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Understanding the effectiveness of cathodic protection under disbonded coatings

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A R T I C I E I N E O

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A B S T R A C T

Factors affecting the effectiveness of cathodic protection under disbonded coatings were studied using a partially covered two dimensional electrode array that simulates a crevice under a disbonded coating and allows for the mapping of electrochemical currents under the influence of cathodic protection (CP). This technique enabled the study of the effects of major factors, including crevice gap size, solution conductivity and applied CP potential on the distribution and evolution of CP currents over the electrode array surface. The effect of each of these factors on the overall current distribution profile has been explained using a new electrochemical model. This model suggests that, despite the detrimental effect of cathodic shielding, the steel under disbonded areas could still be protected, independent of the crevice geometry and solution resistivity, by means of concentration polarization instead of direct electrochemical polarization. A set of conditions for maintaining CP potentials more negative than -850 mV_{CSE} along disbonded coating areas was deduced from the proposed model and validated against potential profiles available in the literature. The possible practical implications of the current mapping technique used in this study for developing in-situ CP monitoring sensors has also been discussed. ã 2015 Elsevier Ltd. All rights reserved.

1. INTRODUCTION

The combination of barrier coatings and cathodic protection (CP) is the most common corrosion prevention method used with buried metallic structures such as energy and water pipelines. Unfortunately, barrier coatings are susceptible to losing their adhesion to the metallic substrate, in particular under CP conditions [\[1,2\],](#page--1-0) thus generating crevices that could be filled with solution from the surrounding environment. This phenomenon is commonly referred to as cathodic disbondment [\[3\]](#page--1-0). Cathodic disbondment occurs in almost all metal-organic coating systems, and has been extensively studied by scanning techniques such as scanning kelvin probe [\[4](#page--1-0)–7] and localized electrochemical impedance spectroscopy [\[8\]](#page--1-0). Coating disbondment is recognized as a major corrosion threat to pipeline integrity, and is commonly associated with several forms of localized corrosion [9–[21\].](#page--1-0) This high corrosion susceptibility is generally attributed to the inability of CP currents to penetrate into the crevices formed by disbonded coatings (cathodic shielding). Cathodic shielding is believed to be caused by significant IR-drops generated as a consequence of the high electrical resistance of the thin solution layer trapped within the crevice. The profile of these IR-drops has been the subject of extensive experimental [\[22](#page--1-0)–31] and modelling research [29–[33\]](#page--1-0) aimed at identifying conditions at which the potential values within disbonded coating areas could be maintained more negative than the commonly accepted 'safe' CP potential criterion of -850 mV_{CSE} [34–[36\].](#page--1-0) It has been suggested that CP induced polarization decreases exponentially along disbonded coatings [\[31,37\]](#page--1-0). Although the application of more negative CP potentials would lead to more negative potential profiles along disbonded coatings areas, very negative CP potentials should be avoided to prevent reduction of water and accumulation of hydrogen bubbles [\[24\]](#page--1-0) as this would further shield CP.

In addition to the significant potential gradients produced by IR-drops, extensive research has also shown that variables such as pH [\[23,27,28,38](#page--1-0)–47], oxygen concentration [\[28,42,43,47](#page--1-0)–54] and ion concentration [\[38,39,55\]](#page--1-0) within disbonded coating areas are likely to differ from the bulk environment. Under such a heterogeneous electrochemical environment, the distribution of current densities within the disbonded coating area could be inhomogeneous. Since current densities can be related to reaction rates, the measurement of their distribution is a valuable resource in terms of identifying the processes that may be occurring under the disbonded coatings. Current density profiles along disbonded coatings have been studied by other researchers [\[37,40,47,56,57\]](#page--1-0)

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using segmented electrodes, where the average current density at each segment of the electrode was individually measured. Unfortunately, the small number (typically 5–8 distinct electrodes) and large size of the electrodes used in those studies limited the spatial resolution of the profiles obtained, making it difficult to get a mechanistic understanding of the processes occurring within the disbonded coating area. In some cases, researchers failed to simulate a continuous metallic surface by separating the electrode segments excessively, leaving large areas of inert material between them [\[40,56\]](#page--1-0). Furthermore, in those previous studies [\[37,40,47,56,57\]](#page--1-0), the electrical connections necessary to perform current measurements were performed manually, which involved interruption of the applied CP, as well as constraining the frequency at which the measurements could be taken.

In this paper, the distribution and evolution of CP currents was studied using a two dimensional (2D) electrode array consisting of small electrodes exposed under a crevice that simulates a disbonded coating. The higher spatial and temporal resolutions of this method allowed for the study of the independent contributions of the oxygen and water reduction reactions to the overall current density profile. The insights provided by this technique allowed us to identify possible conditions at which CP potentials more negative than $-850 \text{ mV}_{\text{CSE}}$ could be maintained, even for extensively disbonded coating areas.

2. EXPERIMENTAL

In this work, a disbonded coating was simulated by means of a 2D electrode array and a polymethyl methacrylate (PMMA) cover used to generate crevices of different gap sizes. The 2D electrode array was a wire beam electrode consisting of 100 carbon steel (UNS G10350) electrodes in a 10 by 10 array. Fig. 1 is a schematic with the basic dimensions of the electrode array and the PMMA

Fig.1. Schematic representation of the electrode array surface and PMMA cover. All dimensions are in mm.

cover. Prior to each test, the electrode array was progressively abraded to 1200 grit using silicon carbide papers and degreased with acetone followed by ethanol. 1 mm and 0.25 mm crevice gaps were achieved by introducing spacers of the same height as the desired crevice gap (indicated in Fig. 1) and fastening the respective PMMA cover to the epoxy body of the array using four AISI SS316 screws. In both cases, a rubber seal was used to limit the solution access to only one edge of the electrode array. Since a larger seal was used for the large crevice gap PMMA cover, a larger rubber expansion gap (indicated in Fig. 1) was present in this case.

Once assembled, the electrode array was installed in a 2.5 L electrochemical cell with the crevice opening facing upwards. A Ag / AgCl / Saturated KCl reference electrode and a Luggin capillary were used to measure the applied CP potentials whilst minimizing IR-drops. All the potentials reported in this paper were converted to the copper saturated electrode scale for direct comparison with industry standards [34–[36\].](#page--1-0) The counter electrodes consisted of two 4.5 mm diameter graphite rods immersed 120 mm into the solution.

In order to measure the distribution of currents over the electrode array surface without interrupting CP, the instrumentation schematically illustrated in [Fig.](#page--1-0) 2 was used. A multiplexer distributed the connections to the 100 electrodes in the array, maintaining 99 of them connected to the WE1 output terminal and the remaining electrode connected to the WE2 output terminal. In order to measure the current flowing throughout the electrode connected to WE2, a Gill AC potentiostat used as a zero resistance ammeter (ZRA), was interposed between WE1 and WE2. In addition to measuring currents, the ZRA kept WE1 and WE2 (i.e. all the electrodes in the array) at the same potential. The array was maintained at different CP potentials using a Bio-logic VMP3 potentiostat in a three electrode configuration, where WE1 acted as the working electrode. The current flowing throughout each electrode of the array was registered by swapping the electrode connected to WE2 every 10 s, following a predetermined sequence that swept the whole array. A make-beforebreak switching sequence between successive electrodes was followed to avoid any momentary disconnection of CP. Current distributions were measured every 20 min during all immersion tests.

All test solutions were prepared from analytical grade reagents and ASTM D1193 type 1 water $[58]$. Solutions were purged with air overnight to ensure dissolved oxygen saturation. Initial solution pH values around 6.3 were measured using a pH electrode. All tests were performed at a room temperature of 22 ± 2 °C. In order to study the effect of solution conductivity and crevice gap size, three experimental conditions denoted: "control", "large crevice gap" and "high conductivity" [\(Table](#page--1-0) 1) were evaluated at CP potentials of -850 mV, -1050 mV and -1250 mV. These CP potentials were selected because they encompass the range of CP potentials typically used in underground pipelines [34–[36\],](#page--1-0) which is one of the areas where cathodic disbondment and the possible subsequent detrimental effects on CP effectiveness can be critical. The average pH developed within the crevice at the end of each 23 h immersion test was measured using pH indicator paper. All tests were performed in triplicate.

3. RESULTS

[Fig.](#page--1-0) 3 illustrates the effect of different applied CP potentials on the current distribution maps obtained for the control condition. In all cases a clear predominance of cathodic currents was observed. Current density values found at the exposed area were larger than those recorded within the crevice area for all three CP potentials. A comparison of the results obtained at -850 mV and -1050 mV showed that, although the obtained current distributions were

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