

CHAPTER 15

RECENT INVESTIGATIONS INTO THE EFFECTS OF ALGAE ON CORROSION

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15.1. INTRODUCTION

The development of the North Sea oil industry during the 1970's stimulated interest in the U.K. in the possible effects which fouling growing on fixed offshore structures could have on the corrosion of the underlying steel. Prior to this most interest in biologically induced corrosion had concentrated on microbial corrosion of buried pipelines and in aircraft fuel systems.

The electrochemical nature of corrosion is illustrated in Figure 1. The metal can be considered as having anodic and cathodic sites. Metal ions go into solution at the anode, electrons pass through the metal to the cathode and a current passes to the cathode through the seawater electrolyte. The form of the cathodic reaction depends upon oxygen availability. Water dissociates and under anaerobic conditions hydrogen atoms and molecular hydrogen accumulate to polarize the cathode thus preventing corrosion. If this cathodic hydrogen is removed corrosion continues and the cathode is said to be depolarized. Under aerobic conditions hydroxyl ions are formed and these react with the ferrous ions from the anodic reaction to form corrosion products which can be complex in nature. In a freely corroding system the initial corrosion rate may be high but the resulting corrosion products can form a barrier preventing oxygen from reaching the metal surface and so retard the corrosion rate.

Many fixed structures in the North Sea have anticipated working lives of 20 years or more and the methods used to maintain structural integrity over such a time period are

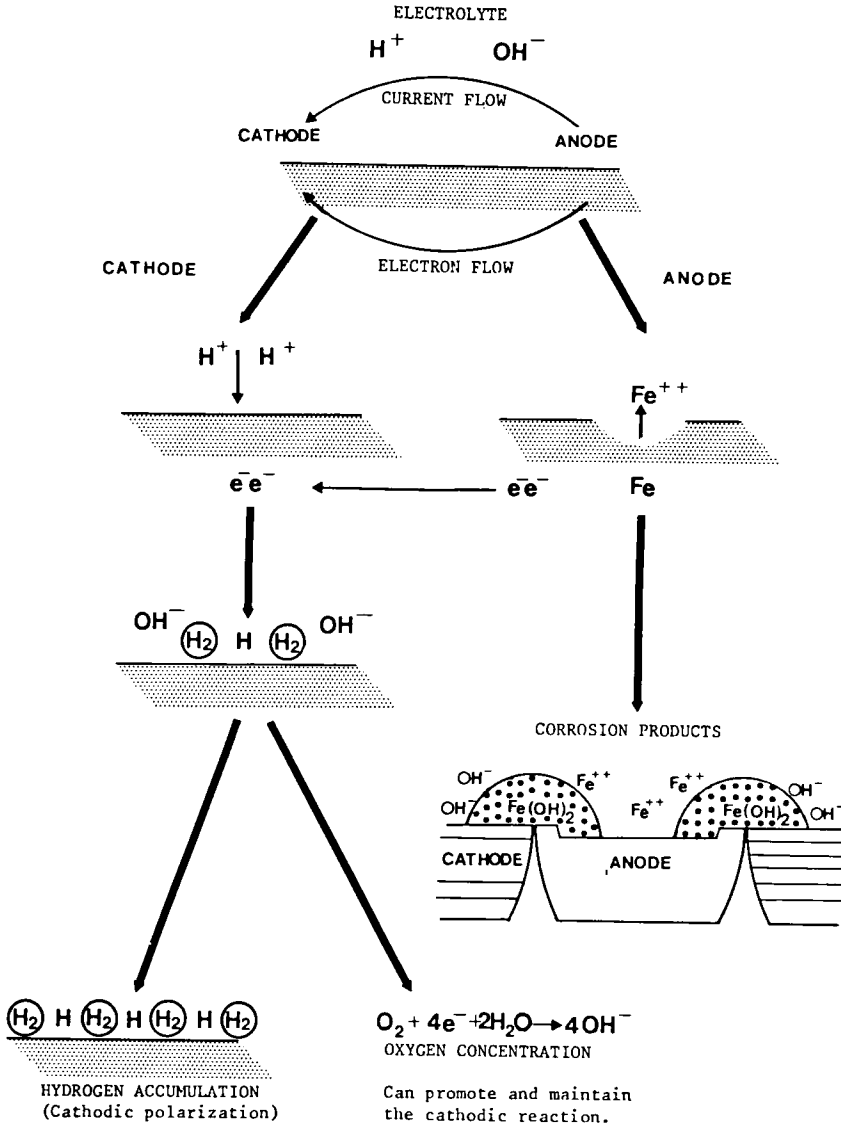


Fig. 15.1. The electrochemical corrosion reactions.

different from those used on shipping which can be brought into dry-dock for maintenance. The protection deployed varies with the position on the structure (Bartlett, 1977; Ridler, 1977; Hodgkiess, 1978). Above the waterline steel is coated with an inorganic zinc primer overlain by paints containing corrosion inhibitive compounds. The splash-zone, where the combination of water movement, oxygen-rich waters and greatest hydrodynamic loading presents a particularly difficult region to protect, often has the added protection of a sheathing of a corrosion resistant copper nickel alloy such as Monel 400 or Kunifer.

The submerged portion is protected by a cathodic protection system, sometimes augmented by a coal-tar epoxy or chlorinated rubber paint system. Two different cathodic protection systems can be used; either impressed current or sacrificial anode. Commonly used sacrificial anode materials are zinc, aluminium and magnesium all of which are substantially anodic to steel. A galvanic cell is formed which results in the anode corroding whilst, in a properly engineered system, the steel remains intact. With the impressed current system a direct current is driven through the structure by a generator with an inert or expendable anode remote from the platform completing the circuit through a seawater electrolyte. Again, the aim is to ensure that the steel effectively becomes a cathode over its entire surface and is protected from corrosion. Both systems generate a high pH at the metal surface and this promotes the deposition of calcereous deposits of calcium and magnesium carbonates, the thickness of which is related to current density and exposure time (Wolfson and Hartt, 1981).

Anti-fouling paints, in contrast to the shipping situation, are rarely used on fixed structures. Their infrequent use has been limited to localised areas such as on signs which aid divers in locating their position on the structure. Consequently, extensive fouling communities develop from the splash-zone to the sea-bed. The fouling communities on some North Sea structures have been described (e.g. Goldie, 1981; Hardy, 1981; Forteath et al., 1982; 1983; 1984; Picken et al., 1983) and the distribution of algae has been documented (Terry and Picken, in press). Algae have been

found to a maximum depth of -40m on installations in the central and northern North Sea and to -5m in the southern sector. The most widespread algae are Enteromorpha spp. in the splash-zone, Ulva sp., Desmarestia viridis, Desmarestia ligulata, Polysiphonia spp., particularly P.brodiaei and P.urceolata and in the central and northern sectors Laminaria digitata and Alaria esculenta.

The effects of fouling on North Sea installations have recently been reviewed (Edyvean et al., 1985a). The impairment of visual inspection is particularly important around welds. The increase in dynamic and hydrodynamic loading, which is most noticeable in the upper 20m of a structure where algae and mussels are dominant, can necessitate costly cleaning for safety reasons. This paper concentrates on the direct and indirect effects which algal fouling can have on corrosion and on corrosion protection systems.

15.2. DIRECT EFFECTS OF ALGAE ON CORROSION

Algae may themselves influence corrosion through their modification of the environment, i.e. the electrolyte, through direct involvement in the electrochemical corrosion reactions or through an influence on mechanically induced corrosion. Although some of these effects are linked closely with the action of bacteria they are discussed here under direct effects.

15.2.1. Modification of the environment

Algae can modify the local environment of the steel by influencing oxygen concentration, changing the pH and through the production of metabolites which create a more aggressive electrolyte. The basic electrochemical nature of corrosion suggests that a reduction in the oxygen concentration would reduce the cathodic reaction rate and lead to a reduction in corrosion. The presence of an algae fouling cover might be expected to produce such a reduction in the local oxygen concentration and studies using steel panels immersed at offshore sites have shown that, initially, corrosion rates were reduced by fouling, with a thin cover of Enteromorpha sp.

providing a particularly effective barrier (Bultman et al., 1977). Once the conditions under such fouling altered so that oxygen was excluded and sulphate-reducing bacteria (SRB) became active then the beneficial effects of the fouling cover were lost as SRB mediated corrosion dominated. Polarization studies, (Edyvean and Terry, 1983b), have shown anodic polarization (i.e. reduction in corrosion) of 50D steel under cultures of both Enteromorpha sp. and a primary film of bacteria and diatoms thus supporting the idea that under some conditions a fouling cover may be beneficial.

Algae, especially microalgae, produce copious amounts of mucilage and release organic compounds into seawater. Recent work has shown that natural seawater containing biologically derived components produces very different surface films and corrosion products on metal surfaces than does artificial seawater without organic components. A study using a 90/10 cupro-nickel alloy (Castle et al., 1983) found very different surface films on the metal in natural seawater containing organic compounds derived from bacteria and microalgae than on metal exposed to sodium chloride solution. The presence of the organic film rendered the metal liable to a loss of cathodic inhibition and the release of aggressive products in the absence of oxygen.

Laboratory studies have shown that the mode of attachment of diatoms can affect corrosion (McDonnell et al., 1984). Steel onto which Achnanthes diatoms were attached by means of a stalk were freely corroding after two weeks in culture whereas specimens with Amphora attached close to the surface produced little loose corrosion products. Attachment in this case was effected by means of a mucilage pad over the surface of the diatom. Such a mode of attachment would have brought about a greater reduction in oxygen concentration at the metal surface than would attachment by a stalk. Subsequent studies, (E.A.McDonnell, personal communication, 1985), have further confirmed the role of mucilage. Polarization experiments have shown the diatom Nitzschia to produce greater cathodic polarization (i.e. reduction in corrosion compared with control specimens) than the diatoms Navicula, Cocconeis, Amphora or Achnanthes. Nitzschia did not attach to the steel but moved across the surface spreading

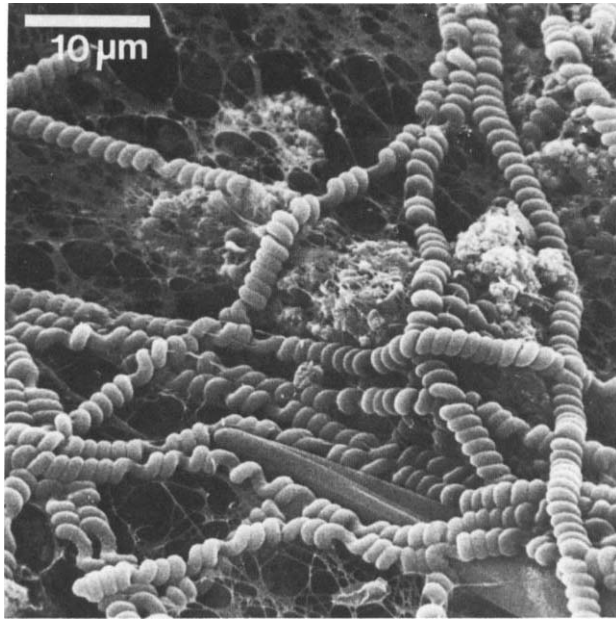


Fig. 15.2. S.E.M. showing corrosion products on unprotected mild steel exposed to flowing seawater for 105 days and covered by a mucilage bound mat of filamentous blue-green algae and a pennate diatom. Reproduced with permission from Terry, L.A. and Edyvean, R.G.J. 1981. *Botanica Marina*, 24: 177-183.

mucilage. Cathodic depolarization was observed with Achnanthes suggesting that its irregular covering of the surface was enhancing corrosion. Figure 2 shows a cover of blue-green algae and diatoms on unprotected steel. The role of mucilage produced by the algae in covering and consolidating the underlying corrosion products can be seen.

Over the normal range of pH values encountered in seawater the availability of oxygen has a greater influence on corrosion than do any changes in the pH per se (LaQue, 1975). In decaying algal cultures, however, pH values as low as pH 1.8 have been recorded (Edyvean and Terry, 1983a). If such low values were found offshore they could be expected to accelerate

corrosion and/or alter any natural passivation of the metal or disrupt protective carbonate scales. Local differences in pH may give rise to local concentration cells (see below).

15.2.2. Effects of algae on electrochemical corrosion

15.2.2.1. Differential concentration cells

Differential aeration cells are probably the most widespread forms of corrosion offshore. Such cells may be formed under all types fouling, bacteria, diatoms and macro-fouling. A differential aeration cell is brought about by the lower concentration of oxygen under the fouling compared with adjacent unfouled or more lightly fouled areas. The area under the fouling becomes anodic to the surrounding, cathodic areas where the higher oxygen concentration promotes the aerobic cathodic reaction. The end result is accelerated corrosion under the fouling.

Other concentration cells, metal ion and pH concentration cells, operate in a similar manner. The pH under algal fouling varies due to the photosynthetic activities. Daily pH changes of up to 2 units have been recorded under cultures of Enteromorpha sp., a filamentous blue-green alga and colonial diatoms (Terry and Edyvean, 1981; 1984; Edyvean and Terry, 1983a). Algal photosynthesis can push pH values above pH 10 (Terry and Edyvean, 1981) whereas under decaying algae the pH values fall well below that of the ambient seawater. The potential for the creation of local pH concentration cells exists although there is no direct evidence confirming the operation of such a mechanism on offshore structures.

15.2.2.2. Pitting corrosion (Active-passive cells)

This is a localised corrosion brought about by the breakdown of natural passivity or by the prevention of the formation of passive films. Differential aeration, reducing the oxygen at the metal surface, can cause considerable pitting corrosion on alloys, such as stainless steel, which rely on passive films for their corrosion resistance. There is a large body of work describing the effects of seawater on the corrosion of various stainless steels and other alloys

(e.g. copper nickel and other copper alloys). There is some work on the effects of differential aeration on crevice corrosion and pitting of stainless steel (e.g. Krougman and Ijsseung, 1984) including the action of bacteria (e.g. Mollica et al., 1984) but there are no details of any algal effects.

Pitting corrosion has been found offshore and pits are known to occur under barnacles (Pipe, 1981). The presence of sulphides increases pitting and hence SRB which produce sulphides during their metabolism can enhance pitting corrosion. A FeS lattice is formed on the steel and hydrogen formed during the anaerobic cathodic reaction is bonded within this lattice thus reducing corrosion. When further sulphides are generated corrosion increases and SRB preferentially remove the hydrogen from the sulphide lattice rather than from the steel and bring about increased cathodic depolarization by increasing this rate limiting step of the corrosion reaction (Sanders, 1984).

15.2.3. Mechanically induced corrosion

15.2.3.1. Hydrogen embrittlement

This form of corrosion also involves the cathodic reaction. Atomic hydrogen generated in the cathodic reaction penetrates the steel resulting in the loss of ductility. A number of detailed mechanisms have been postulated to account for the embrittlement effect (Hinth and Johnson, 1976) which, when combined with the presence of local regions of high stress, can result in severe cracking of the metal (see below). Hydrogen embrittlement is enhanced by the high levels of hydrogen which can be generated by SRB under certain conditions and which is generated by the over-protection by cathodic protection systems (Gooch, 1984). If the levels of cathodic protection are increased too high in order to combat SRB corrosion there is a danger that hydrogen embrittlement may be enhanced. The presence of H_2S , which can be produced by SRB, is known to retard the formation of molecular hydrogen on the metal surface and to enhance the pick-up of atomic hydrogen by the metal. Whenever algae provide conditions for SRB they may consequently enhance hydrogen embrittlement. Any evolution of hydrogen by the algae themselves would also

affect hydrogen embrittlement. Although some work has been carried out (e.g. Healey, 1970) the possibility of this occurring has not been fully investigated.

15.2.3.2. Corrosion fatigue

Fatigue is a form of deterioration involving the initiation and subsequent slow growth of cracks under the influence of cyclic stress. The presence of a corrosive environment, such as seawater, containing hydrogen sulphide usually causes an acceleration in both the crack-initiation and crack-propagation rates producing corrosion fatigue. Offshore stresses can arise from hydrodynamic loading, from high frequency machinery vibrations and from low frequency transient stresses generated by wind and cargo movement. Algae can contribute directly to the first of these stresses - hydrodynamic loading. Until recently very little work has been carried out on this effect of soft fouling on offshore structures. The effect of 100% cover of kelps on the inertia co-efficient has been shown to be nearly double that of a 100% mussel cover in laboratory experiments (Wolfram and Theophantos, 1985) and it is recognised that soft growths may contribute more to hydrodynamic loading than previously thought.

Metabolites, such as H_2S , have long been recognised to enhance crack growth rates due to hydrogen embrittlement and usually H_2S is added to seawater in laboratory tests on crack growth rates. Recently, work using biogenic H_2S derived from a decaying Enteromorpha sp. culture (Edyvean et al., 1985b; Thomas et al., 1986) suggested that there is a threshold level for such enhancement as similar rates were produced from levels of 600ppm biogenic H_2S as were produced with seawater saturated with 3100ppm H_2S .

15.3. INDIRECT EFFECTS OF ALGAE ON CORROSION

Even a thin algal cover may provide conditions enabling bacterial growth. The corrosion process can be affected by the activities of some bacteria, both aerobes and anaerobes.

15.3.1. Aerobic bacteria

Two groups of aerobic bacteria can affect corrosion. The sulphur-oxidising bacteria, Thiobacilli spp., oxidise inorganic sulphur and produce sulphuric acid, (Iverson, 1972), which is corrosive to steel. The nitrate-reducing bacterium, Pseudomonas sp., has been shown experimentally to bring about anodic depolarization (an increase in the anodic reaction) of mild steel (Obuekwe et al., 1981a; 1981b). Ferric compounds were reduced to ferrous ones either removing or preventing the formation of protective ferric coatings. A similar mechanism was suggested to account for the anodic depolarization of 50D steel observed with cultures of the blue-green alga Oscillatoria sp. (Edyvean and Terry, 1983b). Although the chemistry involved in such reactions has been documented (e.g. Cragnolino and Touvinen, 1984), the extent to which they are an influence offshore has not been determined.

15.3.2. Anaerobic bacteria

The role of the sulphate-reducing bacteria (SRB) has received considerable attention as they are known to affect many offshore operations (Sanders, 1984). Although they are present in aerated seawater at low levels and may be found in the primary film within 3 to 20 day's exposure, they are active only under anaerobic conditions (Sanders, 1983; Hamilton and Sanders, 1984).

The classical theory of SRB-mediated corrosion is that of cathodic depolarization (von Wolzogen Kuhr and van der Vlugt, 1934). SRB stimulate the normal electrochemical corrosion mechanisms by the removal of the hydrogen produced in the anaerobic cathodic reaction and the formation of a corrosion product, FeS, which is itself cathodic to steel. Recently, however, doubts have been expressed as to how the cathodic depolarization mechanism can work in practice (for discussion see Cragnolino and Touvinen, 1984) and more recognition has been given to the role of the products, particularly FeS, and H₂S which are produced during bacterial metabolism. Iron sulphides, although cathodic to iron, cannot act as permanent cathodes but their continued production by SRB brings fresh sulphides into contact with the steel and promotes corrosion. Polarization studies have shown that

bacterial activity in decaying cultures of Enteromorpha can bring about both anodic and cathodic depolarization of 50D steel with the conclusion that both the utilization of cathodic hydrogen and the action of biogenic sulphides can be involved (Edyvean and Terry, 1983b). Whatever mechanism is involved, whenever algae provide micro-environments for bacterial corrosion they can enhance corrosion indirectly.

The hydrogenase enzyme system is responsible for cathodic depolarization by SRB. This enzyme is not restricted to SRB and has been found in Ulva lactuca, Ascophyllum nodosum, Porphyra umbicalis, Porphyridium creurentum and some blue-green algae (Frenkel and Rieger, 1951).

15.4. EFFECTS OF ALGAE ON CORROSION PROTECTION SYSTEMS

15.4.1. Disruption of coatings

Although antifouling coatings have little offshore applications, coal-tar epoxy paints are used for corrosion protection. Algal rhizoids can penetrate weaknesses in such coatings and the removal of fouling may accentuate this. Unprotected steel may develop natural passivating films. The removal of fouling can disrupt such films and has been known to result in the removal of metal (Forteath et al., 1984).

15.4.2. Interaction with cathodic protection systems

Algae settle readily on cathodically protected steel (see Figure 3). Both impressed current and sacrificial anode cathodic protection systems generate a protective calcareous scale at the metal surface. The properties of this scale are influenced by several factors including the bulk seawater chemistry, particularly the oxygen concentration and the organics present, local profiles (e.g. pH) of the seawater adjacent to the metal surface, temperature and current density (Hartt et al., 1984). The high pH generated by algae during photosynthesis may enhance scale formation (Edyvean and Terry, 1983a). Fouling can become entrapped in the scale which continues to be deposited around the organisms and the presence of such fouling may alter the properties of the scale (Edyvean, 1984). Removal of embedded fouling can result in

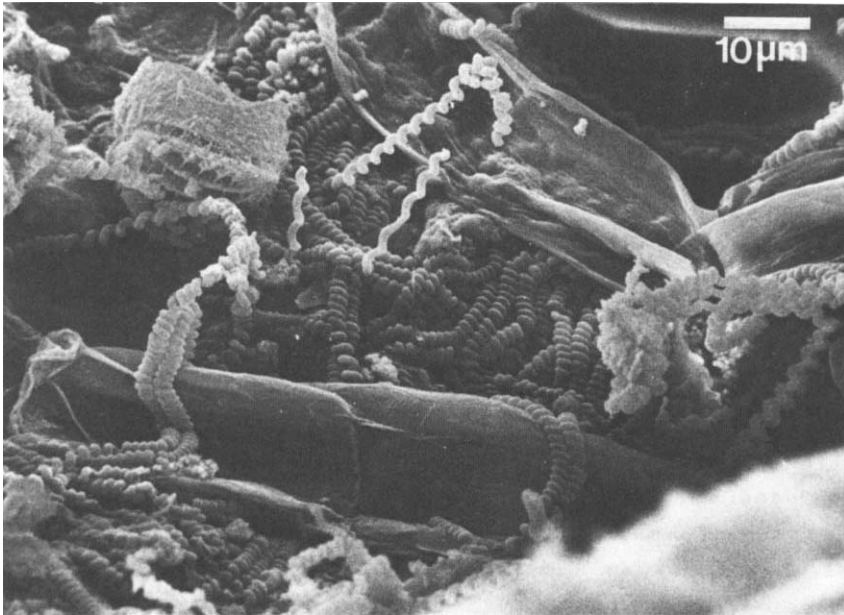


Fig. 15.3. S.E.M. showing a dense covering of diatoms and blue-green algae on cathodically protected, unpainted steel after 100 days immersion in flowing seawater. From Edyvean, R.G.J. and Terry, L.A. 1983. In: *Biodeterioration 5*, Oxley, T.A. and Barry, S. (eds.). Reproduced by permission of John Wiley and Sons Ltd.

damage to the scale and can expose steel which becomes anodic to the scale-protected steel (Terry and Edyvean, 1984). The possibility of localised corrosion is therefore enhanced if the cathodic protection is shut down, if it has not been designed to cope with the increased current demand at such locations of exposed steel or if the pre-existing adjacent fouling organisms interfere with the cathodic process.

UNPROTECTED AND INTERMITTENTLY PROTECTED STEEL

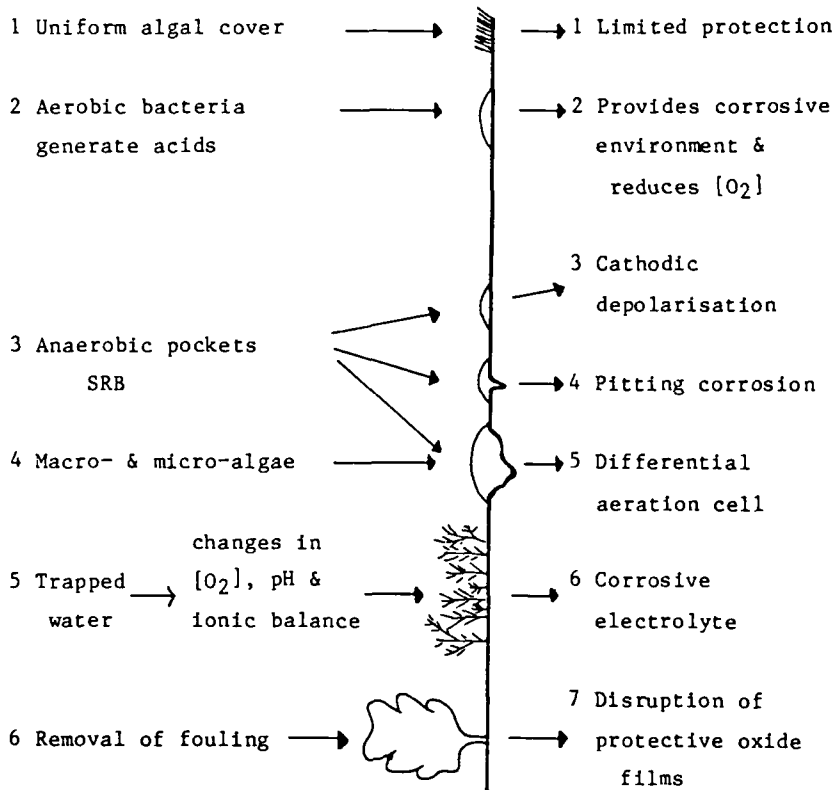


Fig. 15.4. Interactions between algae and corrosion which can occur on unprotected and intermittently protected steel.

PROTECTED AND UNPROTECTED STEEL

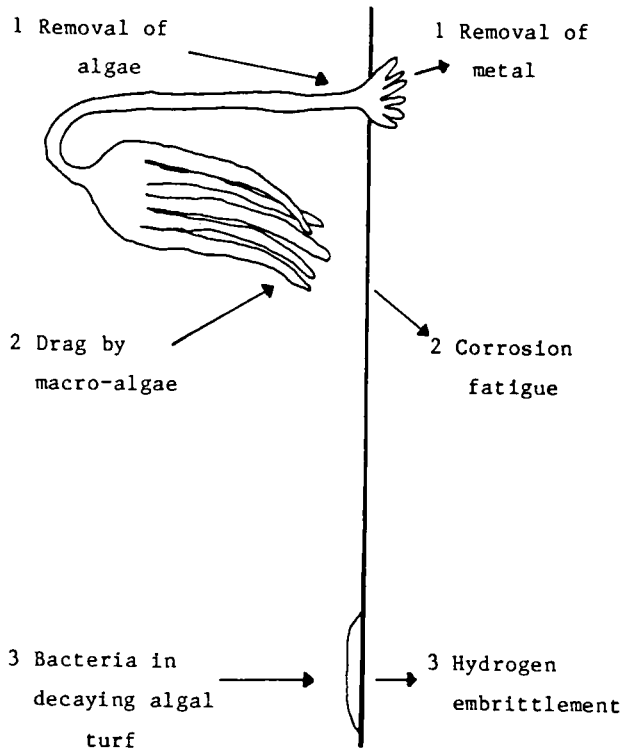


Fig. 15.5. Interactions between algae and corrosion which can occur on both protected and unprotected steel.

15.5 THE EXTENT OF CORROSION ON OFFSHORE INSTALLATIONS

The extent to which fouling is a problem offshore is not easy to assess since if all the protection systems work properly corrosion should not happen at all. Generally, despite some initial problems on certain structures (e.g. Tischuck, 1984), corrosion protection systems have performed well in the North Sea. An impressed current system, however, may not be installed until several months after the platform and both cathodic protection systems often require modification after installation. During periods of inadequate protection structural steel is vulnerable to general corrosion and the biologically induced corrosion depicted in Figures 4 and 5. Some minor structural failures have been reported (Skrebowski, 1978; Vennett, 1979) of risers which carry hot oil from the seabed to the platform and vulnerable areas such as welds require frequent structural integrity monitoring. Corrosion products have been found in samples of marine growth collected offshore for onshore analysis (Forteath et al., 1984) and SRB corrosion can affect a variety of offshore operations in addition to effects on the structural integrity of installations (Sanders, 1984).

15.6 SUMMARY OF ALGAL/CORROSION INTERACTIONS

A number of algal/corrosion scenarios can be formulated for different situations depending on the type of corrosion protection adopted. These scenarios are shown in Figures 4, 5 and 6. These interactions have been derived largely from laboratory studies and theoretical considerations since direct observations from offshore are limited. Some of the interactions are known to depend upon bacterial activity and it is not clear to what extent algae contribute to processes such as pitting corrosion in the absence of bacteria.

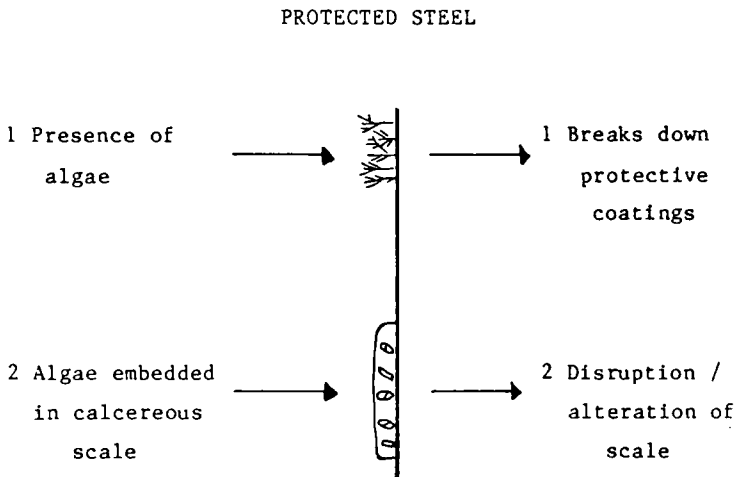


Fig. 15.6. Interactions between algae and corrosion which can occur on protected steel.

15.7 ACKNOWLEDGEMENTS

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