Characterization of steel surface under cathodic protection in seawater

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Characterization of steel surface under cathodic protection in seawater

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Abstract

Purpose – The purpose of this paper is to characterize the surface of steel under cathodic protection while submerged in seawater, to understand the mechanism that controls the operation of the protection system.

Design/methodology/approach – Steel rods were immersed in seawater and NaCl solution with applied cathodic protection. The experimental methodology included monitoring of corrosion potential (E_corr), galvanic current (I_galv), protection potential (E_protection) and the depolarization potential of steel during the time of exposure. In addition, the chemical composition of the steel surface was assessed using a Scanning Electron Microscope (SEM).

Findings – In this research it was determined that the effectiveness of the CP system was mainly attributable to the formation of an iron oxide film on the steel surface.

Research limitations/implications – It is necessary to carry out analysis of the chemical composition of deposits formed on the steel surface, perhaps using X-ray diffraction (XRD), to verify the presence of a protective oxide.

Practical implications – Deposits on the steel surface have the beneficial effect of reducing the current required for efficient protection. Deposit formation therefore is of economic interest, as it decreases the cost of protection.

Originality/value – A unique feature of cathodic protection in seawater is the formation of calcareous deposits on metal surfaces. Advantageous aspects of these deposits, such as decrease in cathodic current requirement, have been investigated by various authors from various viewpoints. However, very little attention has been paid to the impact of any iron corrosion product films; the present paper contributes useful understanding and explains the importance of the mechanism that controls the operation of the protection system.

Keywords Steel, Cathodic protection, Films (states of matter), Seawater, Steel rods, Galvanic current, Surface properties of materials

Paper type Research paper

1. Introduction

Cathodic protection (CP) has been used as an effective technique to prevent corrosion of metallic structures in the oil, gas and marine industries, (Rousseau et al., 2010; NCHRP SYNTHESIS 398, 2009; Miyata and Wakabayshi, 2006; Kim and Scantlebury, 2004).

CP is defined as “electrochemical protection achieved by decreasing the structure potential to a level whereby the corrosion rate of metal is significantly reduced.” However, this definition still fails to provide information regarding the nature and role of the metal/electrolyte interface, or the influence of surface films that form at this interface during the CP process (Leeds and Cottis, 2004). When applying CP for the first time to a structure, it is well known that a higher current and more negative structure/electrolyte potential than the original open circuit potential (OCP) is observed. Over a period of a week or more after the CP is connected, the current decreases and the potential becomes more negative than the initial value (i.e. the potential value just minutes after the anode is connected to the structure) until it

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were used as blanks in the respective electrolytes. B4-B6 in NaCl solution were not cathodically protected and the monitoring of depolarization and galvanic currents. The anode/cathode area ratio was 1:1. Both metals were individually connected, outside the acrylic cells, to facilitate the monitoring of depolarization and galvanic currents. Depolarization measurements for the six protected specimens in seawater showed increased polarization compared to those immersed in NaCl solution, and this difference was attributed to the chemical composition of the electrolyte.

2.2 Potential and current measurements
The monitoring period for all of the specimens was 230 days. Corrosion potential (Ecorr) was measured according to ASTM C876. The protection potential (Eprotection) and the depolarization current galvanic decreased until values close to Eprotection of 250 mV in NaCl solution, and this difference was attributed to the sacrificial anodes. The displacement of potential from the OCP value was obtained due to its interaction with the sacrificial anodes. The potential difference between the “instant off” value and the potential values obtained after 4 and 24 h was more positive than 100 mV. However, although all of the CP systems were effective, the steel rods immersed in seawater showed increased polarization compared to those immersed in the NaCl solution, and this difference was attributed to the chemical composition of the electrolyte.

3. Results

3.1 Corrosion potential
The Ecorr values of the blank steel rods (B1-B6) after 20 days immersion varied between 50 and 750 mV vs SCE for both electrolytes, see Figure 2. The potential values of the specimens indicated corrosion problems according to ASTM C876.

3.2 Protection potential
The potential values of steel rods P1-P6 within the first seven days of immersion indicated corrosion problems, but afterwards a potential shift in the negative direction was obtained due to its interaction with the sacrificial anodes. The displacement of potential from the OCP value was between 50 and 250 mV in the negative direction in all cases (P1-P6) (recorded values were about Eprotection of 100-200 mV vs SCE). This value remained constant during the rest of the monitoring period (Figure 3).

3.3 Steel potential depolarization
Depolarization measurements for the six protected specimens in (P1-P6) were performed after 58, 118 and 205 days after anode/rebar connection. The results are shown in Table I. All pairs (rebar/anode) match the 100 mV criterion established by NACE RP 0285 and TM 0101. The potential difference between the “instant off” value and the potential values obtained after 4 and 24 h was more positive than 100 mV. However, although all of the CP systems were effective, the steel rods immersed in seawater showed increased polarization compared to those immersed in the NaCl solution, and this difference was attributed to the chemical composition of the electrolyte.

3.4 Current densities
Current densities were measured between the zinc anode and the protected steel rods (P1-P6), see Figure 4. The galvanic current decreased continuously until day 120, with values close to 1 mA/m² for the seawater, while for NaCl solution the current galvanic decreased until values close to 2 mA/m². Afterwards, these values were almost constant (Figure 4). At the end of the experiments the specimens polarized in the seawater required the smallest current density compared to specimens polarized in 3.5% NaCl. The reason for this could be due to the thicker calcareous films that were formed on specimens polarized in seawater.
**Figure 1** Electrochemical cell

![Electrochemical cell diagram](image1)

- Reference electrode (SCE)
- Anode (zinc wire)
- Work electrode (steel rod)

**Figure 2** Corrosion potential variation

![Corrosion potential variation graph](image2)

**Figure 3** Protection potential of the galvanic pair CS-Zn

![Protection potential graph](image3)

**Table 1** Depolarization potentials

<table>
<thead>
<tr>
<th>Seawater</th>
<th>Specimen</th>
<th>After 58 days with CP</th>
<th>After 118 days with CP</th>
<th>After 205 days with CP</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Inst. off. 4 h 24 h</td>
<td>Inst. off. 4 h 24 h</td>
<td>Inst. off. 4 h 24 h</td>
</tr>
<tr>
<td>Seawater</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>P1</td>
<td></td>
<td>-1.047 -928 -815</td>
<td>-1.048 -942 -873</td>
<td>-1.051 -929 -873</td>
</tr>
<tr>
<td>P2</td>
<td></td>
<td>-1.072 -935 -860</td>
<td>-1.046 -950 -897</td>
<td>-1.031 -895 -841</td>
</tr>
<tr>
<td>P3</td>
<td></td>
<td>-1.072 -936 -865</td>
<td>-1.046 -945 -895</td>
<td>-1.031 -891 -839</td>
</tr>
<tr>
<td>3.5% NaCl solution</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>P4</td>
<td></td>
<td>-1.030 -830 -742</td>
<td>-1.030 -953 -796</td>
<td>-1.034 -896 -776</td>
</tr>
<tr>
<td>P5</td>
<td></td>
<td>-1.017 -821 -743</td>
<td>-1.028 -810 -759</td>
<td>-1.034 -812 -752</td>
</tr>
<tr>
<td>P6</td>
<td></td>
<td>-1.033 -852 -775</td>
<td>-1.026 -829 -775</td>
<td>-1.031 -842 -775</td>
</tr>
</tbody>
</table>
3.5 Visual changes
After five days of CP in seawater, dispersed bubbles were observed on the rebars surfaces (cathodes), and as time passed these surface bubbles changed to form an adherent and uniform white coating on the surface (Figure 5). According to the difference in surface appearance between specimens (B1 and P2) it was evident that the CP connection helped in the formation of the compound layer on the rebar surface. In the NaCl solution, on rebar surfaces with CP, dispersed bubbles were observed but did not change to form an adherent and uniform layer.

3.6 SEM and EDS examination
Rebar surface immersed in seawater without CP
After 49 day of exposure in seawater, Figure 6 shows two zones of the steel rod (B1). Table II presents the chemical composition determined at these zones. The layer in Zone 1...
(oxide layer) was formed by iron, manganese and oxygen, and at the Zone 2 (rebar) consisted only of iron and manganese.

Rebar surface with CP immersed in seawater
Specimen P1 (protected) was taken out from the electrolyte (seawater) after 41 days of the CP connection with a zinc anode wire, and its surface was examined using the SEM, see Figure 7. Using EDS the area identified as Zone 1 was the composition of the outer layer of the white product, Zone 2 was the composition of the intermediate oxide layer, Zone 3 was the composition of oxide adhering to the steel rod (inner layer), and Zone 4 corresponded to the steel rod composition.

Table III shows the chemical composition of specimen P1 after 41 exposure days in seawater under CP.

4. Discussion

Current density and deposits on the surface of the steel
When cathodically polarizing a metal surface the following processes occur at the metal/electrolyte interface: increase in solution pH, decrease in anodic dissolution kinetics, increase in oxygen reduction kinetics (though this may be limited by mass transport) and increase in hydrogen evolution kinetics (if the potential is sufficiently negative). As a result of the above processes, various changes happen to the metal surface. For all of the polarized specimens, morphological changes to the metal surface occurred during the test period. No specimen was found to be the same shiny metal at the end of the experiment as it was at the start.

For steel rods immersed in seawater (P1-P3) it was observed over time that the current density decreased to a steady value (Figure 4). This result was attributed to the chemical composition the electrolyte. Seawater consists of many salts and numerous organic and inorganic particles in suspension. Its main characteristics are salinity and chlorinity and, from the corrosion point of view, DO content which ranges from 4 to 8 mg/l, depending on temperature and depth. Seawater is slightly alkaline with a pH about 8.0 but when it is contaminated by acids, such as in coastal regions near power stations burning fossil-fuels generating acidic rains, the pH can diminish to 6 or 5. An important feature of CP in seawater is the formation of calcareous deposits. It is generally agreed that the calcareous deposit that forms comprises a relatively thin, uniform, Mg-rich inner layer, presumed to be magnesium hydroxide, and a thicker outer layer of overlapping aragonite needles (Luo et al., 1991; Zamanzade and Shahraei, 2007). During the calcareous deposit formation, the active surface progressively decreases,
and then the anode dissolution and the rate of reaction are lowered. Hence, calcareous deposit has the beneficial effect of reducing the current required for an efficient protection. The deposit layer acts as a physical barrier that can cause polarization of the interface as a result of oxygen diffusion limitation, thereby protecting the surface (Solis and Genesca, 2011). Thus, the current densities of all of the specimens studied were found to decrease with time, suggesting that an insulating coating was progressively blocking the steel surface.

No calcareous deposits were identified in the blanks. This showed that films on the metal surface are direct result of applying CP.

On the other hand, according to the criteria for protection under the NACE RP 0285 and TM 0101, the CP system was effective for the samples immersed in seawater (P1-P3).

The current density in NaCl solution (P4-P6) also decreased as time passed, although there was no presence of calcareous deposits because the chemical composition of the electrolyte was different. Leeds showed that on specimens exposed to pure 3.5% NaCl where no calcareous deposits were present, the most coherent films formed on specimens that were polarized between −1.3 and −1.4 V (Ag/AgCl/3.5% NaCl). These specimens had the lowest corrosion rates and surface films were composed of magnetite (Leeds, 2009). Other studies carried out by Leeds identified iron corrosion products as a major constituent of the surface films. Magnetite was found to form on the metal surface as the potential was made more negative and it also formed a coherent film that was protective in nature (Leeds and Cottis, 2004).

According to the criteria for protection under the NACE RP 0285 and TM 0101, the CP system was effective on steel rods immersed in the 3.5% NaCl solution (P4-P6). This meant that the presence of calcareous deposits contributed to reduced current density, but is not primarily responsible for the effectiveness of CP.

The current decreased for all specimens between the start current and the end current. At the end of the experiments, the specimens polarized in seawater required the smallest current density compared to specimens polarized in 3.5% NaCl. The reason for this could be due to the thicker calcareous films that form on specimens polarized in seawater. Something, such as the surface film, caused a very significant reduction in current by blocking off the specimen surface, leaving less steel exposed to receive current. Also important is the fact that the films must be relatively non-conducting by insulating away the specimen surface.

**SEM and EDS examination**

*Morphological changes of specimens*

Table III shows for specimens exposed in seawater under CP, the chemical composition of the inner layer, or the composition of oxide adhering to the steel rod (Zone 3), had the highest Fe content, accompanied by oxygen, chloride, magnesium, manganese and calcium concentrations. This indicates that this layer comprised mainly steel corrosion products. The analysis results from layers formed in Zones 1 and 2 showed that the chemical elements were similar. The presence high of zinc in the Zone 1 (composition of the outer layer of the white product) was attributed to oxidation of the anode present in the electrolyte and the salts content was attributed to seawater salts, e.g. Cl⁻, SO₄²⁻ and Mg. In Zone 2 (composition of the intermediate layer) the presence of calcium and the salts were attributed to the chemical composition of the seawater.

Considering the opinion of Leeds (2009), who identified using X-ray diffraction and energy dispersive analysis that as the applied potential was made more negative (with CP), the constituents of the film/deposit changed from consisting of predominantly iron corrosion products to consisting of calcium carbonate containing products, calcite and aragonite (Leeds, 2009), the present research confirms that the application of cathodic current leads to the formation of calcareous deposits on the protected steel surface. In the blanks (without CP), no calcareous deposits were formed on the surface.

In NaCl solution, no visible deposit was perceived on the steel surface. However, Leeds (2009) reported that corrosion products formed on the freely corroding specimen immersed in NaCl solution were akaganeite (b-FeOOH), goethite (a-FeOOH), lepidocrocite (γ-FeOOH) and magnetite (Fe₃O₄), and as the applied potential became more negative only the iron corrosion products goethite (a-FeOOH), lepidocrocite (γ-FeOOH) and magnetite (Fe₃O₄) were identified.

Further research is necessary on the chemical composition of such deposits to clarify the composition of products formed on steel surfaces under CP.

**5. Conclusions**

- As the \( E_{\text{protection}} \) and potential depolarization values measured meet the criteria of 100 mV in the seawater and 3.5%, NaCl solution, the steel rods were adequately protected.
- Reduced galvanic currents measured after a certain time under CP were associated with the formation of deposits on the steel surfaces, suggesting that the film acts as an insulator blocking access to the metal surface.
- The effectiveness of CP can be attributed mostly to the formation of an iron oxide film.
- In seawater, the formation of calcareous deposits contributes to reduced current density, but is not primarily responsible for the effectiveness of the CP.

**References**

ASTM A496 (2001), Standard Specification for Steel Wire, Deformed, for Concrete Reinforcement.


NCHRP SYNTHESIS 398 (2009), A Synthesis of Highway Practice Cathodic Protection for Life Extension of Existing Reinforced Concrete Bridge Elements, Transportation Research Board, Washington, DC.


Further reading


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