



Self-validating electrochemical methodology for quantifying ionic currents through pipeline coatings



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ABSTRACT

An enhanced electrochemical method for accurately measuring cathodic protection (CP) currents through protective coatings has been developed as a means of quantifying the permeability and ‘cathodic shielding’ characteristics of nominally intact coating films. This method takes advantage of the fact that cathodic currents could significantly affect the alkalinity of areas under disbonded coatings to self-validate the correctness of current density measurements. In addition, the method provides a high level of accuracy and control over the environment. The method was evaluated using a series of ideally CP-shielding and non-CP-shielding materials, as well as, commercial pipeline coatings. A robust correlation of the measured current with generation of hydroxyl ions and the local alkalinity was established in all cases. For some commercial field joint epoxy pipeline coatings, results suggest that low CP levels could allow sufficient ionic current through a coating to promote a high-alkalinity local environment. However, this may not be the case for fusion-bonded epoxy coatings, which shielded CP and maintained a near-neutral pH under the coating.

1. Introduction

Organic coatings and cathodic protection (CP) are the most widely used methods in the pipeline industry for protecting buried steel pipes against corrosion. Coatings act as a first line of defence, while CP is designed to protect the exposed metal in case of coating failure. However, the effectiveness of CP systems can be locally impaired at coating disbondment areas due to the coating’s electrolytic barrier properties, which can often prevent CP ionic current from reaching the substrate. This phenomenon is commonly known as CP-shielding and it may be linked to corrosion issues such as stress corrosion cracking [1–5] pitting [4,6,7] and microbiologically induced corrosion [8,9]. If untreated, cathodic shielding problems could lead to catastrophic failures such as the major oil spill from a Saskatchewan oil line [10].

Protective organic coatings are not always ideal barriers and may allow water absorption and transport of ions through their polymeric structure. Both processes are known to be enhanced under CP [11–13], and are critical to coatings’ delamination rate [14,15] and pipeline corrosion. There is a general belief in the industry that some coatings are “non-CP-shielding”, meaning that they would allow the flow of ions upon the application of CP (also known as CP current), providing

corrosion protection when detached from the metal substrate [16,17]. Coatings of an epoxy nature, including field joint epoxy coatings and fusion-bonded epoxy (FBE) coatings, are frequently regarded as non-CP-shielding coatings, whilst polyolefins are commonly identified as CP-shielding materials [17–22]. This classification is often based on field observations that may be subjective and not necessarily accurate. Thus, further evidence is needed to determine which coatings are “non-CP-shielding” and how such behaviour affects corrosion.

A coating is commonly classified as non-CP-shielding if a high pH local environment is detected between the metal and the disbonded coating during digging-up operations [17–22]. It should be noted, however, that an ionic current through organic coatings is not the only possible cause for the generation of a high pH local environment under disbonded coatings. For instance, a high level of CP applied at an adjacent macroscopic coating defect, and subsequent diffusion of alkali under the disbonded coating could also result in a high pH local environment [23–28]. Therefore, field evidence of elevated alkalinity level under a coating is not sufficient to determine the non-CP-shielding nature of a coating and a more objective evaluation methodology is needed.

Most previous research on corrosion under disbonded coatings

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simulated elongated crevice geometries and ideal CP-shielding coatings [6,24–30] using thick sheets of polymers such as polymethylmethacrylate (PMMA) which do not allow ions to pass through them. Such research clarified that cathodic currents through a macroscopic opening could produce a high pH and polarisation of the metal within the crevice [24–28], with these effects becoming less important further away from the opening. However, such experiments do not consider the passage of ions through the coating and might not accurately reproduce the conditions at the far end of a long coating disbondment, where through-coating transport contributions would become an increasingly dominant factor. This missing piece of information could be the key to explain why certain coatings have a significantly better service track record than others.

Further studies by Fu et al. [31] and Kuang et al. [32] focussed on the measurement of CP driven ionic currents through coatings. Their methodologies simulated disbonded coatings by placing nominally intact films in a two-chamber cell and measuring the current of ions flowing exclusively through different coating materials. These authors reported that significant CP currents could pass through FBE [31,32] and medium density polyethylene [31], whereas CP was shielded by high density polyethylene (HDPE) [32] and a high performance powder coating (HPPC) [31]. However, some aspects of these results are troubling. Foremost, physically irreconcilable net anodic current densities were reported to pass through several coatings whilst CP was applied. These current densities were between $0.1 \mu\text{A}/\text{cm}^2$ and $0.2 \mu\text{A}/\text{cm}^2$ for HPPC [31] and HDPE [32], while values for FBE coatings were as large as $0.9 \mu\text{A}/\text{cm}^2$ during the first day of testing [32]. Furthermore, the slight increase in pH reported by Kuang et al. [32] for HDPE is inconsistent with the net anodic current densities measured for the same coating, because net anodic current would lead to local acidification of the working electrode chamber when sustained for a few days. These internally inconsistent results suggest that some of the reported current densities might have been not physically meaningful, but perhaps a product of the insufficient accuracy of the instrumentation and methodology used.

These previous reports demonstrate the technological difficulties associated with accurate capture of the small ionic currents through pipeline coatings and indicate the need for a greater level of methodological refinement as well as the need for a method to validate the results.

The present work introduces a more accurate technique able to capture the subtle, yet potentially significant, CP-driven ionic currents through pipeline coatings. This technique implies a paradigm shift from previous research, as it does not attempt to replicate the full complexity of a coating disbondment. Instead, it aims to simplify the system to the bare minimum elements that would allow accurate and reliable quantification of ionic currents through real pipeline coatings, as well as self-validate these results against the local pH changes produced at the cathode.

2. Experimental

2.1. Methodology development

The testing arrangement consisted of a specially designed two-chamber cell in which a coating film was placed in between the chambers. The cell was made of glass with several ports and special fittings to avoid the use of sealants that may cause contamination of the solution inside, affecting its pH. As shown in Fig. 1, a small (15 ml) cathode-chamber, containing working and pH electrodes, was used to simulate and study the environment under a disbonded coating. On the opposite side of the coating, the anode-chamber was twice the volume, and contained the counter and reference electrodes used for CP application.

The cells were filled with 0.1 M NaCl aqueous solution. Effects of using more complex electrolytes with buffering capabilities, and mixes

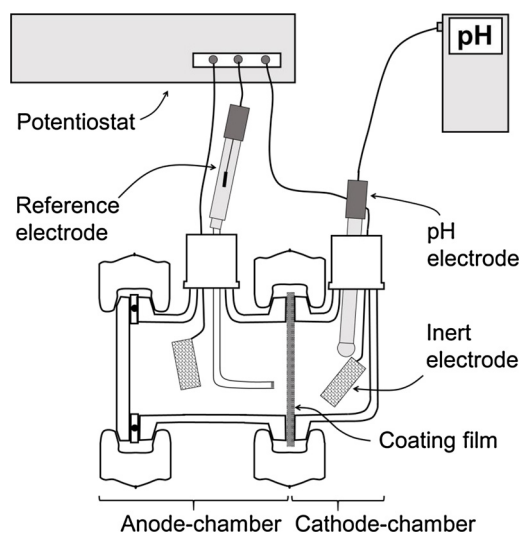


Fig. 1. Cross-sectional view of the experimental arrangement.

of soil, air and electrolyte environments were excluded from the present study for the sake of simplicity. The cell ports were closed with rubber seals to minimise access from atmospheric CO_2 which may lead to formation of carbonate-bicarbonate systems affecting the pH of the solution [33].

Working and counter electrodes were made of a titanium mixed-metal oxide mesh of approximately 1 cm^2 surface area. An inert working electrode was chosen for two important reasons. The first is to simplify the present study, since the use of steel as working electrode may result in the formation of complex iron oxides and scale build-up that could affect the values of current measured. The second reason is that iron oxides could, in turn, consume some of the hydroxyl ions generated in the cathodic reactions, thus affecting the local pH.

A three-electrode configuration was used for CP application and measurement of current, as shown in Fig. 1. A Ag|AgCl|KCl (sat.) reference electrode and Luggin capillary placed in the anode chamber were used to control a constant CP potential equivalent to -850 mV vs. Cu|CuSO₄ between it and the working electrode located in the cathode chamber. The electrical current between the counter and working electrodes was continuously monitored as means of measuring the net ionic current through the coating.

The pH in the cathode-chamber was continuously measured throughout the test with a combination-type pH electrode with an internal double junction Ag|AgCl gel reference. A three-point pH calibration was performed before the tests. Experiments were conducted at room temperature.

As part of the test program, two potentiostats with different specifications were compared. The first was a conventional potentiostat, with a resolution of up to 760 pA ($7.6 \times 10^{-10} \text{ A}$) and a maximum accuracy of 20 nA ($2 \times 10^{-8} \text{ A}$), and the other was a high sensitivity potentiostat, capable of a resolution of 80 fA ($8 \times 10^{-14} \text{ A}$) and a maximum accuracy of 20 pA ($2 \times 10^{-11} \text{ A}$). The experiments using the latter potentiostat were set up in a Faraday cage to minimise electromagnetic interferences from the environment.

2.2. Calculation

The calculation described below was used as a self-validation method for the current measurements by corroborating their consistency with the pH measurements taken in the cathode chamber.

In a disbonded coating scenario where a coating allows passage of ions through it, the application of CP would result in a net cathodic ionic current through the coating and cathodic reactions (i.e., oxygen reduction Eq. (1) and/or hydrogen evolution Eq. (2), for aqueous

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