TNO report

Industrial Innovation
Van Mourik Broekmanweg 6
2628 XE Delft
P.O. Box 49
2600 AA Delft
The Netherlands

www.tno.nl

T +31 88 866 30 00
F +31 88 866 30 10

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Protecting with Nature (PwN)

PwN concept (bio-)corrosion prevention

Date	18 December 2014
Author(s)	Harald van der Mijle Meijer, TNO Edwin Foekema, IMARES Felipe leon, Endures
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Contents

1 Introduction

Harbour infrastructures, civil engineering structures and offshore structures are exposed to a very aggressive maritime environment. The local corrosion mechanism bio-corrosion or microbial influenced corrosion (MIC) seems to be the life determining failure mechanism for these structures.

More than 90% of the harbour structures suffer from MIC based on a research study in the UK . TNO research showed that MIC is a major problem for the sea harbours in the Netherlands. The last decade MIC became a more dominant failure and there are a several International research projects performed to find the solution for this problem.

There is a need for durable solutions to protect and maintain these structures. Different corrosion protection methods and systems are commercially available but each application requires a specific protection system. The optimal solution is not available yet.

On the other hand it is also an asset management issue; finding the right balance between capital investment with selection of more durable materials and protection systems and operational expenses to optimize inspection, monitoring, maintaining and repair operations.

Last but not least the impact on the environment of these structures and corrosion protection methods became more important with the environmental policies. Life cycle analysis and eco-design methodologies will be part of the design and investment process.

1.1 Evolution of corrosion rates

Corrosion of steel that is brought in a marine environment follows different phases. The study of corrosion forms an interdisciplinary science, studying details that are beyond the scope of our goals. When oversimplified the evolution of factors affecting corrosion rates of a metal substrate exposed in (sea)water three phases can roughly be distinguished:

- Phase 1, no biofilm: high corrosion rate as dissolved oxygen in the water is in direct contact with the metal surface.
- Phase 2, thin biofilm of micro-organisms (colonisers): corrosion rate is somewhat reduced as oxygen levels at the metal surface are reduced due to respiration of the biofilm
- Phase 3, thicker biofilm of micro and macro-organisms with local anaerobic areas: corrosion rates increase due to microbial activity in anaerobic areas that can create corrosive conditions, by becoming anodic with respect to other uncovered areas of the metal surface.

Especially when MIC appears (phase 3) the underlying mechanisms become very complex. Most MIC is localized corrosion and there are numerous mechanisms and causative organisms for MIC that can vary among metals and environmental conditions. It has become clear that corrosion rates resulting from MIC can be extraordinarily fast (Little & Lee, 2007). A brief description of MIC and factors involved is given in chapter 3.

1.2 Objectives

In the MIIP Protecting with Nature a pre-study was performed to combine the above issues in a case study to protect a harbor infrastructure against MIC with methods which stimulate or use the environment to protect the steel.
The objectives of the MIIP are;

1) Mapping the costs due to corrosion and degradation of steel structures in seawater.
2) A quick scan of biological mechanisms which contribute to corrosion and degradation.
3) A quick scan of potential “Protecting with Nature” solutions.
4) Check if there is support among the stakeholders for a JIP, based on the insights from the objectives 1), 2) en 3).

2 Business case

The business case will be focused on harbor infrastructures. Based on discussion with stakeholders the following business case can be drawn.
Harbor infrastructure like walls and piling are designed for a life time of 50 years.

The majority of the seawater harbors originally applied unprotected carbon steel structures. The last decade different corrosion protection systems are used like protective coatings and cathodic protection; passive with sacrificial anodes (GACP) and active with impressed current (ICCP). Also different innovative techniques are tested like ultrasonic noise.

Building a complete harbor quay with carbon steel walls with water depth of 9 m it will cost about kEUR 18 per meter[1]. The port of Rotterdam has 89 km of harbor quay so the total investment is 1.6 Billion EUR. The design life is 50 years, so the calculated investment is about EUR 360 per meter per year excluding the operational costs for maintaining the harbor quay.

Recent corrosion cases investigated by TNO in harbours in The Netherlands showed that MIC resulted in failure of 12 mm wall thickness after 5 – 10 years exposure time!

Harbours like Scheveningen and Den Helder decided to install cathodic protection on existing walls and pilings with sacrificial anodes welded on the steel structure. The costs for this modification are about EUR 500 per meter length. Alternative is to apply a protective coating system (organic coating, metal sprayed coating or cementious coating). This is an additional investment cost.

Finally the costs dealing with the effect on the environment are not calculated. However, to complete this we can use as called shadow prices in the cost calculation for CO_2 emission and effect on the sea life. At this moment this is not included in the cost calculation.

Based on this there is interest in protection methods which will reduce both the CAPEX and OPEX[2]. For instance alternative protection methods but also alternative inspection and repair methods.

[1] Service Life Assessment of Harbor Structures, H. Wall, 2014
[2] CAPEX = Capital Expenses, OPEX = Operational Expenses

3 Microbiological mechanisms involved in corrosion

Corrosion results from a series of electrochemical reactions at the metal interface which depend greatly on environmental factors. Because microorganisms are active at surfaces, their activities can have a great influence on corrosion processes. The process by which the presence and activities of microorganisms lead to increased and unexpected corrosion is known as Microbiologically Influenced Corrosion (MIC).
MIC is not a different corrosion mechanism in itself but rather a particular set of environmental conditions influencing corrosion rates and types. Microorganisms are found in almost all environmental niches and can adapt readily to changing or extreme conditions. Although traditionally, it has been assumed that the main groups of microorganisms involved in bio corrosion are those belonging to the sulphate-reducing group, it is now evident that sulphate-reducing bacteria influenced corrosion is just one of the possible mechanisms.

A fundamental characteristic of MIC is the ability of microorganisms to attach to a substratum (e.g., metallic structure) and form biofilms. Biofilms are composed of attached microorganisms and their extracellular polymeric products (slime). Biofilm formation starts as soon as (unsterile) water enters in contact with target surfaces. Most of the times biofilm formation is preceded by the accumulation of organic and inorganic compounds at the interface. It is still controversial if these adsorbed substances are a prerequisite for biofilm formation but indeed they contribute to its development. In this respect and because biofilms continue to be places of accumulation, a vibrant community of microorganisms can thrive even though if nutrients at the water phase are low.

Corrosion can be stimulated by the mere presence of biofilms. Biofilm formation results in the formation of concentration cells. In this direct interaction, the types of microorganisms are irrelevant provided the biofilm is patchy and localized. Consumption of oxygen in these “patchy” biofilms can be so high that oxygen cannot reach the metallic surface under the biofilms. Oxygen exclusion from certain localized areas of the metal structure forms concentration cells which result in pitting corrosion as illustrated in Figure 1.

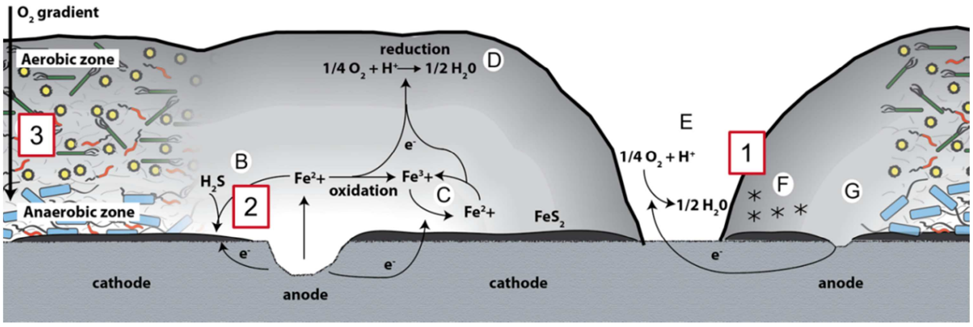

Figure 1. Biofilms can be corrosive by the formation of aeration cells (1) or the production of corrosive metabolites such as H2S (2). Within the biofilm a steep oxygen gradient is created with very low oxygen concentration close to the metal surface as compared to the exterior. An electrochemical cell is then formed in which the region under the biofilm acts as the anode (corrodes) and regions with no biofilm act as cathode. Source of image: (Li, Whitfield, and Van Vliet 2013).

Certainly MIC is not limited to concentration cell effect due to the bare biomass accumulation. Diverse microbial activities within the biofilm also play a major role on determining MIC. The oxygen concentration gradient created in biofilms will result in diverse communities driven by the available electron donors and acceptors. As oxygen gets consumed in upper parts of the biofilms, anaerobic communities can thrive underneath with processes highly relevant for corrosion. One of the most important is the production of hydrogen sulphide (H_2S) which is a highly corrosive acid, catalysing the penetration of hydrogen into steels in a process called H_2S-induced cracking.
Furthermore, the corrosion rate of iron in the presence of H_2S is accelerated by the formation of iron sulphide minerals. With electrical current established, carbon steel behaves as an anode and electron transfer occurs through the iron sulphide. The organisms responsible for this process are known as sulphate-reducing bacteria (SRB).

3.1 Overview implicated organisms and mechanisms

3.1.1 Slime and biofilm forming bacteria

As mentioned earlier, the formation of biofilms is a pre-requisite for the onset of bio-corrosion. Slimes composing biofilms are extracellular polymeric substances (EPS) produced by microorganisms, especially after attachment to the substratum. The production of EPS and biofilm formation has been often reported as a microbial strategy to survive adverse environmental conditions. EPS production in the quantities needed to give structure to the biofilms is an energy consuming process. Therefore most EPS producers are highly aerobic microorganisms. Typical “slime” bacteria belong to the pseudomonads group and although some might produce corrosive metabolites the main effect would be on creating differential aeration cells.

3.1.2 *Acid producing bacteria*

Several microorganisms have the capacity to produce acid from a wide variety of organic compounds. Acid can result from the oxidation of sulphur, thiosulphates and H_2S among others to sulphuric acid. This process is driven by sulphur-oxidizing bacteria (SOB). Another source of acid is the heterotrophic fermentation of organic substrates which results in the production of organic acids by acid-producing bacteria (APB). The impact of acidic metabolites is intensified when trapped at the biofilm-metal interface. Local acid production by microorganisms can accelerate corrosion of metals (Figure 2). When active, anaerobic acid producing microorganisms can acidify the medium in which they are growing in a matter of 1 or 2 days. The MIC risk posed by acid producing microorganisms is by creating local acid environments within biofilms which might increase corrosion rate of many metals including carbon steel. These localized low pH environments might not be detectable with standard water testing procedures.

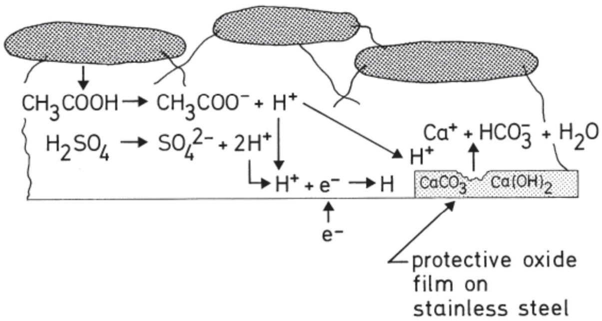

Figure 2. Acid production by biofilm bacteria resulting on electron removal from cathode by hydrogen or dissolution of protective calcareous layer on a stainless steel surface. Source: (Flemming and Geesey 1991).

3.1.3 *Iron and Manganese related microorganisms*

The complementary activities of iron oxidizers and iron reducers (IOB, IRB) are determinant on the stability of iron and therefore are key on corrosion processes in which some form of iron is involved. In acidic conditions, acidic iron oxidizers (AIO) can promote the oxidation of ferrous iron to ferric iron which results on the deposition of iron oxides and hydroxides and/or the formation of iron chloride salts which can be highly corrosive (Figure 3). On the other hand iron reducers can reduce ferric iron to ferrous (mobile) iron. By doing this, iron reducers can disrupt passivation layers which are known to protect several metals from corrosion. The main difference of these two processes is that microbial induced iron oxidation occurs in aerobic conditions, while iron reduction is an anaerobic respiration process.

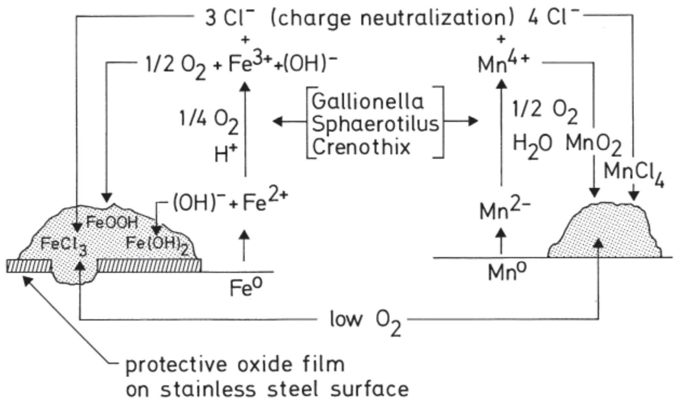

Figure 3. Iron and manganese oxidation and precipitation in presence of bacteria. Pitting occurs due to the presence of chloride ions concentrated at surface because charge neutralization of ferric and manganic cations. Source:(Flemming and Geesey 1991).

3.1.4 *Sulphate-reducing bacteria*

Traditionally, SRB are believed to be major players in biocorrosion. There have been several theories about the exact mechanisms but basically SRB are believed to accelerate corrosion by: (a) generating H_2S; (b) creating oxygen concentration cells; (c) forming insoluble sulphides when metal ions combine with sulphur and (d) by cathodic depolarization (Figure 4). In most environments SRB are participating in the cycling of sulphur in which SOB participate by oxidizing reduced sulphur compounds generated by SRB metabolism.

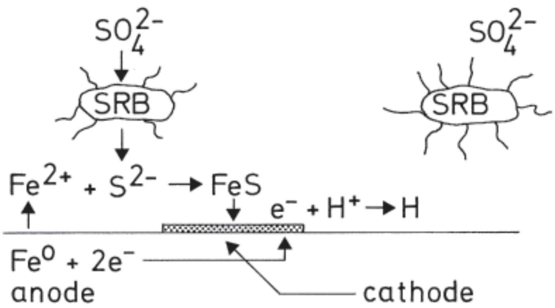

Figure 4. Cathodic depolarization caused by iron sulfide as a consequence of the reduction of sulphate by SRB. Source: (Flemming and Geesey 1991).

If SRBs are in direct contact with the metal, and if there is metal dissolution, either caused by the bacteria or by a galvanic process, SRBs are also able to use electrons directly from metal oxidation (Venzlaff et al. 2013).

4 Potency of macro-fouling to protect against corrosion

In the over simplified evolution of bio-fouling in relation with corrosion as described in paragraph 1.1, phase 2 thus delivers the highest protection against corrosion. Unfortunately as being part of the natural colonization process this phase will rapidly develop into phase 3 were MIC can occur resulting in localized acceleration of corrosion. The thicker biofilm that develops in phase 3 might include organisms that completely seal-off the metal surface from the environment like an industrial coating, and thus protecting the surface from corrosion. In this project we will refer to this as bio-coating.

4.1 Biofouling and corrosion

In literature some indications can be found that biofouling can have a protective feature against corrosion, e.g. (de Messano et al., 2009) (De Brito et al., 2007; Palanichamy et al., 2012). But, mechanisms behind these observations still are not completely clear. It seems that biofouling reduces general corrosion but can increase localized corrosion rates (De Brito et al., 2007). The latter (in many cases MIC) can be expected in phase 3 described above, when the fouling layer becomes thicker and leaves room for developing anoxic conditions. Such a situation can easily develop when sediment and/or organic matter can accumulate between larger organisms that are settled on the substrate. For instance between the shells of mussels substantial amounts of organics rich material can be present, where ideal conditions for MIC can develop. For being protective organisms should be attached directly to the steel surface, leaving little room for accumulation of material and microbial activity. This could be in the form of a thin biofilm of a dense community of larger organisms.

In thin biofilms sessile algae (diatoms) have a substantial contribution to the biomass (Landoulsi et al: 2011). As primary producers diatoms extract CO_2 for consumption which will result in localized reduction of the pH. At the same time the diatoms release dissolved oxygen to the surrounding water. This two related processes create conditions that favors corrosion. As primary production requires light it has been described that the corrosive potential of steel covered with diatoms follows a day and night regime, with higher corrosion rates in daylight (Eashwar et al., 1995) (Landoulsi et al: 2011). On the other hand diatoms can produce compounds that may play a beneficial role in protecting steel as H_2O_2 (Landoulsi et al: 2011). Eashwar and co-workers showed that corrosion was reduced for steel exposed to a normal day and night regime in comparison to steel placed in complete darkness. The biofilm that developed under the day/night conditions was dominated by primary producers which were logically absent in the biofilm that developed in the dark. This could indicate a nett protective property of primary producers in a biofilm.

The authors however do not claim a specific role for the primary producers but state that the underlying mechanism are related to passivity enhancement through photoinhibition and suppression of cathodic kinetics through photoinactivation of microbial redox reactions. They suggest illumination as a novel approach for the mitigation of SS corrosion in seawater ((Eashwar et al., 2011).

Encrusting bryozoans can also form a thin biofilm. Bryozoans live in colonies and produce mineralized exoskeletons. For encrusting species these skeletons form netlike structures that can cover relatively large areas. In theory such a bryozoan colony could work as a barrier that reduces the oxygen availability at the steel surface. However, the only paper known to us that describes a relation between encrusting bryozoans and corrosion shows a significant positive correlation between bryozoan coverage and corrosion rates (de Messano et al., 2009). The authors suggest that due to the porous structure of the bryozoan's exoskeleton the membranous base can permeate water and body fluids to the metal surface. This can change oxygen concentration and pH around and below the bryozoan colony. This observation was only related to the presence of two species (*Membranipora membranacea* and *Schizoporella errata*). The only other relevant observation known to us also concerns *S. errata* and concludes that the dominance of the bryozoans did not reduce the corrosion rate (De Brito et al., 2007). As bryozoans come in many forms it is possible that other bryozoans might give other results. But as far as we know no data on other species is available.

Barnacles are another general fouling organism that given the right season can rapidly colonize substrates in the marine environment. The base plate of barnacles is directly attached to the substrate surface, in theory isolating it from the oxidative environment and leaving little room for microbial activity. It has been reported that a high coverage with barnacles can reduce the uniform corrosion rate of a surface (De Brito et al., 2007). On a local scale the presence of barnacles can however increase corrosion. Corrosion pits on surfaces beneath barnacle settlement (Vedaprakash et al., 2013) suggests that the covering does not have to be a protective sealing in all cases. In addition there is no discussion that the barnacles' carapax wears down the metal surface resulting in localized ring shaped corrosion attacks (crevices) around the calcareous basis (de Messano et al., 2009) (Palanichamy et al., 2012) (De Brito et al., 2007).

Like the base plate of barnacles, oysters (with the Japanese Oyster, Ostrea gigas as the most common representative in Europe) grow their shells directly to the surface of the substrate on which the larvae settles. This substrate is thus protected from the oxidizing seawater, which could in theory thus be protective as was observed with barnacles (De Brito et al., 2007). As far as we know, until now no documentation is available on the influence of oysters on corrosion. Personal communication with people involved in the inspection of harbor quays however suggests that the presence of oysters reduced the corrosion rates. On the other hand oysters shells could cause crevices in steel (Palanichamy et al., 2012).

Sponges have the ability to cover surfaces with layer of living material. In literature no information was found on the impact of sponges on steel surfaces. Personal communication with sponge experts confirms that there is little interest in what happens underneath a sponge.

The general impression is that surfaces below sponges are clean, and shows no indications of being negatively impacted. As sponges are relatively soft, it is unlikely that they will cause crevices, and it seems likely that at the substrate oxygen concentrations will be reduced, due to the sponge‘s respiration without becoming anoxic. Sponges can survive at almost all water depths, as long as it’s below the low water line. Encrusting sponges have the best potential for material protection.

4.2 Potential approaches

4.2.1 Protective biofouling

As presented above thin biofilms can to some extend reduce corrosion rates, although in other situations increased rates can occur. As environmental conditions and the natural development are hard to control thin biofilms are probably less suitable to be used for durable protection of steel constructions. Encrusting bryozoans can form more stable thin biofilms, but the protective potential is doubtful.

Although solid knowledge about their impact on corrosion rates is lacking, oysters and sponges seems to show the highest protective potential. The actual impact on corrosion rates of these organisms must be determined in pilot lab scale studies that will help to identify the most promising species amongst those that are locally available. Introduction of non-native species cannot be considered. Once the optimal species have been identified the next challenge will be to ‘seed’ them on the steel surface and to maintain a stable population. For oysters this will be less a challenge.

4.2.2 Indicative biofouling

Knowing that a relation between biofouling and material protection can be expected, the type of bio-fouling might give indications about the maintenance status of the steel that is covered. If this relation can be established for certain types of fouling communities/organisms it can reduce inspection costs, as inspections can now focus on those part that are covered with biofouling that has no positive (or even negative) impact on the corrosion rates. To establish this relation it is necessary that during future inspections the type of bio-fouling is described and related to the state of the steel that it covers. Such an inventory could also result in the identification of other protective biofouling species/communities that those addressed above.

5 Use of bioelectricity for cathodic protection

The potential difference in (marine) sediments generated by microbial respiration has been investigated as an environmentally friendly way of electricity generation (http://www.nwo.nl/en/research-and-results/cases/bio-batteries-in-the-seabed.html). Although the technology has been in development for years, it has not been widely applied due to the rather low amount of electricity generated. The use of this technology as a realistic energy source has proven difficult to achieve.

The generated electricity, however, might be sufficient for the application of cathodic protection in structures exposed to corrosive aquatic environments. Impressed current cathodic protection techniques are widely applied. Bioelectricity could therefore be used for e.g. the cathodic protection of mild steel or stainless steel. This environmental friendly and inexpensive method could be a good alternative for the methods for cathodic protection used at the moment: the sacrifial anode or the impressed current method, which can be complicated and expensive.

The principle of getting current from an active sediment is simple. Sediment naturally contains a wide variety of microorganisms and therefore can be used as part of a Microbial Fuel Cell (MFC). In the MFC, the sediment serves as the media, the inoculum (the bacteria) and the proton-exchange membrane at the same time. It further requires an anode stuck in the sediment for the bacteria to use it as electron acceptor and a cathode e.g. an electrode in the seawater or stainless steel (cathodic protection). In this way, the microbial respiration is used to convert chemical energy into electrical energy.

The more organic rich a sediment (i.e. typical of harbours), the more microorganisms will live in it and the more electric power that could be generated from it. Several investigations have been done regarding this subject. Reimers et al. (2001) were able to obtain current from a marine sediment – water interface system using platinum or graphite electrodes. The sediment (anode)-seawater(cathode) configuration was found to create enough power to operate e.g. oceanographic instruments.

Laboratory experiment with sediment from river water were done by Sudhakar (2012) where they successfully generated electricity using a zinc anode put in river mud and a graphite cathode put in river water, resulting in electricity with a maximum potential difference of 0.5V.

Orfei et al.(2006) did some lab-scale experiments with graphite electrodes buried in marine sediment. They were able to cathodically polarize stainless steel exposed to seawater with this being the only source of electric power. They found that this method was able to protect the stainless steel in a way that the material would show no failure.

A research group of the Aarhus University claim to have found bacteria in the seabed that function as living electric cables. This bacteria are said to be able to transport electrons of centimeters of distance and therefore facilitating the electric current in the sediment (Pfeffer et al. 2012).
The big advantage of using sediment as a source for electric power is that the fuel is naturally present and constantly renewed.

6 Proposed pilot studies

For the further development of this protecting with nature concept (Figure 5) a couple of pilot studies are proposed in which the practical applicability of the basic elements will be tested. These elements all have their own potential for application and are not mutual depended.

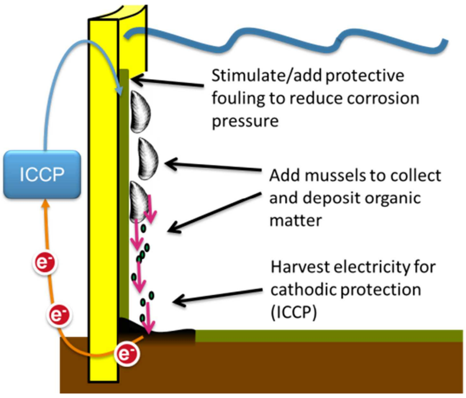

Figure 5. Complete Protecting with Nature against corrosion concept

6.1 Indicative bio-fouling

Goal: Trying to establish the relationship between the type of fouling and the state of the underlying material.
Approach: Working together with companies that preform regular inspections, collecting additional data on fouling types.
Cost indication: EUR 50,000.-.

6.2 Protective macro-fouling

Goal: Determining the impact of sponges on corrosion rates. Identifying the most promising species.
Approach: Sponges collected in the field will be transferred to steel elements that will be exposed under controlled semi-field conditions. Cortisone rates will be followed. In addition various approached to ‘seed’ sponges on a steel substrate will be tested.
Costs: EUR 75,000.-.

6.3 Impressed current cathodic protection

Goal: Determining the performance and energy demand of impressed current cathodic protection in various environmental conditions.
Approach: The effectiveness of ICCP will be tested on different field locations. For this, electricity will be from traditional sources, not bio-electricity.
Costs: EUR 75,000.-.

6.4 Applicability of bio-electricity

Goal: Determining the potential of various marine sediments, with emphasis on harbors, for producing bioelectricity.
Approach: The potential of sediments collected in the field will be tested under controlled lab conditions. In addition a field location will be tested.
Costs: EUR 50,000.-.

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8 Signature

Delft, 24 December 2014

Jan Hoegee
Director Maritime and Offshore

TNO

Harald van der Mijle Meijer
Project leader