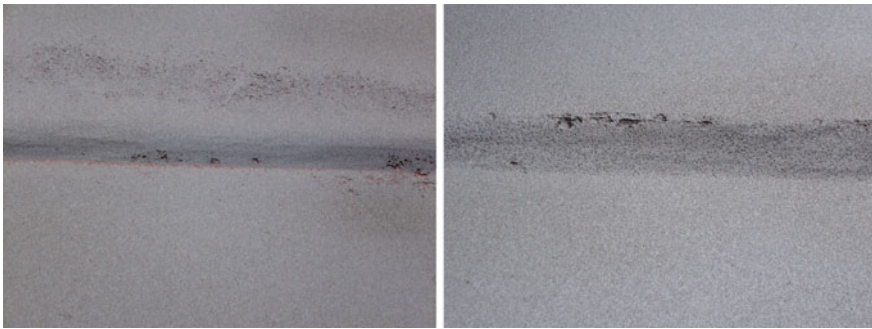


Fig. 5.6 Severe pitting resulted from the water *left* in a vessel after hydrotesting which is an example of a wrong/inadequate hydrotesting. The pitting varied from 1.5 to 2.0 mm in depth and was about 2–5 mm diameter. (Courtesy of Extrin Consultants)

²⁶Javaherdashti R (2003b) Enhancing effects of hydrotesting on microbiologically influenced corrosion. *Mater Perform (MP)* 42(5):40–43.

pressure that the system will undergo in real practice.²⁷ To carry out the hydrotest, most of the time untreated water (well water, river water or seawater) is used that may carry corrosion-related bacteria such as sulphate-reducing bacteria (SRB) or iron bacteria (IB). Figure 5.6 shows the pitting in the interior side of a tank after the tank was hydrotested with untreated water and the water was let stay in the tank for some weeks. As it can be seen from Fig. 5.6, very severe pitting has occurred all over the surface.

To have a better understanding about possible relationship between hydrotest and MIC, it is worth to distinguish between two types of hydrotest implementation methods defined as the following (see footnote 26):

1. Wrong hydrotest: meaning that untreated water has been used for the test. The untreated water is the one on which no chemical treatment, mainly by biocides, to remove corrosion-enhancing bacteria has been done.
2. Incomplete hydrotest: meaning that operations such as draining and drying immediately to be done after the test either have not been carried out or poorly done so that, as an evidence, one can still see water in the system.

As said above, normally untreated water is used for hydrotest. This is perhaps due to two contradicting ideas about hydrotesting and its importance:

- (1) *Hydrotest is important* because it measures how strong the component is and what is the possibility of leaking so that the system under test can be assessed regarding its performance before actually putting it into the service.
- (2) *Hydrotest is NOT important* because it is not part of the manufacturing process itself. Also, it is cheaper to conduct it with the available water sources than going to rather “fancy” options.

The resultant practice from these two different approaches is that due to the necessity of the job, it is done but it is done in a way that appears to be “cheaper”. Nevertheless, it is true that the alternatives often recommended instead of using untreated water are not presented as inexpensive options. Table 5.2 presents some of such alternatives.

In these instances, a simple balance between what you get (mitigation programs) and what you lose (corrosion) could be instructive. Javaherdashti²⁸ in his study of the economy of the treatment of MIC induced by hydrotesting emphasises on some important aspects of applying a successful mitigation program, a brief of this study is given below.

²⁷Iranian Petroleum Standards, “Engineering standards for start-up and general commissioning procedures”, IPS-E-PR-280 (0), Sect. 7.2.7, June 1999.

²⁸Javaherdashti R (2003a) A note on the economy of MIC mitigation programs. In: Proceedings of corrosion control and NDT, 23–26 November 2003, Melbourne, Australia.

Table 5.2 Pros and cons of some alternatives to untreated water for hydrotesting

Alternative	Pros	Cons
Demineralised water (DW)	<ul style="list-style-type: none"> • Provided draining and drying the system at the earliest opportunity after hydrotest, it is recommended • Disposal usually is not a problem 	<ul style="list-style-type: none"> • Costly • Difficult task of drying a large process system after testing
High-purity steam condensate (HPSC)	<ul style="list-style-type: none"> • Provided draining and drying the system at the earliest opportunity after hydrotest, it is recommended • Depending on the chemicals present in the condensate, disposal may be a problem 	<ul style="list-style-type: none"> • Costly • Practical problems with finding a chemically clean, large steam system for testing a large process system • More problematic than DW approach

Stoecker G (1993) MIC in the chemical industry. In: Kobrin G (ed) A practical manual on microbiologically influenced corrosion, NACE International, Houston, TX

Some Points Regarding the Feasibility of Mitigation of Hydrotesting—Assisted MIC

MIC caused by hydrotesting is certainly a case requiring mitigation programs to be launched. For very clear reasons, although all mitigation programs aim at reducing and elimination of unwanted corrosion, it differs in both extent and application principles. However, it must be noted that the approach discussed here can be applied to any case of corrosion whether it is MIC or not.

Mainly before and after any mitigation program, some steps must be checked; these steps are “confirmation”, “mitigation”, “control” and “feed back”.

What is meant by “**confirmation**” is to prove that the case has been caused by MIC and not, for instance, stray current. Some of the factors that contribute to confirmation step are

- Vulnerability of the material to corrosion under the working conditions: it is a well-known fact that certain materials are expected to fail more rapidly under certain working conditions.
- Vulnerability of physical, chemical and, in case of MIC, biological conditions of the system towards corrosion: for instance, when the design of piping system is such that it produces “dead corners” where a fluid like water can come to stagnant conditions and MIC becomes very likely.

The second step is “**mitigation**”; this step contains factors such as physical mitigation, chemical mitigation, improving working conditions, design modification requirements and corrosion knowledge management (CKM). These items have been addressed and discussed in Chaps. 2 and 3 of this book.

The third step is “**control**”: when the case is challenged and some mitigation programs are advised, it will be good practice to control and see if the proposed program will work as expected. When one has achieved how to control the case, it will be very useful if the case history along with all the details of confirmation,

Table 5.3 Four steps for a good MIC mitigation program

Steps	Factors to be considered
Confirmation	Vulnerability of material to MIC, physical, chemical and biological vulnerability of the system and working conditions to MIC including factors such as pH, temperature, the availability of nutrients and required chemical species such as carbon and nitrogen, the availability of energy source, low-flow or stagnant water, existence of too many branches, or dead corners (in piping systems), existence of corrosion-enhancing bacteria in the system, finding corrosion by products unique to corrosion-enhancing microorganisms (such as FeS for SRB), in some cases with high care, pit morphology (pit-within-pit), ...
Mitigation	Physical mitigation such as pigging for pipelines, chemical mitigation such as use of inhibitors and/or biocides, improving working conditions like avoiding water stagnation, adjusting pH so that it will not help microorganisms to grow and act, design modifications of the system, applying corrosion management, ...
Control	Comparing corrosion rates before and after applying mitigation, comparing performance of the system before and after, cost effectiveness of the mitigation program, ...
Feed back	Documentation of working conditions before and after applying mitigation, documentation of the mitigation method(s) for later use, ...

mitigation and control are documented (feedback) so that in the future, it will be easy to refer to and consider the mitigation program for any modifications required. More details of these four steps are shown in Table 5.3.

On the other hand, a very important factor in applying a successful mitigation program is to know how to evaluate if it was both suitable and cost effective. In other words, one has to see how beneficial the mitigation program was, both technically and economically (see footnote 28).

Based on several case studies, Kobrin et al.²⁹ have recommended some practices that may be useful to prevent MIC as induced by hydrotesting. Some of these practices may be addressed as follows:

- Always use the cleanest water available, that is, demineralised water, potable water, steam condensate and the like.
- Within a maximum of 3–5 days after a hydrotest, drain and dry the water. “Make this a requirement on purchase orders, engineering specifications, fabrication procedures and drawings”.
- Get as minimal as possible fabrication crevices.
- Specify good quality welds and avoid heat tint scales (use inert gas back up procedures, for example). Remove the heat tint scale mechanically (grinding, electropolishing and/or abrasive blasting) and/or chemically (pickling).

²⁹Kobrin G, Lamb S, Tuthill AH, Avery RE, Selby KA (1997) Microbiologically influenced corrosion of stainless steels by water used for cooling and hydrostatic testing. Nickel Development Institute (NiDI) Technical Series No. 10 085. Originally from the paper presented at the 58th Annual International Water Conference, Pittsburgh, Pennsylvania, USA, November 3–5, 1997.

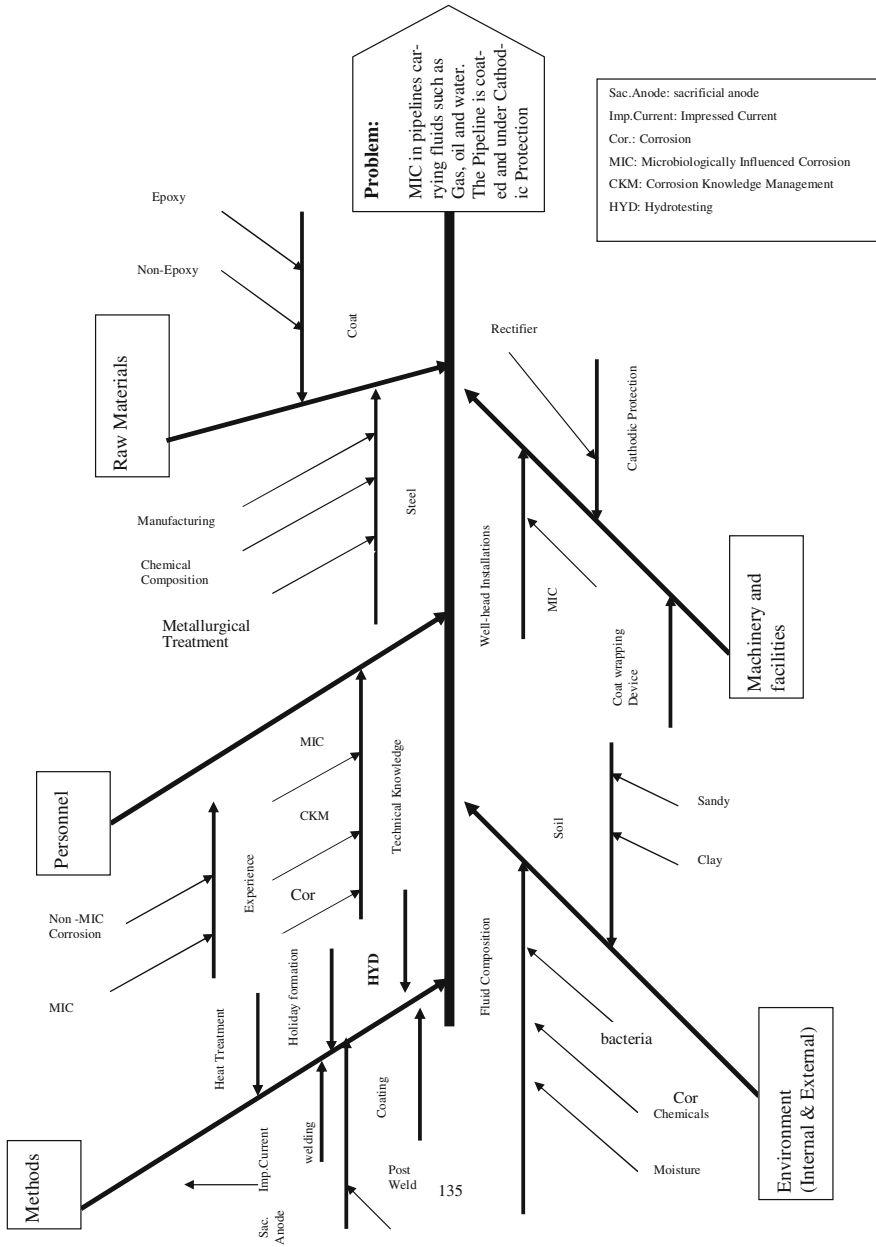


Fig. 5.7 Important factors that must be taken into account regarding the possibility of making a system vulnerable to MIC

- Design horizontal pipelines and heat exchangers as to be “self-draining”.
- At flanged connections, non-wicking gaskets shall be used.
- While high flowing water may still develop MIC, avoid designs that promote water stagnation. Design for flow velocities higher than 1.5 m/s.
- Good material selection and upgrading the existing ones to more corrosion resistant ones can always be a choice.

We add into all these a vibrant, open-minded CKM system especially designed for hydrotesting applications. Figure 5.7 summarises important factors that have to be taken care of regarding the possibility of making a system vulnerable to MIC.

5.4 Summary and Conclusions

The answer to the question of “what makes a system vulnerable to MIC?” is certainly a multi-dimensional one. There are many factors involved in increasing the likelihood of making a system susceptible enough to become deteriorated by microbial corrosion. These factors can be divided into two large categories, physico-mechanical factors such as water velocity, or roughness of the surfaces and chemical factors such as the effects of alloying elements and TDS. Welding and hydrotesting are also very important because if they are not carried out completely and precisely, this can put the system into the danger of MIC. What happens in real life is that systems become not only vulnerable but also contaminated with MIC too soon to be easily picked up. For this reason, it is a must to know how MIC can be detected and what the advantages and disadvantages of these methods are.

The next chapter will look at the methods and techniques that may be applied to detect MIC.

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Chapter 6

How MIC Is Detected and Recognised?

Abstract Two very important practical aspects about MIC is how to detect and treat it. There are various ways to carry out these two tasks. All these tasks have their own pros and cons. In this chapter we will discuss these methods along with their limitations and advantages.

Keywords Pit morphology · Culture dependent methods · Culture independent methods · Electrochemical investigation methods

6.1 Introduction

In previous chapters, the importance of biocorrosion and its possible mechanisms were discussed. Also, we looked at some crucial factors that could increase the likelihood of MIC in a given system. Especially in Chap. 5, the concern was to avoid microbial corrosion. However, almost all the time, what happens in real life is that the system of concern has already been contaminated and the outstanding question is no longer how to prevent, but rather, how to estimate the severity and extent of MIC. For instance, while for SRB-induced MIC, some investigators believe that no relationship exists between corrosion rate and the number of the

The original version of this chapter was revised: Some text have been updated with revised content; Figure 6.8 and its legends have been removed and other figures were renumbered accordingly; Table 6.2 and its legends have been removed. The erratum to the chapter is available at DOI: [10.1007/978-3-319-44306-5_12](https://doi.org/10.1007/978-3-319-44306-5_12)

bacteria cells,¹ the number of acid-producing bacteria in a system has a profound effect on the corrosion rate.

The distinction between “recognition” and “detection” of MIC has been introduced here to separate those methods that use microbiological means to assess MIC from those that do not. Therefore, our convention here is that the “recognition methods” do not use biology, but other methods and technologies to deal with the “criminal scene investigation” of what the bacteria have done. The “detection methods”, on the other hand, are mainly focused on the application and implementation of biological techniques by making use of the features of the bacteria.

Recognition Methods:

¹Little BJ, Wagner P (1997) Myths related to microbiologically influenced corrosion. Mater Perform (MP) 36(6):40–44. In this regard, see also: Ilhan-sungur E, Cansever N, Cotuk A (2007) Microbial corrosion of galvanized steel by a freshwater strain of sulphate reducing bacteria (*Desulfovibrio* sp.). Corros Sci 49(3):1097–1109. The general criteria for evaluation of soil microbial corrosivity based on SRB counts alone have been reported by Mizia RE, Alder Flitton MK, Bishop CW, Torres LL, Rogers RD, Wilkins SC (2000) in their report, “Long Term Corrosion/degradation Test First Year Results”, Idaho National Engineering and Environmental Laboratory, Sept 2000. On the other hand, for a general criteria for MIC in soil including bacteria such as SRB and iron bacteria, among others, see Stein AA (1993) MIC treatment and prevention. In: Kobrin G (ed) A practical manual on microbiologically-influenced Corrosion. NACE, Houston, TX, USA. The source for both the cited studies regarding a relationship between SRB numbers and the severity of corrosion is the paper by Ronay D, Fesus I, Wolkober A (1987) New aspects in research in biocorrosion of underground structures. Corrosion’ 87, Brighton, UK. According to this investigation, if the number of SRB per gram is less than 5×10^3 , there is no risk of MIC whereas a count of 10^4 or more of SRB per gram of soil, is alarming a severe case of MIC. Kuwait oil company is reportedly targeting the following as maximum allowable bacterial counts (From: Al-Shamari AR, Al-Mithin AW, Prakash S, Islam M, Biedermann AL, Mathew A (2013) Some empirical observation about bacteria proliferation and corrosion damage morphology in Kuwait oilfield waters. Paper No. 2748, CORROSION 2013, Houston, TX, USA.

Bacteria type	Sessile bacteria count	Planktonic bacteria count
SRB	$<10^2/\text{cm}^2$	$<1/\text{ml}$
GAB	$<10^2/\text{cm}^2$	$<10^4/\text{ml}$
GAnB	$<10^2/\text{cm}^2$	$<10^4/\text{ml}$

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I would like to emphasise that these numbers can only have “operation significance” in the sense that they will set a target for operators and perhaps a practical measure to compare the fluctuations of the system due to certain applications (e.g., application of certain biocides). However, these figures by its own carry no meaning especially for SRB-related cases

6.2 Investigating Vulnerable Systems and Components

More often than not, a large percentage of the risk (>80 %) is found to be associated with a small percentage of the equipment item (<20 %).² In other words, there are certain components in a system that could be vulnerable to MIC and also certain types of materials which are prone to experiencing risk of biocorrosion.

Almost every system that uses untreated liquid water in contact with rough surfaces³ does have the potential of risking MIC for which time-management is crucial. Currently, there is a relatively good understanding of what particular industries are prone to MIC and where to expect this type of corrosion. Some examples of the components and parts that may suffer most from MIC can be named as open (or closed) cooling systems, water injection lines, storage tanks, and residual water treatment systems, and filtration systems, different types of pipes, reverse osmosis membranes and potable water distribution systems.⁴ Also MIC can be expected to occur more often at welds and heat affected zones (HAZ), under deposits and debris and after hydrotesting (inadequate drainage/drying),^{5,6}

Therefore, for example, the possibility of getting MIC in power generation industry is high and in this particular industry, cooling systems are more susceptible to MIC than, say, the fire-side of the water walls in the boiler.

Another important issue, of course, is the material itself. A review of case histories shows that, in general, MIC-related failures probably account for less than 10 % of total corrosion failures in stainless steel systems,⁷ (thus putting them well above mild steels). However, in some cases, it is the mild steel that as a material shows good performance with regard to susceptibility to microbial corrosion to MIC: Olesen et al.⁸ in their investigation of corrosive effects of manganese-oxidising bacteria observed that these bacteria do not cause high rates of corrosion by the deposition of manganese oxides in systems that have been built from mild steel only.

²Hovarth RJ (1998) The role of the corrosion Engineer in the development and application of Risk-based inspection for plant equipment. Mater Perform (MP) 37(7):70–75.

³Javaherdashti R (2007) How to deal with MIC? tips for industry. In: “MIC An International Perspective” Symposium, Extrin Corrosion Consultants-Curtin University, Perth-Australia, 14–15 Feb 2007.

⁴Al-Darbi MM, Agha K, Islam KR (2005) Modeling and simulation of the pitting microbiologically influenced Corrosion in different industrial systems. Paper 05505, CORROSION 2005, NACE International, Houston TX, USA.

⁵Of course here the reader will notice that using untreated water is also an important issue (wrong hydrotesting) as mentioned in Chap. 5.

⁶Scott PJB (2004b) Expert Consensus on MIC: Prevention and Monitoring, Part 1, Mater Perform (MP) 43(3):50–54

⁷Jack TR (2002) Biological Corrosion Failures. Published by ASM International.

⁸Olesen BH, Nielsen PH, Lewandowski Z (2000) Effect of Biomineralized Manganese on the Corrosion Behaviour of C1008 Mild Steel. CORROSION 56(1):80–89.

Moreover, it must also be noted that different classes of stainless steels do not behave the same when exposed to biological environments. For instance, apparently, grade 304 stainless steel may be regarded inferior to grade 316 stainless steel from the standpoint of resistance to MIC.

6.3 Pit Morphology

In their outstanding review of MIC, B. J. Little et al.⁹ have summarised the trend in MIC literature regarding the efforts that have been made to establish a relationship between the shape of the pit (pit morphology) and MIC.

Some researchers and investigators (see footnote 7)¹⁰ have used or advised the “characteristics pit morphologies” in their assessments of MIC cases as indicators. Generally, it was believed that a certain pit-shape exists that can be applicable to, at least, materials of the same rank. An example is the “gauge” like pits found in 300-series of stainless steels, Fig. 6.1, where there is a narrow opening and a wide interior space.

Nowadays, it is not believed that such relationships between pit morphology and classification of the attack as microbial corrosion can particularly exist. There are reported cases (see footnote 9) where the diagnoses have been made based only on the pit morphology as an indication of MIC, but have been found to be caused by factors other than MIC. Tatnall and Pope¹¹ have also noted this point by giving the example of corrosivity of ferric chloride on stainless steels or welds and addressing it as “not necessarily...biologically produced”. Stray DC currents, for example, may create corrosion morphologies resembling MIC.

Recently investigations have revealed that the initial stages of pit formation by certain types of bacteria indeed have special characteristics. Some of these cases have been reported by Little et al. (see footnote 9) In a series of investigations on microbial corrosion of pure iron (99.99 %)¹² and carbon steel¹³ in the presence of SRB (*D. desulfuricans*, de Romero et al. also showed that severe pitting occurred where the bacteria had been formed as colonies. However, in none of these cases, any indication for pit determination by naked eye has been given so far. In carbon steels, a characteristic “pit-in-pit” morphology may be taken as a sign of suspecting

⁹Little BJ, Lee JS, Ray RI (2006) Diagnosing microbiologically influenced corrosion: a state-of-the-art review. CORROSION 62(11):1006–1017.

¹⁰Cubicciotti D, Licina GL (1990) Electrochemical aspects of microbially induced corrosion. Mater Perform (MP) 29(1):72–75.

¹¹Tatnall RE, Pope DH (1993) Identification of MIC. Chapter 8. In: Kobrin G (ed) A practical manual on microbiologically-influenced corrosion. NACE, Houston, TX, USA.

¹²de Romero M, 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, NACE International, Houston, TX, USA.

¹³de Romero M, Duque Z, Rodriguez L, de Rincon O, Perez O, Araujo I (2005) A study of microbiologically induced corrosion by sulfate-reducing bacteria on carbon steel using hydrogen permeation. CORROSION 61(1):68–75.

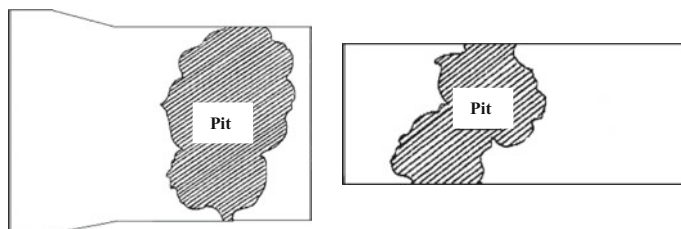


Fig. 6.1 Two examples of the so-called “characteristic pit morphologies” associated with MIC in stainless steels



Fig. 6.2 Two examples of MIC-related failure featured as pit-in-pit in a carbon steel pipeline’s external surface that had both coating and under CP and buried in a soil with pH of 5.5. © NACE International 2013

MIC activity, Fig. 6.2.¹⁴ However as we will explain in more details later (Fig. 6.9), one must not judge the case of corrosion to be MIC-related just based on its looks: one has to be sure that it was MIC and then use the failure morphology to re-confirm it.

It seems that with regard to trials aimed at establishing a relationship between the pit morphology and classification of the attack as MIC, the words of wisdom by Tatnall and Pope (see footnote 11) can be better understood: “surface morphology relates to the chemistry at the metal surface, not to the presence or absence of micro-organisms”.

6.4 Mineralogical Finger Prints

Another approach that can be used to identify cases of microbial corrosion is by determination of the minerals formed, as some of them do only form under microbial conditions.

¹⁴Brooks WW (2013) Microbiologically influenced corrosion riviera park case study. Paper no. 2525, CORROSION 2013, Houston.

The presence of SRB can be often justified by the presence of Fe_xS_y minerals such as troilite (FeS), pyrrhotite ($\text{Fe}_{0.875-1}\text{S}$), mackinawite ($\text{FeS}_{0.93-0.96}$), greigite (Fe_3S_4), or amorphous iron sulphide ($\text{FeS}_{\text{amorph}}$).^{15,16} It has been reported¹⁷ that the primary films formed by SRB on steel are mackinawite and protective film of siderite (FeCO_3).

Both then are transformed to cubic greigite and greigite with rhombohedral structure, i.e. smythite. Eventually, the final stage of all these transformations is the formation of non-protective pyrrhotite under anaerobic conditions. Pyrrhotite may form after 9 months (see footnote 9). For copper–nickel alloys affected by SRB, the finger print minerals could be djurleite, spinonkopite, and high-temperature polymorph of chalcocite (see footnote 9). Figure 6.3a, b show iron sulphide film formed on two types of mild steel coupons exposed to SRB culture. Figure 6.2a¹⁸ shows the iron sulphide film formed on carbon steel with a composition (wt%) of carbon (0.25 %) and chromium (0.3 %). The composition (wt%) of the carbon steel shown in Fig. 6.2b¹⁹ is also carbon (0.39 %) and chromium (0.11 %). As it seen from the figures, both steels show cracks, indicating that the films formed are not mechanically stable enough to resist external forces such as shear forces caused by intermittent flow patterns. We should open a parenthesis here and tell the readers about an important point: insufficient treatment of MIC is, in most instance, worse than no treatment at all. An example is an increasing flow of water or inducing oxygen after a period of stagnation without having a versatile mitigation program. In both “treatments” mentioned above, if necessary pre-cautions are not taken, the existing situation may become worse: for instance, by increasing the flow, the shear forces thus produced are capable of damaging the non-protective, brittle films and therefore producing cracks and enhancing corrosion.

When a crack forms, the local oxygen concentration (pressure) within the crack and in the area around it will be different. Due to the lack of access to the inside of the crack, the oxygen partial pressure within the crack decreases whereas the adjacent area is still rich in oxygen. These cracks can furthermore establish electrochemical cells such as differential aeration cells where the low partial pressure of oxygen in one side makes it anode and, as a consequence, the likelihood of corrosion also increases.

¹⁵Lee AK, Buehler MG, Newman DK (2006) Influence of a Dual-species Biofilm on the Corrosion of Mild Steel. *Corros Sci* 48 (1):165–178.

¹⁶Liu 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.

¹⁷Tiller AK (1983) Microbial Corrosion. In: Proceedings of microbial corrosion, 8–10 March 1983, The Metals Society, London, UK.

¹⁸Javaherdashti R (Javaherdashti 2005) Microbiologically influenced Corrosion and cracking of mild and stainless steels. Ph.D. thesis, Monash University, Australia.

¹⁹Javaherdashti R, Sarioglu F, Aksoz N (1997) Corrosion of drilling pipe steel in an environment containing sulphate-reducing bacteria. *Int J Pres Ves And Piping* 73:127–131.

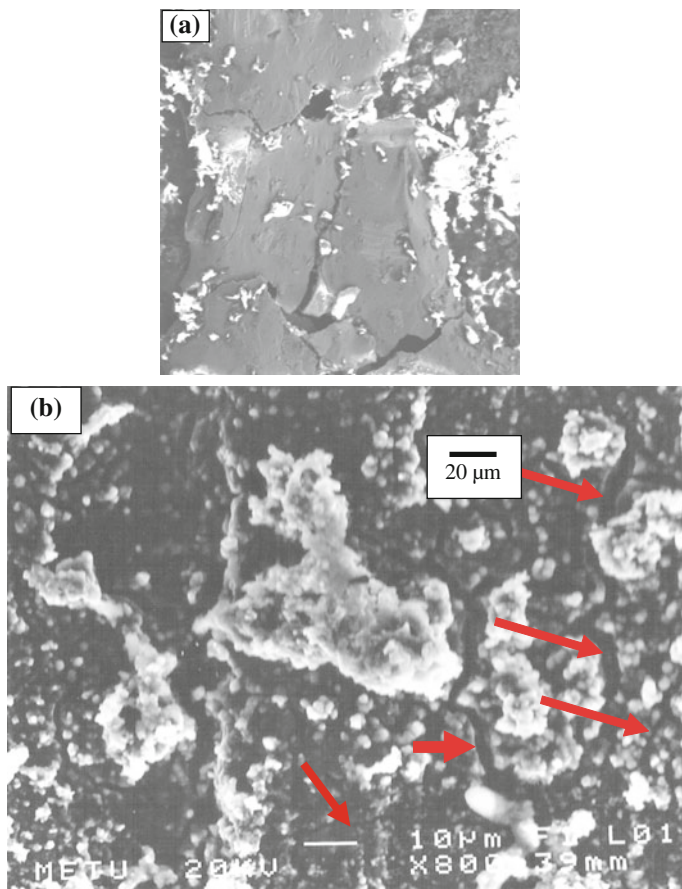


Fig. 6.3 **a** Scanning electron microscope (SEM) micrograph of the cracked corrosion product film (most probably FeS) that had been formed on mild steel electrode exposed to pure SRB environment after the biofilm removal **b** SEM of another type of carbon steel (N-80) after being exposed to SRB culture. Some of the cracks are shown by *arrows* in both pictures

6.5 Appearance and Colour of Corrosion Products

The colour of the corrosion products can also provide good clue to investigate MIC and, probably, the likely species involved.

The black colour, smelly iron sulphide corrosion products and reddish-brown colour deposits may be good indicators to consider the involvement of SRB and

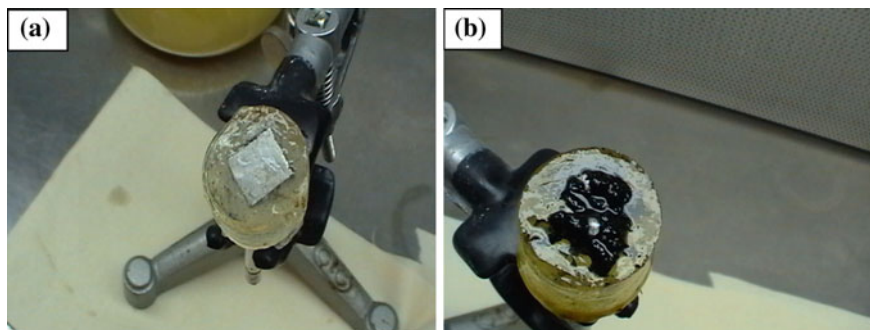


Fig. 6.4 Appearance of mild steel **a** before and **b** after about two months of exposing to SRB culture (see footnote 17)

Fig. 6.5 Cultures of active IRB, the two test tubes on the *left* show positive ferric iron reducing culture in different cell concentrations, the last tube on the *right* shows negative ferric iron reducing culture. (Courtesy of Extrin Consultants)



iron-oxidising bacteria, respectively.²⁰ Figures 6.4a, b show a piece of carbon steel before and after exposing to an SRB culture. On the other hand, when iron reducing bacteria are present and actively reducing iron, the dark greenish colour is a good indication of the presence of these bacteria, Fig. 6.5.

In the case of sulphur-oxidising bacteria (SOB), the colour of the corrosion products is reportedly yellow.²¹

²⁰Blackburn FE (2004) Non-BIOASSAY Techniques for Monitoring MIC. Paper 04580, CORROSION 2004, NACE International, Houston, TX, USA.

²¹Scott PJB (2004a) Expert consensus on MIC: failure analysis and control. Part 2, Mater Perform (MP) 43(4):46–50.

6.6 Characteristics of Microbial Attack

There are a few patterns to address the microbial attack that can be used to evaluate a case of MIC, as very briefly addressed and described below²²:

- (1) Attack by physical presence and attachment of microbial cells onto the surfaces (as it occurs in the electronic industry by adhering cells onto the electronic chips, thus requiring having very clean air in the laboratories),
- (2) Attack by the excretion of mineral or organic acids of a biological source such as hydrated hydrogen sulphide gas (by SRB, for example) or nitric acid (by, for instance, nitrifying bacteria) that results in hydrolysis of the material,
- (3) Attack by organic solvents that are produced as results of the actions of fermentative bacteria,
- (4) Attack caused by the salt which itself may have been produced as the result of reactions between anions (which are final products of microbial metabolism) and cationic components of ceramic materials. The results of these reactions could range from swelling of the porous material (due to the hydration of these often highly water soluble salts) to blasting (caused by dryness and thus formation of voluminous crystals) to freeze-thaw attack (the physical attack that may be the result of the swelling originally resulting from microbial activity),
- (5) Attack by the effect of biofilms that may cause, among others, problems such as localised corrosion and reduced flow velocity,
- (6) Attack by enzymes excreted by micro-organisms that live on insoluble compounds to turn them into smaller fragments. An example is the deterioration of cellulose (wood) into glucose. This matters if the insoluble compounds are impregnated by organic substances (such as resins or waxes) used to improve their features and characteristics. Therefore, degradation of such organic additives by certain micro-organisms may caused serious problems for the performance of the material,
- (7) Attack which is stimulated by the solubility action of most of organic acids, capable of complexing metal ions which may be otherwise insoluble/low soluble products. Also, emulsifying agents produced by micro-organisms (e.g. phospholipids) can degrade “insoluble” materials such as pyrite or low soluble items such as elemental sulphur.

Additionally, there are some other pertinent points, summarised as the following (see footnote 20),²³:

²²Sand W (1997) Microbial mechanisms of deterioration of inorganic substrates-a general mechanistic overview. *Int Biodeterior Biodegradation* 40(2-4):183-190.

²³Scott PJB (2000) Microbiologically influenced corrosion monitoring: real world failures and how to avoid them. *Mater Perform (MP)* 39(1)54-59.

- If osmium compounds such as osmium tetroxide are used for fixation of the sample chemically, the osmium picked by the micro-organism can make it easier to distinguish samples with biological cells from inorganic debris and crystals of approximately the same dimensions and shape.
 - If using methods such as EDXA or atomic absorption spectroscopy, total or organic carbon is above 20 % and the sulphur is about 1 % or more (in the absence of any other source of sulphur), or wet chemical methods show that there are high concentrations of chlorides in fresh water and iron or manganese in non-ferrous materials, or phosphorus in corrosion products (unless coming from treatments such as phosphate treating) and very low nickel (below the material ratio), all these clues can signal the possibility of a microbial attack.
 - There could be other methods such as the use of sulphur isotopes that have a lighter atomic number so that when they react with micro-organism driven sulphate reduction (for example SRB), they can easily identified from the non-biologically formed heavier sulphur isotope compounds.
- (8) There is still no united idea regarding the so-called biogenic iron sulphide as to be a good indicator of bacterial activity when compared to abiotic sulphide films (please also refer to the footnote given in Page XXX, Chap. 4, regarding Smith and Miller's review). Some researchers²⁴ have postulated that the presence of mackinawite may be used as an indication of MIC by SRB. On the other hand, some other experimenters²⁵ believe that while SRB may affect the crystallisation mode of iron sulphides, they reject the idea that mackinawite is the "unique" SRB-influenced corrosion product. So until researchers agree on one or another idea, it is not recommended to use sulphide films as the only way of identification of MIC.

Detection Methods:

Detection methods can be grouped into two subgroups: the methods that are used in the laboratory studies and the methods that are used in the field. The former methods can be called as "Laboratory methods" and the latter as "Field methods". The laboratory methods can further be classified as "Culture-dependent" and "Culture-independent" methods. It may seem confusing but Filed tests at least at the moment and to the best knowledge of this author- are all classified as "culture-dependent". This must be remembered when the reader is studying the following sections. All these methods have their pros and cons. We will be dealing with each very briefly here without going through the microbiological details of each. Obviously, more details can be found from the given references.

²⁴McNeil MB, Little BJ (1990) Technical note: mackinawite formation during microbial corrosion. CORROSION 46(7):599-600.

²⁵Newman 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.

6.7 Laboratory Methods

6.7.1 Culture-Dependent Methods

By culturing what is meant is, basically, that the nutrients and the temperature necessary for the growth of certain types of bacteria are prepared and in the course of time, the bacterial species of interest are grown. Even with this definition, one can easily see the main drawback of culturing methods: you get what you have asked for. In other words, if the environment (in terms of chemicals used as nutrients, oxygen and the temperature) are within the range of a pre-arranged band, this means that the bacterial species that do not meet those criteria will not grow. That is why in a culture prepared for room-temperature (mesophilic), neutral-pH tolerant, strictly anaerobic bacteria such as some species of strictly anaerobic SRB, one can not grow, say, aerobic (oxygen-demanding), acidophil (acid-loving), thermophilic (high-temperature) sulphur-oxidising bacteria. In addition to this, culturing can reveal only 1 % or less of the total bacteria present in a given sample.²⁶ Therefore culturing methods may not be regarded as very reliable methods on their own, as they may produce dubious results which are open to discussion. Two examples of culture-dependent methods are Serial Dilution and Most Probable Number (MPN).

Maxwell et al.²⁷ oppose such shortcomings of culturing methods by stating that the very low percentage of culturable species “is not unique” to a certain industry such as the oil industry. They also emphasise upon the importance of many issues such as (a) the possible positive impacts of more investment by industry to enable the laboratories to use a wider range of culture media, (b) increasing the reliance and qualification of the testing methods by applying statistically relevant techniques (such as triplicate Most Probable Number method) and also (c) the “fact” that “in the hands of trained microbiologists, similar techniques [such as Culturing and Extinction serial dilution] are employed as useful tools in clinical, pharmaceutical, and other industrial situations”.

While it is very true that without more funds, progress in the field of MIC—like other disciplines—is almost impossible, comparing culturing method outcomes in medical applications with industrial (engineering) applications is oversimplifying the situation. For one thing, when a disease and its cause are concerned, there is not a wide range of micro-organisms that can be considered as being related. Every time a similar pathological situation arises, it is that particular type of micro-organism which is responsible. However in the case of, for example, accelerated low water corrosion and buried pipelines (to be studied in more details in Chap. 7), certainly more than one type of bacteria can be involved. Therefore, by

²⁶Yee GG, Whitbeck MR (2004) A microbiologically influenced corrosion study in fire protection systems. Paper No. 04602, CORROSION 2004, NACE International, Houston, TX, USA.

²⁷Maxwell S, Devine C, Rooney F, Spark I (2004) Monitoring and control of bacterial biofilms in oilfield water handling systems. Paper 04752, CORROSION 2004, NACE International, Houston, TX, USA.

just relying on the culturing method, one can miss a lot of such bacteria. Another interesting example is when a slime sample from a cooling water system is diagnosed as having high numbers of *Pseudomonas*. Practically, such diagnoses may not be that important as “rather than being a single strain, *Pseudomonas* is a diverse genus of common, ... aerobic organisms associated with everything from industrial biofouling to urinary tract infections” (see footnote 11). Therefore, the complexity of MIC in industrial systems used for engineering purposes make culturing method an easy, and inexpensive yet least reliable as a complete method of detection.

Little et al.²⁸ have reported a very interesting case where the corrosion rate of the mild steel specimen exposed to a mixed culture of SRB and oil-oxidising bacteria changed according to the medium used, demonstrating how the culture medium composition can affect the corrosion rate and intensity. Stare and Javaherdashti²⁹ compared the precision of some SRB detection cultures and found out that by modification or using new formulations of relatively well-known culture media such as API RP38 and Butlin, the resultant synthetic cultures could perform relatively better in terms of getting more positive results. These results justify once more that there is no such thing called as “the best standard culture”, as long as you know what you want to find.

Table 6.1 summarises pros and cons of some of common detection methods that are used for dealing with bacterial samples suspected of containing corrosion-related bacteria. One has to keep in mind that although all these methods have their own drawbacks, they have been used (and as matter of fact, still being used) by many laboratories and in many researches. The reason for this is not always their technical competence (especially compared with culture-independent methods) but rather their relatively inexpensive and easy-to-do nature.

A very significant issue with culturing methods is that the samples needed for them have to be taken under the best possible conditions. Sampling is so important that, for instance, Sects. 6.5 and 6.6 in the NACE Standard Test Method “Detection, Testing, and Evaluation of Microbiologically Influenced Corrosion on Internal Surfaces of Pipelines”, NACE Standard TM0212-2012 (Year 2012) and Sects. 6.2–6.4 of the NACE standard Standard Test Method, “Field Monitoring of Bacterial Growth in Oil and Gas Systems”, NACE TM0194-2014 (Year 2014) have been devoted to sampling.

Normally, what is being done is that, most of the time, a water sample from the suspected failed section of the system is taken and it is sent to a qualified laboratory to be processed by inoculating it into a given microbial growth medium. In addition to the conditions that the samples must not become contaminated and frozen during transportation to the laboratory, the time factor is of crucial importance. The best time interval between sample-taking and laboratory processing must not exceed 24 h.

²⁸Little B, Lee J, Ray R (2007) New development in mitigation of microbiologically influenced corrosion. In: “MIC An International Perspective” Symposium, Extrin Corrosion Consultants-Curtin University, Perth-Australia, 14–15 Feb 2007.

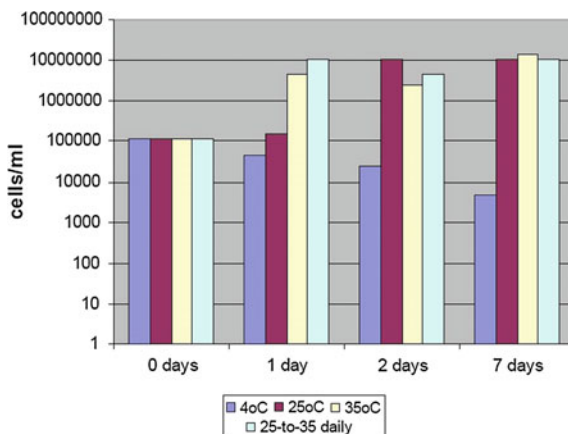
²⁹Setareh M, Javaherdashti R (2003) Precision comparison of some SRB detection methods in industrial systems. Mater Perform (MP) 42(5):60–63.

Table 6.1 Pros and cons of some common detection methods used in MIC studies (see footnotes 11 and 19)

Detection method	Some advantages	Some disadvantages
Culturing	Rather simple and routine, comparatively unsophisticated and cost effective	Only a very small portion of the whole micro-organisms are cultivable; it may be too time consuming; the culturing environment can be different from the natural environment of the micro-organism; it is selective, i.e. it allows growing of “pre-selected” micro-organisms
Direct Microscopic Examination	It is a good way to estimate total number of bacteria using staining/counting techniques; It can be used for direct inspection of certain large, distinctively shaped micro-organisms (such as filamentous iron bacteria and stalked iron oxidisers such as <i>Gallionella</i>)	This method cannot identify a large number of bacteria, so this method must not be used alone and requires involvement of other detection methods as well
Adenosine Triphosphate (ATP) assay	This method has been used to estimate relative total bacteria number in environments where “non-bacteria” ATP is rare (e.g. oil field water samples); It can be carried out within much shorter times (less than an hour)	This method can not distinguish between ATP extracted from bacteria and other organic debris in the sample; the amount of ATP is not predictable in SRB and some other common environmental bacteria giving rise to very rough approximate values for total bacteria count
Anti-body tests	Commercially available only for SRB; it is rapid (from 20 min. to less than an hour), inexpensive (provided that there is microscope available)	The sensitivity limit is normally approximately 10^3 cells/ml, however, its “total number of bacteria” counts must be checked with culturing methods as well; cannot distinguish between living and dead bacteria
Fatty acid analyses	Commercially available; its precision is better than anti-body techniques in “marking” available micro-organism types	Relatively expensive; less quantitative; limited library of fatty acid signatures of bacteria; cannot detect certain bacteria such as iron oxidisers

Le Borgne S, Jan J, Romero JM, Amaya M (2002) Impact of molecular biology techniques on the detection and characterization of micro-organisms and biofilms involved in MIC. Paper No. 02461, CORROSION 2002, NACE International, Houston, TX, USA

Fig. 6.6 The impact of storage conditions (Time and temperature) on the precision of SRB quantification (Kilbane J (2014) Effect of sample storage conditions on oilfield microbiological samples. Paper No. 3788, CORROSION 2014, Houston, TX, USA). As seen from the figures, the samples kept at 25 °C or daily cycled between 25 and 35 °C show increase in SRB cells. © NACE International 2014



Obviously, these requirements for taking a sample with all these conditions in place cannot be always observed in the field. The storage conditions of samples is highly likely to induce errors in the results. These errors can sometimes be in the form of fluctuations (increase or decrease) in the number of bacterial species that in either case will cause underestimation or overestimation in the number of the bacteria. For many bacteria such as acid-producing bacteria (APB), there is a positive correlation between their numbers and corrosion rate (the higher the bacteria, the higher the expected corrosion rate). Figure 6.6 shows an example of what can happen to the number of sulphate-reducing bacteria based on storage conditions.

No discussion about detection methods applied in MIC studies is complete without mentioning molecular biology methods which are becoming more and more popular in this area. We will briefly discuss these methods here, without going through all the details.

6.7.2 Culture-Independent Methods

Due to the shortcomings of traditional, relatively inexpensive techniques like culture-dependent methods,³⁰ other methodologies have been developed. These methods are called “culture-independent methods” or “Molecular Microbiology Methods” (MMM). They are based on molecular biology techniques and use the

³⁰One of culture-dependent methods is the Most probable Number (MPN) that has been reported to “underestimate the size and misrepresent the composition of microbial communities”, see Ref. Kilbane (2014).

genetic material (DNA and RNA) of the bacteria. Referring to them collectively as “genetic techniques”, they have the capacity to³¹:

- highlight the dominant bacteria in a natural sample (an ecological system) that contains other species as well with no worries regarding the serious limits of common viable counting methods,
- determine the relative proportion of MIC-related bacteria within the whole bacterial community,
- identify the bacteria which are resistant to biocides,
- evaluate the population size changes imposed using biocide or nutrient modifications,
- be counted as a more reliable method for sampling biological samples which is not affected by time or transportation factors³²

Some of culture-independent methods are as follows:

- Polymerase Chain Reaction (PCR)
- Denaturing Gradient Gel Electrophoresis (DGGE)
- Fluorescence in situ Hybridisation (FISH)
- Microbial Diagnostic Microarray (MDM) {Gene Chips}
- Metabolic activity Measurement techniques such as ATP measurement
- Next-Generation Sequencing (NGS)

Genetic techniques mainly analyse the DNA extracted from cultures or environmental samples. The extracted DNA will be used to find “molecular fingerprints” using techniques such as PCR (Polymerase Chain Reaction). PCR is used to “amplify” in vitro the DNA fragments that then can be used to identify the bacteria (see footnote 29). Figure 6.7 schematically presents the main steps involved in genetic techniques using PCR.

To make the traditional PCR methods, new techniques such as real-time quantitative PCR (qPCR) have been developed and used, whose advantages over traditional PCR have been reported to be³³ (a) providing more accurate and reproductive quantitative data regarding microbial communities (b) having a detection range of six orders of magnitude or more (c) no need for post-PCR manipulation and treatment and (d) much better analysis capability.

³¹Videla H (2007) Biofilms in pipelines and their treatment in the oil industry. In: “MIC An International Perspective” Symposium, Extrin Corrosion Consultants-Curtin University, Perth-Australia, 14–15 Feb 2007.

³²Sampling and preserving the samples could be a really tough issue especially due to practicality of these practices. If sampling and handling are carried out in a manner that the microbial samples get contaminated or die during transportation, the results could become highly dubious.

³³Zhu XY, Modi H, Ayala A, Kilbane JJ (2006) Rapid detection and quantification of microbes related to microbiologically influenced Corrosion using quantitative polymerase chain reaction. CORROSION 62(11):950–955.

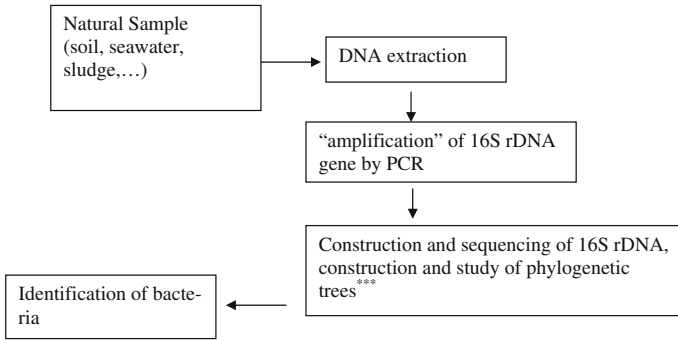


Fig. 6.7 Basic steps involved in genetic techniques to be used for MIC studies

If we want to compare the MMM with conventional culture-dependent methods (such as MPN), we can see that while MPN results may not be matched with the risk of MIC, culture-independent methods (q PCR) are both applicable in more convenience to risk-based inspection and assessments and do show a good correlation with the risk of MIC.

One has to keep this in mind that at the moment all these methods (both culture-based and culture-independent methods) are classified as laboratory methods in the sense that in order to perform them, one has to have both a well-equipped laboratory and trained personnel. This may appear as a disadvantage for those clients who count beans” but one has to observe that the highly precise results that are obtained from MMM tests with regards to MIC risk does compensate the cost spent on these methods.

6.8 Quick (Or Rapid) Check Tests

Most of the time, what is required is to know whether or not MIC and particularly SRB form a part of the problem. In these conditions, one needs a prompt answer that although it may not be very accurate, at least it will give an idea about the “presence” or “absence” of SRB. However, one must be very cautious with using this terminology as they may also be misleading, as it will be discussed below.

These methods can be classified as “absence/presence tests”, in terms of microbiological tests. Most frequently tests of this kind that used in the field are “acid test” and “lead acetate test. In acid test, a few droplets of diluted hydrochloric acid are added on the corrosion products. If there is a smell of “rotten egg”—characteristic of hydrogen sulphide gas—then, the corrosion products do contain sulphides. The “lead acetate test” is basically using moist lead acetate [Pb (C₂H₃O₂)₂.3H₂O] papers, that in contact with sulphides, the paper turns into black.

While these test methods are easy and straightforward, one should bear in mind that:

- They are only useful when it has been established with confidence that the case is indeed MIC and does involve SRB. The reason is that by conducting these tests, what is actually tested is the presence of sulphide not SRB. In other words, if the case is confirmed as MIC and it is also confirmed that SRB are involved, then these tests can be called “absence/presence test” in their microbiological context, meaning that they can be used to provide proof for the existence of any micro-organism that are capable of producing sulphides. Otherwise they just show presence of sulphides and these sulphides may have been created by non-biological means.
- These tests, at the best, are capable of confirming the presence of SRB. They can not be used to test the presence of manganese-oxidising bacteria. So, if you have a mixed sample (more accurately, a mixed culture) that contains many types of bacteria, using the acid test and lead acetate test may not be useful.

As a result, bearing in mind the limitations of both of these rapid test methods, they may become very handy to help build a story for a corrosion case where there is no immediate access to laboratory facilities.

Therefore, if the detection test is not sophisticated, in terms of both the testing techniques and the means, it can be done on site and requires no background science of either microbiology or corrosion, we call these tests as “rapid check tests”. In this regard, a majority of tests called by some experts (see footnote 11),³⁴ as “rapid check tests” will need to be re-assigned. To have an idea of what these so-called quick check tests are, a list of the test types are given below:

1. Microscopic direct method evaluation
2. ATP Luminescence
3. Hydrogenase test
4. Desulphoviridin test
5. APS-reductase test
6. Enzyme linked immunosorbent assay (ELISA)
7. Auto-radiography
8. Fatty acid analyses

Both the APS-reductase and hydrogenase tests work on the basis of tracing enzymes, one tracks down hydrogenase and the other APS-reductase. However, it must be noted that while the hydrogenase test can only be done on SRB that have this enzyme only, APS-reductase based tests are applicable to all the SRB. The

³⁴King 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 Feb 2007.

Fig. 6.8 SRB-positive, as evidenced by blackened Sanicheck® SRB kit (Courtesy of Extrin Consultants)



main drawback is, of course, it can only detect SRB. Besides, although the commercial kits are user-friendly, there is still a certain level of hands-on experience is needed for carrying out the tests more confidently.

Another point is that some of the commercially available SRB-detection quick tests normally rely on visual effects caused by SRB presence. One of these visual factors is the blackening, as shown in Fig. 6.8.

6.9 Electrochemical Recognition Methods and Their Application to MIC

Microbial corrosion is a multi-disciplinary topic. Therefore, many disciplines must become involved for the assessment of its effects. Electrochemistry is definitely one of these disciplines. When electrochemical experimental techniques are applied to non-living objects, there is no fear of altering/modifying the environment. However, when it comes to living micro-organisms, it becomes another story.

The examples below suggest how applying a voltage on microbial communities can have adverse effects:

- A report on cathodic protection effects of steel pipes against MIC³⁵ suggests that, under laboratory conditions, applying voltages with values more negative

³⁵Kajiyama F, Okamura K (1999) Evaluating cathodic protection reliability on steel pipes in microbially active soils. CORROSION 55(1):74–80.

than $-0.95V_{\text{Cu-CuSO}_4}$ may decrease the number of iron bacteria as a result of environmental changes caused by cathodic protection process.³⁶

- Again with regard to cathodic protection criteria (applying voltages more negative than $-0.95V_{\text{Cu-CuSO}_4}$), it has been reported³⁷ that applying voltages up to $-1.1V_{\text{Cu-CuSO}_4}$ not only failed to prevent the growth of bacteria on the metal surfaces, it rather prompted the growth of certain microbial species and rate of corrosion.
- Little et al. (see footnote 9) reported in one of their investigations, in which applying electrochemical polarisation could influence the number and types of bacteria associated with the surface.

The following is a list of some pros and cons of traditional electrochemical methods when they are applied to biocorrosion studies)^{38,39,40,41}:

Open-circuit potential (corrosion potential), or briefly, OCP:

- By this method, corrosion potential of a corroding metal is measured by determining the voltage difference between the metal immersed in a corrosive medium and a suitable reference electrode which is usually a saturated calomel electrode.
- Advantage: because of its simplicity, the measurement of the corrosion potential has been used in MIC studies for many years. It can be used either in the laboratory or in the field.
- Disadvantage: it measures both anodic and cathodic processes simultaneously and only assesses trends.

³⁶Although in this report the type of the bacteria (IOB or IRB) has not been specified, from general recognition of iron bacteria [see “Standard Test Method for Iron Bacteria in Water & Water-formed Deposits”, ASTM D932-85 (Re-approved 1997), ASTM annual book, ASTM, USA, 1997.], it may be anticipated that it was iron-oxidising bacteria whose number had been adversely affected by applying voltage.

³⁷Pope DH, Zintel TP, Aldrich H, Duquette D (1990) Efficacy of biocides and corrosion inhibition in the control of microbiologically influenced corrosion. *Mater Perform (MP)* 29(12):49–55.

³⁸Videla HA (1996) *Manual of biocorrosion*. CRC press, Inc.

³⁹Stott JFD, Skerry BS, King RA (1998) Laboratory evaluation of materials for resistance to anaerobic corrosion caused by sulphate reducing bacteria: philosophy and practical design, the use of synthetic environments for corrosion testing. In: Francis PE, Lee TS(eds) *ASTM STP 970*, ASTM, pp 98–111.

⁴⁰Dexter SC, Duquette DJ, Siebert OW, Videla HA (1991) Use and limitations of electrochemical techniques for investigating microbial corrosion. *CORROSION* 47(4):308–318.

⁴¹Dexter SC (1995) Microbiological effects. In: Baboian R (ed) *Corrosion tests and standards: application and interpretation*. ASTM Manual Series: MNL 20, ASTM.

Reduction–oxidation (Redox) potential:

- It is pertinent to the relative potential of an electrochemical reaction under no net flow of electrical current (equilibrium conditions). The redox potential in general is a measure of the oxidising power of the environment.
- Advantage: it can be used in both lab or in the field.
- Disadvantage: it is not useful for evaluating corrosion rates. It requires the simultaneous measurement of the medium pH, because it may result in difficulties in both taking accurate measurements and interpreting the obtained data. Such cases happen when immersion times are not chosen carefully, so that microbial colonisation of the measuring electrode occurs and the measured value will correspond to the chemistry at the electrode under the biofilm rather than to that of the bulk environment. Also, the redox potential measurements of electrochemical reactions must be made under equilibrium conditions where it is usually unlikely to be encountered in real-life experiences performed on living systems such as microbial communities.

Tafel polarisation:

- In this method, applied potential to the system is plotted versus the logarithm of the current density. The resulting curves would intersect at a point representing the corrosion potential and the corrosion current density. In the vicinity of the corrosion potential, the measured log current versus potential curves both deviate from linearity. Nevertheless, both often contain linear segments referred to as Tafel regions.
- Advantage: it can be used in the laboratory or in the field because of easy interpretation of data.
- Disadvantage: the measurement of corrosion current is dependent on both a steady corrosion potential and ability to identify the linear Tafel region. Electrolytes in which more than one reduction reaction takes place or in which concentration polarisation occurs exhibit less distinct linear regions. Large polarisations may change the electrochemical conditions at the metal surface and could be deleterious to micro-organisms in the biofilm. For systems like some stainless steels in seawater, in which corrosion potential drifts or fluctuates with time, Tafel polarisation is practically meaningless.

Potentiodynamic sweep techniques:

- The applied potential is increased versus log current and plotted. For a given corroding metal, the corrosion potential and corrosion current will be determined by the point at which the cathodic curve intersects the anodic curve. One of the main experimental variables that can be manipulated is the sweep rate. High scan rates (about 60 V/h) are used to show regions where intense anodic activity is likely. Slower scan rates (1 V/h) are used to identify regions in which relative inactivity is likely such as stable metal surface conditions.

- Advantage: useful to predict the corrosion behaviour of passive metals in biotic media containing biofilms. Quantification of microbial effects and rapid scan rates for film-free metals are possible.
- Disadvantage: results depend on the sweep rate and experimental conditions. Slow sweep rates can affect localised conditions at the metal/solution interface.

Polarisation resistance method:

- The method is based on the linear relationship between changes in the applied potential and the resulting current density when the applied potentials are within ± 10 mV of the corrosion potential. The slope of the potential/current curve is approximately linear and has the units of resistance.
- Advantage: rapid and easy interpretation of the results, it shows a good correlation with weight-loss method.
- Disadvantage: it is not useful to assess localised corrosion. The presence of biofilms complicates the linear polarisation interpretation by introducing additional electrochemical reactions, which can lead to nonlinear polarisation behaviour.

Generally, all direct current polarisation methods, that is Tafel polarisation, potentiodynamic sweep techniques, and polarisation resistance method, apply voltage to the test environment, that in the case of MIC studies is the microbial environment. The net result of this is altering the environment in such a way that is likely to affect the micro-organisms. Some examples of such adverse effects will be addressed later in this study. It appears that the method showing less adverse influence to the microbial environment is the open-circuit potential measurement. Nowadays, the general trend among investigators seems to prefer OCP and electrochemical noise potential (EPN) as the safest electrochemical recognition methods as they do not impose voltages upon microbial communities (see footnotes 8 and 37),^{42,43}

6.10 Summary and Conclusions

The first step for recognition and detection of MIC is to try to prove that the case is not MIC-related at all! By doing so, many prejudices and problems associated with it can be solved⁴⁴ Fig. 6.9 shows the required chain of action in the form of a flow

⁴²Jack TR, Ringelberg DB, White DC (1992) Differential Corrosion Rates of carbon Steel by Combinations of *Bacillus* sp., HAFNIA ALVEI and DESULFOVIBRIO GIGAS Established by Phospholipid Analysis of Electrode Biofilm. Corros Sci 33(12):1843–1853.

⁴³Michael JF, White DC, Isaacs HS (1991) Pitting Corrosion by Bacteria on Carbon Steel, Determined by the Scanning Vibrating Electrode Technique. Corros Sci 32(9):945–952.

⁴⁴Just imagine the situation which is not MIC-related but due to the insistence of the engineer, the management goes through heaps of money spending and then it is realised that the case was not an

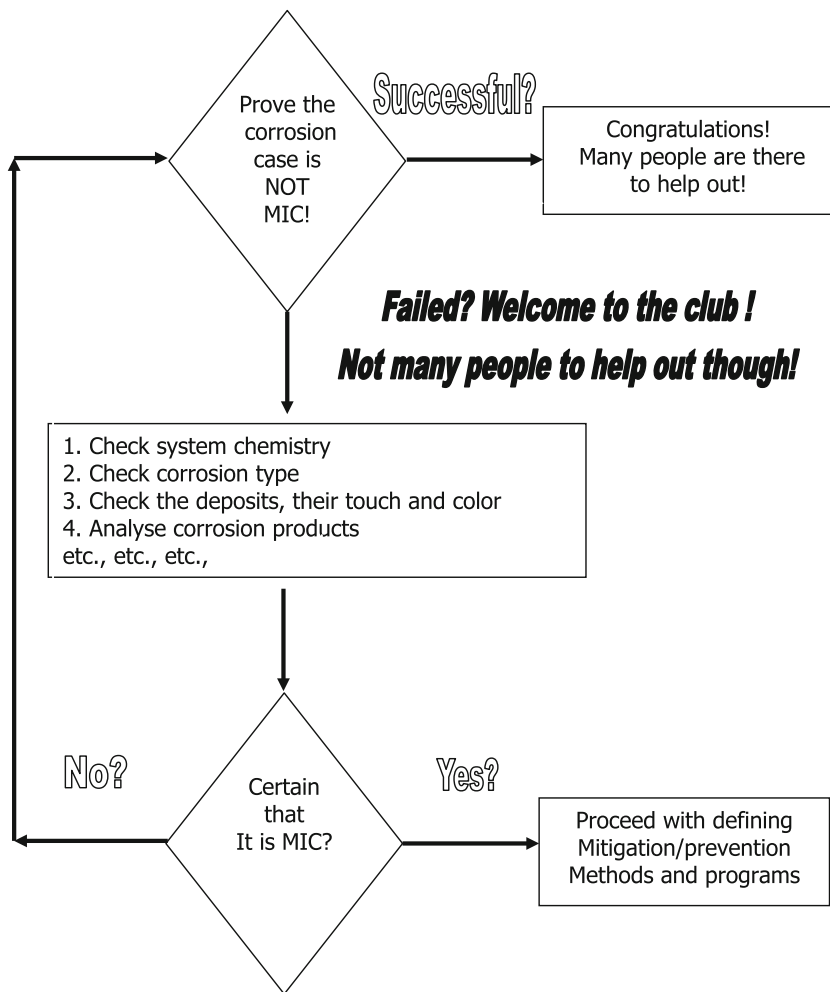


Fig. 6.9 A guide for the confirmation steps that may need to be taken to prove the corrosion case can “really” be MIC

(Footnote 44 continued)

example of microbial corrosion at all. It must be the hardest imaginable task to convince the same management about another case that indeed could be microbially induced corrosion. All this could have been prevented if the engineer in charge had first investigated the possibility of non-MIC corrosion. Another extreme is, of course, denying MIC all together; Tatnall describes such misinterpretations as addressing cases where microbial tuberculation corrosion of steels being called water corrosion or under-deposit corrosion by “those [corrosion engineers] who do not understand (or believe in) the biological factors”, [see Tatnall RE (1991) Case histories: biocorrosion. In: H-C Flemming, GG Geesey (eds) Biofouling and biocorrosion in industrial water systems. Springer, Berlin, Hedelberg, Germany].

chart of the “do’s” and “don’ts” that in the first place a corrosion engineer should consider. After you are convinced that the case is microbial in nature, the microbial detection and nonmicrobial recognition techniques and methods can be applied. This chapter explained some of these methods with a brief on some of their pros and cons.

The following Chapter takes the examples of some industrial systems and looks at some common characteristics that can result in MIC despite that the systems are not technically and industrially similar to each other.

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Chapter 7

Examples of Some Systems Vulnerable to MIC

Abstract It may come to mind that different systems will have different patterns for MIC. While this is true for many systems, there is a general pattern for MIC that can repeat itself in seeming far different industrial systems. This chapter describes some of these systems.

Keywords Pipeline · Jetty · Offshore platforms · Firewater system

7.1 Introduction

It is not a rare accident to meet people who, despite having no blood connection, look so similar to each other.



How two different individuals may look alike!¹

No matter how different such individuals may be in other details of their lives, the most interesting features are that they look so much like each other. These “similar, yet, different” characteristics can also be seen in many industrial systems and their problems, especially if MIC is the problem.

As we shall see, the proposed cyclic mechanisms of MIC are very similar in a buried pipeline to accelerated low water corrosion of steel piles of a jetty or wharf. Although there are many aspects of biocorrosion not yet clear, some “rules of thumb” can still be developed to allow estimating the vulnerability of a system to MIC, as stated in details in Chap. 5. Despite the limitations and related uncertainties, it is still possible to come up with some patterns that repeat themselves in systems where corrosion is enhanced by microbial corrosion mechanisms. It is these general patterns and global features that we are trying to address in this chapter for some industrial systems as diverse as fire water lines, offshore platforms, buried metallic pipelines and immersed piles.

7.2 Buried Metallic Pipelines

According to the principles of CKM, as discussed earlier in Chap. 3, the first step in understanding corrosion is to be able to define the system in which one is interested to detect, define and mitigate corrosion or more specifically as the topic of this book is concerned, microbial corrosion. As Fig. 7.1 suggests, the following corrosion systems can be defined in a buried pipe:

1. External corrosion system that includes corrosion problems such as those occurring in the soil surrounding the buried pipe, the coating, the cathodic protection system, ...
2. Internal corrosion system, including corrosion problems that are likely to occur with regard to the fluid (water, gas, oil, its temperature and pH, its velocity, its TDS, ...), the lining, ...
3. The corrosion system itself, the pipe, where corrosion can be the result of wrong/incomplete hydrotesting, the steel characteristics (physical, chemical, metallurgical), ...

As far as corrosion-related bacteria are concerned, in this chapter we will focus on both external and internal corrosion systems of a buried metallic pipeline in this chapter.

A very important point, however, is the appearing discrepancy between our use of “external corrosion” and the way that it is addressed in corrosion literature: most of the time, when external corrosion of buried pipes is mentioned in the literature, the damage to the coating and the “exterior” wall of the pipe is meant. As the reader can easily understand, our use of the term external corrosion includes this type of

¹Source: www.marshall-modern.org.

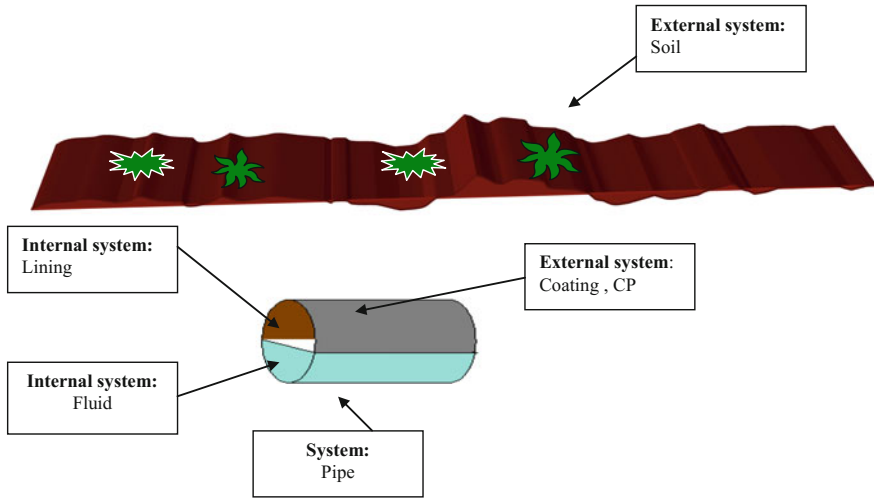


Fig. 7.1 Corrosion systems and subsystems in a buried pipe (Javaherdashti R, Marhamati EG (2005) A computerised model incorporating MIC factors to assess corrosion in pipelines. Mater Performance (MP) 44(1):56–59, Jan 2005.)

corrosion classification too. Therefore, we may use these terminologies interchangeably, bearing in mind that defining the surroundings of a buried pipe as the external system of corrosion, will define a wider domain than just addressing what happens on the exterior wall of the pipe.

A study about failures of on-land oil and gas pipelines from 1970 to 1984 has shown that more than 16 % of the damage was due to corrosion with 40 % of it being external corrosion, and 17 % internal corrosion.² Jack et al.³ have also reported that the primary mechanism of deteriorating pipeline integrity was external corrosion of the buried pipes. It is a common practice to address coating and CP as measures of protecting underground pipelines from “the effects of the environment”.⁴ However, while external corrosion has been reported to be the main cause of underground pipe failures, a study⁵ regarding the share of contribution of chemical, microbial and cathodic protection factors (such as the pipe-to-soil

²Eiber RJ, Jones DJ, Kramer GS (1992) Analysis of DOT-OPSR data from 20-day incident reports, 1970–1984 as quoted in Potts, A.E Accident analysis and reliability of offshore pipelines. Monash University, Offshore Engineering Program, June 1992.

³Jack TR, Van Boven G, Wilmott M, Sutherby RL, Worthingham RG (1994) Cathodic protection potential penetration under disbonded pipeline coating. Mater Performance (MP) 33(8):17–21.

⁴Touzet M, Lopez N, Puiggali M (1999) Effect of applied potential on cracking of low-alloyed pipeline steel in low pH soil environment. In: Jackman PS, Smith LM (eds) Advances in corrosion control and materials in oil and gas production (EFC 26). Woodhead Publishing.

⁵Li SY, Kim YG, Kho YT (2003) Corrosion behaviour of carbon steel influenced by sulphate-reducing bacteria in soil environments, Paper No. 03549, CORROSION 2003, NACE International, USA.

potential) to the underground corrosion of steel in anaerobic environments, concluded that the microbial factor was the most important element.

Biofilms are reported to mainly form on the bottom of the internal surface of pipelines (over a sector of approximately 30° angle⁶), making them different from scale and corrosion products that are, for instance, generated over the whole surface in injection water pipelines.⁷

Figure 7.2 summarises some of the most well-known failure mechanisms in buried pipelines. Some of these mechanisms have been explained and discussed in previous chapters in this book such as the effect of hydrotesting on MIC (Chap. 5)

It must be noted, however, that while MIC could be an initiator of corrosion, it could well be a result as well. For instance, as shown in Fig. 7.2, if the line is passing through different soils where the difference in the average diameter of the soil particles will allow different oxygen ingress gradients to be formed, this may increase the possibility of having differential aeration cells formed on the exterior wall of the underground pipeline. If, also, the coating is performing poorly, then, due to coating disbonding some areas with poor or no coating cover (holidays) are formed. Chances are that these holidays will be the best spots at which electrochemical corrosion starts. Being exposed to the community of the soil micro-organisms, including SRB and SOB, a “sulphureta”⁸ may be created, depending on many factors including weather conditions, as will be addressed later in this chapter.

When condensed moisture and water are collected under disbonded coatings, at least two scenarios can occur:

1. The collected water is quite conductive
2. The collected water is not very conductive.

If the trapped water has good conductivity and the pipeline is under CP, this will allow the current to pass and the required potential to be established so that the steel under the disbonded coat may be protected.⁹ However, one should not forget that this water with relatively good conductivity is also a good electrolyte thus raising the possibility of electrochemical corrosion under the disbonded area. On the other hand, if the trapped water is not a good conductor, the CP criteria will not have the

⁶King RA (2007a) 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 Feb 2007.

⁷King RA (2007b) Microbiologically induced Corrosion and biofilm interactions. In: MIC—an international perspective symposium, Extrin Corrosion Consultants-Curtin University, Perth-Australia, 14–15 Feb 2007.

⁸Sulphureta is a term used to address alternating oxidised and reduced sulphur environments, such as a bacterial consortia containing SRB (that reduce sulphur compounds) and SOB (that oxidise sulphur compounds). See footnote 18.

⁹Jack TR, Wilmott MJ, Sutherby RL (1995) Indicator minerals formed during external corrosion of line pipe. Mater Performance (MP) 35(11):19–22.

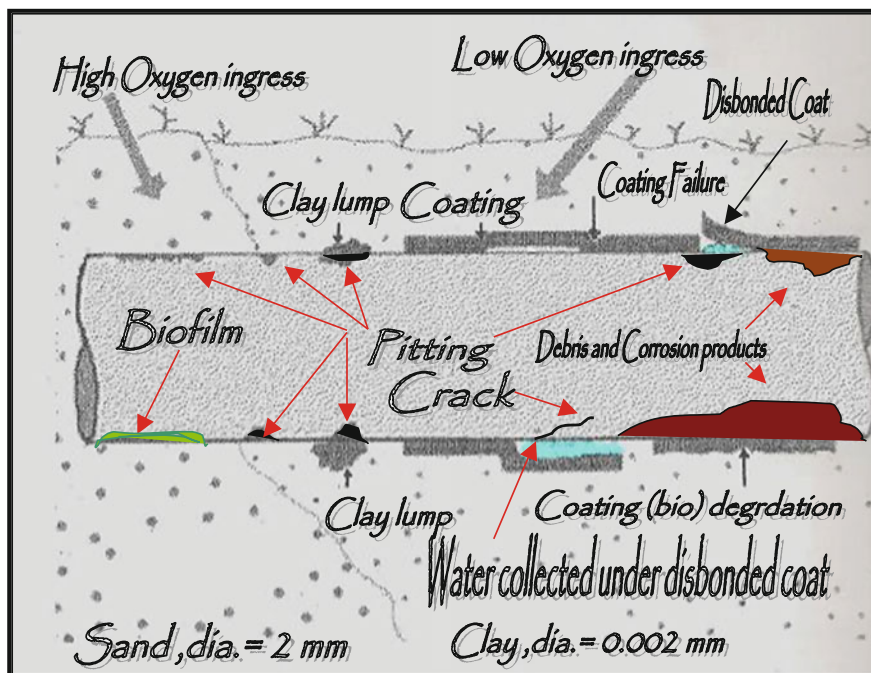


Fig. 7.2 A review of some of the factors contributing to corrosion and particularly, MIC (Javaherdashti R (2000) A review of microbiologically influenced corrosion of buried, cathodically protected, coated gas pipe lines, in Persian, Department of Technical Education, Iranian National Gas Company, Tehran, Iran, Winter 2000)

opportunity of being maintained. If the water trapped under the coat is saturated with cations such as calcium or carbonate ions, making it quite alkaline, scaling may occur and this plus an elevated pH may protect the underlying steel (see footnote 3).

It may also be interesting to know that if the soil around the pipe contains SRB and SOB, as these two almost always accompany each other,¹⁰ they can work in “shifts” so that when the environmental conditions are suitable for the aerobic SOB—such as dry soil where interparticle spaces and cavities are filled with oxygen—The SRB will wait, for example, until in the wet soil resulting from a rainy day, the oxygen trapped in the interparticle spaces is expelled. This makes the environment so low in oxygen that the SRB can start to proliferate. This coexistence can enhance the corrosion even further.

¹⁰Tatnall RE (1993) Introduction. In: Kobrin G (ed) A practical manual on microbiologically influenced corrosion. NACE, Houston, TX, USA.

7.3 Maritime Piled Structures (Jetty and Wharves)

A commonly seen problem with steel piles in ports and jetty structures is a type of electrochemical corrosion called “Accelerated Low Water Corrosion” or ALWC for short. An integral part of ALWC could be MIC.¹¹ In fact, some definitions of ALWC do consider MIC as an integral part of the definition.¹² This type of corrosion has been observed and reported in ports all around the world, including the USA,¹³ Europe (see footnote 12) and Australia.¹⁴ In many cases of ALWC, microbial corrosion manifests itself as a mass which is orange in colour and collectively referred to as “orange bloom”, Fig. 7.3a–d.

In essence, orange bloom can be regarded as a microbial community where SRB are definitely a part, due to the black iron sulphide mass associated with the orange bloom, Fig. 7.4. Upon removal of the orange bloom, the liberated hydrogen sulphide produced by the SRB and the remaining black iron sulphide products can be detected. Orange bloom is capable of flagging very serious pitting of the steel piles and thus endangering their mechanical integrities, Fig. 7.5.

There are still debates about the exact mechanisms that could be operative in ALWC. However, the involvement of bacterial species such as SRB and SOB has always been reported.¹⁵ Figure 7.6 shows the factors that are important in ALWC and its occurrence.

An accepted scenario on the effect of SRB and SOB¹⁶ can schematically be shown in Fig. 7.7. As it is seen in the figure, when there is high tide and thus limited or no oxygen available, the anaerobic SRB will be able to use the anaerobic environment thus produced and reduce sulphates to sulphide that, when taken into consideration with the anodic reaction of dissolving iron and availability of iron ions, iron sulphides will be produced (thus the black colour of the “orange” bloom,

¹¹Javaherdashti R (2006) Microbiological contribution to accelerated low water corrosion of support piles. *Port Technol Int* 59–61, 29th Edition, Spring 2006. At a conference on Durability of Steel Piling in Soil and Marine Environments in 1984, it was reported that “bacterial corrosion of steel piling in marine environments was not significant and... marine fouling appeared to be mostly beneficial”. See footnote 15 for more details.

¹²Gehrke T, Sand W (2003) Interactions between micro-organisms and physicochemical factors cause MIC of steel pilings in harbours (ALWC), Paper No. 03557, CORROSION-2003, NACE International, Houston, Texas, USA, 2003.

¹³Hannam MJ, Clubb DL (2002) Experience and considerations on the corrosion protection of harbour steel sheet piling. In: *The institute of corrosion conference*, Cardiff, UK, 23rd Oct 2002.

¹⁴Hutchinson CPA, Vallini FD (2004) The effectiveness of petrolatum tapes and wraps on corrosion rates in a marine service environment, Paper 033, Corrosion and Prevention 2004 (CAP04), Perth, Australia, 21–24 Nov 2004.

¹⁵Gubner R, Beech I (1999) Statistical assessment of the risk of the accelerated low water corrosion in the marine environment, Paper No. 318, CORROSION-99, NACE International, USA.

¹⁶Little 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.

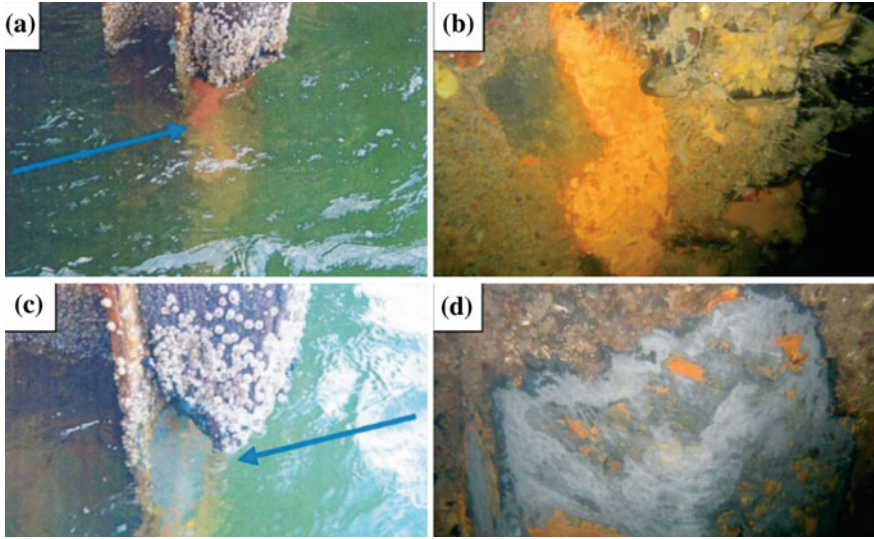


Fig. 7.3 **a** “Orange bloom” (arrowed) as seen from above the water level, **b** close up of the same mass under water, **c** the steel underneath the orange bloom and **d** its close up after removal of the orange bloom (All images Courtesy of Extrin Consultants)

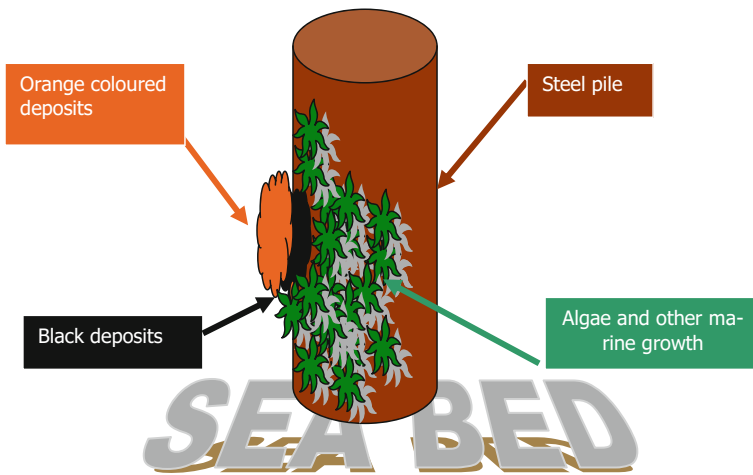


Fig. 7.4 Schematic presentation of orange bloom on a steel pile (Javaherdashti R (2005) Microbiological contributions to accelerated low water corrosion (ALWC) of steel—piled structure: a review. In: Proceedings of corrosion and prevention 2005 (CAP05), Gold Coast, Australia, November 2005.) (Not to scale)

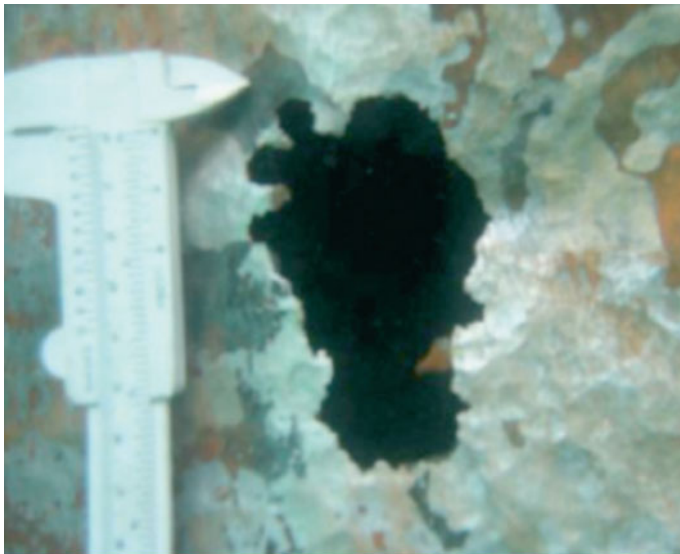


Fig. 7.5 Perforation on the steel under the orange bloom (Courtesy of Extrin Consultants)

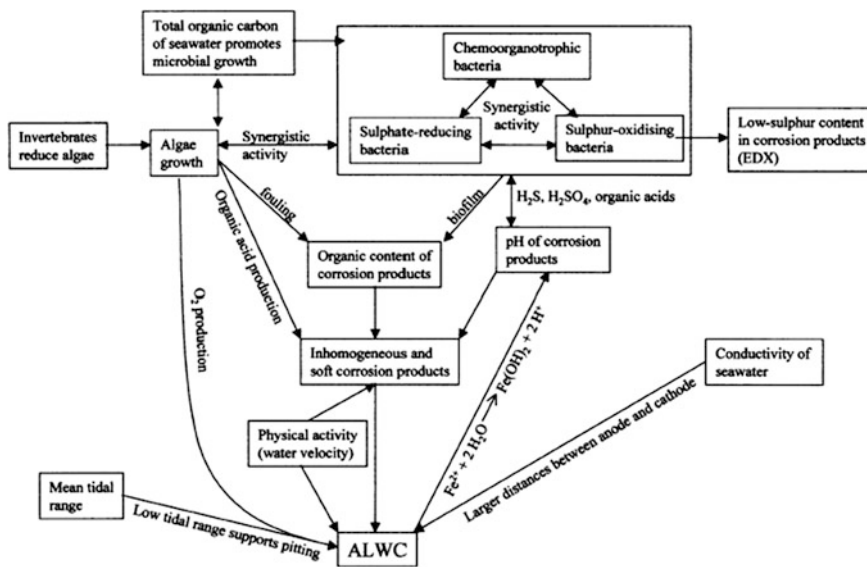


Fig. 7.6 A presentation of factors that can be important in ALWC (see footnote 15)

see Fig. 7.4). When, however, there is a low tide, oxygen becomes available to the sulphur oxidising bacteria (SOB) where these bacteria are capable of using the situation to produce acidic conditions and very low pH.

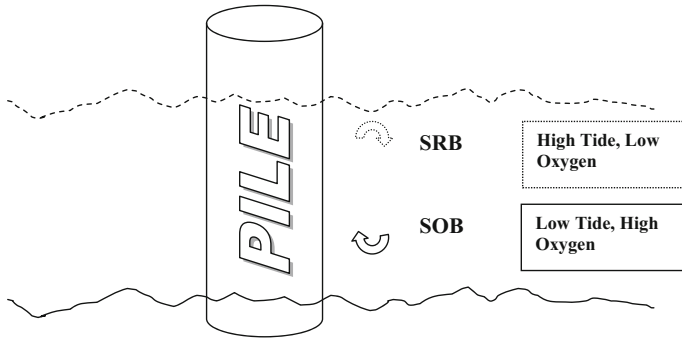


Fig. 7.7 Possible cyclic effect of SRB and SOB on ALWC of steel piles

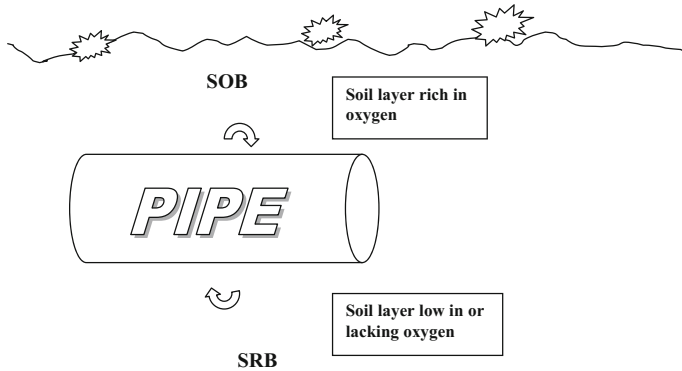


Fig. 7.8 Possible cyclic effect of SRB and SOB on a buried pipe

By comparing Fig. 7.7 with Fig. 7.8, a general pattern may be reached: a cyclic corrosion effect of which SRB are an important part helps in intensifying corrosion in an environment that also contains SOB.

To prevent f ALWC, use of coatings such as coal tar epoxy or glass flake composite along with application of CP have been recommended (see footnote 15). While replacing the piles which are beyond economic repair can always be an option, the repair techniques that can normally be applied are one or a combination of the following.¹⁷

¹⁷Christie J (2007) Dealing with MIC on maritime piled structures. In: MIC—an international perspective symposium. Extrin Corrosion Consultants-Curtin University, Perth-Australia, 14–15 Feb 2007.

- Welding patch plates (for small areas showing sign of MIC)
- Welding strengthening plates (for areas where the effect of corrosion is more extensive, either U-plates or profiled plates can be used for the damaged areas)
- Plating with reinforced concrete infill (especially in Z sections)
- Concrete as in-situ collars or reinforced concrete plugging (e.g. as encasement on H piles)
- Splicing, it may be possible to cut out damaged sections of single piles (H, box or tubular) and joining the replacement sections.

7.4 Offshore Platforms

Offshore platforms are, in essence, similar to buried pipelines as in both of them external and internal surfaces are exposed to corroding environments: in buried pipelines the external surface of the pipe is exposed to the soil which is a corrosive environment and its internal surface is under the corrosive impact of the fluid that is going through, either water, oil or the like. In case of offshore platforms, the whole immersed structure is exposed to the seawater (a corrosive medium) and the internal surfaces of the systems such as seawater injection systems or oil storage facilities can be considered as locations at which corrosion is occurring internally.

While there could be many ways to classify offshore platforms and structures, one approach to address the basic types of offshore platforms (or, alternatively within the context of this book, offshore drilling units) is as follows:

1. Fixed platforms;
2. Submersibles;
3. Semi-submersibles;
4. Jack-ups;
5. Drilling ships;
6. Tension-legs platforms.

In an offshore platform most of the MIC problems may happen in the following spots¹⁸ some of which have been shown in Fig. 7.9:

- Marine fouling
- Drill cuttings around the platform legs
- Oil storage and transport
- Water-filled legs
- Production system
- Seawater injection system
- Downhole pipework
- Reservoir problems.

¹⁸Edyvean RG, Dexter SC (1993) MIC in marine industries. In: Kobrin G (ed) A practical manual on microbiologically influenced corrosion. NACE, Houston, TX, USA.

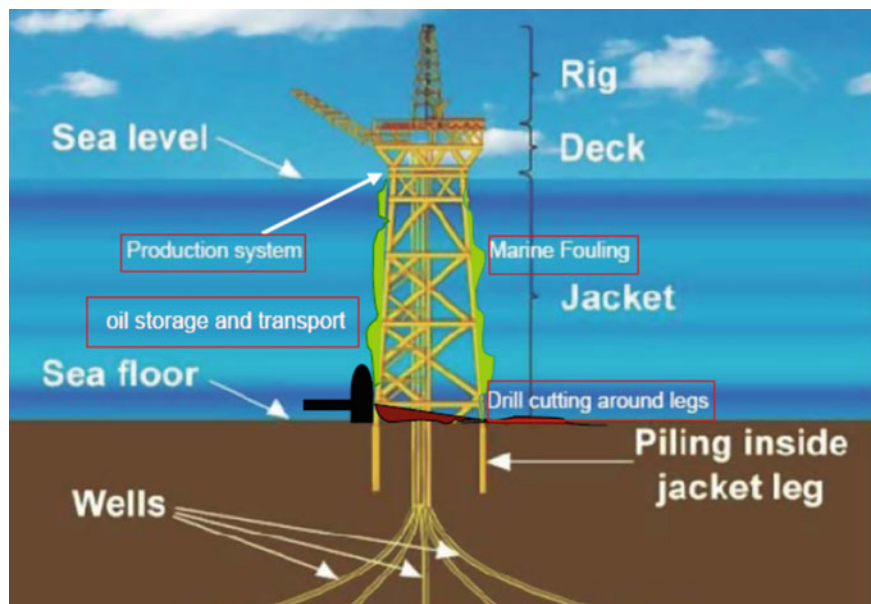


Fig. 7.9 Some locations vulnerable to MIC in offshore platforms (The figure has been taken from www.consrv.ca.gov/dog/picture_a_well/offshore_platform.htm with some modifications for our purpose here)

In addition to a series of problems,¹⁹ two main problems resulting from bacterial growth in offshore structures are²⁰ (1) hydrogen sulphide production (generated, for example, by SRB) that besides being volatile and toxic, thus serious to the personnel safety, causes corrosion and souring of the products (crude oil, for instance) which ultimately affects the quality and final price²¹ and (2) the production of bacterial metabolites which could give rise to accelerated materials deterioration.

The effects on offshore structures can be categorised as external (such as environmental effects on external surfaces of these structures) and internal effects (such as MIC problems in water handling system and oil production system).

¹⁹Some of such problems are reservoir souring and/or filter blockages in diesel systems (Communication with Dr. A. MOrshed, Production Services Network, Aberdeen, UK, 01/June/07).

²⁰Wilkinson TG (1983) Offshore monitoring. In: Microbial corrosion: proceedings of the conference d sponsored and organised jointly by The National Physical Laboratory and The Metals Society, 8–10 March 1983. The Metals Society, London, UK, 1983.

²¹Evans P, Dunsmore B (2006) Reservoir simulation of sulphate-reducing bacteria activity in the deep sub-surface, Paper No. 06664, CORROSION-2006, NACE International, USA, 2006.

Fig. 7.10 A semi-submersible offshore platform (Source <http://www.rigjobs.co.uk/oil/semisub.shtml>)



The impact of MIC on the internal systems is more apparent and immediate than those on the external surfaces. Careful monitoring, regular maintenance, and prudent use of biocides (such as chlorine and chlorine-releasing compounds, phenolics, aldehydes and quaternary ammonium compounds) are some of practices that can be recommended.

The type of MIC-related problems that may be expected in, for example, submersible and semi-submersible platforms are, more or less, similar to stagnant water problems caused in firewater lines or pipelines. Such platforms have pontoons and columns that, when flooded with seawater, cause the pontoons to submerge to a predetermined depth. Figure 7.10 shows an example of a semi-submersible offshore platform.

In such platforms, the stagnant water becomes deaerated and oxygen-free so it becomes a good place for SRB to become active. In addition, it has been investigated that²² the decay of macro-organisms in sea water, in the presence of light, could encourage phototrophic sulphur bacteria's role in increasing anaerobic corrosion of metals. A routine countermeasure is the use of biocides. However, the biocide should not simply be introduced into the platform leg as it takes a

²²Eashwar M, Maruthamthu S, Venkatakrishna Iyer S (2004) A possible role for phototrophic sulphur bacteria in the promotion of anaerobic metal corrosion. *Curr Sci* 86(5): 639–641, 10 March 2004.

substantial time (maybe many weeks) to distribute. Real life experiences have shown²³ that it will be necessary to overdose the biocide if a long life time is expected.

7.5 Fire Water Lines

At an emergency when water is required to extinguish a fire, having a reliable fire water system that can handle stagnant water is of vital importance. Figure 7.11a, b show two examples of MIC within such systems.

It has been reported²⁴ that the main cause of pitting in fire sprinkler systems is oxygen, as these systems use locally supplied potable water. This water, being rich in oxygen, can easily establish differential aeration cells along the piping. It is then possible for oxygen to diffuse out of the system; rendering it more anaerobic (see footnote 20). Interestingly, an investigation²⁵ has detected aerobic types of corrosion-enhancing bacteria, such as iron-oxidising bacteria (IOB), for example, *Gallionella* and *Siderophacus* which may also contribute to the corrosion seen in

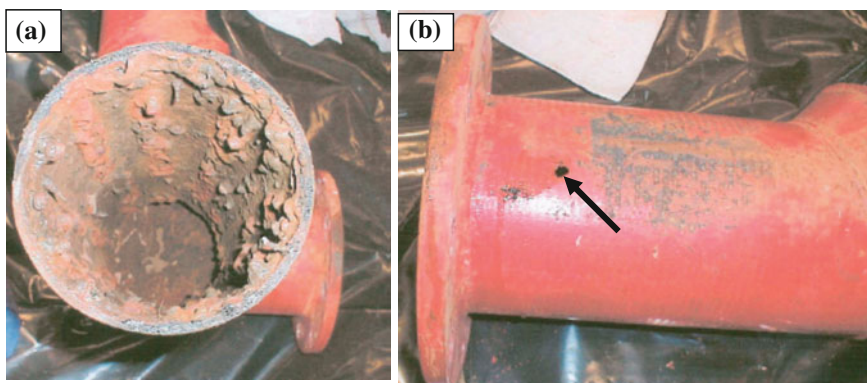


Fig. 7.11 **a** Internal wall of a fire water pipeline in which water has been stagnant and **b** observed perforation on the pipe (arrowed) (Fernance N, Farinha PA, Javaherdashti R (2007) SRB-assisted MIC of fire sprinkler piping. Mater Performance (MP) 46(2) Feb 2007.)

²³NACE CORROSION NETWORK discussion group, "corrosion within Offshore jacket legs", November 2002.

²⁴Brugman HH (2004) Corrosion and microbiological control in fire water sprinkler systems, Paper No. 04512, CORROSION-2004, NACE International, USA, 2004.

²⁵Yee GG, Whitbeck MR (2004) A microbiologically influenced corrosion study in fire protection systems, Paper No. 04602, CORROSION-2004, NACE International, USA, 2004.

failed fire protection systems. Therefore, it may be assumed that a cyclic action of anaerobic SRB and aerobic IOB like anaerobic SRB and aerobic SOB in buried pipelines and steel piles (ALWC) could also be operational in fire water systems too.

7.6 Summary and Conclusions

No matter how different the two systems may seem at first sight, when it comes to MIC, some general patterns of corrosion can be recognised for both. These patterns such as those operative in a buried pipeline may well be similar to those of a submerged steel pipe and its ALWC problem. The stagnant water and the type of problems it produces have the same mechanisms for the involvement of MIC, whether in a firewater pipe or the water-filled legs of an offshore platform.

MIC may seem to be difficult to be explained but, if recognised promptly and accurately, could have simple general patterns to look at, both for mitigation and prevention.

An integral part of evaluation and assessment of the severity of MIC rests on the type of material that has been used. Examples of some materials that are frequently used in industry will be the topic of the next chapter.

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Chapter 8

Examples of Some Materials Vulnerable to MIC

Abstract While almost all engineering materials are susceptible to MIC, there are three engineering materials that in this chapter we want to study their MIC behaviour and susceptibility with more details. There are three reasons for that: either these materials have a reputation to be toxic to micro-organisms and thus MIC-proof, or that due to their alloying elements are resistant to corrosion and thus MIC or they are considered to have a rather straightforward MIC mechanism (s). In this chapter we will see why these are not true!

Keywords Copper and its alloys • Duplex stainless steel • Concrete

8.1 Introduction

Without a doubt, the choice of material is an important factor to make a system resistant or vulnerable to MIC. Case histories show that carbon steel is a more susceptible material in comparison with stainless steels and that stainless steel SS316 is more resistant than SS304.

This chapter will focus on three types of materials: duplex stainless steel, copper and copper-nickel alloys and concrete. The main reason for selecting these materials was that they are of frequent use in industry. For example, copper and copper alloys have this reputation that no micro-organism can colonise them, as copper is poisonous to living organisms. This “copper reputation” has given this material a very wide range of applications. Duplex stainless steels are better known for their upgraded corrosion resistance versus the “ordinary” stainless steels such as grade 316, 304 and their varieties.

On the other hand, concrete, thanks to its composite structure that takes the advantage of both steel and cement, has given this material an impossible-to-ignore position among other materials especially in the sewage treatment industry.

We start this chapter with copper alloys, as none of other materials have the so-called “bio-resistance” of copper.

8.2 Copper and Cupronickels

Localised corrosion of copper can occur in four types as summarised and addressed by Yakubi and Murakami¹ and tabulated in Table 8.1.

It was “known” for quite some time that the copper sheets that had been used to cover the bottoms of wooden ships corroded in seawater such that the environment could be kept toxic to barnacles and similar organisms,² thus biofouling-free. Copper and copper alloys are still praised³ today for their resistance to biocorrosion.

However, the involvement of some types of micro-organisms with relatively high tolerance to copper has been reported. In their review of the behaviour of cupronickels alloys in sea water, Parvizi et al.⁴ had reported of *Thiobacillus thiooxidans* being able to withstand copper ion (cuprous) concentrations as high as 20,000 ppm, Palanichamy et al.⁵ have also observed endospore-forming genus *Bacillus* and non-endospore forming genus *Propionibacterium* on copper surfaces. Critchley et al.⁶ have reported the isolation of copper-resistant species such as *Sphingomonas* and *Acidovorax*.

Microbial corrosion has been proposed as a possible cause for “blue water” corrosion (see footnote 6). Blue water corrosion is a term to address the release of copper corrosion by-products into the water, especially drinking water. It has been reported that (see footnote 6) this type of copper corrosion has been most often observed when the water has been stagnant for several hours or days, and typically containing 2–20 ppm copper concentration (the recommended copper concentration in drinking waters is 2 ppm). Blue water corrosion generally occurs randomly. Blue water has been reported⁷ not to significantly compromise the pipe integrity in general, though.

¹Yakubi A, Murakami M (2007) Critical ion concentration for pitting and general corrosion of copper. *Corrosion* 63(3):249–257, March 2007.

²Burns RM, Bradley WW (1967) Protective coatings for metals, 3rd edn. American Chemical Society, Monograph Series.

³See, for example, reviews by Schleich W, Steinkamp K (2003) Biofouling resistance of cupronickel-basics and experience. Paper No. P0379, Stainless steel world. Maastricht, The Netherlands, 2003 and also Schleich W (2004) Typical failures of CuNi 90/10 seawater tubing systems and how to avoid them. Paper No. 12-0-124, EuroCorr 2004, Nice 2004. Also, Powell C, Michels H (2004) Review of splash zone corrosion and biofouling of C70600 sheathed steel during 20 years exposure. EuroCorr 2006, Event No. 280, 24–28 September 2006, Maastricht, The Netherlands.

⁴Parvizi MS, Aladjem A, Castle JE (1988) Behaviour of 90–10 cupronickel in sea water. *Int Mater Rev* 33(4):169–200.

⁵Palanichamy S, Maruthamuthu S, Manickam ST, Rajendran A (2002) Microfouling of manganese-oxidising bacteria in tuticorin harbour waters. *Curr Sci* 82(7):865–869.

⁶Critchley M, Taylor R, O'Halloran R (2005) Microbial contribution to blue water corrosion. *Mater Perform (MP)* 44(6):56–59.

⁷Webster BJ, Werner SE, Wells DB, Bremer PJ (2000) Microbiologically influenced corrosion of copper in potable water systems-pH effects. *CORROSION* 56(9):942–950.

Table 8.1 Classification of Copper corrosion types in water

Type	Water type	pH range	Water temperature	Features
I	Hard	7–7.8	Cold	Not reported
II	Soft	Below 7.2	Hot	Deep, narrow pit morphology and existence of a basic copper sulphate product
III	Soft	Above 8.0	Cold	Wide and shallow pit morphology, evidenced by production of “blue water”, and pipe blockage
Moundless	Containing high sulphate ion and silicon dioxide	Not reported	Not reported	Open-mouth pit morphology, no “mounds” of corrosion products present on such pits

Two models can be proposed to explain MIC of copper. As Webster et al. (see footnote 7) put it, these models can be explained as follows.

Model I: the EPS (extracellular polymeric substances)-which is mainly the biofilm-create preferential cathodic sites by the “cation-selective nature of the EPS”.⁸

Model II: This model describes MIC of copper in terms of formation of copper ion concentration cell by the EPS and generation of a weakly acidic environment.

Webster et al. consider that the second model, which is based on a decrease in pH, is probably the prevailing mechanism.

Cupronickels (either 90/10-that contains 10 % nickel—or 70/30 with 30 % nickel or Monel 400) have been used for many years in applications where sea water has been involved for their good corrosion resistance. This fitness for purpose is specifically because of the cupronickels passive cuprous oxide (Cu₂O) film which retards both the anodic dissolution of the alloy and the rate of oxygen reduction.⁹ Based on studies by Gouda et al. and reported by Lee et al.,¹⁰ alloy 400 (=Monel 400 containing 66.5 % nickel, 31.5 % copper and 1.25 % iron) is much more susceptible to SRB-induced MIC when compared to 70/30 cupronickel or brass.

⁸Biofilms are negatively charged.

⁹Shalaby HM, Hasan AA, Al-Sabti F (1999) Effects of inorganic sulphide and ammonia on microbial corrosion behaviour of 70Cu-30Ni alloy in sea water. *British Corrosion J* 34(4):292–298.

¹⁰Lee JS, Ray RI, Little BJ (2003) A comparison of biotic and inorganic sulphide films on alloy 400. In: *Proceedings of corrosion science in the twenty-first Century*, vol 6. Paper C057, UMIST, UK.

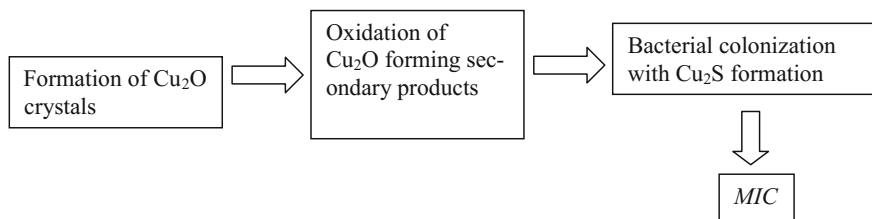


Fig. 8.1 Possible MIC pattern for MIC of Cu-10 %Ni in non-chlorinated brackish water according to de Romero

de Romero et al.¹¹ have also suggested patterns as possible mechanisms for MIC of Cu-10 %Ni in non-chlorinated brackish water, where because of a lack of chlorine and possibility of surviving micro-organisms, MIC is possible. Their proposed mechanism for MIC of Cu-10 % Ni in brackish water with no chlorine can be schematically summarised as in Fig. 8.1.

8.3 Duplex Stainless Steels

Carbon steel and stainless steels and their behaviour with regard to microbial corrosion have been relatively well studied and documented compared to duplex stainless steels.

Duplex Stainless Steels (or briefly, DSSs) are being used in many industries, such as chemical processing, electrical energy generation¹² and also oil and gas industry where they are susceptible to corrosion (mainly SCC) in environments such as Packer fluid and acidising fluid.¹³

DSSs have two phases, austenite and ferrite where their presence and particular ratio influences the way by which these steels interact with the environment.¹⁴ An example of a typical microstructure of a duplex stainless steel has been shown in

¹¹de 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*, 56(8):867–876.

¹²Chaves R, Costa I, de Melo HG, Wolyne S (2006) Evaluation of selective corrosion in UNS S31803 duplex stainless steel with electrochemical impedance spectroscopy. *Electrochimica Acta* 51:1842–1846.

¹³Rhodes RR, Skogsberg LA, Tuttle RN (2007) Pushing the limits of metals in corrosive oil and gas well environments. *CORROSION* 63(1):63–100.

¹⁴Archer ED, Brook R, Edyvean RGJ, Videla H (2001) Selection of steels for use in SRB environments. Paper No. 01261, *CORROSION-2001*, NACE International, USA.

Chap. 9. The austenite phase provides features, such as toughness and weldability whereas the ferritic phase contributes to strength, corrosion resistance and SCC resistance.¹⁵

The probability of chloride SCC in some DSS known as SAF2205 has been reported at less than 10 %.¹⁶ However, when hydrogen sulphide is present in the environment, the danger of hydrogen-assisted chloride SCC for DSSs increases with temperatures in the range of 60–100 °C and decreases with higher Cr, Mo and N contents (see footnote 13).

Mechanisms regarding DSSs characteristics of corrosion resistance are still not well understood, some of the theories in this regard are (a) combined effect of corrosion potentials in each phase and its impact on crack initiation and propagation in either austenite or ferrite or both phases,¹⁷ (b) difference in potential of grain boundaries relative to the ferrite per se¹⁸ and (c) mechanical effect of austenite and ferrite and the impact of hydrogen diffusion in ferrite to compensate for the produced stresses (see footnote 14).

Duplex stainless steels are also vulnerable to microbial corrosion, SAF 2205 has been reported as being vulnerable to MIC,^{19,20} particularly in the presence of SRB,^{21,22}

The vulnerability of DSSs to MIC is important; as it once again proves that just by increasing some alloying elements that have a reputation for inducing corrosion resistance, such as chromium, one can not overcome MIC. A careful material selection must be accompanied by scrutinising the service conditions and serious follow up on monitoring how the material is performing to avoid the risk of MIC.

¹⁵Siow KS, Song TY, Qiu JH (2001) Pitting corrosion of duplex stainless steels. *Anti-Corros Meth Mater* 48(1):31–36.

¹⁶Stainless Steel Selection Guide Central States Industrial Equipment & Service, Inc., <http://www.al6xn.com/litreq.htm>, USA.

¹⁷Gunn RN (1997) Duplex stainless steels, Chap 7. Woodhead Publishing Ltd.

¹⁸Danko JC, Lundin CD (1995) The effect of microstructure on microbially influenced corrosion. In: Proceedings of international conference on microbiologically influenced corrosion, New Orleans, Louisiana, NACE international, USA, May 8–10 1995.

¹⁹Kovach CW, Redmond JD (1997) High-performance stainless steels and microbiologically influenced corrosion. www.avestashfield.com, acom 1-1997.

²⁰Neville A, Hodgkiess T (1998) Comparative study of stainless steel and related alloy corrosion in natural sea water. *British Corros J* 33(2):111–119.

²¹Johnsen R, Bardal E (1985) Cathodic properties of different stainless steels in natural seawater. *CORROSION* 41(5):296–302.

²²Antony PJ, Chongdar S, Kumar P, Raman R (2007) Corrosion of 2205 duplex stainless steel in chloride medium containing sulphate-reducing bacteria. *Electrochimica Acta* 52:3985–3994.

8.4 Concrete

As Rogers et al. quoted to The U.S. Nuclear Regulatory Commission, “Service Life of Concrete”, compiled in 1989, there are at least seven major chemical/physical factors reported to be major causes of concrete degradation, these are²³

1. Sulphate and chloride attack,
2. Alkali aggregate reactions,
3. Water leaching,
4. Freeze/thaw cycling,
5. Salt crystallization,
6. Corrosion with resulting expansion of reinforcing bars,
7. Acid rain.

As it is seen, biodegradation of concrete is not among these causes. This is an example of how authorities can be oblivious to the biodeterioration of concrete. As Rogers et al. put it: “an understanding of concrete degradation may be incomplete without including the effects of microbial influenced degradation, or briefly, MID”.²⁴

There are case histories,^{25,26} reporting SRB-induced infection of the concrete columns (up to 70 % in some areas) of an occupied building. What is thought to be the main mechanism for attacking concrete itself is by the act of SOB bacteria such as *Thiobascillus thiooxidans* that excrete very low pH acid (H_2SO_4) which dissolves the concrete.²⁷ In sewer pipes, SOB can contribute to corrosion rates of up to 1 cm/year²⁸

More precisely, it is a process that can be schematically shown in Fig. 8.2. The MID-assisted deterioration of concrete can happen in three phases. So far, nothing is known regarding the time intervals between each step but it seems that the concrete becomes vulnerable first by chemical corrosion (deterioration) because of factors such as the formation of carbonic acids. This will lower the pH from above 12 to somewhere around 9–9.5. Then “microbial succession” starts, where neutrophilic SOB are replaced by another group of SOB which are capable of further reducing the pH, thus dissolving the concrete.

²³Rogers RD, Knight JJ, Cheeseman CR, Wolfram JH, Idachaba M, Nyavor K, Egiebor NO (2003) Development of test methods for assessing microbial influenced degradation of cement-solidified radioactive and industrial waste. *Cement Concrete Res* 33:2069–2076.

²⁴Corrosion, and thus MIC, is used to address degradation in metals. We will use the term “microbial influenced degradation, or briefly MID, to address degradation of non-metallics.

²⁵Scott PJB, Davies M (1992) Microbiologically influenced corrosion. *Civil Eng* 62:58–59.

²⁶Davies M, Scott PJB (1996) Remedial treatment of an occupied building affected by microbiologically influenced corrosion. *Mater Perform (MP)*, 35(6):54–57.

²⁷Little BJ, Ray RI, Pope RK (2000) Relationship between corrosion and the biological sulphur cycle: a review. *CORROSION* 56(4):433–443.

²⁸Knight J, Cheeseman C, Rogers R (2002) Microbial influenced degradation of solidified waste binder. *Waste Manag* 22:187–193.

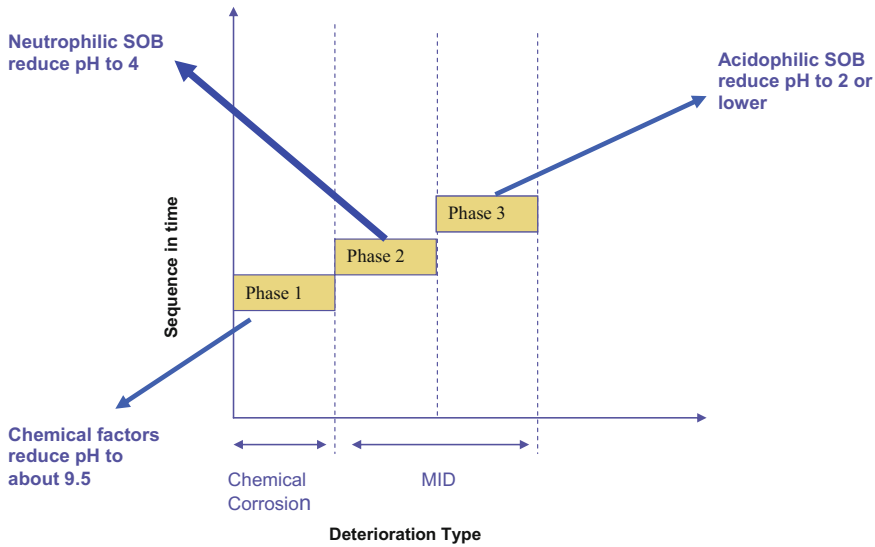


Fig. 8.2 Schematic summary of deterioration of concrete with the involvement of MID (Javaherdashti RPA, Farinha PK, Sarker HN (2006) On microbial: causes, mechanisms and mitigation. Concrete Australia 32(1). Pipe)

MID can be seen as a three-phase process whose phases are schematically summarised as in Fig. 8.2.

As seen from Fig. 8.2, the three phases can be explained as follows²⁹:

Phase 1: Combined corrosive effects of atmospheric carbon dioxide and hydrogen sulphide reduce pH to about 9.5.

Phase 2: First stage of “microbial succession” where, provided that sufficient nutrients, moisture and oxygen exist, some species of sulphur-oxidising bacteria (e.g. *Thiobacillus sp.*) can attach themselves onto the concrete surface and grow. Mostly, these species of SOB are neutrophilic sulphur oxidising bacteria (NSOM). These bacteria produce some acidic products and convert the sulphides present to elemental sulphur and polythionic acids.

Phase 3: Being the second step of microbial succession, it is normally followed after Phase 2 where the pH has been reduced fairly, another species of SOB known as acidophilic sulphur-oxidising bacteria (ASOM) such as *T. thiooxidans* colonise the concrete surface and further reduce the acidity. It has been proposed that³⁰ during Phase 2 the NSOM reduces pH to four where during Phase 3, pH is further reduced by the ASOM to one or two.

²⁹Roberts DJ, Nica D, Zuo G, Davis JL (2002) Quantifying microbially induced deterioration of concrete: initial studies. Int Biodeter Biodeg 49:227–234.

³⁰Davies JL, Nica D, Shields K, Roberts DJ (1998) Analysis of concrete from corroded sewer pipe. Int Biodeg Biodeg 42:75–84.

Studies show (see footnote 29) microbial succession can start with very low number of both types of the sulphur oxidising bacteria so that MID can develop entirely. Quoting from Bock and Sands' work, Rogers et al. (see footnote 29) report that a cell density of chemolithotrophic SOB's such as *Thiobacillus* of about 10^4 – 10^6 cells per grams of concrete is required before MID is detected.

When concrete is used in environments such as sewer systems, it can be exposed to a cyclic action of SRB and SOB, Fig. 8.3, in a sense, similar to ALWC (Chap. 7). In this way, SRB and SOB will have synergistic effect on each other in terms of enhancing corrosion, Fig. 8.4.

At low sulphate ion concentrations (less than 1000 ppm), the corrosion product is ettringite ($3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{CaSO}_4 \cdot 12\text{H}_2\text{O}$ or $3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 3\text{CaSO}_4 \cdot 31\text{H}_2\text{O}$) whereas gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) is the main cause of deterioration at high sulphate ion concentrations. It follows then, that, the mechanism of attack depends on the concentrations of the SO_4^{2-} ions in the solution.³¹ It has been reported that³² ettringite is produced when the pH levels are higher than 3 whereas gypsum is likely to be formed at pH levels less than 3. Also, it must be noted that (see footnote 29) ettringite is expansive and causes internal cracking which is actually providing

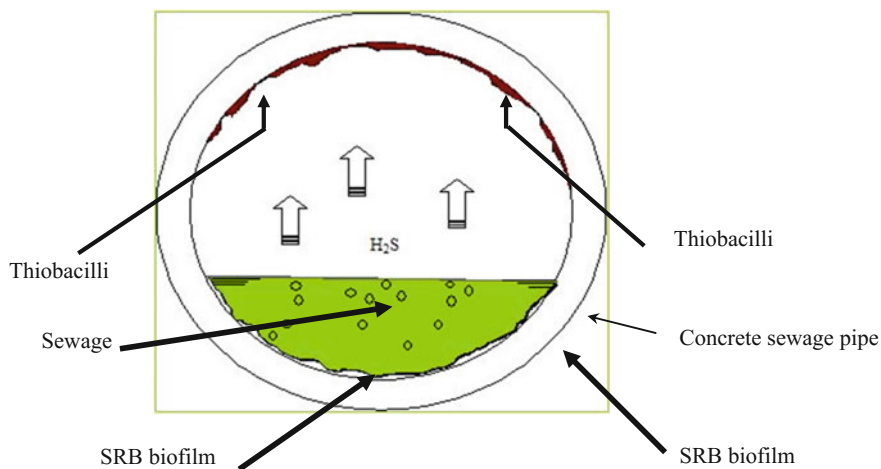


Fig. 8.3 Schematic representation of possible microbial consortium in a concrete sewage pipe (Javaherdashti R (2004) A review of microbiologically influenced corrosion with emphasis on concrete structures. In: Proceedings of corrosion and prevention 2004 (CAP04), 21–24 Nov 2004, Perth, Australia.)

³¹Monteny JE, Vincke A, Beeldens N, De Belie L, Taerwe D, Van Gemert W, Verstraete (2000) Chemical, microbiological, and in situ test methods for biogenic sulfuric acid corrosion of concrete. *Cement Concrete Res* 30:623–634.

³²Mori T, Nonaka T, Tazaki K, Koga M, Hikosaka Y, Noda S (1992) Interactions of nutrients, moisture and pH on microbial corrosion of concrete sewer pipes. *Water Res* 26(1):29–37.

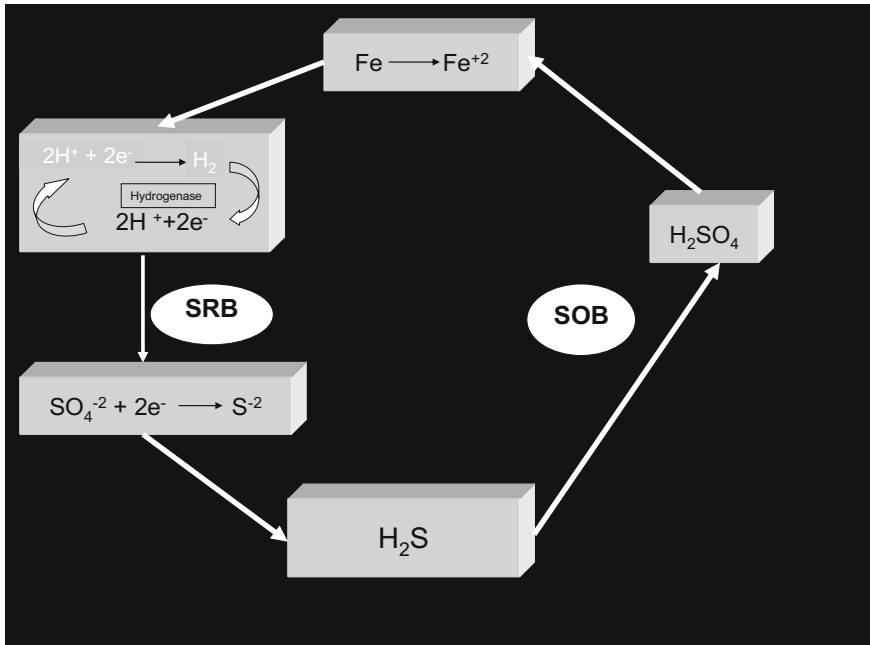


Fig. 8.4 Possible cyclic action between SRB and SOB

a larger surface for chemical reactions to occur, thus resulting in more sites of penetration into the concrete.

The conversion of the concrete into gypsum and ettringite reduces the mechanical strength of the concrete which is followed by reducing the structural integrity of the concrete and may result in total failure and collapse of the structure.

In their review, Ribas Silva and Pinheiro,³³ they quote from the work done by Salvadori with regard to the impact of some biocides on some inorganic materials including concrete. This impact can be tabulated in Table 8.2. In addition to chemical treatment of concrete by using biocides, other techniques of dealing with concrete such as mechanical and biological measurements have been reviewed elsewhere (see footnote 33).

³³Ribas Silva M, Pinheiro SMM (2007) Mitigation of concrete structures submitted to biodeterioration. In: MIC-An International Perspective Symposium, Extrin Corrosion Consultants-Curtin University, Perth-Australia, 14–15 February 2007.

Table 8.2 Impact of some common biocides on the bacteria within the concrete

Biocide type	Action
Acids	Cell death
Alkalis	Breaking up the bacteria acting on organic matters
Oxidant agents	Release oxygen or other active compounds
Surface-active agents (detergents)	Cause loss of structural organisation of cellular membranes
Phenols	Effective on cellular membranes and bacterial walls
Heavy metals	Toxic actions on proteins
Alcohols	Cause dehydration
Nitrogen-organics	Interfere with photosynthesis
Phospho-organics	Interfere with the biosynthesis of some aminoacids

8.5 Summary and Conclusions

In this section, some materials and their vulnerability to MIC were briefly reviewed. These materials were copper and cupronickels, duplex stainless steels and concrete. We showed that all these materials are actually susceptible to microbial corrosion, so there is no material that can be regarded as to be totally safe to MIC. Chapter 9 will be concentrating on the treatment of MIC.

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Chapter 9

How Is MIC Treated?

Abstract Treatment of MIC can be done only by four methods: physical-mechanical, chemical, electrical and microbiological. We will discuss these methods along their alternatives as well as the pros and cons associated with them.

Keywords Pigging · UV-UT-Biocide · Dual biocide treatment · Natural biocide · CP-Coating · Biological treatment

9.1 Introduction

No matter how good and reliable the techniques and methods are for defining, recognising and detection of MIC, all will become pointless if the problem cannot be cured.

Treatment programs can be divided in two, either to mitigate an existing problem or to prevent the initiation of a problem, right from the beginning. For reasons which are beyond this book, and have been explained to some extent somewhere else,¹ most of the time what is required is mitigation.

There are very innovative ways to deal with a biocorrosion problem. Davies and Scott^{2,3} explain a very interesting case where the paint on many of the sheathings of the structural columns of a fully occupied university medical building. Shortly after the building opened, the paint started to blister and “bled a colourless liquid that quickly became rust-coloured”. In fact, 45 % of all the columns tested showed sign

The title of this chapter should have been “How is MIC technically treated?” to also address the nontechnical CKM-related treatment of MIC. However, the application of CKM to MIC problems is not different from applying it to corrosion, either microbial or “non-microbial”.

¹Javaherdashti R, “Corrosion Knowledge Management: How to deal with Corrosion as a Manager?”. To be published.

²Davies M, Scott PJB (1996) Remedial treatment of an occupied building affected by microbially influenced corrosion. *Mater Perform (MP)* 35(6):54–57.

³Scott PJB, Davies M (1992) Microbiologically induced corrosion. *Civ Eng* 58–59.

of corrosion. Despite many practical restrictions and limits, the investigators could isolate microbial consortia containing sulphate-reducing bacteria. The source of the problem was attributed to contaminated, untreated water that had been used in making the concrete. However, no conventional way of using biocides could be applied due the fact that the building was already occupied. As a biocide, the chemical that was selected and applied was denatured ethanol-based chlorhexidine digluconate, used in some mouthwashes to treat gum diseases.

Another example of such non-conventional, innovative methods is applying immunoglobulin solutions films on the surface of carbon steel and stainless steel that has been shown to prevent the adherence of *Pseudomonas fluorescens* on these metallic surfaces, thus inhibiting biofilm formation.⁴ However this method could not become popular in industry, perhaps because of reasons such as relatively high cost of immunoglobulin and lack of communication between the involved disciplines.⁵

In addition, in nature there are mechanisms from which many industrial biocidal treatments have been imitated, W.F. McCoy⁶ has given some examples of such systems. For example; when water reacts with chlorine, bromine or iodine, hypohalous acids are formed. These acids are of biocidal use in industry. Equivalently, in nature, in addition to the human immune system, this acid is also produced on the surface of some aquatic plants, keeping them free from germs.

All the above examples can serve to show that the treatment of microbiologically influenced corrosion cases may not always be taken as expensive or environmentally unfriendly practices. With lateral thinking and multidimensional planning based on understanding of the mechanisms of microbial corrosion, it is possible to make a change, when necessary.

Microbial corrosion can be treated in four ways

- Physical-mechanical,
- Chemical,
- Electrochemical,
- Biological

This chapter explains some physical-mechanical treatments (such as UV and pigging), chemical treatment (use of biocides, the advantages and disadvantages of some biocides and the treatments regimes such as dual biocide treatment,) electrochemical treatment (use of cathodic protection and coatings) and finally, introducing some biological treatments that are being researched and applied recently.

⁴Guiamet PS, Gomez de saravia SG, Videla HA (1991) An innovative method for preventing biocorrosion through microbial adhesion inhibition. J Int Biodeter Biodegradation 43:31–35.

⁵Private Communication with Professor Hector A. Videla, 15 August 2006.

⁶McCoy WF (1998) Imitating natural microbial fouling control. Mater Perform (MP) 37(4):45–48.

9.2 Physical-Mechanical Treatments

9.2.1 Pigging

PIG, being the abbreviation for “Pipeline Inspection Gauge”, is a tool by which, among many other tasks and benefits, pipelines are cleaned and/or inspected internally. Figure 9.1a shows an example of a pig to be used for cleaning natural gas pipelines. Figure 9.1b illustrates the relative size of a pig.

Some of the reasons for running pigs are⁷

- Improving the flow efficiency of the pipe line
- Improving or insuring gaining useful and good data on inspection by running a pig
- Feed back on the results of chemical treatment programs that aid in increasing the service life of the pipeline
- Removing more debris and solid products.

In addition, by running pigs, targets such as the removal of collected water and corrosion tubercles can be achieved if the facility (pipeline, for example) has been designed to allow pigging and well equipped with appropriate launchers and receivers.⁸ In this chapter, reference (Schmidt 2004) reports some of the cases where the problem of “unpiggable pipelines” has been dealt with successfully, where factors such as existence of over-or under-sized valves, different size repair sections, short radius or mitred bends have caused no accessibility for pigging. The options to overcome the problem of dealing with a pipeline being unpiggable are (Schmidt 2004) either modification of the pipeline so that it becomes piggable (which is costly and may cause operation interruptions and in some cases—due to the nature of the performance—it is just impossible) or modification of the inspection equipment in accordance with the existing conditions. This option means that, while there may be overlaps in terms of design and operation for modified pigs, each case needs to be dealt with individually.

Looking at Fig. 9.1a more closely may reveal the brushes around the main structure of the pig. Due to extreme conditions of temperature, moisture and mechanical abrasion to which pigs are exposed, these wire brushes start to degrade and also corrode. In case of the so-called “intelligent pigs” that for their operation use “magnetic flux leakage” techniques, the necessary electrical contact between the pig and the wall of the pipe is provided by these steel brushes. Neither austenitic steels (as they lack ferrite, thus cannot be magnetised) nor ferritic steels (due to their relatively low work hardening rates) may be used for making these brushes, leaving

⁷Verleun T (2004) Cleaning of oil and gas pipelines. Pigging Products and Services Association (PPSA). www.ppsa-online.com/papers.php.

⁸Jack TR (2002) Biological corrosion failures. ASM International.

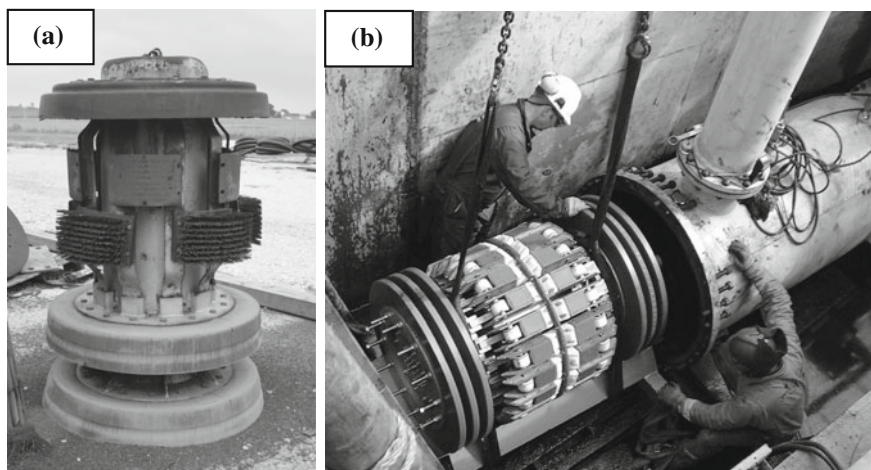


Fig. 9.1 a An example of a ‘pig’ used to clean natural gas pipelines (<http://en.wikipedia.org/wiki/Pigging#Images>). b A pig being installed into a part of a pipeline (Schmidt R (2004) Unpiggable Pipelines-What a Challenge for In-Line Inspection. Pigging Products and Services Association (PPSA). www.ppsa-online.com/papers.php)

the door open to other types of steels such as martensitic steels and duplex stainless steels⁹ (where both austenite and ferrite are present, Fig. 9.2). As it may be seen, materials selection play an important role here in terms of suggesting a material that can improve the performance of an inspection/cleaning tool and thus, perhaps indirectly, add to the increased life of the pipeline.

Pigging has always been advised by experts,^{10,11,12} as a very feasible way to keep the system clean and to manage the possibility of MIC.

9.2.2 Use of Ultraviolet Radiation

Ultraviolet (UV) can be defined as a physical process in which the targeted organism(s) are not killed but their genetic material (DNA) is altered so that their

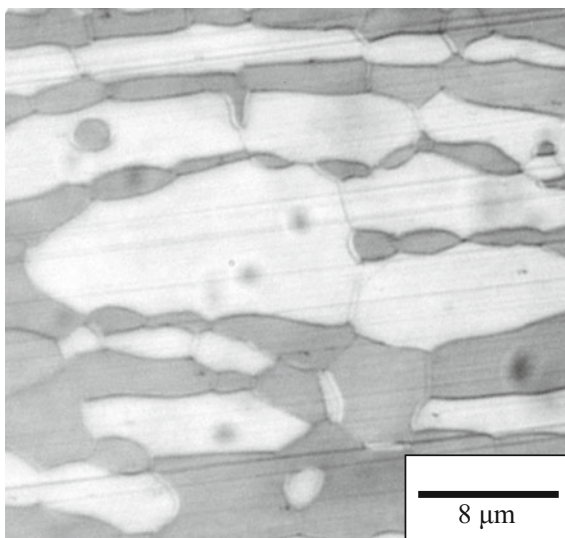
⁹Archer ED, Brook R, Edyvean RG, Videla HA (2001) Selection of steels for use in SRB environments. Paper No. 01261, CORROSION 2001, NACE International.

¹⁰King RA (2007a) 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 Feb 2007.

¹¹Scott PJB (2004) Expert consensus on MIC: prevention and monitoring, Part 1. Mater Perform (MP) 43(3)50–54.

¹²See footnote 8.

Fig. 9.2 An example of a duplex stainless steel sample, microstructure of duplex stainless steel SAF 2205 containing about 0.003 % carbon and 22.55 % chromium (*bright* Austenite, *dark* Ferrite) (Javaherdashti R, Raman Singh RK, Panter C, Pereloma CV (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 Nov 2004, Perth, Australia)



production is prevented.¹³ While some investigators have addressed UV application as an “alternative to biocides”,¹⁴ perhaps due to the efficiency of UV in a 99.9999 % reduction in viable bacterial numbers,¹⁵ it has been reported that¹⁶ only on surfaces directly irradiated by UV may biofilm growth be prevented, so that as soon as non-living particles can shield the micro-organisms from UV by adhering onto the surface, the growth can be restarted. Also, due to the poor penetrating power of ultraviolet light, this method has been reported (see footnote 15) to affect the planktonic but not the sessile bacteria in biofilms.

Some of the shortcomings of UV treatment can be briefly addressed as the following (see footnote 13):

- The UV lamp can be covered with micro-organisms thus decreasing the UV radiation that could be available for deactivation. For example, if the bacteria are

¹³Al-Majnouni AD, Jaffer AE (2003) Monitoring microbiological activity in a wastewater system using ultraviolet radiation as an alternative to chlorine gas. Paper No. 03067, CORROSION 2003, NACE International.

¹⁴Saiz-Jimenez C (2001) The biodeterioration of Building Materials. In: Stoeckel JG II (ed) A practical manual on microbiologically influenced corrosion, vol2, 2nd edn, NACE International.

¹⁵Mittelman MW (1991) Bacterial growth and biofouling control in purified water systems. In: Flemming H-C, Geesey GG (eds) Biofouling and Biodeterioration in Industrial water systems, proceedings of the international workshop on industrial biofouling and biocorrosion, Stuttgart, 13–14 Sept 1990, Springer, Berlin, Heidelberg.

¹⁶Flemming H-C, Schaule G (1996) Measures against biofouling. In Heitz E, Flemming H-C, Sand W (eds) Microbially influenced corrosion of materials, scientific and engineering aspects, Springer, Berlin, Heidelberg.

a spore-former, it may require as 10 times more dose of the UV light to be reduced 90 % in counts than its non-spore former equivalent strain.

- Some micro-organisms, specially certain types found in wastewater treatment, are not inactivated by UV radiation; this could be a matter of scrutiny especially in drinking water applications.

9.2.3 Ultrasonic Treatment

Another method that may be useful is applying power ultrasound (UT). The possible mechanisms by which UT can affect MIC are explained as follows¹⁷: through UT, an acoustic pressure is produced that induces cavitation bubbles in the liquid. Later when these bubbles collapse, the high and intense pressures (in the order of hundreds of atmospheres) and temperatures (in the range of thousands of degrees) thus locally generated will have two detrimental effects (1) they are capable of destroying the cells and (2) by formation of chemical species such as hydrogen peroxide—which has biocidal effects—and hydroxyl radicals, the chemistry of the environment becomes very hostile to micro-organisms.

Ultrasonic energy has been reported as having “good efficacy” (see footnote 16) and a “promising method [against] soft biofilms”.¹⁸ However, the feasibility of applying this method for mitigation of MIC depends on (see footnote 17) generation of enough cavitational forces to kill large enough numbers of MIC-assisting bacteria so that the regrowth¹⁹ is low enough to ensure minimisation of corrosion.

¹⁷Pound BG, Gorfu Y, Schattner P, Mortelmans KE (2005) Ultrasonic mitigation of microbiologically influenced corrosion. *CORROSION* 61(5):452–463.

¹⁸Flemming H-C (1991) biofouling in water treatment. In: Flemming H-C, Geesey GG (eds) “Biofouling and biodeterioration in industrial water systems”, proceedings of the international workshop on industrial biofouling and biocorrosion, Stuttgart, 13–14 Sept 1990, Springer, Berlin, Heidelberg.

¹⁹“regrowth”, “aftergrowth” or “recovery” all refer to rapid returning of biofilms back immediately after a biocidal treatment. There could be five reasons for regrowth, (1) if the remaining biofilm still has enough viable organisms to let the bacterial community jump from “lag phase”-where a critical size of bacterial population is needed to arrive at rapid growth (or, log phase where the increase in bacterial population is very rapid)- then, after a shock treatment, the bacterial number on such surfaces increases skyrocket in comparison with a previously clean surface, (2) the remaining biofilm offers a “rough” surface to the planktonic bacteria that can use it more efficiently than a clean surface, thus facilitating formation of more sessile bacteria, (3) biocides like chlorine may not be able to penetrate deep enough to affect the biofilm cells, in this case, while chlorine removes the outer cells and EPS, after chlorination stops, the “deep-down” cells will have a better access to nutrients so that their growth is enhanced, (4) the surviving “deep-down” cells will start to rapidly create EPS to counteract the effect of chlorine and (5) if there are micro-organisms that could be “less susceptible” to a biocidal treatment, they can rapidly proliferate between biocide treatment programs. See footnote 18.

Ultrasonic treatment may destroy the underlying material and be restricted to surfaces where UT can be applied (see footnote 18).

9.3 Chemical Treatments

Using biocides is the most profound characteristic of chemical treatment. Biocide, literally meaning “killer of living [things]”, can be divided into two large categories, oxidising and non-oxidising biocides. Oxidising biocides penetrate and destroy the bacterial cells whereas non-oxidising biocides penetrate the biofilm and damage the cell membrane or destroy the mechanisms used by the micro-organism to process energy²⁰

In the literature of chemical treatment of MIC by biocides, a very commonly used term for a biocide is being “broad spectrum”. That means that the “broad spectrum biocide” must be able to kill as many diverse types of micro-organisms and as many of the same micro-organism as possible. In other words, if a certain biocide is capable of killing both bacteria and fungi, it is a broader spectrum biocide than a biocide that just kills bacteria. In the same way, if a biocide can kill several types of a certain bacteria, it is broader spectrum biocide than the one that kills just one type of the same bacteria. Some of the biocide selection criteria are as the following²¹:

- The type of micro-organisms involved
- The prior operating history of the system
- The type of process cooling water system
- The chemicals being used for scale and corrosion control
- Chemical and physical characteristics of the water in the system
- Environmental limitations and restrictions.

It is important to notice that inhibitors are chemicals used mainly for treatment of non-microbiological corrosion where biocides are used for killing micro-organisms. However, practices like adding inhibitors such as chromates in concentrations ranging from 50 to 1000 mg/l into systems where the pH of the system is kept in a non-scaling range by adding acid, may render the corrosion inhibitor toxic to many of the micro-organisms capable of inducing MIC.²² In this way both nonmicrobial electrochemical corrosion and MIC could be treated.

²⁰Grondin EY Lefebvre N Perreault K (1996) Given, “strategies for the effective application of microbiological control to aluminium casting cooling systems”. In: Presented at “ET 96”, Chicago, USA, 14–17 May 1996.

²¹Lutey RW (1995) Process cooling water, Sect. 3.3.6. In: Rossmore HW (ed) Handbook of biocide and Preservative Use. Blackie Academic & Professional (Chapman & Hall), Glasgow, UK.

²²Ibid footnote 21, Sect. 3.2.4.

9.3.1 Pros and Cons of Some Biocides

As mentioned earlier, biocides, by their effects, can be divided into two large groups: oxidising and non-oxidising biocides. Some examples of biocides mainly used in oil industry are presented below with their pros (+) and cons (-)^{23,24,25}

Oxidising biocides:

Chlorine:

(+):

- Economical
- Broad spectrum activity
- Effective
- Monitoring dosages and residuals is simple.

(-):

- Hazard concerns for the operator
- Ineffective against biofilm bacteria
- Ineffective at high pH
- Inactivation by sunlight and aeration
- Corrosive to some metals
- Adverse effect on wood
- Feeding (Dosing) equipment is costly and requires extensive maintenance
- Limitations imposed by environmental authorities on the discharge of chloramines and halomethanes.

Chlorinating compounds (bleach [NaOCl], dry chlorine [Ca (OCl)₂]):

(+):

- Circumvent the danger of handling chlorine
- As effective as chlorine

(-):

- Can cause scaling problems
- Expensive
- Larger quantities needed than when using gaseous chlorine.

Chlorine dioxide (ClO₂)²⁶:

(+):

²³Ibid footnote 21, Sect. 3.4.

²⁴Boivin J (1995) Oil industry biocides. Mater Perform (MP) 34(2):65–68.

²⁵Videla HA, Viera MR, Guimet PS, Staibano JC Alais (1995) Using Ozone to control biofilms. Mater Perform (MP) 34 (7):40–44.

²⁶See also Cochran M, “Extending ClO₂s Reach in Anti-microbial Applications”. www.engelhard.com/aseptrol.

- pH insensitive
- Good oxidising agent for biomass
- Tolerates high levels of organics
- Dissolves iron sulphides.

(-):

Special equipment is required for generation and dosing

- Toxic
- Expensive.

Chloramines (like ammonium chloride):

(+):

- Good biofilm activity
- Good persistence in long distribution systems
- Has reduced corrosivity
- Low toxicity

(-):

- Ammonia injection is required
- Costs more than chlorine alone
- Poor biocidal properties compared to free chlorine.²⁷

Bromine:

(+):

- More effective than chlorine at higher pH
- Broad spectrum activity on bacteria and algae over a wider pH range than hypochlorous acid
- Bromamines are environmentally less objectionable and less reactive with hydrocarbons, etc. reducing the production of halomethane.

(-):

- Similar to chlorine compounds
- Expensive.

Ozone²⁸:

²⁷Scott PJB (2000) Microbiologically influenced corrosion monitoring: real world failures and how to avoid them. *Mater Perform (MP)* 39(1):54–59.

²⁸One of the chemicals that in the role of a nutrient supports the growth of micro-organisms is assimilable organic carbon (AOC), which is a fraction of the organic matter that naturally exists in water. When ozone is added as a part of an ozonation process, it increases AOC as a result of breaking up organic carbon large molecules into smaller molecules. (see: Cantor AF, Bushman JB, Glodoski MS, Kiefer E, Bersch R, Wallenkamp H (2006) “Copper pipe failure by microbiologically influenced Corrosion. *Mater Perform (MP)* 46(6):38–41). In other words, using ozone may kill the bacteria but, if not treated with intensive care, could cause regrowth promptly due to making organic matter more available to the micro-organisms.

(+):

- A natural biocide, effective as a detachment agent against sessile bacteria on stainless steel surfaces
- Resembles advantages of chlorine
- Non-polluting and harmless to aquatic organisms.

(-):

- Like chlorine, it is affected by pH, temperature organics, etc.
- Its oxidising effect does not resist throughout the system, so ozone is used in small systems or specific sites within larger systems
- Ozone must be generated on site, requiring investment for installation and running the equipment.

Sodium and Hydrogen peroxides²⁹:

(+):

- Used as a sanitising agent
- Have many of advantages as ozone.

(-):

- Requires high concentrations and extensive contact time [to kill the micro-organisms]
- Cheaper and more safe than ozone
- Careful use not to stimulate corrosion.

Non-oxidising biocides:

Aldehydes:

1. *Formaldehyde (HCHO)*:

(+):

- Economical

(-):

- Suspected of being carcinogen
- High dosages are required
- Reacts with ammonia, hydrogen sulphide and oxygen scavengers.

2. *Glutaraldehyde*:

(+):

- Broad spectrum activity
- Relatively insensitive to sulphide

²⁹Biocidal effect of hydrogen peroxide may be due to it providing other alternative cathodic reduction in addition to oxygen reduction, thus enhancing the possibility of ennoblement, see: Videla HA (1995) Biofilms and corrosion interactions on stainless steel in seawater. Int Biodeterior. Biodegradation 245–257.

- Compatible with other chemicals
- Tolerates soluble salts and water hardness.

(-):

- It is deactivated by ammonia, primary amines and oxygen scavengers.

3. *Acrolein*:

(+):

- Broad spectrum activity
- Penetrates deposits and dissolves sulphide constituents
- In highly contaminated waters, it is generally more economical/cost effective than chlorine
- No particular environmental hazards.

(-):

- Difficult to handle
- Reactive with polymers, scavengers and violently reacting with strong acid and alkalis.
- Potentially flammable
- Highly toxic to humans.

Amine-type compounds:

1. *Quaternary amine compounds*:

(+):

- Broad spectrum activity
- Good surfactancy
- Persistence
- Low reactivity with other chemicals

(-):

- Inactivated in brines
- Foaming
- Slow acting.

2. *Amine and diamine*:

(+):

- Broad spectrum activity
- Have some inhibition properties
- Effective in sulphide-bearing waters

(-):

- React with other chemicals, particularly anionics
- Less effective in waters with high levels of suspended solids.

Halogenated compounds:1. *Bronopol*:

(+):

- Broad spectrum activity
- Low human toxicity
- Ability to degrade

(–):

- Available as a dry chemical
- Breaks down I high pH.

2. *Dbnpa*:

(+):

- Broad spectrum activity
- Fast acting and effective (at a pH above 8, it must be used for quick kill situations)
- No apparent difficulties related to effluent discharge with these materials when applied as recommended.

(–):

- Expensive
- Affected by sulphides
- Must be adequately dispersed to ensure effectiveness due to low solubility in water
- Although effective against bacteria at low concentrations, higher concentrations are required to control most algae and fungi, making them less cost effective
- Overfeeding causes foaming and skin contact problems.

Sulphur compounds:1. Isothiazolone³⁰:

³⁰The most frequently used types of isothiazolone are 3:1 ratio 5-chloro-2-methyl-4-isothiazoline-3-one (CMI), 2-methyl-4-isothiazolin-3-one (MIT) (see: Williams TM (2006) “The mechanism of Action of isothiazolone Biocides. Paper No. 06090, CORROSION 2006, NACE International, USA), and also 4,5-dicholo-2-n-octyl-4-isothiazolin-3-one (DCOI) (see: Williams TM (2004) Isothiazolone Biocides in water Treatment Applications. Paper No. 04083, CORROSION 2004, NACE International, USA). It has also been reported that (Williams 2006 CORROSION) isothiazolones use a two-step mechanism to affect micro-organisms: step 1. takes minutes and it involves rapid inhibition of growth and metabolic activities, step 2, taking hours to become effective, is an irreversible cell damage that is basically a kill process and end up in loss of viability. An investigation (see: Jacobson A, Williams TM (2000) The environmental fate of isothiazolone biocides. *Chimica Oggi* 18(10):105–108 reports that when isothiazolone molecule is degraded, it releases chlorine as chloride ion and “not as an organochlorine metabolite or by-product”. Therefore, if chloride-induced corrosion is a concern in a system, it is prudent not to use this biocide or use it with high degree of care. In addition, It has also been reported that isothiazolones have an active –SH group, that in the presence of sulphide, it can be affected (see: King RA (2007b) Microbiologically

(+):

- Broad spectrum activity
- Compatible with brines
- Good control of many aerobic and anaerobic bacteria (like anti-sessile bacteria) and have activity against many fungi and algae at acidic to slightly alkaline pHs
- Low dosages are required
- Degradable.

(-):

- Cannot be used in sour systems
- Expensive
- Less cost effective when the system contains significant amounts of sessile or adhering biomass. In such cases, the use of a penetrant/biodispersant enhances the effectiveness of the biocide
- Extreme care required because of potential adverse dermal effects, automated feeding systems are strongly recommended.

2. *Carbamates (alkyl thiocarbamates):*

(+):

- Effective against SRB and spore formers
- Effective in alkaline pH
- Useful for polymer solutions.

(-):

- High concentrations are required
- React with metal ions and other compounds

3. *Metronidazole (2-methyl-5 nitroimidazole-1-ethanol):*

(+):

- Effective against SRB
- Compatible with other chemicals

(-):

- It is specific to anaerobic organisms.

Quaternary phosphonium salts (quats):

(+):

(Footnote 30 continued)

Induced Corrosion and biofilm Interactions. In: "MIC An international perspective" symposium, extrin corrosion Consultants-Curtin University, Perth-Australia, 14-15 Feb 2007).

- Broad spectrum of killing activity and good stability. They are generally most effective against algae and bacteria at neutral to alkaline pH
- Low toxicity
- Stable and unaffected by sulphides.

(-):

- Not effective fungicides at any pH
- Their activity is mostly reduced by high chloride concentrations, high concentrations of oil and other organic foulants and by accumulations of sludge in the system
- Excessive overfeed of some types of quats may contribute to foaming problems especially in open recirculating systems with organic contaminations.

Another way of grouping biocides is in accordance with their mechanisms of action, in this way, the biocides will be divided into two subgroups as seen in Fig. 9.3:

Figure 9.3 illustrates an alternative way of looking at how biocides can be effective through their “mechanisms of action”. With regard to one of these biocidal chemicals, silver, an important note must be said here; sometimes silver is recommended as a biocide to industrial inquirers who are not allowed to use copper or mercury, obviously for environmental concerns. It has been reported that (see footnote 16) although silver is a “killer” to micro-organisms at very low concentrations (less than 10 µg/l), within a few weeks, the micro-organisms become not only tolerant but also start to multiply in the presence of concentrations as high as 1 mg/l of Ag ions.

Talking about developing resistance to some biocidal agents, we should explain a misunderstanding. It may be believed that bacteria change and modify their genetics features by undergoing periodic mutation, therefore after a period of time, they become resistant to a given biocide. Al-Hashem et al.³¹ differentiate between adaptation and developing resistance to a biocide from an antibiotic. These differences can be summarised as in Table 9.1

From the table, it may be observed that bacteria would need to alter the structure of every protein in the cell to enable it to become resistant to a biocide. This would require that the bacteria would need a large number of mutations at the same time or in a short time to become resistant to a biocide. Such patterns of mutations, however, must occur over time spans much longer than what is normally available in an industrial system. The main reasons that explain why a biocide that seemed to be working previously is not working any more can be summarised as follows (see footnote 31):

³¹Al-Hashem AH, 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, USA.

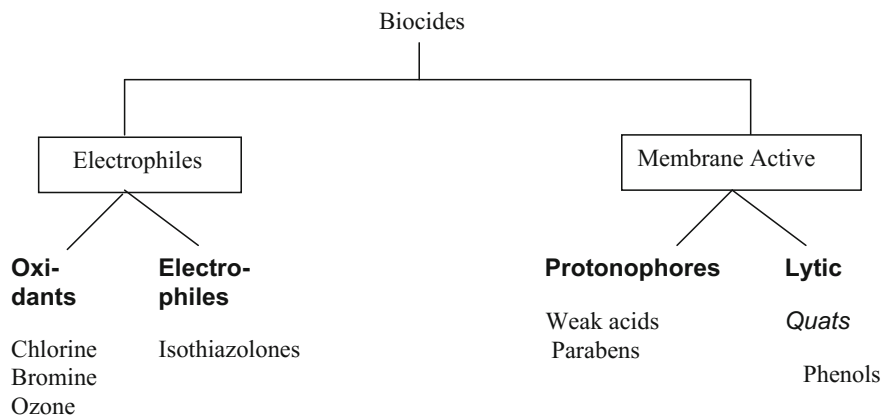


Fig. 9.3 A Brief of Industrial Biocides' Mechanisms of Action (see footnote 30, Williams TM (2004) CORROSION)

Table 9.1 Comparison between antibiotic and biocide resistance modes

Characteristics of Developing Resistance to <i>Antibiotics</i> by bacteria	Characteristics of Developing Resistance to <i>Biocides</i> by bacteria
Antibiotics act by selective biochemical blocking of important binding sites of bacteria	Biocides act by mechanisms like precipitation of proteins, solubilisation of lipids etc. with attack on multiple sites in the bacterial cell simultaneously

1. change in biocide dosing regime,
2. change of the manufacturer of the biocide
3. change of factors such as the system's temperature and pH
4. lack of biocide uses optimisation so that it was effective on the small-sized initial bacteria population but with increase in size and biological activity over the time, the initial dosage of the biocide has been proved to be ineffective.

Here we would like to also say a word on “colour coding” of biociders based on their relative risk to the environment. This code system can assist a great deal in the environmental assessment of the biocide and must be observed in any industry in which use of biocides is allowed.

Base on this colour code system,³² the toxicity of the biocide is coded as given in Tables 9.2 and 9.3 (complete names for the abbreviations of the selected biocides have been given in the reference)

Environmental fate of biocides is a very important issue in dealing with MIC. However it must be noted that all the factors related to a biocide selection and

³²Williams TM, Cooper LE (2014) The environmental fate of oil and gas biocides: a review. Paper No. 3876, CORROSION 2014, Houston, TX, USA.

Table 9.2 Colour coding of biocide toxicity hazard rating

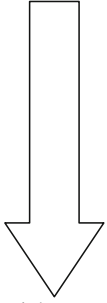
Hazard rating	Designated colour code
 <p>Lowest Hazard</p> <p>Highest Hazard</p>	Gold
	Silver
	White
	Blue
	Orange
	Purple

Table 9.3 Summary of UK North Sea ratings for some oil and gas biocides

Biocide	North Sea colour rating
DMO	Gold
Glutaraldehyde, DBNPA, THPS, DDAC	Gold-Silver
Bronopol	White
Dazomet, ADBAC, TTPC	De-Listed
CMIT/MIT, CTAC, THNM, cocodiamine	No data

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application (economical, ecological, not antagonistic impacts on other chemicals,...) are very important parameters in a chemical treatment program of an MIC-related case if it is a feasible option in the first place.

9.3.2 A Note on Dual Biocide Treatment

It must be noted that physiological resistance of biofilms to oxidising biocides is much less pronounced than for non-oxidising biocides. Combinations of both oxidising and non-oxidising biocides in one treatment help to offset the physiological resistance of biofilms because of their dual mechanism of action.³³

Almost in the same way that in composite materials, the properties of the components (phases) are combined to give a better result, dual biocide treatment may also prove to be useful, for example, by combining the good killing features of an aldehyde with high penetration abilities of a quaternary amine, the poor

³³Ludensky ML, Himpler FJ, Sweeny PG (1998) Control of biofilms with cooling water biocides. Mater Perform (MP) 37(10):50–55.

penetration characteristics of the aldehyde and low killing efficiency of the amine are compromised (see footnote 31).

However, Al-Hashem et al. (see footnote 31) report another example of dual biocide treatment where a high concentration batch treatment by a biocide has been followed by a low concentration of continuous biocide treatment. The first step had been introduced to reduce the numbers of the bacteria (batch treatment) and keep it low (continuous treatment). These authors, after not finding such treatments feasible enough both in terms of the extra time to be allocated for each treatment and the costs of the chemicals and facilities, prefer a batch dose of high concentration with special consideration of factors such as the frequency of biocide application and pretreatment of the water entering into the system.

Another example (see footnote 15) is using chlorinated (or brominated) compounds with surfactants to oppose biofilm formation. However, removal of the surfactants after the application can be a problem, for example in terms of the volumes of water needed to rinse them.

It seems that no matter how one interprets dual biocide treatment, either in terms of using two non-oxidising biocides or a combination of an oxidising and a non-oxidising biocide or even using different regimes and concentrations of the same biocide, these all depend on factors such as biocide selection, system requirements and the economy of the application and posttreatment concerns. Therefore, although dual biocide treatment can be advisable, ignoring the factors just mentioned may result in a practice which will be hardly applicable.

9.3.3 “Natural” Biocides

Biocides can further be divided into two groups: synthetic biocides and ecofriendly biocides. Ecofriendly biocides then are grouped into “green” biocides and “natural” biocides. Natural biocides (or, for that matter, inhibitors) are extracted from totally natural sources (such as, but not limited to, plant extracts). Here we do not explain such natural inhibitor; a good review of some examples of natural inhibitors and the mechanisms by which they affect corrosion has been given elsewhere.³⁴

We will mainly concentrate on a natural biocide whose source is Neem tree (*Azadirachta Indica*). We will briefly present the results of some research done on the biocidal effects of this plant, bearing in mind that Neem tree also shows corrosion inhibiting effects, as also has been mentioned in footnote 33. Neem laves, bark extracts and neem oil all have antibacterial and antifungal effects^{35,36} However

³⁴Abdullah Dar M (2011) A review: plant extracts and oils as corrosion inhibitors in aggressive media. *Ind Lubr Tribol* 63(4):227–233.

³⁵Rasooli I (2007) Food preservation—A biopreservative approach. *Food m* 1(2):111–136.

³⁶Jahan T, Ara Begum Z, Sultana S (2007) Effect of neem oil on some pathogenic bacteria. *Bangladesh J Pharmacol* 2:71–72.

its effect so far has been studied on SRB.^{37,38} The biocidal effect of Neem could possibly be due to the formation of “Terpenes” that can adversely affect cell walls and membranes.³⁹

With increasing public awareness about environment and how to deal with it in a most ecofriendly manner, it makes sense if industry becomes much more interested in management of corrosion by “natural” means. Natural biocides can indeed offer a very healthy option to both manage MIC and care about the environment at the same time.

In one of our publications,⁴⁰ we have contemplated on the link between environment and corrosion and required mechanisms that need to be in place to address environmental impacts of corrosion. This author would call a corrosion management approach as “Natural” only if it uses natural inhibitors and biocides, as a minimum to deal with corrosion and particularly microbiologically influenced corrosion. Till that day, none of our corrosion management approaches can be addressed as being “natural” means in dealing with corrosion even if they have started to apply green biocides and inhibitors.

9.4 Electrochemical Methods

It may appear a little strange to categorise items such as cathodic protection and coating under electrochemical methods. However, it will make sense when we think of these methods in terms of their effects on building up an electrochemical cell [see Chap. 1, electrochemical triangle]. In other words, coating is mainly replacing the role of electrolyte by separating electrodes (anode and cathode) from finding a medium through which electron and ions can be transferred. In the same way, by applying cathodic protection, the electrons lost from the metal during anodic reactions are provided by the CP system, thus the role of anode becomes less important.

³⁷Bhola SM, Alabbas FM, Bhola R, Spear JR, Mishra B, Olson DL, Kakpovbia AE (2014) Neem extract as an inhibitor for biocorrosion influenced by sulfate reducing bacteria: A preliminary investigation. *Eng Fail Anal* 36:92–103.

³⁸Kuta FA, Abdulasak ST, Saidu AN, Adedeji AS (2014) Antimicrobial effects of *Azadirachta indica* leaves on corrosion causing microorganism (*Desulphovibrio* sp.). *Med Aromat Plant Res J* 2(2):33–36.

³⁹Ocando L, de Romero MF, Urribarri A, Gonzalez D, Urduaneta E, Fuenmayor H (2013) Evaluation of Sulfate-reducing bacteria biofilms in the presence of biocides. Paper No. 2782, CORROSION 2013, Houston, TX, USA.

⁴⁰Javaherdashti R, Nikraz H (2010) A global warning on corrossions and environment: a new look at existing technical and managerial strategies and tactics. VDM Germany

9.4.1 Cathodic Protection (CP)

The cathodic protection criterion of -0.95 V (Vs. Cu-CuSO₄ reference electrode) to protect steel against SRB-induced MIC, first appeared as the result of thermodynamic considerations in 1964 by Hovarth and Novak,^{41,42} to be later experimentally verified by Fischer in early 1980s (see footnote 33),⁴³

While the “ -950 mV” criterion has been widely used, there are reports that show this criteria is not as straightforward as it may seem. Two such reports were cited in Chap. 4, Sect. 6.2.2.1, where two examples of investigations done in the early and the late 1990s have supported the idea that the “ -950 mV” CP criteria may not be actually working the same everywhere. Recently, the results of an investigation of CP effects on pure iron surfaces in the presence of SRB⁴⁴ have demonstrated that applying cathodic polarisation of -1070 mV versus Cu-CuSO₄ has not been sufficient to prevent the growth of SRB.

The accepted theory to explain the feasibility of CP on MIC is that⁴⁵ CP increases the local pH at metal/medium (water and/or soil) interface, thus causing the release of hydroxyl ions and decreasing the solubility of calcium and magnesium compounds. This would result in the formation of calcareous deposits. It is this high pH generated by CP that has made some researchers speculate why CP is effective on MIC,⁴⁶ as it is believed that micro-organisms cannot normally tolerate such high pH values. This is despite that, the presence (and not growth and vitality) of alkaliphilic micro-organisms in highly alkaline ($\text{pH} \geq 11$) media has been reported.⁴⁷

⁴¹Kajiyama, F, Okamura K (1999) Evaluating cathodic protection reliability on steel pipes in microbially active soils. CORROSION 55(1):74–80.

⁴²Tiller AK (1986) A review of the european research effort on microbial corrosion between 1950 and 1984. In: Dexter DC (ed) Biologically induced corrosion. NACE-8, NACE, Houston, TX, USA.

⁴³Fischer KP (1981) cathodic protection criteria for saline mud containing SRB at ambient and higher temperatures. Paper No. 110, CORROSION/ 81, NACE International, USA.

⁴⁴de Romero MF, Parra J, Ruiz R, Ocando L, Bracho M, de Rincón OT, Romero G, Quintero A (2006) Cathodic polarisation effects on sessile SRB growth and iron protection. CORROSION, Paper No. 06526, NACE International, USA.

⁴⁵de Gonzalez CB, Videla HA (1998) Prevention and control. In: Ferrari MD, de Mele MFL, videla HA (eds) In CYTED, Ibero-American programme of science and technology for development, practical manual of biocorrosion and biofouling for the industry, Subprogramme XV, Research Network XV.c. BIOCORR, Printed: POCH&INDUSTRIA GRAFICA S.A., La Plata, Bs.As., Argentina, 1st Edn. March 1998.

⁴⁶Geesey GG (1993) Biofilm Formation. In: Kobrin G (ed) A practical manual on microbiologically-influenced corrosion. NACE, Houston, TX, USA.

⁴⁷Pedersen K (1999) Subterranean micro-organisms and radioactive waste disposal in sweden. Eng Geol 52:163–176.

9.4.1.1 How CP Is Effective on MIC?

As pointed earlier, a possible mechanism could be chemical nature of the environment which is created after the application of CP in terms of increasing the local pH and inhibiting the bacterial reproduction of microbes⁴⁸ in such a high alkaline environment. But there are two seemingly rival theories in this respect. We will briefly explain these theories and interpretations below.

A. Electrostatic-chemical theory

In late 90s it was reported by J.W. Arnold,⁴⁹ a microbiologist then working at the ARS Poultry Processing and Meat Quality Research Unit at Athena, Georgia, USA, that electropolished surfaces had been much less vulnerable to biofilms build-up when compared with the surfaces prepared by other methods such as polishing, sand-blasting and grinding. A possible reason for observing such behaviour, it was theorised, could be due to the charge change induced by electropolishing of the metal surfaces (that other polishing and surface treatments methods were not capable of), thus rendering the surface negatively charged. Therefore, the bacteria which can be taken as a charged particle due to their negative charge,^{50,51} would not be able to attach themselves onto the surfaces easily.

If this interpretation is correct, then the negatively charged metallic surface (energised by CP and especially impressed current CP) repel the negatively charged bacteria as schematically shown in Fig. 9.4.

In this model, the interaction between the negatively charged metallic surface and the negatively charged bacteria causes a lag phase before the chemical effect of CP starts to play a role. In other words, according to this model, that we call electrostatic-chemical model, or briefly, EC model, when CP is on and the structure energised, the repulsion forces thus produced would serve to keep the bacteria away from the structure as the negatively charged bacteria cannot be attracted to the structure unless the distance is in the order of nano-metres. While all this is happening, cathodic reactions are still on-going so that hydroxyl ion release that occurs as a result of CP, increases the pH locally and the alkaline environment manages to affect the bacteria adversely. The outcome will be lowering the risk of corrosion. The EC mechanism can be schematically shown as Fig. 9.5.

As seen from Fig. 9.4, when the bacteria come into contact with the metallic surface that, due to an induced current cathodic protection, or briefly ICCP, has already been negatively charged, the repulsion forces thus produced prevent the

⁴⁸Stein AA (1993) MIC treatment and prevention. In: Kobrin G (ed) A practical manual on microbiologically-influenced corrosion. NACE, Houston, TX, USA.

⁴⁹Lee J (1998) Bacterial biofilms less likely on electropolished steel. Agric Res 10.

⁵⁰Percival SL, Knapp JS, Wales DS, Edyvean RGJ (2000) Metal and inorganic ion accumulation in biofilms exposed to flowing and stagnant water. Brit Corros J 36(2):105–110.

⁵¹Sreekumari KR, Nandakumar K, Kikuchi Y (2004) Effect of metal microstructure on bacterial attachment a contributing factor for preferential MIC attack of welds. CORROSION 2004, Paper No. 04597, NACE International.

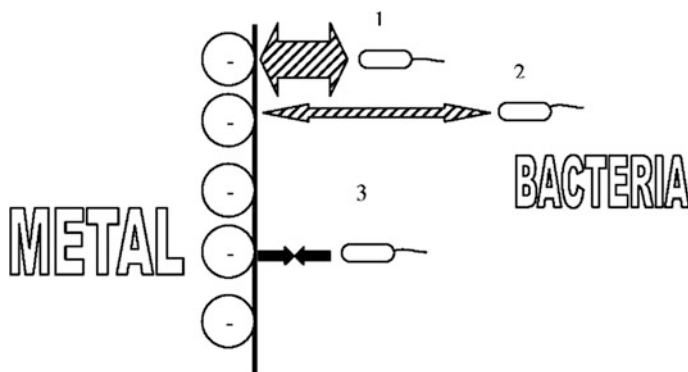


Fig. 9.4 Possible interaction between negatively charged surface and negatively charged bacteria. The power of the repulsion forces (shown as *dashed*) is schematically represented by the thickness of the *arrows*. For example the magnitude of the repulsion forces against the bacterium ① is much bigger than that of the bacterium ②. If the bacteria come close enough [0.4 nm or less (Geesey GG, Wigglesworth-Cooksey B, Cooksey EK (2004) Influence of calcium and other cations on surface adhesion of bacteria and diatoms: a review. *Biofouling*. 15 (1–3):195–205)], then chances are that the interacting forces become attractive forces to let bacterial attachment onto the surface

attachment of the bacteria onto the surface. This, in turn, would mean that the biofilms formation would be avoided. In Fig. 9.5, possible stages involved in the CP that may be effective in reducing MIC are shown; the electrostatic effects are shown in Figs. 9.5a, b. Taking the example of a pipe, it is schematically shown that due to CP, there is a fairly uniform charge distribution on the exterior wall of the pipe or a given segment of it (Fig. 9.5a) where the pipe is surrounded by relatively nonuniformly distributed negatively charged bacteria (Fig. 9.5b). The net effect will be repulsive forces that will push the bacteria away from the metallic surface. The chemical effect (Figs. 9.5c, d) is that as the CP practice continues, the local concentration of protons (H^+) decreases by being used up in the cathodic reaction. By a further increase in pH, calcareous sediments formation is more assisted. As the local pH is too high, the micro-organisms that may be still adhering to the surface of the metal will die off.

Some examples of works favouring electrostatic repelling of negatively charged bacteria by the negatively charged metallic surfaces under CP have been quoted by Mains et al.⁵²

An alternative theory, that we call chemical bridge theory, is not considering electrostatic forces of significant importance and rather relies on chemical binding, as will be discussed below.

⁵²Mains AD, Evans LV, Edyvean RGJ (1992) Interactions between marine microbiological fouling and cathodic protection. In: Sequeira CAC, Tillere AK (eds) *Microbial corrosion*, proceedings of the 2nd EFC workshop, Portugal 1991. European Federation of Corrosion Publications, Number 8, The Institute of Materials.

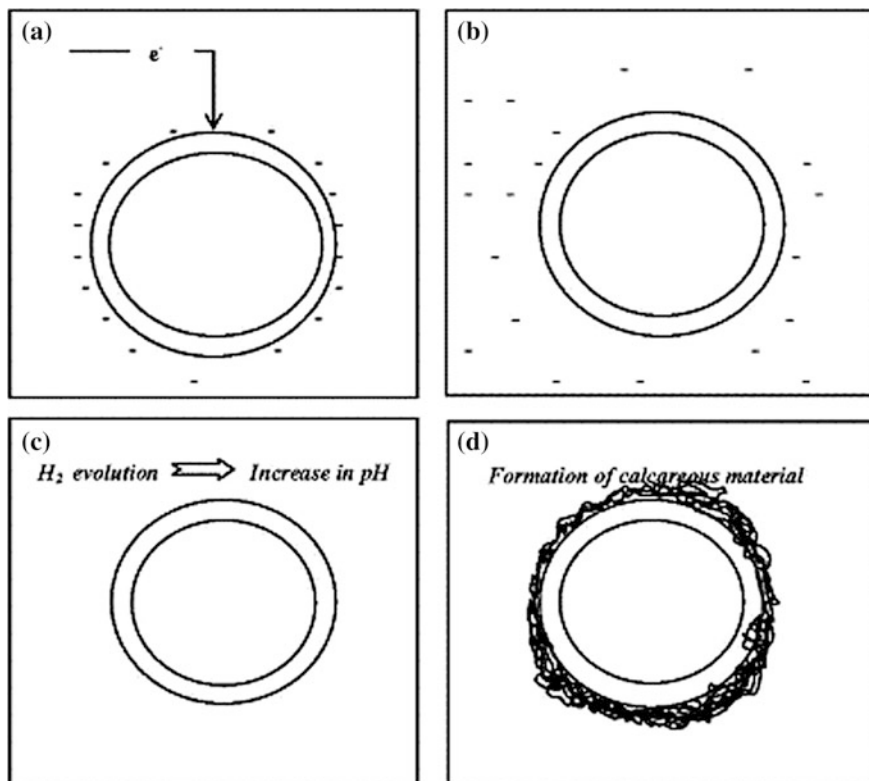


Fig. 9.5 Possible EC effects on the ICCP of a pipeline (Javaherdashti R, Mathematical justification of applying over-voltage in cathodic protection systems to avoid MIC. Unpublished work)

B. Chemical bridge theory

Mains et al. (see footnote 45), in trying to explain why applying CP to stainless and structural steel surfaces immersed in seawater can inhibit the settlement and attachment of aerobic bacteria to these surfaces, call the use of electrostatic repulsion theory in explaining such phenomena as being “oversimplification”. Instead, they propose an alternative mechanism. We call their proposed mechanism the chemical bridge theory, or briefly, CB.

Based on studies done on the adhesion of bacteria onto the surface of materials such as glass and tooth enamel and other studies addressed in their paper (see footnote 45), their theory can schematically be shown as Figs. 9.6a, b:

Stage 1: the bacteria use divalent ions such as calcium or magnesium to attach themselves onto the negatively charged metallic surfaces

Stage 2: As CP increases, the local chemistry changes dramatically resulting in a pH increase. This will turn the environment locally alkaline so that due to the

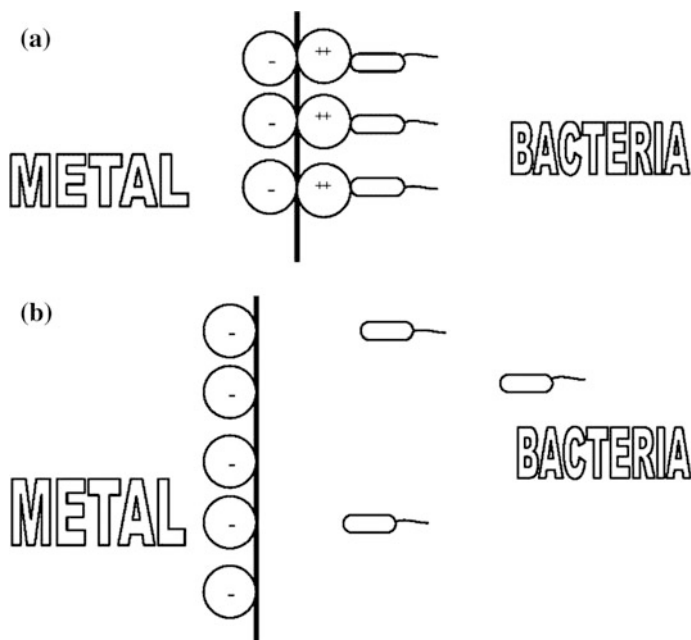


Fig. 9.6 Stages involved in CB theory

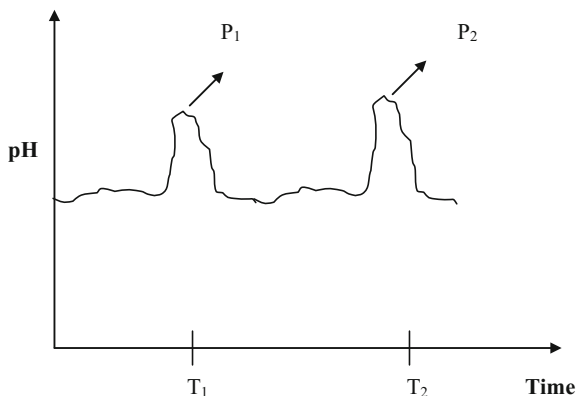
precipitation of calcium and magnesium, these ions become unavailable to the bacteria.

One question here is why calcium and not anything else? One possible reason could be that (see footnote 43) polycations such as calcium ion or magnesium ion decrease electrostatic repulsion during the primary stage of cell adhesion onto negatively charged surfaces. However, the same study (see footnote 43) also reports that irreversible attachment of bacterial cells to solid surfaces could involve both monovalent and divalent cations.

It is not explained in the CB theory what will happen to the bacteria that have lost their “bridges”. Therefore, we may assume that the fate of these bacteria will be left to the locally increasing alkalinity so that they may not be able to survive under those circumstances. In fact, another question that may come to mind is the possible events that can happen in between stages 1 and 2 from the standpoint of an increase in pH. Figure 9.7 schematically shows the change in pH with regard to what is expected to happen according to CB theory.

The CB theory implies that there must be at least two rises in pH, one that is necessary to precipitate divalent ions such as calcium ions, that in Fig. 9.7 has been marked by P_1 at the time T_1 . Another rise in pH, marked by P_2 at time T_2 , is when the pH becomes detrimental to the micro-organisms. At the moment there is no evidence, to the best of the knowledge of the author, to suggest if these pH rises are

Fig. 9.7 Hypothetical pH change over time (arbitrary scale) according to CB theory



characteristically different from each other ($T_2 - T_1 > 0$) or the time difference is so infinitesimal ($T_2 - T_1 \approx 0$) that practically it is nil, suggesting that in Fig. 9.7 there is only one peak not two. This, in turn, means that one single pH rise is sufficient to both remove the bridging ions and make the environment hostile to the micro-organisms. However, it seems logical to imagine that if there is a lag time of $T_2 - T_1 > 0$, the micro-organisms repelled by the electrostatic forces, would have a chance, however slim, to arrange themselves for a regrowth, should the lag time becomes long enough.⁵³ Basically, we cannot even be sure about how the curve in Fig. 9.7 may look like.

In fact, there are several other theories proposed to explain the mechanisms by which microbial adhesion on a surface can take place. These include, but may not be limited to, the Derjaguin Landau Verwey and Overback (DLVO) theory (that involves considering the effects of hydrophobicity and surface charge) and the theory of thermodynamics of attachment (that involves surface-free energy). These theories and their different aspects have been explained elsewhere⁵⁴ and we will not introduce those details here.

9.4.1.2 CP Criteria and Uncertainty in Design

The main purpose of this section was to show that the so-called -0.95 V criteria for having a secure CP against MIC may not be as straight forward in practice than it may seem in theory.

⁵³Due to any possible reason ranging from poor practice of CP to irregularities in its application which are not rare when it comes to the field conditions.

⁵⁴Habash M, Reid G (1999) Microbial biofilms: their development and significance for medical devices-related infections. *J Clin Pharmacol* 39:887–898.

Around the world for many engineering CP applications, only the effect of SRB and the -0.95 V criteria are considered when it comes to calculate the impact of MIC on design. However, it is very important to realise that the -0.95 V criteria (and many more of its kind such as relating “certain” numbers of “certain” types of bacteria with a “certain” corrosion rate or assessment of MIC by the pit morphology) can, at their best, be regraded as the “minimum to expect”. In other words, both the corrosion professionals and their clients must be educated to become aware of the existing shortcomings of these approaches and take them not as “solid rules” but “flexible guidelines”. In the case of CP design and application, it may be a good idea to more accurately test the actual voltage at which for a particular environment CP can affect the microbial community either by reducing their numbers or keeping them “inactive” enough not to interfere with corrosion in any shape or mode. Needless to say that such practices can only occur in a perfect world where the cost of corrosion, in general, and MIC, in particular, is not an industrial joke.⁵⁵

9.4.2 Coating

According to some surveys, “almost all” of cases of corrosion of underground gas pipelines can be attributed to disbonded coatings.⁵⁶ Yet, an important issue with coating is no matter how good a coating system is, as long as the application is not standard, the coating system may not be expected to perform well. In other words, although the idea of using protective coating is not new, there is still no ideal coating material that is adherent, coherent, completely nonporous, mechanically resistant to the hazards encountered during delivery, laying and backfilling and chemically resistant to prolonged contact with all kinds of natural environments. Table 9.4 summarises the pros and cons of some coatings used for buried pipelines.⁵⁷

In addition to reportedly well-performing silicon-based coatings,⁵⁸ new technologies that incorporate micro-fine copper flakes into an epoxy resin base to

⁵⁵See the last two paragraphs of the “introduction” of the paper by 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, NACE International, USA.

⁵⁶Li SY, Kim YG, Kho YT (2003) Corrosion behaviour of carbon steel influenced by sulfate-reducing bacteria in soil environments. Paper No. 03549, CORROSION 2003, NACE International.

⁵⁷Javaherdashti R, Vimpani P (2003) Corrosion of steel piles in soils containing SRB: a review. In: Proceedings of corrosion control and NDT, 23–26 Nov 2003, Melbourne, Australia.

⁵⁸Wiebe D, Connor J, Dolderer G, Riha R, Dyas B (1997) Protection of concrete structures in immersion service from biological fouling with silicone-based coatings. Mater Perform (MP) 36 (5):26–31.

Table 9.4 Some features of commonly used coatings (see footnote 49)

Coat name	Advantages	Disadvantages
Coal tar-based	More stable and water proof than Asphaltic bitumen-based	Organic reinforcements to these coatings can be attacked and broken down by cellulose-decomposing microbes, carcinogenic thus its use is banned in some countries
Asphaltic bitumen-based	Better to be reinforced with fibreglass	
Concrete	Alkalinity	Permeable to air, water and stray currents unless they are tick and hence expensive
Zinc coating on steel	With suitable thickness can prevent corrosion in neutral or alkaline soil for quite long time	Not to be used for acid conditions
Spray applied Zinc-Aluminium coating	Promising	–
Lead coats	Good performance	Once the coating fails, rather rapid corrosion occurs.
Plastic	Resistant to electrochemical corrosion	Bonding to metal
Fibre-glass resin and epoxy resin coatings	Highly protective	Comparatively expensive

reduce biofilm adhesion⁵⁹ may seem promising for MIC-related corrosion issues, however it is still too soon to express an idea-positive or negative-on this subject.

Reportedly, some coats known as “soft-coat” or “semi-hard coatings” use vegetable oils. Needless to say how dangerous these coats could be with regard to MIC as they would provide a “food” for the bacteria present in the untreated water coming into contact with them.

As some of the coatings could be polymer materials, it is useful to rank some frequently used polymers against microbial attack. Table 9.5 shows a selected series of such polymeric materials. It is advised, however, to study each related case individually and then make the decision as how one defines “stability” either with regard to their applicabilities such as mechanical properties or structural integrity for any particular case.⁶⁰

⁵⁹Metosh-Dickey CA, Portier RJ, Xie X (2004) A novel surface coating incorporating copper Metal Flakes for Reducing Biofilm attachment. *Mater Perform (MP)* 43(10):30–34.

⁶⁰Filip Z, Pommer E-H (eds) (1992) Microbiologically influenced deterioration of materials. In: *Microbiological degradation of materials and methods of protection*. European Federation of Corrosion Publications, Number 9, The Institute of Materials.

Table 9.5 Stability of some polymers to microbial attack (Geesey et al. 2000)

Polymer	Stability ranking
Polyethylene	Very stable to medium stable
Polypropylene	Very stable to medium stable
Polystyrene	Very stable
Polyurethanes	Less stable ³
Epoxy resins	Very stable

Some of the micro-organisms that often attack plastics are *Pseudomonas aeruginosa*, as well as *micrococcus* and *bacillus* species. See Ref. Geesey et al. 2000

9.5 Biological Methods

In recent years, the feasibility of another method of MIC mitigation is being examined in which a certain type of bacteria is used against the other. As the reader may guess, the experiments are being done on the possibility of reducing MIC as induced by SRB.⁶¹

From some reports, it is known that some SRB (such as *Desulphovibrio desulphuricans*⁶² and *Desulphovibrio gracillis*⁶³) are capable of reducing nitrate.⁶⁴ Excluding such “weird” SRBs, some methods have been proposed and exercised to use nitrate-reducing bacteria (NRB) against SRB. Two examples of these methods are,⁶⁵ (a) bio-competitive exclusion and (b) bio-augmentation. The essential components of the definitions of these methods (see footnote 54) can be schematically presented as Fig. 9.8a, b.

⁶¹A Possible, yet still theoretical, use of magnetic bacteria (Chapter 4) could be using them in a system contaminated with, say, SRB to corral the SRB and, literally speaking, “pushing” them to a spot under the effect of a magnetic field and then apply biocide to them. See Javaherdashti R (1997) Magnetic bacteria against MIC. Paper No. 419, Corrosion 97, NACE International, USA.

⁶²Dzierzewicz Z, Cwalina B, Chodurek E, Bulas L (1997) Differences in hydrogenase and APS-Reductase activity between desulfovibrio desulfuricans strains growing on sulphate or nitrate. ACTA BIOLOGICA CRACOVIENSIA Series Botanica 39:9–15.

⁶³Dunsmore BC, Whitfield TW, Lawson PA, Collins MD (2004) Corrosion by sulfate-reducing bacteria that Utilize Nitrate. Paper No. 04763, CORROSION 2004, NACE International, USA.

⁶⁴Nitrite has inhibitory effect on SRB, because of mainly two reasons: (a) nitrite is toxic to SRB and with their nitrite reductase, the bacteria will produce a detoxifying reaction. The end result is that while the bacteria are still alive, no growth happens and their sulphate reduction activity will be inhibited, (b) nitrite can directly affect the enzyme required for reducing sulphite to sulphide, see footnote 58.

⁶⁵Little B, Lee J, Ray R (2007) New development in mitigation of microbiologically influenced corrosion. In: MIC “An international perspective” symposium, extrin corrosion consultants-Curtin University, Perth-Australia, 14–15 Feb 2007.

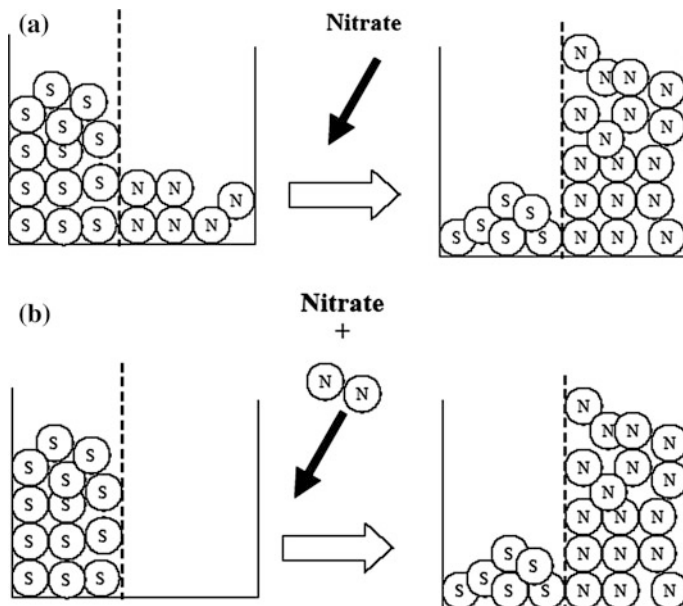


Fig. 9.8 Explanation of two microbiological methods (bio-competitive exclusion and bio-augmentation) to mitigate MIC. **a** *Bio-competitive exclusion*: by adding nitrate, nitrate-reducing bacteria (presented by circles with letter N), will outnumber sulphate-reducing bacteria (shown by circles with letter S). **b** *Bio-augmentation*: Addition of ex situ grown nitrate-reducing bacteria and nitrate into a system that may have no “indigenous nitrate-reducing bacteria

Little et al. (see footnote 54) report successful trials of bio-competitive exclusion as exercised on oil platforms where the corrosion rates were, at least, reduced 50 %. On the other hand, with respect to bio-augmentation, while researchers such as Hubert et al.⁶⁶ and Bouchez et al.⁶⁷ have reported failures regarding introduction of bacteria into natural mixed cultures, Zhu et al.⁶⁸ have reported the simultaneous application of nitrate and denitrifying bacteria as “the most effective way” for controlling MIC induced by SRB. However, the research in this area is not completed yet.

⁶⁶Hubert C, Voordouw G, Arensdorf J, Jenneman GE (2006) Control of souring through a novel class of bacteria that oxidize sulfide as well as oil organics with nitrate. Paper No. 06669, CORROSION 2006, NACE International, USA.

⁶⁷Bouchez T, Patureau D, Dabert P, Juretschko S, Delgenes J, Molette, Ecological study of a bioaugmentation failure. As reported in footnote 56.

⁶⁸Zhu XY, Modi H, Kilbane JJ II (2006) Efficacy and risks of nitrate application for the mitigation of SRB-induced corrosion. Paper No. 06524, CORROSION 2006, NACE International, USA.

9.6 Summary and Conclusions

Treatment of MIC can be done, with the present knowledge, in four categories, physical-mechanical, chemical, electrochemical and biological. While all of these techniques have been refined and advanced with respect to just a couple of years ago, some of them such as biological treatment of MIC, or suggestion for use of coatings with nano-size copper flakes, are quite new. An important part of this section focused on cathodic protection and its effect(s) on MIC, helping the reader acknowledge that in the field of MIC there is hardly anything that has not been, or is not currently, under challenge. This, we hope, will once again justify the vital need for more research and more communication among different disciplines of science and engineering with each other and with the industry.

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Chapter 10

(Mathematical) Modelling of MIC by Fuzzy Logic

Abstract For a rather complex phenomenon like MIC that not only involves the interaction between lifeless elements of electrochemistry but does also involve the activity of living things such as bacteria, it may seem too ambitious a target to be able to define a predicatable model based on mathematics. Fuzzy logic and calculations have the capability for this purpose and in this chapter we present one example of application fuzzy logic to describe/predict MIC.

Keywords MIC models · Fuzzy logic and calculations · Carbon steel-SRB

10.1 Introduction

Modelling in itself is an important issue. When we look at the four principles of “Corrosion knowledge Management” (Chap. 3, “Non-technical Mitigation of Corrosion: Corrosion Knowledge Management), we see that modelling is one of these principles.

But why can modelling be so important? If we define modelling as an imitation of reality, it becomes evident that when we cannot have full access to describe a reality, we need to make “something” that will resemble it “to some extent”. This “something” is the model itself and the “to some extent” is another way of saying that all models do suffer from intrinsic drawback of not being completely the reality itself.

Use of models is necessary for us to be able to not only better understand the present state of a system but also to predict how it may behave in the future. This chapter will briefly focus on the application of fuzzy logic as a powerful tool to construct mathematical models of MIC.

10.2 MIC Models

When it comes to MIC, two types of modelling can be recognised:

1. Bacteria-Specific Models

- 1.1 “Melchers” Model
- 1.2 “Gu” Model
- 1.3 Maxwell-Pots Model

2. Process-Specific Models

- 2.1 “Linear microbial Corrosion rate” model
- 2.2 Checworks Predictive Model (CW)
- 2.3 Union Electric Callaway MIC index (Ue)
- 2.4 Lutey/Stein MIC index (L/S)
- 2.5 MIC risk factor model
- 2.6 Javaherdashti MIC risk model

We have explained about these models elsewhere (Javaherdashti et al. 2013) and the references are given there. Of these models, some are not mathematical at all, namely “Melchers” or “Gu” model. But models such as those given as “Process-Specific Models” have a majority of mathematical models, as the names themselves can explain for them. The examples of these models can be further extended, for example the mathematical model (Ahammad et al. 2011), proposed by Ziauddin Ahammad et al. that describes the interactive action of SRB and methanogens can be classified as a bacteria-specific model whereas the mode proposed by Salek et al. (2011) is more a process-specific model that elucidates the corrosive effect of biofilm and its corrosion accelerating effect. However, all these models are based on simple maths applied into a framework of microbiology–electrochemistry. Otherwise, all of these models have two common features:

1. They rely on a chemical–microbiological platform,
2. They have conventional mathematics in the sense that conditions for the model to be true either exist or not. In other words, parameters of the model are assumed to be “static” not “dynamic” with time.

However, natural systems are not static, they change in time and the best example for that is the dynamic nature of biofilm construction and deconstruction cycle. We need mathematics that will take into consideration the “grey” nature of MIC processes without assuming it totally “black” or “white”.

The best means to achieve a model that is studying the impact of varying factors in a given parameter is fuzzy calculations/logic. There are millions of documents, including papers, books, conference papers, etc. written and is still being written on the subject of fuzzy logics and fuzzy calculations and we have used them in many of our previous publications (Javaherdashti et al. 2012, 2004, 2000a 2000b). We will briefly explain the general guidelines that may be used to apply fuzzy logics and calculations for MIC considerations.

10.3 Fuzzy Calculations

The very nature of processes involved in MIC dictates that they are not of the type we could have otherwise called as “binary” in the sense being totally false (having a value of “0”) or totally true (a value of “1”). In fact, when one looks at the physical as well as chemical properties of both the corrosive environment and the vulnerable material in the context of microbial corrosion, one cannot help but think of an artistic work by “Jackson Pollock”: on the surface, chaotic but deep down, of its own order.

More or less the same “fuzzy-ness” is ruling the material–environment mutual relationship (See Fig. 5.1, in Chap. 5 “How Does a System Become Vulnerable to MIC?”).

How fuzzy logic and calculations may work in relation to MIC? In fact it is no different from any other applications of fuzzy logic: you have a set of parameters (parameters of interest) that you want to know how close they can be to the members of another set of parameters (target parameters). In fact, you try to find a “ranking function” that would tell you how close the parameters of interest will be to the target parameters. The “ranking function” may alternatively be called as the “membership function”, Fig. 10.1.

The way we can apply fuzzy logic/calculations into any MIC problem can be described in the same way that has been conceptually shown in Fig. 10.1: we can define a set of parameters and then define a membership function (F , in Fig. 10.1) so that it will measure how close (that is, with what probability) the set of interest and its elements can be matched with the target set elements. More details of basic concepts of fuzzy logic are given in many publications, including one of our works (Javaherdashti 2000b).

Below we will give an example of how fuzzy logic can be applied in dealing with engineering problems with a background in microbial corrosion.

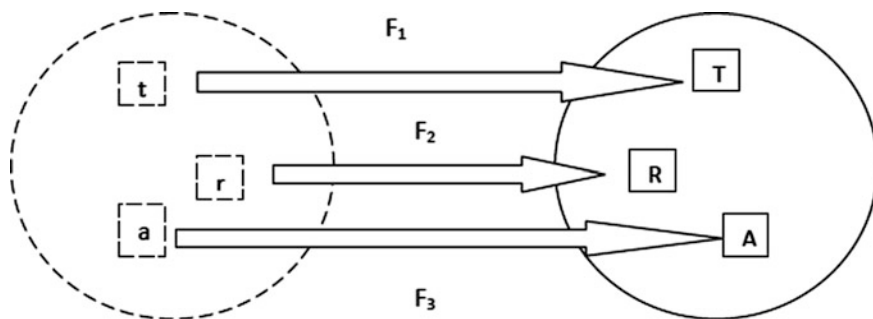


Fig. 10.1 Between two “interest” and “target” sets, three parameters are linked. Each “F” shows how close a member of the interest parameters set (*dashed line*) can be matched with its corresponding element in the target set (*solid line*)

10.4 Fuzzy Modelling of Microbial and Non-microbial Corrosion of Carbon Steel in a Post-cracked Stage in Reinforced Concrete Structures by Their Open Circuit Potential Patterns

An essential component of Reinforced Concrete (RC), steel, has been reported to have a global production magnitude of 5.8×10^8 ton/year where about 10 % of that goes to RC. Among all causes of progressive deterioration and corrosion, it has been observed that biodeterioration of structural materials may contribute significantly to the continued loss of capacity of some structures located in aggressive environments; for example, in sewer pipes, sulphur-oxidising bacteria can contribute to corrosion rates of up to 1 cm/year. Microbial corrosion of steels and mainly carbon steels which are the metallic phase of any RC structure was a known phenomenon since early 1930s (Ribas Silva and Pinheiro 2007) Sulphate-reducing bacteria (SRB) are known for their corrosive impact on almost all engineering materials, metallic or non-metallic and especially concrete structures, probably through their association with other micro-organisms such as sulphur-oxidising bacteria. There is tremendous amount of research about microbial corrosion in general and SRB in particular. When RC concrete structures are cracked and the steel rebar is exposed to the surrounding environment, SRB can be increased inside the bulk of the concrete composite and thus enhance the corrosion of the rebar. In the context of this section of our book, we will be exclusively looking at the corrosion of the steel rebar, mainly by sulphate-reducing bacteria (SRB). The obvious reason is that when the steel phase in an RC structure fails, the whole integrity of the structure will be jeopardised. In addition to that, as the interaction between the bacteria and the material is of critical importance and very complicated, fuzzy logic is used to model this relationship. The significance of fuzzy logic in mathematical modelling of many corrosion-related complex issues is a known matter (Najjaran et al. 2004; Moura et al. 2008).

10.4.1 Basic Concepts

10.4.1.1 The Main Assumption of the Model

The initiation time of reinforcement corrosion depends highly on the diffusion coefficient and on the critical chloride ion threshold, which is a property of the material. Apart from biodeterioration, diffusion increases with water–cement ratio and temperature. The corrosion of reinforcement results in an expansion of corrosion products, which exceeds the tensile strength of concrete, causing cracking. Figure 10.2 illustrates Tuutti’s model where the process of corrosion-induced cracking is divided into two stages: (1) crack initiation and (2) crack propagation.

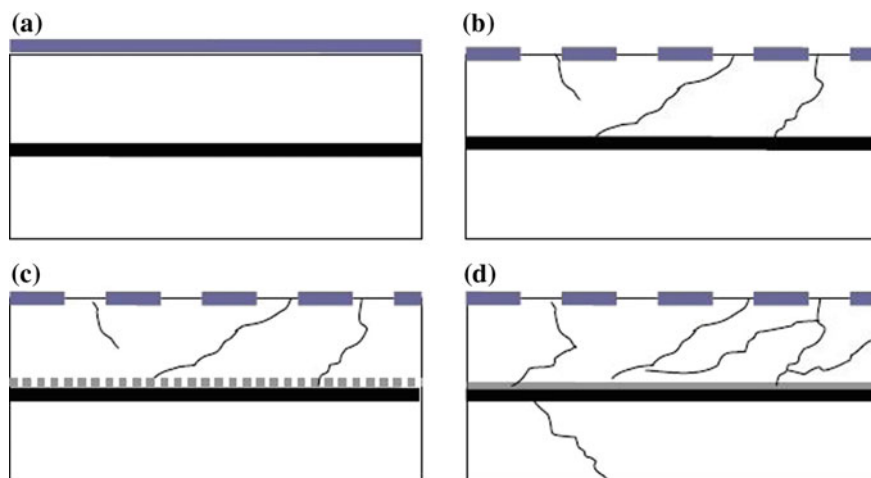


Fig. 10.2 Schematic presentation of Tuutti's model for crack initiation and propagation in RC structures

Figure 10.2 schematically shows a possible scenario of reinforced concrete structures: due to high pH of the concrete surface, the structure is sound and without crack (A) but during course of time, due to some “external factors” the outer surface of the concrete becomes conditioned as to allow cracks to develop internally (B). As the cracks develop, water ingress from outside can find its way deep into the reinforced metallic phase (C). Under these circumstances rust is developed. The developed corrosion products (rust) in physical terms will need more space that cannot be accommodated by the gap between the metallic phase and the concrete around it. The end result is that due to the internal tensile stresses thus produced, the non-metallic phase fails and cracks, thus allowing more water ingress through increasing the number of capillaries and cracks.

Crack initiation is defined by the time for which cracks of a certain width are formed. The value for the limiting crack width at the end of the crack propagation phase depends on the limit state considered. Sakai et al. (1995) defined the limit crack width as 0.3–0.4 mm for durability limit states and ACI-209 (ACI 1978) suggests a value of 0.8 mm for serviceability (aesthetics) requirements.

Main assumption of the model is that the concrete has already been cracked so that water (and micro-organism) ingress is already taking place. The justification for this fundamental assumption is that when the concrete is cracked, some organism's ingress through cracks generating tensile stresses that deteriorate the concrete by increasing the crack size and concrete porosity. It must be noted that the water absorbed into the concrete via cracks not only acts as a highly conductive electrolyte to let electrochemical process of corrosion take place, but it can also act as a good habitat for living micro-organisms that may corrode the RC structure very rapidly. The combined action of micro-organisms and the expansive pressures from

steel oxidation increase the concrete cracking rate, spalling and delamination. The significance of this assumption is that the model is confined to stages where the concrete “sheath” around the carbon steel rebar is no longer functional in inducing alkalinity and thus passivation due to crack initiation and water ingress into the concrete.

10.4.2 *Environment Versus Material*

When it comes to corrosion, two scenarios can be suggested:

- (a) Suitable Environment
- (b) Susceptible Material.

A suitable environment can be defined as an environment in which corrosion is favoured. A good example of such a suitable environment is seawater (synthetic or natural).

When defined as per microbial corrosion, a suitable environment is an environment in which “biofilm” formation is favoured. Biofilms are matrix-enclosed bacterial population’s adherent to each other and/or to surfaces or interfaces (Costerton et al. 1995) and they are the main cause of inducing corrosion. Alternatively, such an environment can also be called as a “biotic” environment. Examples of such suitable biotic environments are natural environments such as seawater or artificial environments such as laboratory-made broths where necessary nutrients for growing micro-organisms are made up. The abiotic environments, on the other hand, are also the control environment that mimics the biotic environments except having micro-organisms so that only the contribution of the micro-organisms will be measured by the biotic environment. Susceptible material is the one which is prone to undergo corrosion and in case of MIC, a materials on which biofilm formation can be developed. (for example, carbon steel). It will be the combination of these two parameters that will increase the likelihood of corrosion and MIC. In other words, there can be three probabilities (The underlined phrases are fuzzy concepts):

- Probability (1) likelihood of corrosion is relatively high if both suitable environment and susceptible material exist, such as carbon steel in seawater,
- Probability (2) likelihood of corrosion is relatively low if either suitable environment or susceptible material exists, such as stainless steel in seawater,
- Probability (3) likelihood of corrosion is too low if neither suitable environment nor susceptible material exists, such as titanium alloy in an alkaline environment

Obviously, the above three probabilities will still hold even if we replace “corrosion” with “microbial corrosion”.

10.4.3 Algorithm and Methodology

For the same susceptible material (carbon steel), three sets are defined as in Eq. (10.1) for two suitable environments, biotic environment (with SRB) and abiotic environment (synthetic seawater):

$$G = \{G_j\}, \quad j = 1, 2, 3, N \quad (10.1)$$

$$S = \{S_i\}, \quad i = 1, 2, 3, M$$

$$A = \{A(i)\}, \quad i = 1, 2, 3, M$$

The set G measures all practically achievable universal properties (mechanical, physical and chemical parameters) of carbon steel in biotic and abiotic environments. Among these parameters are the alloying elements, mechanical properties, crystal structure, electrochemical properties and the like.

The set S measures the required ranges of the above mentioned universal properties of carbon steel in biotic and abiotic environments favouring both non-microbial and microbial corrosion.

The set A , on the other hand, measures the fuzzy probability of each member of the sets G to become a member of the set S . In other words, A would measure the fuzzy possibility of risk of corrosion (both MIC and non-microbial corrosion) within the given universal parameters. Therefore, a membership function $F_{A(i)}$ measures the fuzzy likelihood of a member of G (such as G_i) to become a corresponding member of S (such as S_i). Our aim is to find out a general algorithm that would allow define A .

The condition of using the same susceptible material (carbon steel) in both suitable environments emphasizes the probability (1) where likelihood of corrosion will be relatively high.

Fuzzy membership functions for each set are defined to arrive at composite function of membership functions. By defining the composite functions fuzzy rules to characterise the environment and its important parameters are defined.

A fuzzy method known as “generalisation of compositional rule of inference” is utilised in this study. In this method, a fuzzy rule is transformed into a general form of multi antecedents (inputs) and consequents (outputs). Also *Kosko decomposition method* for decomposing a fuzzy rule and *Mamdani minimum fuzzy implication* will be used.

By utilising *Mamdani minimum fuzzy implication*, the minimum value of membership functions of the given fuzzy sets is calculated. Then, by maximum-minimum technique, first the minimum values of membership functions are calculated. After that, among the selected minimum values, the maximum value is picked up. If in any case, the membership functions of some elements are equal, one of the functions is chosen.

10.4.4 Fuzzy Model

10.4.4.1 Universal Properties of Carbon Steel in Biotic Environment

Assume that there are various U universal features that can favour (microbial) corrosion of carbon steel and not necessarily be related to each other (such as the surface roughness of the metal and the metal's alloying elements). We may assume that for each G_j , there is a feature such as K so that $K = 1, 2, 3, \dots, U$.

When G_j is considered for a special universal feature such as K , it may also be assumed that the parameter will be a random variable such as $x(j, K)$ that obeys a normal distribution function. For any factor that can help corrosion, and especially MIC, and is expressed as S_i , one may assume that $m(i, K)$ and $M(i, K)$ are, respectively, the permissible minimum and maximum thresholds for the universal feature K to be expressed by S_i .

This will be translated as Eq. (10.2) in terms of fuzzy probability function:

$$F_{A(i,K)}(G_j) = \text{Prob}(m(i, K) \leq x(j, K) \leq M(i, K)) \quad (10.2)$$

where $K = 1, 2, 3, \dots, U$, $i = 1, 2, 3, \dots, M$, $j = 1, 2, 3, \dots, N$

Equation (10.2), in terms of a membership function $F_{A(i,k)}(G_j)$, defines the fuzzy likelihood of an existing universal feature such as K from the range of universal features G_j to become an element of S_i . Roughness is, for example, an important feature that can promote MIC by "harbouring" bacteria. Equation (10.2) can then be used to calculate the best membership function value that will allow the roughness of the surface to make it vulnerable and receptive of biofilm formation and thus undergo MIC. Likewise, we can also think of electrochemical features of carbon steel as measured by open circuit potential-that essentially measures corrosion potential-in the biotic environment.

10.4.4.2 Universal Properties of Carbon Steel in Biotic Environment

Assume that there are various V universal features that can favour non-microbial corrosion of carbon steel and not necessarily be related to each other for instance the impact of alloying elements such as decreasing concentration of chromium in grain boundaries due to factors such as carbide formation that will make it possible for the micro-organisms to prefer to colonise the grain boundaries.

We may assume that for each G_j there is a chemical feature such as L so that $L = 1, 2, 3, \dots, V$.

When G_j is considered for a universal feature such as L , it may also be assumed that the parameter will be a random variable such as $x(j, L)$ that obeys a normal distribution function. For any factor, expressed as S_i , that can help biofilm formation and induce microbial corrosion, one may assume that $m(i, L)$ and $M(i, L)$ are, respectively, the

permissible minimum and maximum thresholds for the universal feature L to be expressed by S_i .

Therefore the related membership function, in terms of fuzzy probability function, can be shown as Eq. (10.3):

$$F_{A(i,L)}(G_j) = \text{Prob}(m(i,L) \leq x(j,L) \leq M(i,L)) \quad (10.3)$$

where $L = 1, 2, 3, \dots, V$, $i = 1, 2, 3, \dots, M$, $j = 1, 2, 3, \dots, N$

Equation (10.3), in terms of a membership function $F_{A(i,L)}(G_j)$, defines the fuzzy likelihood of an existing feature such as L from the range of the universal features G_j to become an element of S_i , suitable for non-microbial corrosion of carbon steel.

10.4.5 Fuzzy Composite Functions

Equations (10.2) and (10.3) define how “close” the value of a given universal feature of carbon steel in biotic and abiotic environments can be to the range of risky values to become eligible for MIC and non-microbial corrosion. Now these membership functions need to be defined as a single function in accordance with fuzzy functions. In other words, a composite function $F_{A(i)}$ must be defined as a function of both $F_{A(i,K)}(G_j)$ and $F_{A(i,L)}(G_j)$.

A composite function for each $G_j \in G$ can be defined for the universal features of the carbon steel in biotic and abiotic environments, respectively, as Eqs. (10.4) and (10.5):

$$F_{K(i)}(G_j) = \frac{\text{Max}}{K} \{F_{A(i,K)}G_j\} \quad (10.4)$$

$$F_{L(i)}(G_j) = \frac{\text{Max}}{L} \{F_{A(i,L)}G_j\} \quad (10.5)$$

The Eqs. (10.4) and (10.5) explain that among the membership functions for each set, the maximum values must be picked up. The fuzzy subset $A_{K(i)}$ (a member of G) defined by the membership function $F_{K(i)}(G_j)$ shows that with what (fuzzy) probability a certain range of the universal features of the biotic environment can have the conditions that will render carbon steel prone to microbial corrosion, as indicated by S_i . Likewise, the fuzzy subset $A_{L(i)}$ (a member of G) defined by the membership function $F_{L(i)}(G_j)$ shows that with what (fuzzy) probability a certain range of the universal features of the abiotic environment can have the conditions that will render carbon steel prone to non-microbial corrosion, indicated by S_i . It must be noted that the values of both $F_{K(i)}(G_j)$ and $F_{L(i)}(G_j)$ can be assumed to be not arbitrary variables which are independent of each other.

Equation (10.6) defines the fuzzy membership function, $F_{A(i)}$, for the fuzzy subset $A(i)$ (belonging to A) in such a way that it can measure the fuzzy possibility, S_i (belonging to S) of a combined range of universal features G_j (belonging to G) for becoming vulnerable to the value necessary for MIC and non-microbial corrosion.

Assuming $G_j \in G$:

$$F_{A(i)}G = \begin{cases} \text{If } \max\{F_{K(i)}G_j, F_{L(i)}G_j\} = 0. & \text{Then } 0 \\ \text{If } \max\{F_{K(i)}G_j, F_{L(i)}G_j\} = 0. & \text{Then } \gamma_{\text{Bio}}F_{K(i)}G_j + \gamma_{\text{Abio}}F_{L(i)}G_j \end{cases} \quad (10.6)$$

where $\gamma_{\text{Bio}} + \gamma_{\text{Abio}} = 1$, $\gamma_{\text{Bio}}, \gamma_{\text{Abio}} \leq 1$.

Equation (10.6) addresses the probability for carbon steel in biotic environment to microbial corrosion (MIC) and in abiotic environment to non-microbial corrosion in terms of coefficients (weights) γ_{Bio} and γ_{Abio} .

Obviously, as the tests will be done in two separate environments, each γ value must be taken for that particular environment. Therefore, when the biotic environment is being tested, $\gamma_{\text{Abio}} = 0$ and likewise, when the abiotic environments is being tested, $\gamma_{\text{Bio}} = 0$. When the γ values for each environment is determined, the comparing them with each other can result in three fuzzy possibilities for a susceptible material in two suitable environments:

- Fuzzy Possibility 1 $\gamma_{\text{Bio}} > \gamma_{\text{Abio}}$ meaning that carbon steel in biotic environment is more susceptible(less resistant) to corrosion in comparison with abiotic environment. Therefore MIC of carbon steel is more likely,
- Fuzzy Possibility 2 $\gamma_{\text{Bio}} < \gamma_{\text{Abio}}$ meaning that carbon steel in biotic environment is less susceptible (more resistant) to corrosion in comparison with abiotic environment. Therefore MIC of carbon steel is less likely,
- Fuzzy Possibility 3 $\gamma_{\text{Bio}} = \gamma_{\text{Abio}}$ meaning that there will be no preference in the corrosion behaviour of carbon steel in either biotic or abiotic environments

γ can be arbitrarily defined as a dimensionless value, $P_{\text{Mean}}/P_{\text{Max}}$, Eq. (10.7):

$$\gamma = [P_{\text{Max}} / P_{\text{Mean}}] \quad (10.7)$$

Where P_{Mean} is the average value of corrosion potential (in mV) of carbon steel in a given environment and P_{Max} is maximum value of corrosion potential (in mV) of carbon steel in that given environment.

10.4.6 Validation

10.4.6.1 Experimentation

Susceptible Material

As the susceptible material carbon steel with the following universal features were selected.

Chemical Composition

The chemical composition of the carbon steel samples that were used for the experimental purposes in this study is given in Table 10.1:

Suitable Environments

Abiotic Environment

As mentioned earlier, in all types of experiments related to microbial corrosion, a control environment is used that in essence, in its chemistry it is similar to the main biotic environment except the target micro-organism(s). Therefore, synthetic seawater test medium was used as abiotic medium. The synthetic seawater used in these series of experiments was prepared as 35 g/l NaCl solution (3.5 % NaCl solution wt%/wt%) whose pH had been adjusted to 8.20 by using 0.1 N NaOH solution.

Biotic Environment

The main media supporting the growth of the corrosion-related bacteria contained 35 g/l of NaCl added to the ingredients listed in Table 10.2 and the pH of the medium before autoclaving was adjusted to 8.20 using 0.1 N NaOH solution. After autoclaving the measured pH was ≥ 7.5 .

Bacterial Cultures

The sulphate-reducing axenic (i.e. single type) culture was isolated from a sub-culture taken from a muddy marine sediment taken from a depth of 14 m. The growth was

Table 10.1 Chemical composition of the carbon steel (as received from the manufacturer)

Element	C	Cu	Al	Nb	V	Ti	P	Mn	Si	S	Cr	Mo	Ni
wt%	0.25	0.50	0.15	0.01	0.03	0.04	0.05	1.6	0.4	0.04	0.3	0.1	0.5

Table 10.2 Composition of postgate B medium

Chemical	g/l of distilled water
K ₂ HPO ₄	0.5
NH ₄ Cl	1.0
CaSO ₄ · 2H ₂ O	1.3
MgSO ₄ · 7H ₂ O	2.0
Lactic acid (88 %)	2.7
Yeast extract	5.0

characterised by both hydrogen sulphide odour and blackening of the test tube. The bacterium was determined by its morphology to be a *Desulfovibrio* sp.

Test Procedure

To evaluate the performance of carbon steel in biotic and abiotic environments, it was decided to perform open circuit potential (OCP) tests on carbon steel in both environments. OCP is a “safe” electrochemical method, contrary to a majority of other methods (See Chap. 6, Sect. 6.3.3).

To determine OCP of the steel in the biotic and abiotic environments, a piece of the steel ($\sim 1 \times 1 \text{ cm}^2$) was placed in resin with a wire spot welded at its back. To protect the wire from the media, it was placed within a glass tube. The potential change of the electrode was recorded with respect to a non-leaking saturated Ag/AgCl reference electrode in a flask with an approximate volume of $\sim 700 \text{ ml}$ via a data taker. The working electrode and Ag/AgCl reference electrodes were connected to a voltmeter that recorded potential changes each 10 min and feeds the data into a data taker. Before each test, conductivity of the working electrode was checked by a voltmeter. Both the steel electrode and the reference electrode were sterilised by autoclaving. All metallic and glass components of the bioreactor were autoclaved at 121 °C for 15 min. Under sterile flow of air, the bioreactor was assembled and 1 ml of the isolated SRB culture was inoculated. Before inoculation, the inoculum was checked to be assured about viability of the micro-organisms. Open circuit potential under anaerobic conditions (for SRB) was measured by filling the OCP test flask with the inoculated medium almost intact (to drive away the air) and then placing a layer of sterile paraffin oil on the surface to prevent the entrance of air.

10.4.7 Results and Discussion

Figure 10.3 shows the OCP of carbon steel in biotic(SRB culture) and abiotic (synthetic seawater) environments. It is seen from Fig. 10.3 is that the carbon steel in abiotic environment shows a rather smooth pattern with a potential around -500 mV versus Ag/AgCl reference (RE) electrode. Figure 10.2 also illustrates how OCP of the carbon steel is changing in SRB-containing biotic environment. As

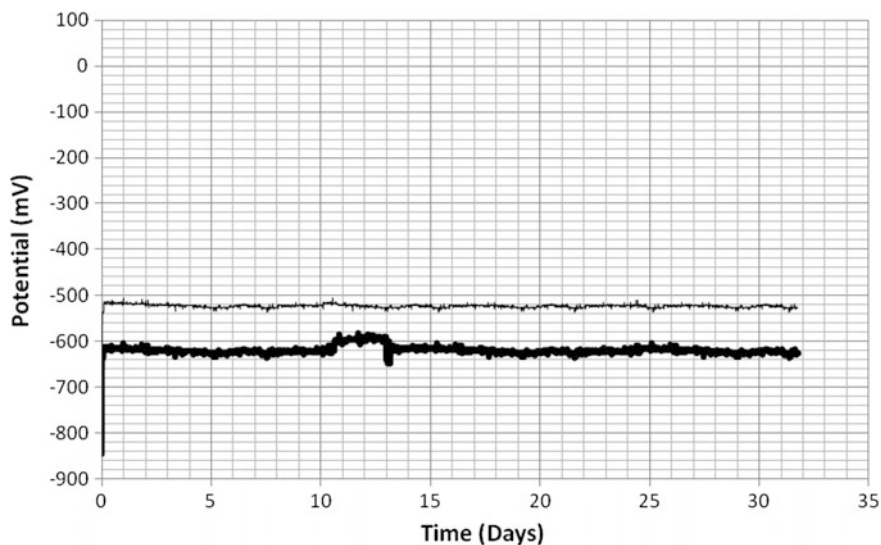


Fig. 10.3 Open circuit potential of carbon steel in SRB-containing biotic (*thin line*) and abiotic (*thick line*) synthetic seawater environments

it appears, fluctuations in the potential show “noble” peaks as high as -580 mV to “active” peaks of about -840 mV in the biotic environment. The OCP remains active at around -600 mV for about 3 days and then rises up to potentials around -580 mV. This pattern of decreasing and increasing the potential is repeated afterwards where after about 21 days, the potential decreases with repeating the same fluctuating pattern of potentials.

The OCP pattern, from time to time, manifests itself in the form of “jumps”, especially in the biotic environment. While at this stage nothing can be said about exact mechanism(s) that may be involved in producing such serrated pattern for OCP data, these fluctuations of potential are a well-known yet not fully explained phenomenon when OCP is used in microbial environments. Therefore, a possibility for continuous build-up and breakdown of protective films, such as ferric oxide film or in biotic environments, a biofilm formation–destruction cycle, should not be ruled out. The fluctuations of potential can be interpreted as mixed effect of bacterial activity and purely chemical effects of some compounds that for example in the case of SRB, could be sulphide. Table 10.3 summarises the maximum and average (mean) values of potentials in biotic and abiotic environments.

However, the cause of these fluctuations in the observed OCP potentials is of secondary importance. For the validation of the fuzzy model we need to know the γ values. Based on the above potentials, the γ values for biotic (γ_{Bio}) and for abiotic environments (γ_{Abio}), respectively, will be as follows (Eqs. (10.8) and (10.9)):

Table 10.3 OCP (mV) for the susceptible material (carbon steel) in the suitable environments containing SRB (biotic environment) and synthetic sea water(abiotic environment)

Environment	Maximum potential (mV)	Mean potential (mV)
Biotic	-582	-619.41
Abiotic	-504	-522.30

$$\gamma_{\text{Bio}} = 0.94 \quad (10.8)$$

$$\gamma_{\text{Abio}} = 0.96 \quad (10.9)$$

As seen from Eqs. (10.8) and (10.9), it is the fuzzy possibility $\gamma(\gamma_{\text{Bio}} = \gamma_{\text{Abio}})$ that is applicable. In other words, there is no preference in the corrosion behaviour of carbon steel in both biotic and abiotic environments. This suggests that under these conditions, carbon steel can be corroded with almost the same possibility of being exposed to sulphate-reducing bacteria or synthetic seawater, at least under the testing conditions.

Perhaps an immediate practical outcome of these results is that the existence and activity of SRB could be as much important as the effect of chlorides. This will mean that the deterioration of RC structure must be monitored very carefully not to cross to post-crack initiation stage and let the structure crack so that the bulk of the structure and the steel rebar are exposed to the corrosive environments, either biotic or abiotic. Therefore,

- Fuzzy logic has the capability of predicting the behaviour of steel rebar inside RC concrete structures,
- Biotic environment containing SRB will have the same effect on the corrosion of carbon steel as abiotic environments containing chlorides, implying that the severity of corrosion of carbon steel can in biotic environments be as severe as abiotic environments.

10.5 Conclusions

Fuzzy logic and Fuzzy calculations can be a powerful tool to tackle MIC modelling problems. The main reason for that is that processes involved in any MIC case are too complicated to be explained by “conventional” methods only. Mathematical modelling is, and must always be, an integral part of any MIC research to allow to not only understand the current situation of a system but predict how it will look like in the future should the conditions vary within certain framework.

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Chapter 11

Diplomacy of MIC Treatment

Abstract If we define engineering importance of any issue in terms of its risk and its cost, any corrosion problem can be looked at from two perspectives: an engineering approach that takes mainly “risk of corrosion” into consideration and a management approach that cares more about the “cost of corrosion” -both economical and ecological costs. This chapter will address the link between these two approaches with an emphasis on MIC.

Keywords Microbial corrosion knowledge management (MCKM) • Microbial corrosion management (MCM) • Future studies • Management strategies

11.1 Introduction

I have been lecturing about MIC all around the world for various industries. An experience of teaching this subject for more than many hours to many technology and research professionals has given me invaluable feedbacks. A question that I am frequently being asked by some is the link between Chaps. 3 and 9: at first glance, Chap. 9 is more “technical” whereas Chap. 3, nontechnical mitigation of corrosion may seem to be of no relevance to the rest of the book.

In this chapter, I am determined to clear the organic link between “microbial” corrosion knowledge management (MCKM) and “microbial” corrosion management (MCM). Obviously, we will be talking about non-corrosion management (CM) and corrosion knowledge management (CKM) in the context of microbial corrosion.

I have chosen the title of this chapter as “Diplomacy” because I believe that the essence of any engineering treatment must be smart use of resources. Spending resources without having a plan in mind or working through trial and error is not smart, it is not diplomatic: it is just a waste of time and money.

In this chapter, I will concentrate on both MCKM and MCM approaches and their interrelated link with each other.

11.2 MCKM and MCM

Any corrosion problem can be looked at from two viewpoints: a technical side (Engineering) and a nontechnical side (Managerial). Obviously, the technical side will be more concerned about the technicality: in the context of MIC for example, this can be the best practice for biocide injection, material selection, feasibility of CP on MIC and the like. On the managerial side, however, the MIC problem is looked at from an strategic point of view: a manager would ask if he has got all his resources oriented towards controlling MIC? Are his engineers well informed about MIC? Is their knowledge updated? Does the company have consultants with updated knowledge about MIC treatment? and all these things. Next section can be taken as a more detailed extension of Chap. 9.

11.2.1 *Microbial Corrosion Management (MCM)*

From 2001 when, apparently for the first time, the term “Corrosion Management” was created in a document by CAPCIS Ltd.¹ till very recent document in 2016 by NACE² the essence of corrosion management has always been one thing: dealing with the risk of corrosion.

As all CM systems would also recommend, the first step in managing the risk of corrosion, in general, and MIC, in particular, will be understanding the threats. In other words, one has to be prepared about what threats could damage one’s system. The rule of thumb here is not to mix up “Risk” with “likelihood”: The fact that no MIC has not happened in your system despite your system potentially susceptible to it (Likelihood), does not mean that your system is immune to MIC for sure (Risk).³ The confusion between Risk and Likelihood is so widespread that it is worth of dealing with it before any mitigation/prevention strategy can be applied. In addition

¹Review of corrosion management for offshore oil and gas processing. Offshore Technology Reports 2001/044, Crown Copyright 2001.

²The International Measures of Prevention, Application, and Economics of Corrosion Technologies study (IMPACT). NACE, March 2016.

³As any HSE (Health, safety, Environment) officer would tell us, the Risk of any hazard is the product (function) of two factors: likelihood of that hazard and its consequences. Therefore, even if a certain hazard may have a low likelihood for happening, if its associated consequences are critical (or at that level), its Risk is reported as being “Very High”. An example is the Risk factor in running a nuclear power plant: although with today’s advancements, running a power plant as such is safe enough to make its potential hazards almost unlikely, if anything goes wrong the severity of consequences will be so important that anything of hazardous nature in such plants is treated as with high level of care because its potential high or very high Risk factor. While this has become a routine with industries such as nuclear due to its public sensitivity, corrosion and particularly has not yet been regarded as a serious Risk in many instances: what happens, unfortunately, in practice in many cases is that the engineer in charge assumes that not having a case of MIC so far, has guaranteed his system against MIC for good.

to what we said in details in Chaps. 2, 6 and 9, the following must also be taken into consideration when the case of corrosion “may seem” to be MIC related, this is what happens most of the time.

11.2.1.1 Strategies that Can Be Suggested to Handle MIC

It may seem so obvious but the very first step in treatment of MIC in a system is a two step process:

- Step 1: The system and its working conditions must render it susceptible to MIC,
- Step 2: The case is indeed MIC related.

Any equipment that undergoes corrosion must satisfy the above two-step criteria so that it can be assured that the case is indeed MIC. Below we will give some examples that may be useful in this context.

The above-mentioned strategies are very important because if not applied carefully, they may result in mistreatment of the case and this, in addition to exacerbating the case, would also disappoint any future attempts to deal with MIC treatment even if the case of corrosion is indeed MIC-related.

“Experience Is the Mother of Science”

What we mean here can be best described by an example about Biofouling. Biofouling could be a severe problem in many water treatment systems, especially in strainers, Fig. 11.1. The very first step for Biofouling to actually form and mature, is that biofilm formation is facilitated through a series of structures, namely a condition film (molecular fouling), a film containing bacteria, microalgae and fungi (Microfouling) to be followed by a film that contains macroalgae and vertebrates (Macrofouling).⁴

Another example can be heat exchangers: in these equipment, Biofouling will cause many problems such as, but not limited to, heat-transfer problems: Biofouling can cause the “leaving temperature difference” (LTD) to increase and thus have a diverse effect on the energy consumption efficiency of the cooling system; it has been quoted that 1 °C increase in LTD will cause roughly 3 % energy consumption increase in the cooling system.⁵ This impact has been schematically shown in Fig. 11.2.

As it can be seen for both the examples shown above (heat exchanger and strainer), the system’s working conditions actually makes it susceptible to experience biofouling which itself is in fact a result of biofilm formation. Thus, looking

⁴Oug E, Tobiesen A, Mortensen TC (2003) Marine growth in cooling plant at drilling installation. Nigeria, Section 1.3, Report SNO-4641-2003 p 6.

⁵Nagai N, Morita A, Tsunoda K, Emori K (2013) New biofouling control program for open recirculating cooling water system with refrigerator/chiller to reduce operating and maintenance costs of the system. NACE, USA.

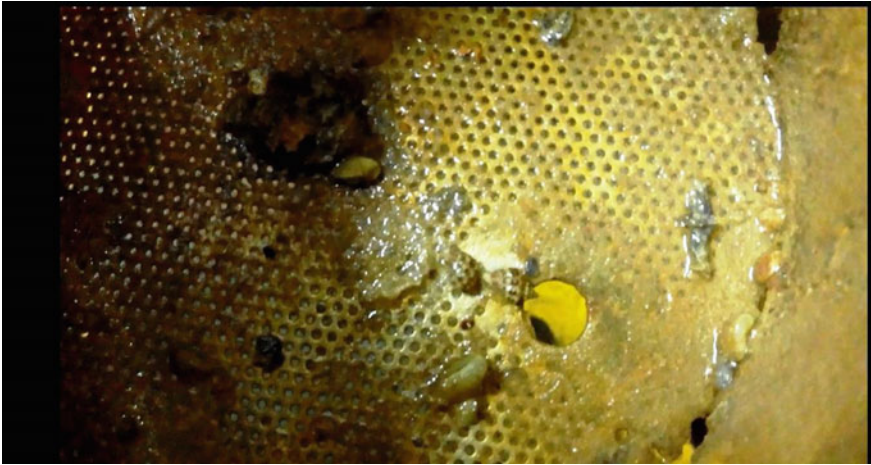


Fig. 11.1 Biofouling as formed on an off-shore platform strainer (Courtesy: Dr. Reza Javaherdashti)

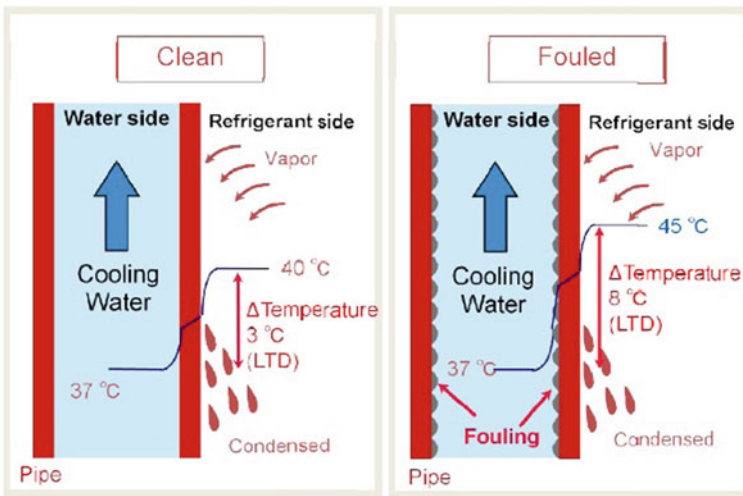


Fig. 11.2 A comparison of LTD in a clean and a fouled Heat Exchanger (see footnote 5) © NACE International 2013

for MIC as a culprit in, say, the fire-side of a boiler, is not a good choice for explaining the cause of corrosion.

Step 2 is even more important: as we briefly mentioned in Sect. 6.2.2. (Pit morphology), moving just by the appearance of the failure to name the corrosion mechanism that may have caused it is an absolute error. Figure 11.3 shows an appearance (mounds) that are very similar to microbial mounds generated by iron

oxidising bacteria, yet it was not MIC but oxygen attack that had caused that appearance.

In the summer of 2011, this author was called into investigate the probable cause of failure in a water pipeline made up of carbon steel. The pipe had no lining, the pH was neutral, there was no CP on the pipe and, as the client reported, there has been a history of finding *Pseudomonas* (a fast biofilm-former) in the line. Within the corrosion products were black-coloured products. Based on the colour of the corrosion products and the history of the system, it had been deduced that the cause of the failure was by microbial corrosion, most probably by SRB.

Obviously, the system was indeed vulnerable to MIC (Step 1). One could easily see that by considering the working conditions, the susceptible material of the pipe and its history of being vulnerable to harbouring CRB. But was it really a case of MIC?

As we advised in Chap. 6 (Fig. 6.6), it is not safe to assume right from the beginning that the case of corrosion presented to us is MIC. It is always logical to assume the opposite, that the case is not MIC-related and try to work out a scenario that would explain the case of corrosion in purely non-MIC terms. Only after failure in explaining the case by not involving MIC, it is safe to consider MIC as a probable scenario.

We followed the same path: obviously the black product could be something resulting from the corrosion process and the best nominee for that was FeS. Although even if it was iron sulphide, we could not assume safely that it had been generated by SRB as a by-product of its corrosive action, still it could have been a clue for us.⁶ We applied the acid test (diluted HCl) to find out if the black-coloured deposit was indeed iron sulphide. The evidence of iron sulphide will be a characteristic rotten egg smell (H₂S). We did not smell the rotten egg scent. The other option was magnetite (Fe₃O₄). This type of iron oxide is magnetic and has also a black colour. We dried the deposit and used a magnet and that was it! Magnetite. This told us that (1) the corrosion product was not iron sulphide and (2) it could have been resulted from a poor oxygen control regime and most probably not MIC.

11.2.2 *Microbial Corrosion Knowledge Management (MCKM)*

As we mentioned in detail in Chap. 3, any corrosion problem has two faces: an engineering face and a managerial face. MCKM is a powerful tool that will allow

⁶There are seven types of iron sulphide and one type of it is magnetic (Fe₃S₄). See: T.S. Khan, M.S. Al-Shehhi, "Review of black powder in gas pipelines—an industrial perspective", *Journal of Natural Gas Science and Engineering* Vol. 25, pp. 66–76, July 2015. Having this magnetic iron sulphide compound in may mean that mechanical removal of it (by pigging, for example) could be a tedious task. In these cases, it is better to first apply a chemical treatment to dislodge and dissolve the scale and then apply mechanical removal.

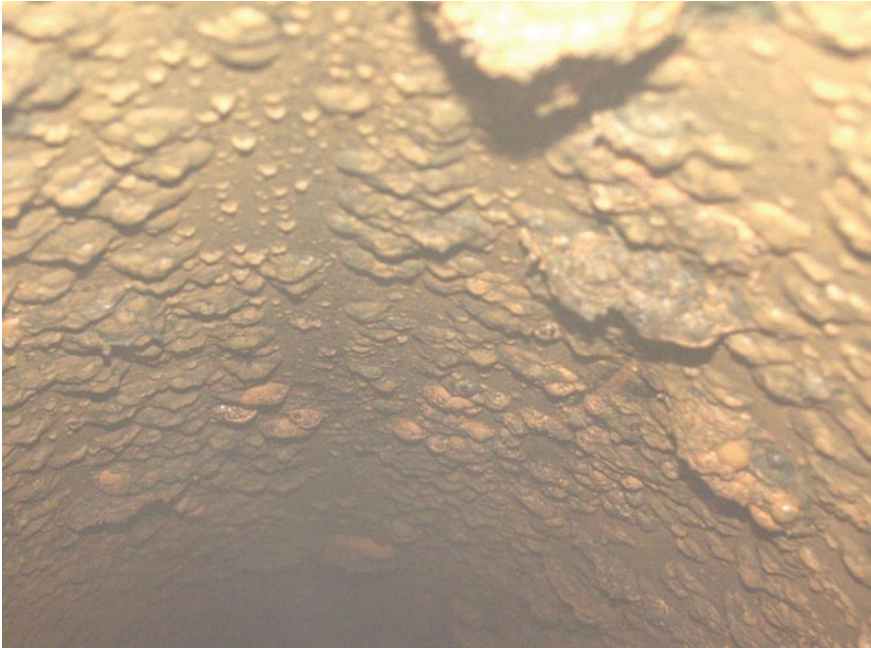


Fig. 11.3 Oxygen attack appearance in a water line. The appearance is similar to microbial mounds generated by IOB (Courtesy: Dr. Reza Javaherdashti)

managers and strategists within a company/plant decide on the management of corrosion in the most feasible and pragmatic way.

Good management practice starts with a transition from a “possible future” to a “desired future” via “creative Planning”. We can define “possible” and “desired” futures based on how “good” or “bad” they are for us: a desirable future has more good incidents for us than bad incidents whereas in a possible future, both types of incidents (good and bad) will have an equal possibility for happening,⁷ Fig. 11.4 schematically describes the general management pattern for any company with a plan for being successful based on the possible scenarios of futures.

If good incidents bring us profit, joy and prosperity bad incidents, on the contrary, will be defined with the damage they will impose upon us and the loss that they would make for us. Obviously, a strategist manager (or management team) will be after maximising their profit (good incidents) and minimising the loss (bad incidents).

Further thinking about good and bad incidents may reveal to us that bad incidents themselves are divided into two groups as shown in Fig. 11.5.

⁷Javaherdashti R, Akvan F (2015) On the Link between Future studies and necessity of including corrosion in a desirable future scenario. *Int J Eng Techn Manage Res* 2(4).

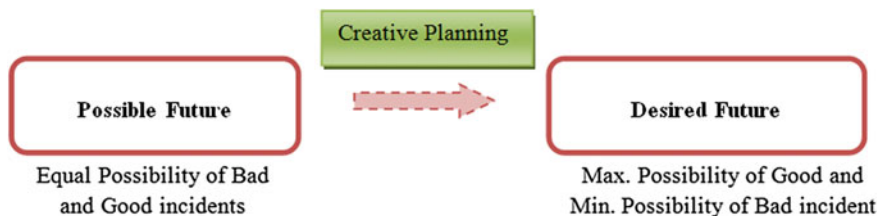


Fig. 11.4 Only those companies can survive the changing pattern of technology that have a clear strategy for transition from a possible future to a desirable future (see footnote 7)

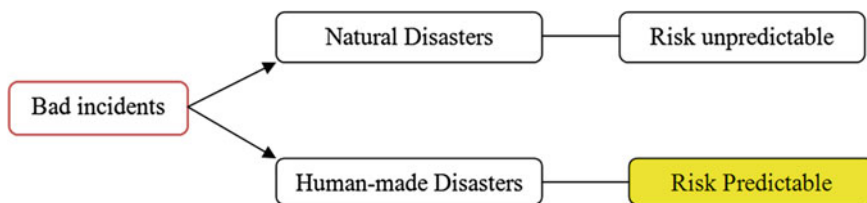


Fig. 11.5 Classification of bad incidents into “natural” and “man-made” disasters (see footnote 7)

While natural disasters such as floods and earthquakes leave us no chance for predicting the risk of their occurring, the risk of a man-made disaster like corrosion is predictable, in fact through our knowledge about monitoring corrosion and measuring its rate, we can say with a good precision that how long will the structure survive by calculating its remaining life.

This is how corrosion must be viewed by the top and middle managers in their plans to move further for achieving highest possible success. They must regard corrosion-and as a matter of fact, microbial corrosion-a bad incident whose risk of occurrence must be minimised should a desired future is to be reached at.

There is no clash between the thermodynamically favoured nature of corrosion and the way we addressed it as man-made. It is a natural process that is only felt in our man-made structures. While corrosion as a natural process is indeed favoured by nature to occur, corrosion as a disaster is the face we see when we face with it in our structures from a pipeline to a bridge, from body implants to air planes and from off-shore platforms to corroded piping of our apartment.

Now that the undeniable role of taking care of corrosion in a management grand plan to embrace a desired future is described, we can turn into Figs. 3.3 and 3.2 in Chap. 3 of this book that related the resources a manager can have with his target(s) via CKM principles. What happens in reality, though, is that a manager only notices the importance of corrosion (and MIC) when he has a deep understanding of both economical and ecological dimensions of the loss that can be imposed on his company should the case of corrosion is only treated as an on-off incident isolated in time and space and not an on-going issue for which a continuous planning is required. In other words, the way it works is that for the manager to be able to

organise his seven resources of budget, training, humanware, R&D, information, energy (motivation) and time to focus on a particular MIC problem, he must first have a sound understanding why MIC is important for him in the first place and this will not happen unless he know what economical and ecological threats he will have to face if he ignores MIC.

Perhaps it is instructive here to give a real life example:⁸ in 1989, a reputable oil exploration company noticed that about 22 % of their 23 km long main subsea pipeline had experienced unusually high corrosion rates in the order of 10 mm per year. Instead of doing a root cause analysis of the problem, they simply did what now has become a routine process: replace it. However within 12 months or so, the replaced section also corroded. So this time the company replaced the whole 23 km. In fact, the company did not replace just 22 % of the line but a huge 122 % of it. Those who work in subsea industry can easily imagine how much money had been wasted in such a “treatment” instead of a “prevention” plan.

While I would like to comment that such disasters have become so rare in number these days, I am afraid to say that it is not true. We still get such disasters here and there, some are echoed in the mass media and some go unnoticed by the public, for many reasons.

11.2.2.1 A Pragmatic Approach Towards MCKM

How can we deal with a microbial corrosion problem as a top manager? This is just impossible and it is so for at least two reasons:

1. As a top manager who is responsible for strategic planning, one has to have a grand plan and not just concentrate on cases. An analogy would be comparing such a top mar with a man who writes the constitutional law for a country: in the constitutional law, you do not mention traffic fines,
2. MIC can never be a one-off issue if it has happened once unless necessary mitigation followed by prevention measures have totally and thoroughly taken care of.

There are six steps in CKM that has be taken by a strategist manager to deal with corrosion. Figure 11.6 shows these steps. As it is been explained in the figure, the very step 1 and 2 will be definition of the corroding system and application a suitable corrosion management (CM) approach. These should not and cannot be carried out by a manger, it is their expected professional approach that a corrosion specialist must do. In other words, it is the duty of a corrosion specialist (or a group of them) to correctly define the corrosion problem, the possible threats to the asset and suggest and apply the best corrosion management technologies to rectify it.

⁸Magot M, Ravot G, Campaignolle X, Ollivier B, Patel BK, Fardeau M-L, Thomas P, Crolet J-L, Garcia J-L (1997) *Dethiosulfovibrio peptidovorans* gen. nov., sp. nov., a new anaerobic, slightly halophilic, thiosulfate-reducing bacterium from corroding offshore oil wells. *Int J Syst Bacteriol* 47 (3):818–824.

Steps 3, 4 and 5 are to be carried out by a manager. In this respect, he must have developed an economical/ecological model of the corrosion cost(s) to his company and re-define and re-arrange the seven managerial resources he has in his possession to achieve the goal of controlling corrosion and its costs. Once again I would like to remind that while the main concern of a corrosion management (CM) approach is controlling the risk of corrosion, main concern of a corrosion knowledge management (CKM) is to control the costs. We will explain Steps 3–5 (managerial share of CKM) in more details below in terms of.

A strategist manager as such needs a grand plan to take care of corrosion, in general and MIC, in particular.⁹ For this aim, he must work out his strategy as the following tasks which are a possible interpretation of Fig. 3.2 in Chap. 3.¹⁰ We will summarise these tasks within steps to be taken as shown in Fig. 11.6.

Task 1. Appreciation of the necessity for having an economical/ecological model for corrosion in your company/plant in place.¹¹ This can alternatively be also called as “Appreciation of the need for “justification” of research in the field of MIC”. For the economical model, we have to determine how corrosion makes the expected depreciation rate faster: any investment must be profitable over time and it is a known fact that all physical assets will lose their value over time too. The rate by which this devaluation occurs can be addressed as “depreciation”. Assuming a certain nominal depreciation rate for the devaluation—ageing of a given structure is quite normal and understanding. The problem starts when corrosion actually increases this rate so that an asset which under its surface value depreciation rate is to go for 30 years and still be profitable, due to corrosion becomes less valuable in, say, a third of this time span. Obviously, this in addition to the costs of repairs and maintenance are amongst the parameters that must be taken very seriously for such a model of corrosion damage. To determine the place of MIC in this economical scheme, one has to be able to identify MIC from other corrosion processes and this will need a well-trained technical personnel as well as having knowledgeable consultants and contractors. To work out, the economical model, the manager has to consider corrosion (and especially MIC) as an “environmental impact” and act accordingly. More about the mutual link between corrosion and environment and

⁹In one of our works, I have shown that in fact it seems that first “non-microbial” corrosion must be taken care of because otherwise, MIC may proceed, See: R. Javaherdashti, “Behaviour of Stainless Steel 316L in a Marine Mixed Culture containing Sulphate Reducing and Iron Reducing Bacteria” Corrosion & Materials, Vol. 36, No. 2, February 2011.

¹⁰Obviously, this is just a recommendation that sounds logical. There can exist other possible ways based on the actual working culture of the company and the innovative and creative way of thinking of the manager himself.

¹¹This may sound like yesterday’s news to some of the readers but an on-line survey that I did on NACE Corrosion Network in 2005, in reply to the question “Is there any official record/report showing economical loss due to corrosion in your company?”, 80 % said “No”.

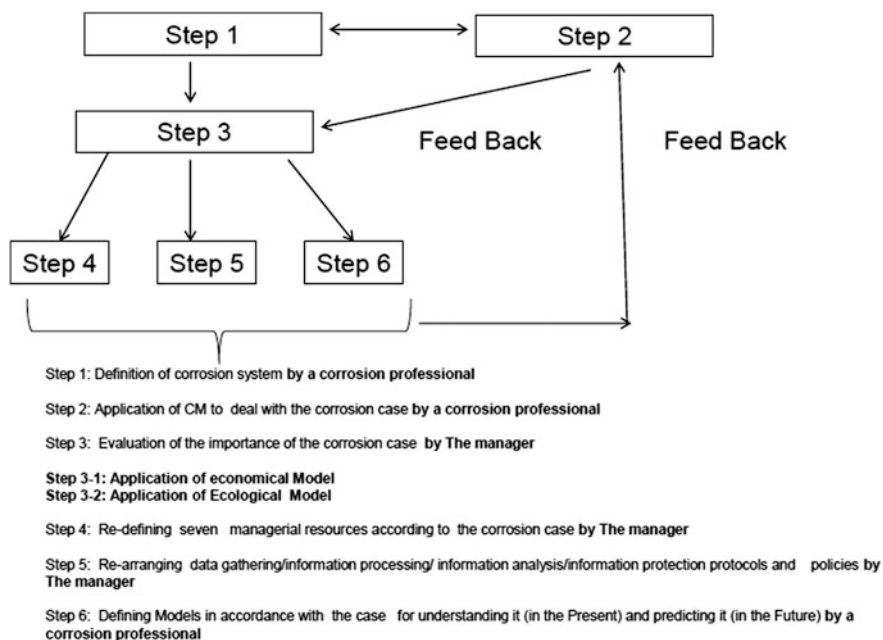


Fig. 11.6 Steps to be taken in a proposed CKM scheme to control corrosion

how this issue must be addressed has been discussed in detailed length elsewhere^{12,13} and will not repeated here

Task 2: Appreciation of the need for establishment of a microbial corrosion research unit within existing R&D plan of the company:

Task 2-1: Specifying applied research areas within the R&D scheme of the company about microbial corrosion mechanisms, its detection and treatment methods and technologies. These research programs must mainly focus on minimising the limitations and maximising the applicability of currently in-use detection and treatment methodologies. Other proposed tasks for such a research scheme within the R&D plan of the company could be:

- Research for new technology/ies/methods to mitigate microbial corrosion such as research on natural biocides, upgrading limitations of culture-independent methods for the identification of CRB,
- Research for materials selection/characterisation in microbial environments encountered within the field of operation of the company (compare the field of operation of a thermal power plant with an off-shore platform)

¹²Javaherdashti R, Nikraz H (2010) A global warning on corrossions and environment: A new look at existing technical and managerial strategies and tactics. VDM, Germany.

¹³Javaherdashti R (2006) Using corrosion management to protect the environment. Mater Perform (MP) 45(6).

- Research into defining best service conditions for the existing infrastructure in terms of coating/lining selection and application,¹⁴ cathodic protection design and application, design optimisation.
- Research on classification and the impact of different types of (indigenous) bacteria on corrosion within the field of operation of the company,

Task four tasks: Organising refreshing courses and workshops with regards to corrosion (in general) and microbial corrosion (in particular) aiming at understanding MIC mechanisms and detection/treatment technologies currently available. The end result must be creating the knowledge/skills required to tackle MIC.

As may have been noticed, Task 2 and Task 3 encompass the “training and research” resources that a Manager can organise and coordinate within a given MCKM scheme.

Task4: While training the personnel is certainly a good way of tackling MIC problems, for immediate needs and also better coordination of activities, it is needed to have the company of MIC experts either as full-time employees or consultants, or even both. Task 4 is what that must be the focus of the department of Human Resources within the company: when an MIC issue has been shown to be of a magnitude worthy of dealing with it company-wide, the true wealth of the company will be its humanware, its employees and consultants. Therefore, care must be given to make the best practice out of this.

The manager has to also come up with plans for upgrading the motivation amongst his employers in terms of increasing their senility towards corrosion and particularly MIC. Financial issues as well as time management are within the domain of critical decision making for such a manager. However important, a manager must never allow mere accounting calculations prevail and tarnish his professional judgement about the Risk of MIC provided that he does have an economical/ecological clue about its importance. Figure 11.6 summarises our proposed interpretation of CKM principles as a roadmap for a top manager who wants to look at MIC problem in his company strategically and not as an on-off fancy issue.

11.3 Conclusion

Corrosion, and for that matter microbial corrosion, should be considered as a critical measure for any company. In transferring from a “Possible Future” scenario to a “Desired Future” one, a manager has to take corrosion in his plant/company/

¹⁴Use of Graphen may be regarded a revolutionary step towards dealing with MIC in terms of coatings, See: Krishnamurthy A, Gadhamshetty V, Mukherjee R, Natarajan B, Eksik O, Shojae SA, Lucca DA, Ren W, Cheng H-M, Koratkar N (2015) Superiority of graphene over polymer coatings for prevention of microbially induced corrosion. *Sci Rep* 5:13858. doi:[10.1038/srep13858](https://doi.org/10.1038/srep13858), Published 09 September 2015.

workplace quite seriously. This can only be achievable through the application of both corrosion management (CM) and corrosion knowledge management (CKM). In this chapter, we tried to give more details on both aspects with a much more emphasis on CKM as applied to microbial corrosion cases (MCKM) in terms of four tasks that a strategic manager must undertake.

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Erratum to: How MIC Is Detected and Recognised?

Erratum to:

Chapter 6 in: R. Javaherdashti, *Microbiologically Influenced Corrosion, Engineering Materials and Processes*, DOI [10.1007/978-3-319-44306-5_6](https://doi.org/10.1007/978-3-319-44306-5_6)

The book was published with incorrect text in Chap. 6 which has been revised now as follows:

In P. 113, Line 340: The paragraph starting with “If we want to compare ...” has been replaced with revised content “If we want to compare the MMM with conventional culture-dependent methods (such as MPN), we can see that while MPN results may not be matched with the risk of MIC, culture-independent methods (q PCR) are both applicable in more convenience to risk-based inspection and assessments and do show a good correlation with the risk of MIC”.

In P. 114, Line 345 in Para 1: The paragraph starting with “Table 6.2” and ending with “these method” has been replaced with revised content “One has to keep this in mind that at the moment all these methods (both culture-based and culture-independent methods) are classified as laboratory methods in the sense that in order to perform them, one has to have both a well-equipped laboratory and trained personnel. This may appear as a disadvantage for those clients who count beans” but one has to observe that the highly precise results that are obtained from MMM tests with regards to MIC risk does compensate the cost spent on these methods.”

The updated original online version for this chapter can be found at [10.1007/978-3-319-44306-5_6](https://doi.org/10.1007/978-3-319-44306-5_6)

R. Javaherdashti (✉)
Perth, Western Australia, Australia
e-mail: Javaherdashti@yahoo.com

Figure 6.8 and its legends have been removed and other figures were renumbered accordingly.

Table 6.2 and its legends have been removed.

Glossary

Anode The electrode at which oxidation occurs, from which the metal ions enter into the solution and the electrons flow away in the external circuit

Cathode The electrode at which reduction occurs, towards which the metal ions in the solution are attracted and the electrons in the external circuit flow

Electrolyte the medium, normally a liquid, containing ions that in an electric field migrate towards (away from) cathode (anode)

Microbial Corrosion Also known as “microbiologically influenced corrosion”, “microbiologically induced corrosion”, “biocorrosion” or “MIC”, refers to an electrochemical corrosion type which is affected by micro-organisms such as certain bacteria. The effect could be accelerating the corrosion rate or decelerating it depending on many factors including the dynamics of biofilms formation, the culture regime and the like

Aerobic Bacteria The bacteria that need oxygen to live

Anaerobic Bacteria The bacteria that can live without oxygen

Facultative Bacteria The type of bacteria that can live either with or without oxygen

Biocide A chemical which is lethal to any living thing such as bacteria

Broad Spectrum Biocide A biocide that can kill as many and as diverse micro-organisms type as possible

Culture A chemical environment (culture medium) designed with certain organic and inorganic materials to support the growth of a certain type of bacteria (or other micro-organisms)

Culture regime In simple terms, the way a culture is refreshed. If the culture is not being refreshed at all, it is called a batch culture. Based on periodic or continuous refreshing, it is called semi-or continuous culture, respectively

Planktonic Bacteria The state at which the bacteria can freely float or swim in a body of water

Sessile Bacteria The state at which the bacteria become motionless after being attached onto a surface.

Mesophilic Bacteria The bacteria that grow best in room temperature

Thermophilic Bacteria The bacteria that grow best at temperatures above 50 °C

SRB The abbreviation for sulphate-reducing bacteria

SOB The abbreviation for sulphur oxidising bacteria

IOB The abbreviation for iron-oxidising bacteria

IRB The abbreviation for iron-reducing bacteria

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