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.

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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.

Туре	Water type	pH range	Water temperature	Features
Ι	Hard	7–7.8	Cold	Not reported
П	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

Table 8.1 Classification of Copper corrosion types in water

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.

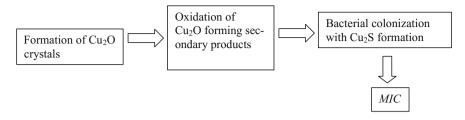


Fig. 8.1 Possible MIC pattern for MIC of Cu-10 $\%\mathrm{Ni}$ in non-chlorinated brackish water according to de Romero

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, Wolynec 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.avestasheffield.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", complied 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 (H₂SO₄) 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.

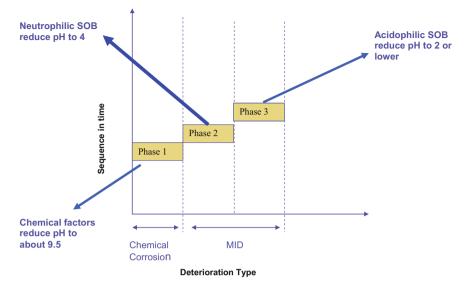


Fig. 8.2 Schematic summary of deterioration of concrete with the involvement of MID (Javaherdashti RPA, Farinha PK, Sarker HN (2006) On microbial: causes, mechanisms and mitigation. Concrete Australia 32(1). Pipe)

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 SOBs 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 (3CaO. Al₂O₃. CaSO₄. 12H₂O or 3CaO. Al₂O₃. 3CaSO₄. 31H₂O) whereas gypsum (CaSO₄. 2H₂O) 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

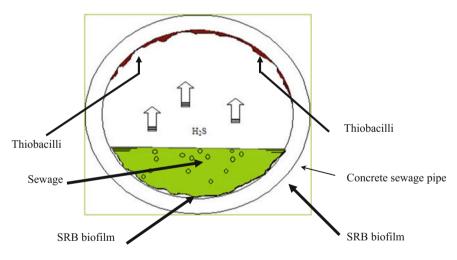


Fig. 8.3 Schematic representation of possible microbial consortium in a concrete sewage pipe (Javaherdashti R (2004) A review of microbiologically influenced corrosion with emphasis on concrete structures. In: Proceedings of corrosion and prevention 2004 (CAP04), 21–24 Nov 2004, Perth, Australia.)

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 corroson of concrete sewer pips. Water Res 26(1):29–37.

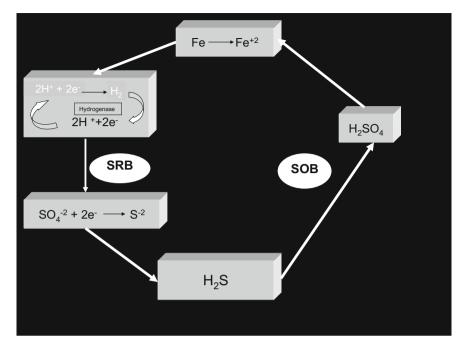


Fig. 8.4 Possible cyclic action between SRB and SOB

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.

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

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

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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