

Overview of Latest Advances in Understanding the Limited Ability of Fusion Bonded Epoxy to Stop Corrosion Within Disbondments

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ABSTRACT

It has been hypothesized that fusion bonded epoxy (FBE) could be partially permeable to cathodic protection (CP), producing an imbalance between cathodic and anodic reactions and inducing a high pH environment within disbonded areas that would impede corrosion. However, this hypothesis arose from incorrectly inverting causes and effects by assuming that the only reason for the presence of a high pH environment under disbonded FBE coatings is their partial permeability to CP current.

This work presents experimental measurements of the CP permeability of FBE coatings and its effects on mitigating corrosion using a recently developed electrochemical self-validating technique. Some degree of CP permeability has been found for FBE only after considerable hydrothermal aging. However, steel corrosion products had been found to significantly hinder the chances of generating a pH capable of inducing passivation, even for the most CP permeable coating tested.

Key words: Disbonded Coatings, Cathodic Protection, Fusion Bonded Epoxy, Epoxy, Shielding, Polyethylene.

INTRODUCTION

Underground pipelines are usually protected against corrosion by a combination of barrier coatings and cathodic protection (CP). Unfortunately, barrier coatings can fail over the service life of the asset and disbond from the pipe forming crevices where CP current has difficulty to reach. Disbonded coatings could potentially lead to a local environment where severe corrosion issues might arise, such as stress corrosion cracking,¹⁻⁵ pitting^{4, 6, 7} and microbiologically induced corrosion.^{8, 9}

Empirical observations of alkaline environments under disbonded field joint epoxy coatings and fusion-bonded epoxy (FBE), have led to hypothesize that these act as “non-CP-shielding” coatings.¹⁰⁻²⁰ This means that they would allow for the passage of a net ionic current under CP that would, in turn, increasing the local pH (pH > 9.5 to 10) providing corrosion protection by passivation.^{13, 21, 22} Although water absorption (which can be enhanced by CP²³⁻²⁵) and aging²⁶⁻²⁸ support the possibility of a net ionic current across these coatings, the non-CP-shielding hypothesis incorrectly assumes that this current is the only possible cause for the development of a high pH environment at disbonded areas.^{29, 30} Under these conditions, increments in pH produced by causes other than ionic current through the coating would lead to overestimate their ionic permeability. Thus, an accurate method to measure ionic permeability through coatings was needed.

Fu et al.³¹ and Kuang et al.³² introduce the use of a dual chamber electrochemical cell to measure CP driven ionic currents through intact coating. Their results indicate that CP driven ionic currents in the order of 1 $\mu\text{A}/\text{cm}^2$ could flow through unaged FBE^{31, 32} and medium density polyethylene³¹. Kuang et al.³² results also indicate that for FBE pH values at the steel cathode chamber of almost 3 cm³ reached values above 9 and 10 at -850 mV (CSE) and -1000 mV (CSE), respectively. These results support the non-CP-shielding coating hypothesis. However, these works also presented indications of insufficient accuracy in the instrumentation employed. In particular, net anodic currents were detected under CP for HPPC,³¹ HDPE³² and FBE coatings³². Thus, further refinement of the methodology to measure ionic currents across coatings under CP is necessary.

This paper is based on our recently published work^{29, 30, 33}. It presents the development of an accurate method to measure CP permeability of coatings and the results obtained for FBE in different conditions. Although some degree of CP permeability was found for hydrothermically aged FBE samples, its effect on pH was less than expected, making challenging to achieve values where passivation could steel occur.

EXPERIMENTAL PROCEDURE

CP permeability tests

In order to assess the ionic current permeability of coatings with enough accuracy to quantitatively evaluate non-CP-shielding hypothesis, the error in the measurements and/or contamination had to be such that it would not induce a significant pH change. Thus, for the development and validation of the technique it was critical to be able to compare measured ionic currents with the pH changes produced at the simulated disbondment.

The experimental arrangement used is illustrated in Fig. 1. It consists of a dual-chamber cell where the evaluated coating film of 40 mm (1575 mil) in diameter is used to separate the anode chamber from the cathode chamber. In order to maintain the possible electrochemical reactions at a minimum, titanium mixed metal oxide mesh was used for both the anode and the cathode. CP was applied at a fix potential of -850 mV_{CSE} using a Ag|AgCl/KCl (sat.) reference electrode with a Luggin capillary which tip was located in the anode chamber at approximately 2 mm (78 mill) from the film. In addition, a combination-type pH electrode with an internal double junction Ag|AgCl gel reference was used to

monitor the pH at the cathode-chamber. The cell was integrally made of glass and clamps were used to keep it watertight without a need for sealers that could affect the solution pH.

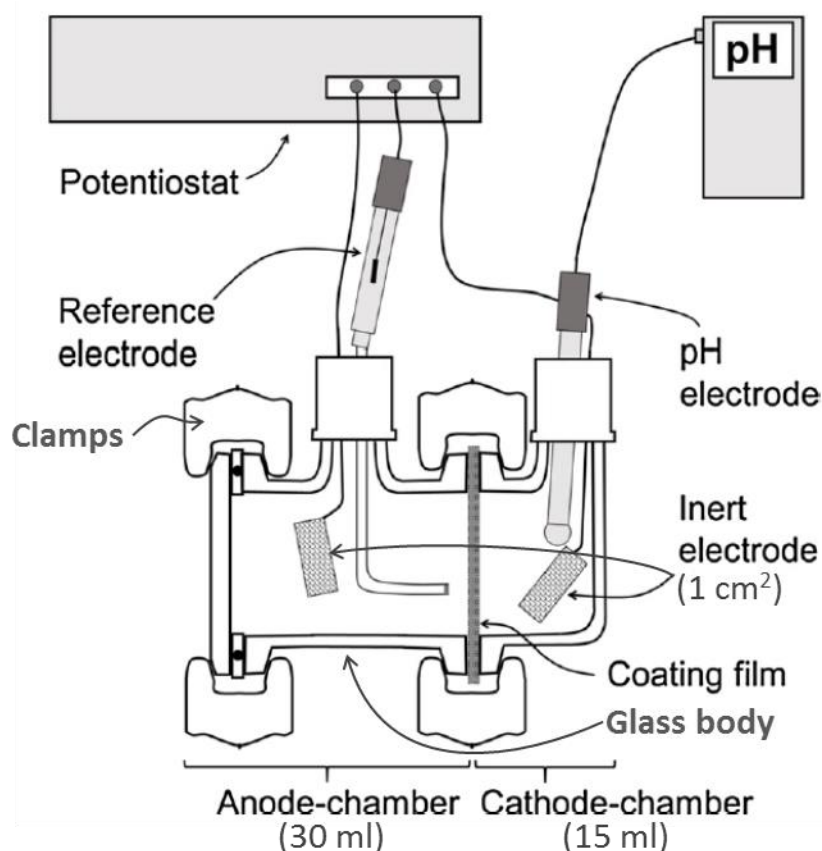


Figure 1: Experimental arrangement.³⁰

The environment produced in the cell aimed to resemble the conditions within a disbondment while maintaining simplicity. Thus, the selected test solution was 0.1M NaCl which ensures high conductivity. The test solution was prepared from analytical grade reagents and ASTM D1193 type 1 water.³⁴ to resemble the easy availability of oxygen produced in unsaturated soils³⁵, the solution was initially saturated with oxygen and left open to air during the test.

The potentiostat used to control CP had an accuracy limit of 20 pA for measuring the current between electrodes, which is significantly lower than conventional potentiostats. This was a key feature that allowed us to ensure that induced pH inaccuracies in at the cathode chamber would only be below 0.04 units after 7 days. To realise the nominal accuracy of the potentiostat, all tests were performed inside a Faraday cage. The test temperature was 22 ± 2 °C (71.6 ± 3.6 °F).

Theoretical pH calculation

In order to validate the technique, ionic current measurements were used to calculate the theoretical pH change at the cathode chamber and then contrasted against actual pH measurements. pH calculation followed the subsequent assumptions:

- The only reactions at the cathode are oxygen reduction and/or hydrogen evolution.
- No Alkali escapes the cathode chamber.
- No H^+ migrates through the coating.

Eq. 1 was derived from Faraday's law of electrolysis and the definition of pH. Here, I is the measured current, Z is equal to 1 mol/equivalent for either of the possible cathodic reactions, F is the Faraday constant, V is 15ml and K accounts for the initial solution pH.

$$pH(t) = 14 + \log\left(\frac{\int_0^t I(t) \cdot dt}{Z \cdot F \cdot V}\right) + K$$

Equation 1

Materials

Unless specified otherwise, all tested films were free of macroscopic defects. This was ensured by the consistency of results observed among replicas. In order to validate the methodology, close to ideal shielding and non-shielding coatings were simulated using, a 1mm (39 mill) layer of polytetrafluoroethylene (PTFE) and an anion-exchange membrane with ammonium and chloride exchange groups, respectively. Following the fabricants recommendation, the ion exchange membrane was soaked in distilled water for 48 h before testing.

High built epoxy and FBE coating were also tested. The high built epoxy consisted of a bisphenol-F-epoxy amine-hardener based system. These coatings were applied using a drawdown film applicator over a removable aluminium substrate. FBE free film samples were prepared on an easy-release silicone substrate by their manufacturer.

In the case of unaged coatings, samples were stored dry before the tests. For hydrothermally aged FBE samples, aging was achieved in distilled water at 85 °C (185 °F) for three, five and seven months. Hydrothermal ageing was expected to accelerate water uptake,^{28, 36-38} which in turn could enhance CP permeability. Thus, in this case samples stored in distilled water before testing. Aging temperature was chosen to be below the Tg of the unaged material in order to avoid excessive deformation. In addition, the films were held between two perforated stainless-steel sheets

Alkalinity retention tests

To evaluate the ability of FBE to maintain a high pH local environment, the initial pH at the cathode chamber was adjusted to 12 by addition of NaOH. At the anode chamber, the test solution was left unchanged. pH changes at the cathode chamber were continuously monitored for a diversity of film thicknesses, aging times and CP conditions.

Steel substrate tests

To evaluate the ability of FBE to prevent steel corrosion, a small crevice was tested with a one-millimetre gap between a steel cathode and the coating. The crevice was prefilled and partially immerse in the test solution to avoid a direct electrolytic path between the solution within and outside the crevice. For this test, this arrangement was chosen over the dual chamber electrochemical cell because pH is expected increase more, the smaller the cathode chamber volume (Eq. 1). Due to the small size of the cathode chamber (aprox. 0.5mL), pH was not monitored in-situ, but ex-situ measurements were performed at the end of the test. The cathode was made of X65 steel mounted in Specifix-20 resin. Its exposed area was 1.5 cm² and its surface was abraded in wet with 220 grit sandpaper and rinsed with ethanol before the tests.

RESULTS AND DISCUSSION

Methodology validation

Fig. 2 presents the measured current density for 1mm PTFE. For this ideally shielding material, measured ionic currents fall predominantly within the uncertainty of the instrumentation. These relatively small currents were expected to produce no significant pH changes at the cathode chamber. This was confirmed by measuring a stable pH around 6.5 for the duration of the test. This result