



# Carbon steel corrosion under anaerobic–aerobic cycling conditions in near-neutral pH saline solutions. Part 2: Corrosion mechanism

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## ARTICLE INFO

### Article history:

Received 30 May 2011

Accepted 2 July 2011

Available online 13 July 2011

### Keywords:

- A. Mild steel
- B. Polarization
- B. EIS
- C. Rust
- C. Pitting corrosion
- C. Oxygen reduction

## ABSTRACT

A corrosion mechanism has been developed to describe tubercle formation along pipeline steels during successive anaerobic–aerobic cycles. Small concentrations of O<sub>2</sub> under nominally anaerobic conditions can lead to the separation of anodes and cathodes. Under subsequent aerobic conditions localized corrosion is then promoted by O<sub>2</sub> reduction on the general magnetite-covered surface. Subsequently, the conversion of magnetite to maghemite passivates the general surface, and focuses corrosion within one major tubercle-covered pit. On switching from aerobic to anaerobic conditions, corrosion is temporarily supported by the galvanic coupling of lepidocrocite (γ-FeOOH) reduction (to γ-Fe-OH-OH) to steel dissolution primarily within the tubercle-covered pit.

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## 1. Introduction

TransCanada Pipe Lines Ltd. (TCPL, Calgary, Alberta, Canada) has developed six possible corrosion scenarios to describe external pipeline corrosion [1,2]. One particularly damaging corrosion scenario for pipeline steels is a change from anaerobic to aerobic conditions [1–4]. In a previous paper [5], we described the changes in corrosion potential ( $E_{\text{CORR}}$ ) and corrosion rate (CR) of carbon steel subjected to a series of anaerobic–aerobic cycles in a near-neutral pH saline solution over an exposure period of 238 days, and discussed the nature of the corrosion product deposits formed and the morphology of the corroded surface. Repeated anaerobic/aerobic cycling caused a gradual evolution in corrosion behavior from a general process to one focused within a single, large tubercle-covered pit. Surface analyses performed at the conclusion of the experiment (i.e., Day 238) revealed two distinct corrosion morphologies. The majority of the surface corroded uniformly to produce a black, magnetite (Fe<sub>3</sub>O<sub>4</sub>)/maghemite (γ-Fe<sub>2</sub>O<sub>3</sub>) layer ~4.5 μm thick. The remaining surface was covered with an orange tubercle, approximately 3–4 mm in cross-section. Analysis of the tubercle cross-section revealed a single large pit ~275 μm deep. In this paper, a more detailed mechanism is developed based on transient changes in  $E_{\text{CORR}}$ , the CR, and electrochemical impedance spectroscopy (EIS) measurements.

## 2. Experimental details

A516 Gr 70 carbon steel (0.23 C; 1.11 Mn; 0.07 P; 0.10 S; 0.26 Si; 0.01 Cu; 0.01 Ni; 0.02 Cr; 0.004 Mo; 0.036 Al; 0.019 V; 0.003 O [wt.%], balance Fe) was used. The solution used was 0.2 mol L<sup>-1</sup> NaHCO<sub>3</sub>/Na<sub>2</sub>CO<sub>3</sub> + 0.1 mol L<sup>-1</sup> NaCl + 0.1 mol L<sup>-1</sup> Na<sub>2</sub>SO<sub>4</sub>, with the pH set to 8.9 ± 0.05 with Na<sub>2</sub>CO<sub>3</sub>. The majority of the experimental details have been described previously [5,6]. All potentials are referenced to the saturated calomel electrode (SCE; 241 mV(SCE) vs. SHE).

During the corrosion experiment,  $E_{\text{CORR}}$  was monitored continuously, except for brief periods every 48 h during which EIS measurements were performed. To record one impedance measurement, 1.5 h was required. EIS was performed using a Solartron 1480 Multistat Potentiostat running Corrware and ZPlot software (versions 2.6 and 2.8, respectively, Scribner Associates), and coupled to a Solartron 1250 or 1255B frequency response analyzer for EIS measurements. Measurements were made using a sinusoidal input potential with an amplitude of ±10 mV at individual frequencies over the range of 10<sup>6</sup> to 10<sup>-3</sup> Hz. To ensure steady-state was maintained over the duration of the experiment, spectra were recorded at one frequency per decade in a reverse scan. Kramers–Kronig transformation of the experimental data was performed using in-house software (version 1.3.0, produced by Z. Qin) to ensure their validity, and fitting of the impedance data was performed using Zview (version 2.80, produced by Scribner Associates).

The experiment involved the following sequence of exposure conditions [5]:

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1. Days 1–44: Anaerobic period (1).
2. Days 44–83: Aerobic period (2).
3. Days 83–109: Anaerobic period (3).
4. Days 109–119: Aerobic period (4).
5. Days 119–126: Anaerobic period (5).
6. Days 126–143: Aerobic period (6).
7. Days 143–202: Anaerobic period (7).
8. Days 202–238: Anaerobic period (8) with  $1 \times 10^{-3} \text{ mol L}^{-1}$  sulfide.

There were two brief in-leakages of  $\text{O}_2$  on Days 102 and 122 during anaerobic periods (3) and (5) when Ar gas cylinders were replaced. The final period after sulfide addition (included to simulate microbial effects) will be discussed elsewhere.

### 3. Results and discussion

#### 3.1. The potential transition under anaerobic conditions (Day 27)

Prior to the transition in  $E_{\text{CORR}}$  (from  $< -800 \text{ mV(SCE)}$  to  $\sim -550 \text{ mV(SCE)}$ ) Raman spectroscopic and EIS measurements show the surface is covered by a porous deposit of magnetite ( $\text{Fe}_3\text{O}_4$ ) and siderite ( $\text{FeCO}_3$ ) formed during electrochemical pre-treatment and over the 25 day nominally anaerobic exposure period [6]. The transition in  $E_{\text{CORR}}$  on Day 27 is accompanied by a very significant change in impedance behavior (Fig. 1). The overall decrease in impedance as the low frequency limit is approached is consistent with the observed increase in CR induced by the transition [6]. This increase was attributed to polarization of the anodic steel dissolution reaction at the base of pores induced by the separation of anodes and cathodes, with the cathodic reaction being proton reduction (supplied by  $\text{HCO}_3^-$  dissociation) on the magnetite surface deposit [6]. The observed increase in CR accounts for the large drop in impedance in the frequency range around 10 Hz (Fig. 1). The low frequency behavior ( $\leq 10^{-2} \text{ Hz}$ , 27 days) suggests a diffusion process may be involved.

#### 3.2. Post-transition anaerobic period (1) (27–44 days)

Immediately following the transition,  $E_{\text{CORR}}$  is unstable over a period of  $\sim 6$  days (Fig. 2). The two transient decreases in  $E_{\text{CORR}}$  in this region may indicate attempts to return to the pre-transition state and appear to be in phase with changes in CR. Once these

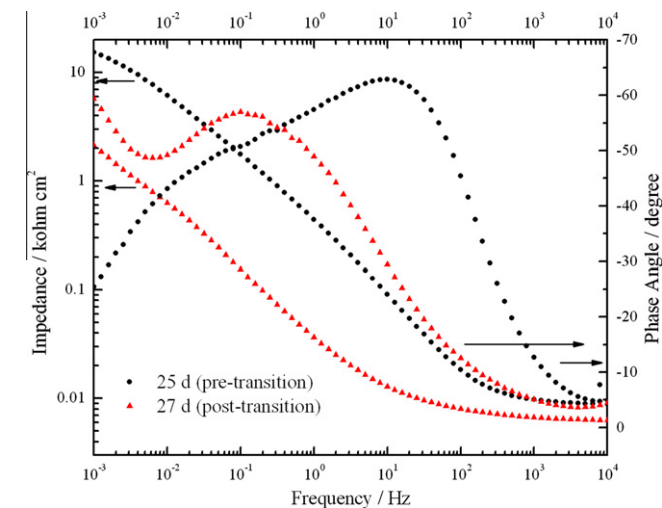


Fig. 1. EIS spectra recorded pre- and post-transition on Days 25 and 27, respectively.

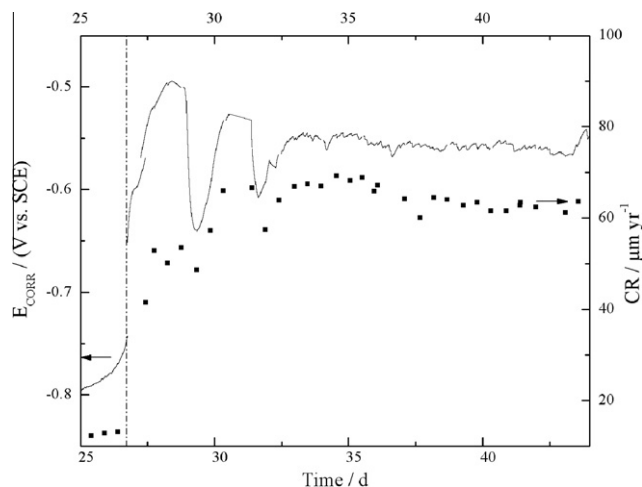


Fig. 2. Changes to  $E_{\text{CORR}}$  and CR with time for the pre- and post-transition anaerobic period (1) between Days 25 and 44.

transients cease, the CR stabilizes at a steady-state value considerably higher ( $\sim 65 \mu\text{m year}^{-1}$ ) than that observed immediately prior to the transition ( $\sim 12 \mu\text{m year}^{-1}$ ). A possible reason for these transients is that a number of additional local corrosion sites initiate and, after unsuccessful attempts to repassivate, stabilize. Alternatively, they represent events within the single tubercle-covered site eventually shown to dominate the corrosion behavior.

Over this post-transition anaerobic period, the impedance spectra show only minor changes (Fig. 3). The peak in the phase angle shows a slight shift to lower frequencies and the value of the phase angle at low frequency decreases in absolute value. The period over which this low frequency change in phase angle occurs coincides with that over which the CR increases (27–32 days) (Fig. 4). These changes suggest the establishment of active sites leading to a decrease in the diffusional impedance of the corrosion process. Since the cathodic reaction involves a plentiful supply of protons in a concentrated bicarbonate solution, and occurs at the  $\text{Fe}_3\text{O}_4$ /solution interface, any transport limitations are unlikely to be associated with the cathodic reaction. A likely scenario is that corrosion is limited, at least partially, by the diffusion of  $\text{Fe}^{2+}$  from anodically dissolving sites.

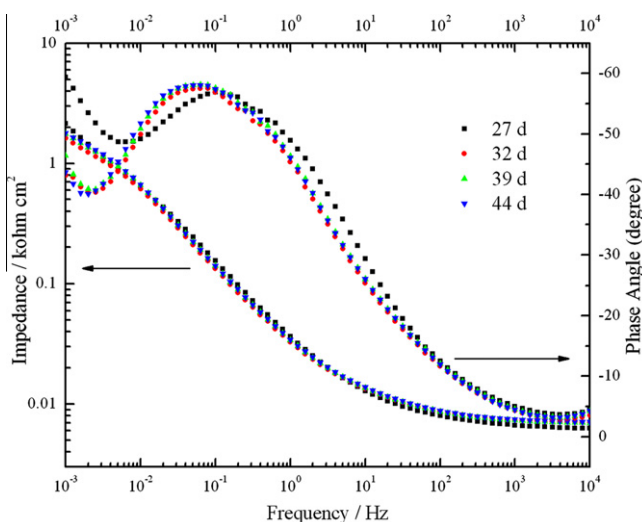


Fig. 3. EIS spectra measured during the anaerobic post-transition period (1) between Days 27 and 44.

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