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 al the details of each technique but rather link it with the theoretical aspects of electrochemistry, as covered in Chap. 1.

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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

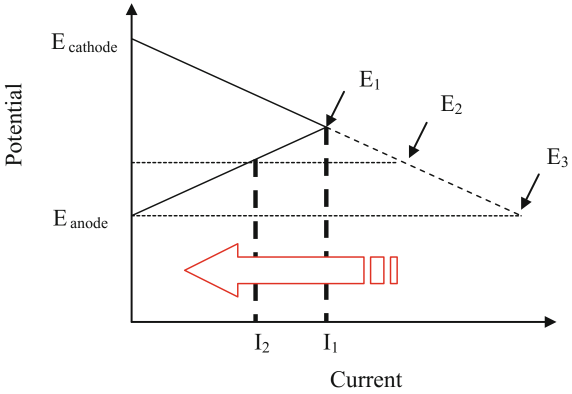

Fig. 2.1 Principle of cathodic protection; at a potential like E_1, a corrosion current (rate) such as I_1 is reached. By making the potential more negative to E_2, the corrosion current is reduced to I_2, as graphically shown by the *red arrow*

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 are[2] 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

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

[2] Byars 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.

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

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

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

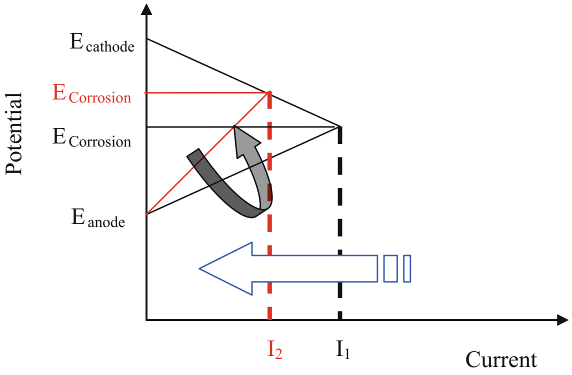

Fig. 2.2 Principle of anodic inhibition; when no anodic inhibitor has been added, the corrosion current (rate) is I_1. When an anodic inhibitor is added, the anodic potential is modified and "rotates up" so that the corrosion rate is reduced (I_2)

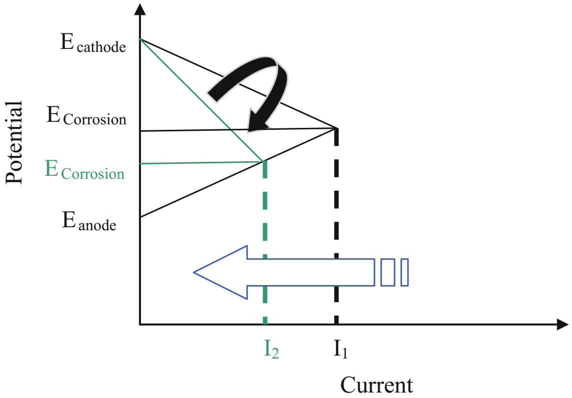

Fig. 2.3 Principle of cathodic inhibition; when no cathodic inhibitor has been added, the corrosion current (rate) is I_1. When a cathodic inhibitor is added, the cathodic potential is modified and "rotates down" so that the corrosion rate is reduced (I_2)

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

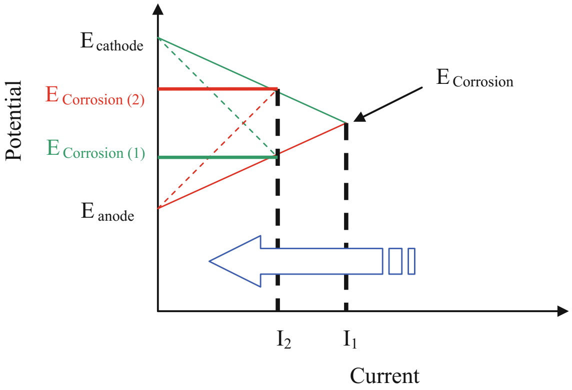

Fig. 2.4 The mixed effect of inhibitors, affecting both anodic and cathodic reactions to reduce corrosion

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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