

CP of Steel in Soil: Temporospatial pH and Oxygen Variation as a Function of Soil Porosity

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ABSTRACT

This paper documents an investigation of pH variations in water saturated sandy soil with steel samples under impressed current cathodic protection (CP). The aim of this work was to evaluate the temporal and spatial variation in pH and oxygen under different protection current density and different soil porosity.

Carbon steel samples were buried in quartz sand saturated with a simulated soil solution. The pH variation was determined by means of planar optical sensors and iridium oxides (IrOx) sensors. The oxygen variation was determined by means of fiber optical oxygen sensors. Different soil porosities were studied by dosing quartz sand with various granulometry.

The increase of pH at the sample surface occurred within the first 10 hours from CP application independently from the soil porosity. The alkalinity produced from CP, and thus the near-field pH, was dependent on the cathodic current density. The pH gradient as a function of the distance from the steel surface was dependent on the soil porosity.

The oxygen consumption rate at the steel surface was dependent on the cathodic current density. The oxygen concentration at the steel surface was reduced by at least 50% within 20 hours of CP application independently from the soil porosity.

Thus, this work confirms that CP increases the pH and reduces the oxygen concentration at the working electrode, thereby strengthening the established view that corrosion protection can be achieved through generating conditions that facilitate passivation.

Key words: Cathodic Protection, Corrosion control, Corrosion monitoring, Oxygen, pH, Sensors, Soil, Underground corrosion

INTRODUCTION

Cathodic protection (CP) is an electrochemical technique used to reduce and control the corrosion of metals. This technique is applied worldwide to protect underground structures, reinforced concrete structures, marine exposed structures, ship hulls, and heat exchangers ¹⁻⁴.

The first application of CP on soil buried iron occurred in the late 1910s with the experiments conducted by Bauer and Vogel in Germany ⁵. In this work it has been reported that the required current density to protect the steel is in the order of 0.1 A m^{-2} , that was described as the amount of current to prevent the iron electrode from corroding ⁵. A second application of CP occurred in the US in the late 1920s during the field test performed by Kuhn ⁶. One of the major results of this study was the criterion of the potential to ensure protection ($-0.85 \text{ V}_{\text{CSE}}$), which led to long-standing controversies until today ⁷⁻¹⁷.

The working principle of CP is based on the polarisation of the metal to be protected in cathodic direction by means of an electrical current. This can be achieved by connecting a less noble metal to the structure that has to be protected, creating a galvanic element; or by impressing a current by means of a DC power source ¹⁻⁴. Considering the example of a pipeline buried in soil, the porous medium around the protected structure has a major effect on the transport processes occurring in the electrolyte (convection, diffusion, and migration). The presence of this medium can be beneficial for the effectiveness of CP. Limiting the transport of the hydroxyl ions (OH^-) produced by the cathodic reactions – oxygen reduction reaction (Eq. 1) and hydrogen evolution reaction (Eq. 2) –, the alkalization of the electrolyte at the steel surface is possible ^{8,9,14}.



In the recent years, multiple studies concluded that the increase in pH, promoted by the generation of OH^- at the steel surface as a consequence of the protection current, is fundamental for achieving corrosion protection of the steel in soil, namely passivation ^{7-9,13,14,16-38}.

During CP, the environment at the steel surface is subjected to changes. For example, the cathodic reactions induce the removal (consumption) of oxygen, but also the generation and accumulation of hydroxyl ions at the steel surface as product of the cathodic reactions. Another example of these changes is related to the migration of ions (chlorides, etc.) as a consequence of the electric field generated by the CP system.

However, the increase in pH at the steel surface in soil as a result of the application of a cathodic current is strongly affected by the environmental conditions, in particular the soil microstructure, composition and bedding conditions, the water movement (stagnant or streaming), and the possible presence of microorganisms. In the last 40 years, many researches tried to find an empirical relationship between protection current density and pH generated at the steel surface ^{18,22,24-26,30,32,36,39}.

For each study, higher protection current density generated higher alkalinity, as expected from the theory. However, from the data reported, the relationship between current density and pH varies between the different studies. This difference can be related to the different conditions at which the experiments were performed.

The comparison with multiple studies demonstrated the complexity in the relationship between protection current density and the generated pH. Many factors can influence this relationship, including experimental time, measurement technique and location, soil properties (ion transport properties, soil chemistry, soil microstructure), water movements (streaming, stagnant), and the possible presence of microorganisms. Thus, it is impossible to predict the pH changes only as a function of one variable (protection current density).

The aim of this work is to provide data on spatial resolution of pH variation during CP condition and on pH variations as a function of the time of the CP application in order to furnish information connected to the necessary time for generating a local environment, which guarantees the steel protection. Furthermore, this study aims to furnish data on the temporospatial variation of oxygen concentration during CP in order to understand the role of oxygen for achieving the steel protection.

EXPERIMENTAL PROCEDURE

Experimental Setup

A three-electrode system was used in this study (**Figure 1**). The working electrode (WE) was carbon steel (DIN 1623) embedded in bi-component acrylic resin. The exposed surface of the WE was 3.61 cm².

The soil was composed by quartz sand with different granulometry, detailed description is provided in the section 'Soil composition'. The composition of the simulated soil solution used for this study was 2.5 mmol/L NaHCO₃ and 5 mmol/L Na₂SO₄·10H₂O with addition of 5ml of 37% HCl to keep the initial pH of the solution to a value of 7. For each experiment, 60 ml of solution were added to ensure the soil saturation.

Three different levels of CP were considered, detailed description is provided in the section 'Cathodic Protection (CP)'. A total of six experimental conditions have been studied. Each protection level has been applied to the WE in the different soil porosities. In this work, only one repetition of each experimental condition was considered.

The counter electrode (CE) was Titanium Metal Mixed Oxide (TiMMO) and it was located approx. 200 mm far from the WE. An Ag/AgCl/sat. KCl (SSE) reference electrode (RE) was placed at 6 mm from the working electrode. All the data are converted to Copper sulfate reference electrode (CSE).

Planar optical sensors (optodes) were placed beside the working electrode surface and glued to the glass of the container. The dimension of the optodes were approx. 20x20 mm².

Four couples of thermally oxidized iridium (IrOx) sensor and additional SSE (Ref) were located in the simulated soil in front of the WE as shown in Figure 1, in order to record the spatial distribution of the pH over the experimental time⁴⁰. The four couples IrOx-Ref were located at 6, 12, 18 and 24 mm from the WE surface.

A fiber optical oxygen sensor was placed at 6mm distance from the WE at a burying depth approx. 10 mm. For compensating the temperature variation in the oxygen concentration a thermocouple (Pt100) was located behind the WE. **Figure 1b** shows a detailed sketch of the top-view of the tank nearby the WE.

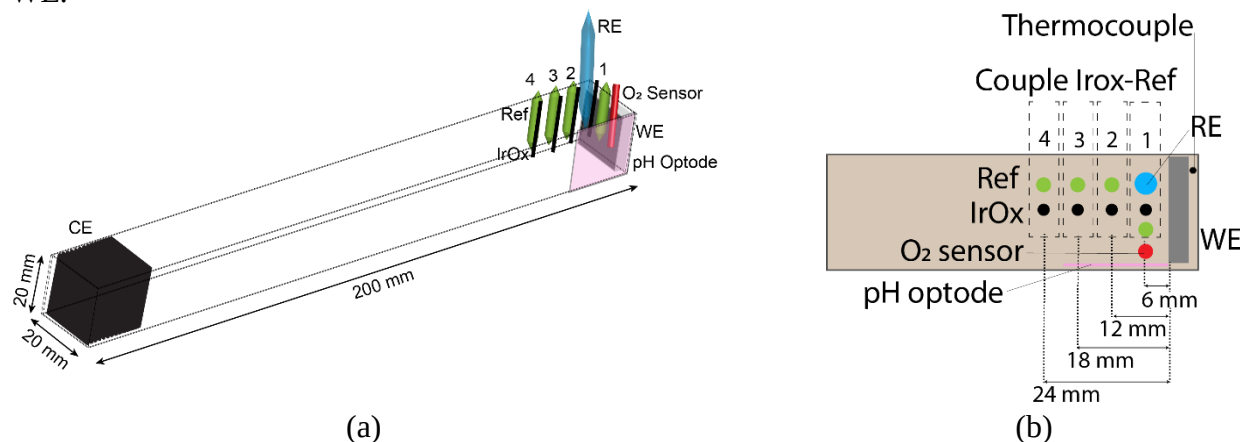


Figure 1: Sketch of the experimental setup. The blue cylinder represent the SSE reference electrode used to measure the potential of the WE during CP. The black cylinders represent the IrOx sensors coupled with the additional reference electrodes represented with the green cylinders. The red rod represents the fiber optical oxygen sensor. The pink rectangle represents the pH optode attached to glass of the container.

Cathodic Protection (CP)

The CP was applied in potentiostatic condition by means of Solartron 1286 electrochemical interface. Three different potential levels were considered in this study. The ON-potentials (E_{ON}) measured with RE (blue circle in **Figure 1b**) were set to $-0.85 V_{CSE}$, $-1.03 V_{CSE}$, and $-1.22 V_{CSE}$. The CP was applied for 20 hours in each experiment.

Soil Composition

Two different mix of quartz sand grains were used to obtain two soil porosities. For the first mix a sand with granulometry between 0.3 and 0.9 mm was used, obtaining a soil porosity of 40%. For the second mix, quartz sand with granulometry lower than 0.3 mm was used, obtaining a soil with porosity of 25%. The soil porosity was calculated with Eq. 3:

$$\text{Soil porosity } (\emptyset) [\%] = \left(1 - \frac{V_{tot} - V_{water}}{V_{wet sand}}\right) \cdot 100 \quad (3)$$

Where V_{water} represents the volume of the water, $V_{wet sand}$ represents the volume of the deposited quartz sand in the water, and V_{tot} represents the sum of V_{water} and $V_{wet sand}$.

pH measurements

Optodes

Optodes were used to monitor and evaluate the oxygen content and the pH changes during the experiment. The working mechanism of these sensors is called fluorescence radiometric imaging (FRIM). Fluorescent chemical dyes are embedded in a polymeric matrix. These dyes react with the environment where the sensor is located in reversible way. When it is subjected to an excitation light (UV), the dyes emit in green and red fluorescence depending on the content of the reacting species in the system.

In this study, the pH detectable range of these optodes varies between 6.5 and 8.5 pH units.

Calibration was performed a priori. In case of pH calibration, quartz sand with granulometry between 0.3 and 0.9 mm was used in addition to buffer solutions to simulate the experimental conditions.

Iridium Oxides (IrOx) sensors

Thermally oxidized iridium (IrOx) sensors were used to monitor the pH variations during CP condition. The equilibrium potential of these IrOx sensors at a given temperature depends only on the pH of the solution.

The sensors were subjected to a 5 points calibration in buffer solutions in pH range between 7 and 13. The calibration was performed immediately before and after each experiment with the corresponding IrOx-Ref couple. The potential measurements for this part of the experiment were performed with Keithley 2701 multimeter.

Oxygen concentration measurements

The oxygen sensor (OXROB3) and datalogger (Optical Oxygen Meter - FireStingO2) were used to monitor the oxygen concentration during the experiment. The calibration of the oxygen sensor was performed before each experiment with one-point calibration function provided in the oxygen logger software.

RESULTS

Protection current density

As a result of the potentiostatic application of the CP condition, the current density varied over time to maintain the steel potential at the desired level of protection. **Table 1** shows the average cathodic

protection current density over the experimental time with the corresponding standard deviation for the different porosities and protection levels.

Table 1

Average cathodic protection current density with standard deviation calculated on 72000 data points for each experimental condition over the experimental time.

E_{ON} [V _{CSE}]	Average protection current density [A m ⁻²]	
	Soil Porosity = 40%	Soil Porosity = 25%
-0.85	$4.06 \cdot 10^{-3} \pm 1.92 \cdot 10^{-2}$	$7.32 \cdot 10^{-4} \pm 6.64 \cdot 10^{-3}$
-1.04	$4.99 \cdot 10^{-2} \pm 7.56 \cdot 10^{-2}$	$5.84 \cdot 10^{-2} \pm 2.91 \cdot 10^{-2}$
-1.22	$3.48 \cdot 10^{-1} \pm 1.08 \cdot 10^{-1}$	$2.30 \cdot 10^{-1} \pm 9.31 \cdot 10^{-2}$

The results presented in **Table 1** show that the increase in E_{ON} corresponds to an increase in protection current density in both the soil porosities. For E_{ON} of -0.85 and -1.22 V_{CSE}, the average protection current density in the soil with porosity of 40% was higher than the protection current density at the same potential level in the soil with 25% of porosity. The opposite behavior is shown for $E_{ON} = -1.04$ V_{CSE}.

pH variation in CP

IrOx sensors

Figure 2 shows the cathodic current density over the experimental time and the pH variation as a function of the distance from the WE surface, CP level determined by the E_{ON} , time of CP application and soil porosity. **Figure 2(a)** and **Figure 2(b)** show the results obtained with $E_{ON} = -0.85$ V_{CSE} and soil porosity equal to 40% and 25%, respectively. **Figure 2(c)** and **Figure 2(d)** show the results obtained with $E_{ON} = -1.04$ V_{CSE} and soil porosity equal to 40% and 25%, respectively. **Figure 2(e)** and **Figure 2(f)** show the results obtained with $E_{ON} = -1.22$ V_{CSE} and soil porosity equal to 40% and 25%, respectively. The values of the cathodic current density over the experimental time are shown in the secondary axis. The distance, d, from the WE surface is indicated in the legend of each figure.