SIGNIFICANCE OF HYDROGEN EVOLUTION IN CATHODIC PROTECTION OF STEEL IN SEAWATER

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Abstract
Current requirement and calcareous scale properties on carbon steel were investigated as a function of applied potential, flow rate and time in natural seawater. The current requirement was dominated by oxygen reduction during the initial stage of polarization after application of cathodic protection. However, as the calcareous scale deposited, oxygen reduction reaction rate decreased, and hydrogen evolution became the dominating cathodic process. Furthermore, the rate of hydrogen evolution appeared to become catalyzed by the presence of the calcareous scale deposit. Maximum Ca/Mg ratio in the calcareous deposit gave the best protection and minimum current requirement. The Ca/Mg maximum was determined by the applied potential and seawater flow rate.

Keywords: Carbon steel, cathodic protection, seawater, hydrogen evolution, calcareous deposits

Introduction
The significance of the oxygen reduction reaction on the formation of calcareous scale during cathodic protection of steel in seawater is widely studied. Factors such as temperature, pH, flow conditions and water composition strongly affect the precipitation of the calcareous deposit at the steel surface. During initial polarization oxygen reduction is the dominating reaction. It is well documented that oxygen reduction rate also affects the properties of the calcareous scale, which in turn determines the extent to which the current requirement is reduced [1, 2, 3], an important aspect in the cathodic protection of steel in seawater.

Little work is available on the significance of calcareous scale on hydrogen reaction rate. Hydrogen evolution can cause hydrogen embrittlement if atomic hydrogen diffuses into the steel material. Determination of hydrogen diffusion into the material is complex. Even though the reaction rate at the surface is measured, it is difficult to quantify the amount of hydrogen that diffuses into the material and the amount that reacts to form hydrogen gas. Andresen et.al. found the hydrogen reaction rate was decreased as a result of cathodic protection in seawater because calcareous deposits at the surface reduced the active area [4]. Similarly, Ou and Wu report that the calcareous scale acted as a barrier for diffusion of hydrogen ions to the steel surface [5], thereby reducing the rate of hydrogen evolution. The purpose of the present work is to investigate the hydrogen reaction during cathodic protection on carbon steel in natural seawater. The approach used was to polarize carbon steel specimens under scaled down laboratory conditions first potentiostatically at selected potentials in the range -800 through -1200 mV\(_{SCE}\) to steady-state conditions with well defined calcareous scale properties. The contribution of hydrogen evolution to the
steady-state current requirement was then investigated by potentiodynamic sweep runs on the polarized specimens without destroying the calcareous deposits formed.

**Scale-down for experiment**

In earlier work in this laboratory, an attempt was made to scale cathodic protection in the field to the laboratory scale by using an algorithm described in Reference [1]. The main principle of downscaling is to assure that the thickness of diffusion layer for oxygen reduction on the steel sample obtained in the laboratory is identical to the thickness expected under realistic conditions on the steel structure in the field. In order to satisfy this condition, the flow rate in the laboratory has to be reduced significantly in relation to the flow rate in the field, assuming that the seawater properties used in the laboratory are identical to those in the field. The result is shown in Figure 1. For example, flow of seawater at a rate of 0.3 and 1 m/s around a 1 m diameter subsea structure can be simulated in the laboratory, respectively, by using flow rates of 1 and 10 cm/s past the small plate specimens.

![Figure 1. Relation between flow rate for sheet specimen (15×35 mm) and a subsea pipeline with diameter 1 m at 0.3-1.0 m at 10°C](image)

**Experimental**

**Specimens**

The test material was carbon steel with composition as given in Table 1.

<table>
<thead>
<tr>
<th>Element</th>
<th>C</th>
<th>Mn</th>
<th>P</th>
<th>S</th>
<th>N</th>
<th>Cr</th>
<th>Ni</th>
<th>Cu</th>
<th>Al</th>
<th>Nb</th>
</tr>
</thead>
<tbody>
<tr>
<td>wt%</td>
<td>0.04</td>
<td>0.22</td>
<td>0.009</td>
<td>0.014</td>
<td>0.003</td>
<td>0.02</td>
<td>0.04</td>
<td>0.01</td>
<td>0.035</td>
<td>0.001</td>
</tr>
</tbody>
</table>

The plate specimens (15 mm × 50 mm) had a thickness of 1 mm. The specimens were polished by using a 320 grit SiC paper, rinsed successively in isopropanol and ethanol and then dried in a silica-gel desiccator. A copper wire was attached to the steel as the electrical connection, as shown in Figure 2. The steel specimen was moulded into a PVC casing by using epoxy. The resulting exposed specimen area was 15 mm × 35 mm. The PVC casing was designed to fit the flow channel used,
shown in Figure 3. A standard calomel electrode (SCE) was used as a reference electrode.

**Apparatus**

Cathodic polarisation tests were performed in flowing fresh natural seawater, which was obtained from a depth 80 - 90 m in the Trondheim's Fjord. Seawater was sand filtered and allowed to enter the flow channel by gravity. The seawater was not recycled.

A cylindrical titanium flow channel was used with a total length of 2 m (Figure 3). The inner diameter of the channel was 52.8 mm. Ten specimen holes were evenly placed along the channel top. Eight sheet specimens and two SCE reference electrodes were mounted through the holes. Four specimens were connected to each of the reference electrodes. The steel sample surfaces were aligned parallel to the flow direction. The distance between the centres of the electrodes was 180 mm. The flow channel was used as a common counter electrode for all specimens. The channel was installed with a slope of $2^\circ$ to prevent trapping of gas bubbles.

![Schematic illustration of the test specimen.](image-url)

Figure 2. Schematic illustration of the test specimen.
A temperature sensor probe was mounted at the seawater inlet, and the temperature was continuously recorded. The temperature was in the range 8-10 °C during all runs. It could not be controlled more accurately. The seawater flow rate was controlled manually and frequently during a run by use of a mechanical valve at the seawater inlet. The flow rates used were 1, 5 and 10 cm/s.

Each steel sample was connected to a separate potentiostat (Wenking MP75/MP81), and the applied potential and the resulting sample current were continuously recorded in the usual manner.

**Procedure**

The electrochemical test procedure consisted of potentiostatic polarization of the steel specimen at selected potentials in the range -800 through -1200 mV_{SCE}. The time of polarization varied between 140 and 320 hours depending on how fast a steady-state current was obtained. At the end of this period, the specimens were polarized potentiodynamically starting from the potentiostatic potential, first in the negative direction to -1300 mV_{SCE}. The potential sweep was then reversed and the specimens were polarized from -1300 mV_{SCE} to zero current. The sweep rate was 0.5 mV/s during the potentiodynamic polarization. Absence of hysteresis in the reverse-sweep data indicated that the calcareous scale, which was formed during potentiostatic polarization was not destroyed during the potentiodynamic run.

After potentiostatic testing a replicate steel specimen surface was characterized in LV-SEM (Low Vacuum Scanning Electron Microscope). EDS (Energy Dispersive Spectroscopy) analysis was used to examine the chemical composition of the calcareous scale. Specimens that were examined in SEM were not subjected to potentiodynamic polarization.
Results and Discussion

**Polarization data**

The cathodic current density is reported as a positive entity, as is often the case in the cathodic protection literature. All potentials are reported relative to SCE. The current density decreased immediately after application of the selected potential. Time to reach a steady state depended on the applied potential and flow rate.

Figure 4 a)-c) show the current density transients for replicate specimens polarized at -800, -1100 and -1200 mV, respectively, at 5 cm/s. At -800 mV the current density attained a steady state after about 100 h. However, a current plateau was observed from about 10 to 30 h of polarization, indicating an induction period before the onset of calcareous scale deposition [1]. A similar plateau region was also observed at -900 mV. This trend was more significant at the higher flow rate, and it was not visible at the lower flow rate. The delay in the deposition of calcareous scale is attributed to longer time required to attain high enough pH at the surface due to a high (positive) applied potential and flow rate. As is well known, the surface pH has to exceed a critical value for the onset of scale deposition, and attainment of the critical value depends on the operating conditions [4]. At -1100 mV applied potential and 5 cm/s flow rate, the current density did not reach a steady state after about one week of polarization, as shown in Figure 4 b). This was also the case for -1000 mV at 5 cm/s, indicating that the deposition kinetics was slow for the entire test period under these conditions. At -1200 mV SCE, fast stabilisation occurred and the steady-state current was obtained after about 50 h, indicating fast deposition of calcareous scale.
**Hydrogen evolution**

The steady-state current on a cathodically-protected surface is essentially determined by the rates of hydrogen evolution and oxygen reduction, assuming that the corrosion rate is negligible,

\[ i_{\text{net}} = i_{H_2} + i_{O_2} \]  \hspace{1cm} (1)

The dominating reaction at the surface is determined by the applied potential, flow rate and quality of the deposit. The contribution of hydrogen evolution to the steady state current was determined by using the potentiodynamic polarization plots obtained at the end of potentiostatic polarization runs. These plots normally consist of a limiting current section if the oxygen reduction reaction is still appreciable on the surface, as shown in Figure 5. The Tafel part corresponds to the hydrogen evolution reaction. The Tafel line was extrapolated to the potential applied during the potentiostatic run before the potentiodynamic run. Thus, the hydrogen current at this potential was determined from the extrapolated Tafel line, and the total current at the same potential was obtained from the measured polarization curve as shown in the figure. The current due to the oxygen reaction was obtained from Equation 1. The fraction of hydrogen current was then plotted as a function of the potentiostatic potential as shown in Figure 6, indicating that hydrogen evolution is the dominating reaction at or close to steady state for applied potentials \( \leq -1000 \text{ mV} \).

![Figure 5](image)

*Figure 5. Potentiodynamic polarization data obtained at the end of potentiostatic polarization at -800 mV. Tafel slope for hydrogen evolution at steel surface with calcareous deposit is determined from the potentiodynamic curve in the manner indicated.*
Calcareous deposits

As already indicated, the properties of calcareous deposit are strongly dependent on the applied potential and flow rate. The deposits are reported to contain Mg(OH)$_2$ and CaCO$_3$. The magnesium and calcium phases deposit, respectively, as a thin film and in the form of discrete crystalline particles [6]. Structure and chemical composition of the calcareous deposits are determined by the pH at the steel surface, which in turn is dependent on the applied potential and the flow conditions. The pH at the surface decreases as flow rate increases due to increased mass transfer of OH$^-$ from the surface. The pH increases with decreasing potential as a result of increased cathodic reaction rate at the surface, thus, increased production of OH$^-$. To obtain a co-precipitation of CaCO$_3$ and Mg(OH)$_2$, the solution has to be oversaturated by both species. Saturation point depends on pH, and CaCO$_3$ will theoretically precipitate at a lower pH than Mg(OH)$_2$ [7]. Mantel et al. have proposed that CaCO$_3$ precipitation is inhibited by magnesium in the solution [6]. Due to the slow kinetics of CaCO$_3$ precipitation at about 10°C [8] and presumable magnesium inhibition, Mg(OH)$_2$ can precipitate at a lower pH than CaCO$_3$.

With the foregoing background, the present results can be viewed. Figure 7a shows that calcium phase precipitated at -900 mV and 1 cm/s, but no calcium appeared at 10 cm/s, as shown in Figure 7b. At -1100 mV the conditions for CaCO$_3$ was improved at 10 cm/s compared to 1 cm/s due to increased pH, shown in Figure 7c and 7d. Figure 7e shows that the calcareous deposit at a surface polarized at -1200 mV and 10 cm/s was covered by clusters of CaCO$_3$ crystals. At -1200 mV and 1 cm/s, a relatively thick Mg(OH)$_2$ layer was precipitated, and no calcium phase was present.

Figure 8 shows the Ca/Mg ratio in the calcareous deposit as a function of potential for 1 and 10 cm/s. Ca/Mg ratio was determined by EDS analysis. Flow rate had a large influence on the chemical composition in the deposit. At -800 mV and 1 cm/s, the scale contained only Mg(OH)$_2$. As the applied potential became more negative (-900 mV), the conditions for CaCO$_3$ precipitation was improved due to increased surface pH. Figure 11a confirms calcium phase is formed at -900 mV and 1 cm/s. At -1000

![Figure 6: Contribution of hydrogen evolution to steady state current density as a function of applied potential.](image-url)
mV, the pH is even higher, which favours CaCO₃ precipitation. Maximum Ca/Mg ratio was obtained at -1000 mV and 1 cm/s, and the ratio decreased with decreasing potential. At low potentials the pH is high and the driving force for Mg(OH)₂ precipitation is also high. In addition, magnesium causes an inhibition of CaCO₃ deposition, as described earlier. Thus, the deposit consisted of only Mg(OH)₂ at -1200 mV and 1 cm/s and no calcium phase was present.

By increasing the velocity to 10 cm/s, the surface pH is decreased. Hence, calcium phase was not precipitated until the potential was decreased to -1000 mV at 10 cm/s. Figure 11b shows the absence of calcium in the scale formed at -900 mV and 10 cm/s. At 10 cm/s, the Ca/Mg ratio increased as the potential became more negative,
and maximum Ca/Mg ratio was obtained at -1200 mV within the test potential range. High calcium content in the calcareous scale at -1200 mV and 10 cm/s, shown in Figure 7e, led to the minimum current demand at this flow rate, as indicated in Figure 6. This indicates that calcium phase caused a lower reaction rate at the surface and a low protection demand at a given flow rate. Increasing flow rate caused a slower build-up of OH⁻ at the surface, and the conditions for precipitation of a pure magnesium deposit were not present. By an additional decrease in potential, however, the Ca/Mg ratio is expected to drop also at the high flow rates.

The slow decay of current towards a steady state at -1100 mV and 1 cm/s, as shown in Figure 4b, is attributed to slow CaCO₃ deposition. Barchiche et al. found that the kinetics for CaCO₃ deposition is slow at 10°C [8]. This leads to slow stabilisation of the current. Present EDS analysis proved also that appreciable CaCO₃ was deposited at -1000 and -1100 mVₛₑₑ at 1 cm/s and 10 cm/s. The same behaviour is expected for 5 cm/s, although complete data at this flow rate is not yet available.

The expected trend in the Ca/Mg ratio is illustrated in Figure 8 as a function of applied potential and flow rate. As the flow rate increases, the maximum Ca/Mg ratio is expected to appear at lower potentials, and the maximum value is expected to increase with increasing flow rate. Increased Ca/Mg with increasing flow rate is also reported by Hartt et al. [7] The present data, indicating a maximum Ca/Mg ratio at a specific applied potential and flow rate has not been reported in earlier studies.

![Figure 8. Ca/Mg ratio in the calcareous deposit as a function of applied potential and flow rate. —— Measured. ----- Estimated.](image)

Summary

The steady-state current increased with decreasing applied potential. Time to obtain steady-state condition increased as the flow rate increased. The kinetics of calcareous scale deposition decreased in the range -800 to -1100 mV with increasing flow rate. At -800 and -900 mV a plateau of current was established initially, indicating an induction period for scale deposition, and the current decreased after this period as a scale providing adequate diffusion limitation was formed.
Hydrogen evolution was the dominating reduction reaction at calcareous surfaces at potentials lower than -950 to -1000 mV. Oxygen reduction contributed to the net current at more positive potentials. The Tafel slope for hydrogen evolution obtained by potentiodynamic polarization of specimens depended on pH at the surface. The Tafel slope increased with increasing potential and increasing flow rates, thus, with increasing pH.

Structure and composition of the calcareous deposits was strongly dependent on the applied potential and flow rate. The kinetics for deposition of CaCO_3 at potentiostatically polarized surfaces was slow at 8-10°C. CaCO_3 precipitation depended on pH and was inhibited by magnesium in the solution. The kinetics for Mg(OH)\_2 precipitation was faster than CaCO_3, and Mg(OH)\_2 was formed at all potentials and flow rates investigated.

Deposits formed at -800 mV contained no calcium phase due to low pH value and partly due to inhibition of calcium phase deposition by magnesium present in the solution. CaCO_3 was precipitated at -1000 and -1100 mV at 1, 5 and 10 cm/s. At 1 cm/s the maximum Ca/Mg was at -1000 mV, and the ratio decreased with more negative potentials due to magnesium inhibition and high driving force for Mg(OH)\_2 precipitation. At -1200 mV and 1 cm/s the calcareous scale contained only Mg(OH)\_2. At 10 cm/s, the Ca/Mg ratio increased from -1000 mV to -1200 mV. The pH at the surface is lower at 10 cm/s compared to 1 cm/s and the driving force for precipitation of a magnesium scale was less. Thus, higher flow rate favoured CaCO_3 deposition.

CaCO_3 was precipitated at increasingly negative potentials as the flow rate increased, e.g., -900 mV at 1 cm/s and -1000 mV at 10 cm/s. The Ca/Mg ratio increased with increasing flow rate at -1100 mV and -1200 mV. At -900 and -1000 mV the Ca/Mg ratio decreased as the flow rate increased.

References