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

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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".

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

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

[3]Scott 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. McCoy[6] 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.

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[4]Guiamet 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.

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

[6]McCoy 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 are[7]

- 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 seels (due to their relatively low work hardening rates) may be used for making these brushes, leaving

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

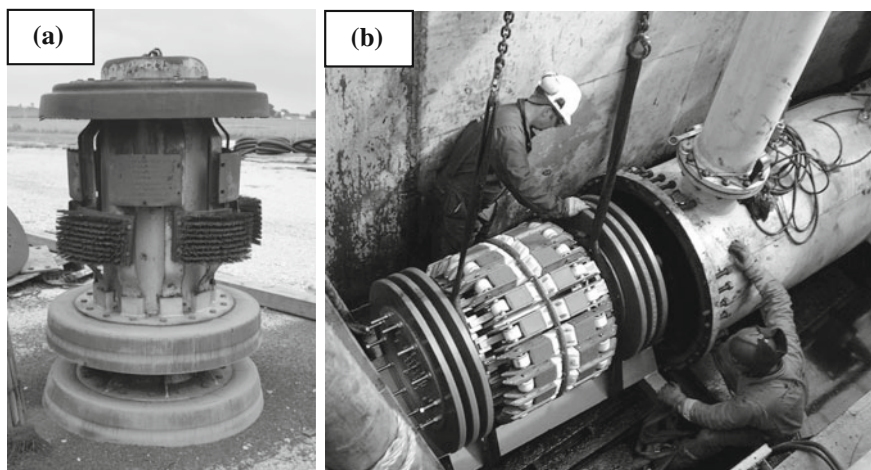[8]Jack TR (2002) Biological corrosion failures. ASM International.

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 steels[9] (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

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

[10]King 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.

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

[12]See 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)

8 μm
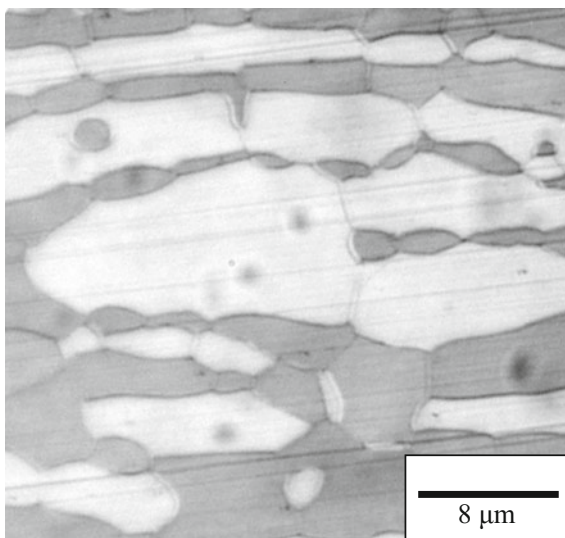
production is prevented.[13] While some investigators have addressed UV application as an "alternative to biocides",[14] perhaps due to the efficiency of UV in a 99.9999 % reduction in viable bacterial numbers,[15] it has been reported that[16] only on surfaces directly irradiated by UV may biofilm growth 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

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[13]Al-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.

[14]Saiz-Jimenez C (2001) The biodeterioration of Bvuilding Materiasl. In: Stoecket JG II (ed) A practical manual on microbiologically influenced corrosion, vol2, 2nd edn, NACE International.

[15]Mittelman 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.

[16]Flemming 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 mater 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 follows[17]: 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 regrowth[19] is low enough to ensure minimisation of corrosion.

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

[18]Flemming H-C (1991) biofoulingin water treatmen. 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 energy[20]

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 following[21]:

- 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.

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[20]Grondin 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.

[21]Lutey 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.

[22]Ibid 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 (ClO$_2$)[26]:

(+):

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[23]Ibid footnote 21, Sect. 3.4.

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

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

[26]See also Cochran M, "Extending ClO$_2$;s 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.

  Ozone[28]:

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

[28]One 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 pert 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 peroxides[29]:
(+):

- 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

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[29]Biocidal 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. Isothiazolone[30]:

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[30]The most frequently used types of isothiazolone are 3:1 ratio 5-chloro-2-methyl-4-isothiazoline-3-one (CMI), 2-methyl-4-isothiozolin-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 bio-cides. Chimica Oggi 18(10):105–108 reports that when isothiazolone molcule 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 isothiazalones 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):

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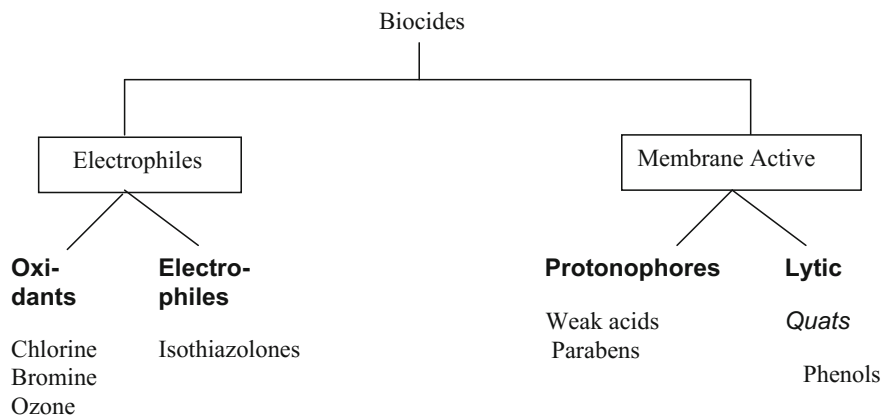
Fig. 9.3 A Brief of Industrial Biocides' Mechanisms of Action (see footnote 30, Williams TM (2004) CORROSION)

Table 9.1 Comparison between antibiotic and biocide resistance modes

Characteristics of Developing Resistance to **Antibiotics** by bacteria	Characteristics of Developing Resistance to **Biocides** 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

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[32]Williams TM, Cooper LE (2014) The environmental fate of oil and gas biocides: a review. Paper No. 3876, CORROSION 2014, Houston, TX, USA.

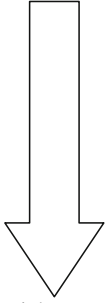**Table 9.2** Colour coding of biocide toxicity hazard rating

Hazard rating	Designated colour code
Lowest Hazard	Gold
	Silver
	White
	Blue
	Orange
	Purple
Highest Hazard	

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

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[33]Ludensky 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 continuos 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 natura 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 lave, bark extracts and neem oil all have antibacterial and antifungal effects[35,36] However

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[34]Abdullah Dar M (2011) A review: plant extracts and oils as corrosion inhibitors in aggressive media. Ind Lubr Tribol 63(4):227–233.

[35]Rasooli I (2007) Food preservation—A biopreservative approach. Food m 1(2):111–136.

[36]Jahan 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 memeberances.[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.

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[37]Bhola 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.

[38]Kuta FA, Abdulrasak 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.

[39]Ocando L, de Romero MF, Urribarri A, Gonzalez D, Urdaneta E, Fuenmayor H (2013) Evaluation of Sulfate-reducing bacteria biofilms in the presence of biocides. Paper No. 2782, CORROSION 2013, Houston, TX, USA.

[40]Javaherdashti R, Nikraz H (2010) A global warning on corrosions 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-CuSO$_4$ 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 SRB[44] have demonstrated that applying cathodic polarisation of −1070 mV versus Cu-CuSO$_4$ has not been sufficient to prevent the growth of SRB.

The accepted theory to explain the feasibility of CP on MIC is that[45] 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 (pH ≥ 11) media has been reported.[47]

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

[42]Tiller 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.

[43]Fischer KP (1981) cathodic protection criteria for saline mud containing SRB at ambient and higher temperatures. Paper No. 110, CORROSION/ 81, NACE International, USA.

[44]de 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.

[45]de 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 biocorrosin 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.

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

[47]Pedersen 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 microbes[48] 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

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[48]Stein AA (1993) MIC treatment and prevention. In: Kobrin G (ed) A practical manual on microbiologically-influenced corrosion. NACE, Houston, TX, USA.

[49]Lee J (1998) Bacterial biofilms less likely on electropolished steel. Agric Res 10.

[50]Percival 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.

[51]Sreekumari 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.
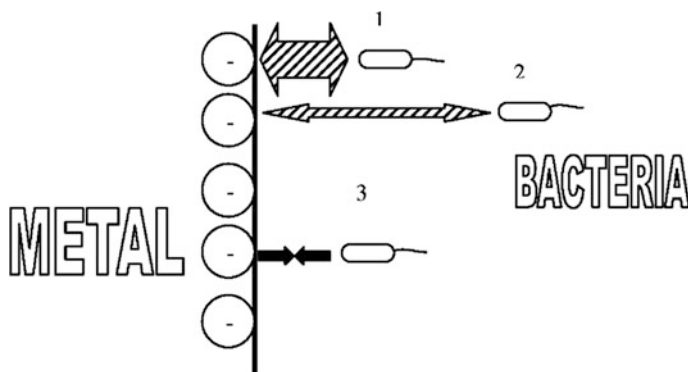
Fig. 9.4 Possible interaction between negatively charged surface and negatively charged bacteria. The power of the repulsion forces (shown as *dashed*) is schematically represented by the thickness of the *arrows*. For example the magnitude of the repulsion forces against the bacterium ① is much bigger 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 diatome: 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.

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[52]Mains AD, Evans LV, Edyvean RGJ (1992) Interactions between marine microbiological fouling and cathodic protection Scale. 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.
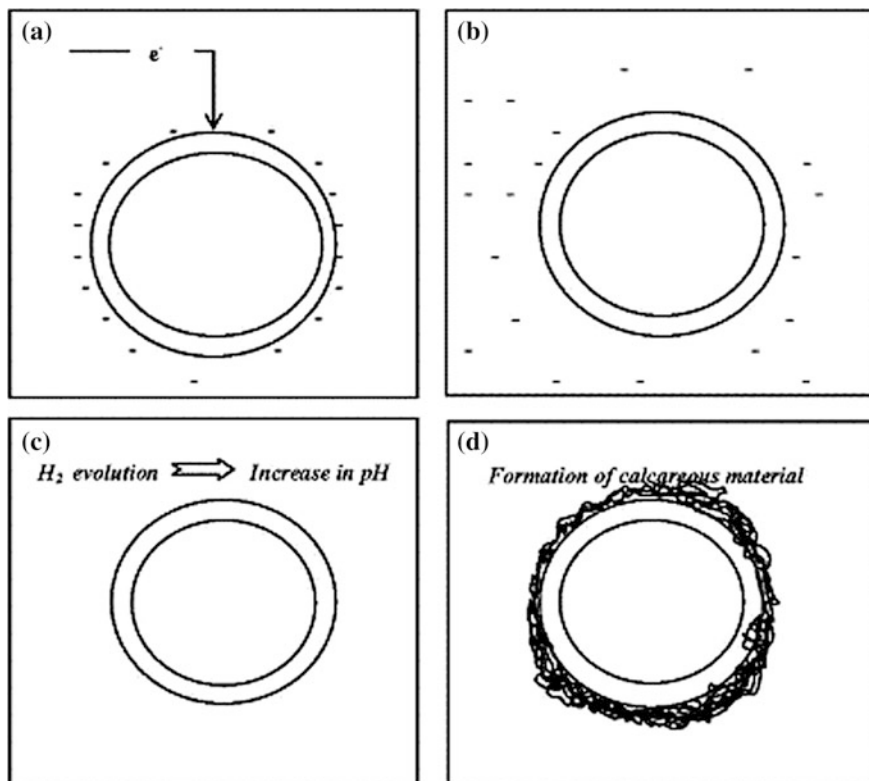
Fig. 9.5 Possible EC effects on the ICCP of a pipeline (Javaherdashti R, Mathematical justification of applying over-voltage in cathodic protection systems to avoid MIC. Unpublished work)

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
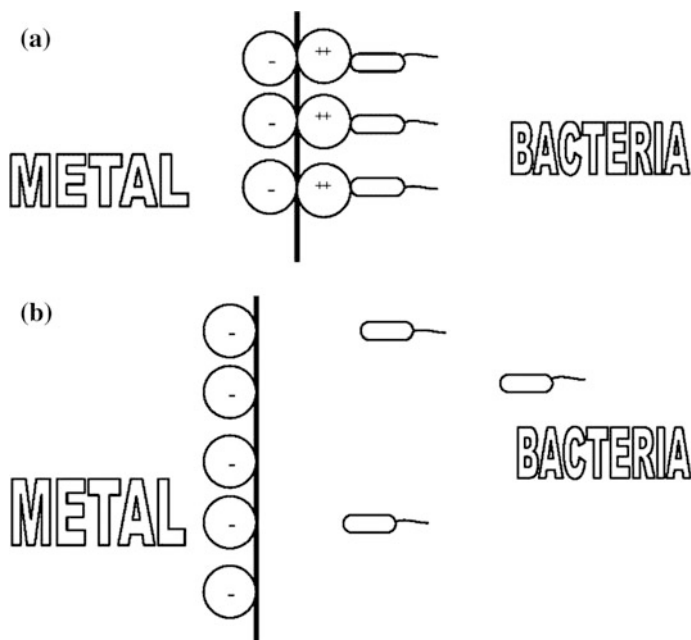
Fig. 9.6 Stages involved in CB theory

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
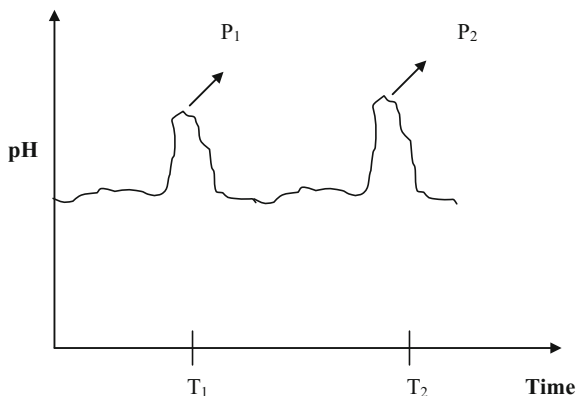
characteristically different from each other ($T_2 - T_1 > 0$) or the time difference is so
infinitesimal ($T_2 - T_1 \approx 0$) that practically it is nil, suggesting that in Fig. 9.7 there
is only one peak not two. This, in turn, means that one single pH rise is sufficient to
both remove the bridging 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 elsewhere[54] 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.

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[53]Due 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.

[54]Habash 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 disbanded 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

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[55]See 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.

[56]Li 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.

[57]Javaherdashti 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.

[58]Wiebe 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 adhesion[59] 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]

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[59]Metosh-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.

[60]Filip 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 stable3
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.

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[61]A 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.

[62]Dzierzewicz Z, Cwalina B, Chodurek E, Bulas L (1997) Differences in hydrogenese and APS-Reductase activity between desulfovibrio desulfuricans strains growing on sulphate or nitrate. ACTA BIOLOGICA CRACOVIENSIA Series Botanica 39:9–15.

[63]Dunsmore BC, Whitfield TW, Lawson PA, Collins MD (2004) Corrosion by sulfate-reducing bacteria that Utilize Nitrate. Paper No. 04763, CORROSION 2004, NACE International, USA.

[64]Nitrite 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.

[65]Little 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.
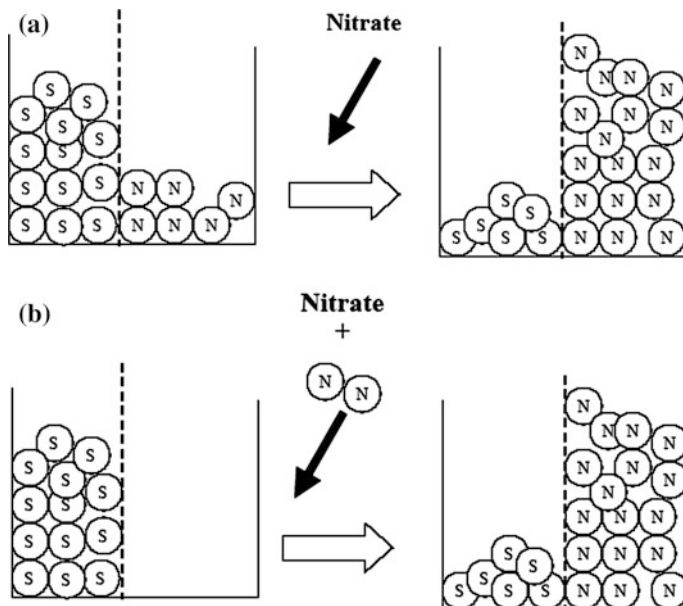
Fig. 9.8 Explanation of two microbiological methods (bio-competitive exclusion and bio-augmentation) to mitigate MIC. **a** *Bio-competitive exclusion*: by adding nitrate, nitrate-reducing bacteria (presented by circles with letter N), will outnumber sulphate-reducing bacteria (shown by circles with 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.

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[66]Hubert 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.

[67]Bouchez T, Patureau D, Dabert P, Juretschko S, Delgenes J, Molette, Ecological study of a bioaugmentation failure. As reported in footnote 56.

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

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

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

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de Gonzalez CB, Videla HA (1998) Prevention and control, in CYTED, Ibero-american programme of science and technology for development, practical manual of Biocorrosin and biofouling for the industry, Subprogramme XV, Research Network XV.c. BIOCORR. In: Ferrari MD, de Mele MFL, Videla HA (eds) Printed: POCH&INDUSTRIA GRAFICA S.A., La Plata, Bs.As., Argentina, 1st Edn, March 1998

Dunsmore BC, Whitfield TB, Lawson PA, Collins MD (2004) Corrosion by sulfate-reducing bacteria that utilize Nitrate. Paper No. 04763, CORROSION 2004, NACE International, USA

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