Understanding factors affecting corrosion under disbonded coatings

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UNDERSTANDING FACTORS AFFECTING CORROSION UNDER DISBONDDED COATINGS

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SUMMARY: This paper presents an overview of findings over the past several years on corrosion under disbonded coatings (CUD) and major influencing factors affecting this behaviour. The effect of cathodic protection (CP) current shielding by disbonded coating film on CUD has also been assessed and quantified using a method developed for precisely measuring CP current penetration. The main results indicate that all tested commercial coatings, with thicknesses typically used in the field, would shield CP currents in the intact condition. Although it has been found that some thin coatings allow some CP current penetration and that a slight increment of CP current through the coating was observed with the ageing of coatings, unfortunately for the types of coating assessed none was able to create a high pH condition sufficient to protect the pipeline steel surface under disbonded coatings. Understanding of major factors affecting CUD was facilitated by an electrochemically integrated multi-electrode array that was used as a unique tool for probing localised electrode processes evolving and propagating dynamically on pipeline steel surfaces under the effect of cathodic shielding and coating disbondment. Taking the advantage of the high temporal and spatial resolution of the electrode array method, various laboratory devices and probes have been designed to simulate a disbonded coating in order to assess the penetration and contribution of CP currents through coating films. Disbondment geometry, pH and soil saturation status have been shown to be key parameters affecting CUD. For instance, it was found that in non-saturated soil CUD behaviour changed significantly with coating disbondment gap size. These findings have been compared with those reported in the literature and in industry reports.

Keywords: Pipeline corrosion, pipeline coating, coating disbondment, cathodic protection of pipelines, corrosion under disbonded coating.

1. INTRODUCTION

Organic coatings, which are widely used for mitigating corrosion of oil, gas and water pipelines, can disband from pipeline surface under certain environmental and cathodic protection (CP) conditions. Disbonded coatings are believed to shield CP current, and therefore localised corrosion occurs under disbonded coatings (CUD). CUD can be considered a worst-case scenario form of electrochemical corrosion that occurs on the external surface of buried steel structures such as underground pipelines causing damage. It is well-known that coating disbondment and CUD are affected by complex and interrelated factors including coating types, soil conditions, CP potential, soil stresses, and the corrosive environment etc., however the actual impact of these factors on pipeline integrity has not been quantified sufficiently. The assessment and quantification of these effects can be difficult due to technical limitations with existing laboratory test methods in measuring cathodic shielding and in monitoring localised corrosion under disbonded coating film. In order to probe the synergistic influence of these factors on CUD, there is a requirement for experimental methods that are able to simulate such complex conditions and measure their effects. Recently we have developed new methods and devices for understanding and quantifying the impact of these factors on coating disbondment and CUD under simulated underground pipeline conditions [1-8]. This paper provides an overview of some key findings on the effects of several key factors affecting CUD.
2. EXPERIMENTAL DETAILS

The chemical composition (wt%) of X65 pipeline steel employed throughout this investigation was 0.04 C, 0.2 Si, 1.5 Mn, 0.011 P, 0.003 S, 0.02 Mo and Fe balance. A multi-electrode array, also known as wire beam electrode (WBE), was applied to simulate the metal substrate under disbonded coatings [1-3]. The WBE was fabricated by 100 square shaped electrodes (2.24mm x 2.24mm) made of X65 steel in a 4 by 25 array. The gaps between neighbouring electrodes were kept small (0.20 ± 0.05 mm). Four rows of the electrodes were exposed to the bulk soil and twenty-one rows of electrodes were covered (see Figs.1(a) and (b)). An artificial crevice with width and length set at 11 mm and 52 mm was formed on the surface of the WBE by using a transparent 3D printed plate (FullCure 720, translucent amber acrylic-based photopolymer) and a silicone rubber for sealing. The thickness of the cover was 3mm. As indicated in the datasheet, the water absorption of the material (measured with the procedure D570-98 24hr) is around 1.5-2.2%. The inner layer of the 3D printed cover was sealed with an acrylic clear coating to avoid the penetration of chemical species, water and oxygen. In this paper, the crevice gap was controlled with the step/space introduced by the printed cover. Three different crevice gaps (0.25mm, 1mm and 2mm) were introduced for the WBE and the crevice opening faced upwards. Before experiments, the WBE surface was mechanically abraded by water emery papers up to #1200 successively and degreased with distilled water and ethanol. The simulated soil used in this manuscript was prepared from the commercially available washed sand. The median of the sand particle size number distribution was around 200μm. Sand was cleaned with de-ionized water and dried within oven at 100°C for 24 h before experiment. The solution (0.01M Na₂SO₄) used in the tests was prepared from analytical grade reagents and ASTM D1193 type 1 water. Fig.1(c) illustrates the schematic diagram of the experimental setup. A 3.5L electrochemical cell was applied. The crevice was filled with Na₂SO₄ solution before adding saturated sand to the cell. An approximately 10 mm supernatant solution was left over the sand to ensure saturation. The CP potential (-733mV) was applied against an Ag/AgCl (saturated KCl) reference electrode (RE) to the opening mouth of the simulated coating disbondment, and a lugin capillary was used to minimise IR drop. This potential was converted to industry standard with the copper/copper sulphate scale (CSE) and equalled with -850mVcse. The experimental setup shown in Fig.1 applies cathodic current over the WBE surface in a similar manner as in the pipeline industry where the reference electrode and a counter electrode (CE) was used to apply cathodic potential to the opening mouth area of the disbondment crevice. The CE used in the experiment was Ti-mesh. After 24h, the valve at the bottom of the cell was opened to let solution come out. Subsequently, the cell was exposed in air at ambient temperature (25 ± 2°C) for 9 days. The current density distributions on the WBE surface were measured by an automatic switcher (CPE systems), programmed to connect one electrode to WE2 and maintain the other 99 electrodes connected to WE1. A Zero Resistance Ammeter (ZRA) was interposed between WE1 and WE2 to measure the local current throughout WE2. The current flowing throughout each electrode of WBE was registered by systematically alternate the electrode connected to WE2 every 1s. More details of WBE measurement could be found in references [7,8]. The current distribution on the WBE surface was measured every 5 min during 10 days. The obtained current signals were post-processed with MATLAB R2015b. After each experiment, the WBE was withdrawn from the electrochemical cell. The cover was removed and the surface was photographed. After that the electrode array surface was cleaned with water followed by acetone and ethanol, and photographed. Corrosion products were then removed using ASTM G1-03 solution followed by being rinsed with water and ethanol. After removing the corrosion products, the surface of the electrode array was photographed again. Surface replicas of the WBE surface were obtained using a Struers repliset-F5 kit. Optical surface profilometry measurements of each electrode in the array were performed over the surface replicas using an Infinite Focus interferometry profilometer. The surface profilometry results were processed to calculate the average metal loss of each electrode. 

The penetration and contribution of CP currents through coating films, as well as the effect of CP current shielding by new and aged disbonded coating film on CUD have been assessed and quantified using a method developed for precisely measuring CP current penetration [4,5]. As shown in Figure 2, a small cathode-chamber of 10ml of volume was used to study the environment under coating disbondment. It contained a pipeline steel working electrode, a Lugging capillary connected to a Ag/AgCl/KCI (sat.) reference electrode to measure the true polarisation of the steel, a combination-type pH electrode with an internal double junction Ag/AgCl gel reference to measure the pH of the solution in contact with the steel, and aeration ports for bubbling gases (not displayed in Figure 2 for the sake of simplicity). The steel electrode was obtained from the external diameter of an X65 grade pipeline. It had an exposed area of 1.5 cm² and the electrical contact and sides were covered with SpeciFix-20 resin. The surface of the electrode was sanded with a 220 grit paper and rinsed with ethanol. The cathode-chamber was separated to the adjacent chamber (intermediate chamber) by epoxy coating films (fresh and aged). More details on the experimental setup can be found in reference [4-8].
Figure 1 Schematic diagram of the probe for simulating and measuring CUD (a, b) and experiment setup to measure the current density distribution maps over the electrode array probe surface under CP [7,8].
3. RESULTS AND DISCUSSION

Previously we have reported technological developments that enabled this study and preliminary results [1-11]. Here we discuss two major factors that have not been discussed in detail, yet could significantly affect CUD. The detection and monitoring of localised corrosion processes under a dynamically changing electrochemical environment under disbonded coatings are major technical challenges. Currently detecting corrosion under disbonded coatings, especially at pipeline joints, relies on in-line inspection tools (intelligent pigs). This is the only current method for detecting and locating defects and damages on the pipeline developed due to CUD, however where in-line inspection is not possible this leaves pipeline operators with little choice. Another approach that should be useful for pipeline corrosion management is the use of corrosion monitoring and warning sensors or probes. Currently the most widely adopted corrosion monitoring sensors in the pipeline industry are steel coupons and electrical resistance probes (ER probes). The ER probes are electrically connected to a pipeline to simulate the bare metal exposed in a coating defect for detecting corrosion data under CP. A major limitation of ER probes is in the simulation and detection of localised corrosion such as CUD, because an ER probe may not be able to simulate corrosion environment and conditions under disbonded coatings, and also because localised damages may not lead to any significant change in electrical resistance detectable by an ER probe. In order to address these issues, new probes have been designed to measure the distribution of electrochemical currents over an electrode array surface partially covered by a crevice that simulates a disbonded coating [1,2,6-10]. Corrosion patterns were estimated based on the current density distributions detected by electrode array probes for CUD detection. The acceptable level of correlation with the corrosion damage observed at the array surface at the end of the tests suggests that the probe surface has the potential to monitor localised corrosion under disbonded coatings. Using probes to simulate and detect early stages of corrosion or to measure corrosion susceptibility under disbonded coatings could provide a valuable and inexpensive means of obtaining in situ monitoring information on the health of a structure. Recently a specially designed multi-electrode array has been utilised to visualise dynamic steel corrosion CUD [7].

3.1 The effects of coating disbondment features on CUD

In order to capture and understand the phenomena empirically observed in the industry, experiments have been carried out using probes and experimental setup shown in Fig. 1, designed to simulate complex corrosion conditions under coating disbondment of different crevice gap sizes (0.25mm, 1mm and 2mm) in soil environment of changing moisture contents. This could help understand facts such as that CUD would not normally occur if a disbonded coating is tightly attached although not bonded to a steel pipe while it occurs if a disbonded coating is loosely bound on a pipe, and that wet/dry seasonal changes affect CUD in the soil. In order to simulate the alteration of soil moisture contents due to wet/dry seasonal changes, CUD experiments were carried out in two stages. The first stage test was carried out in saturated soil, approximately 10mm supernatant solution left over the soil to ensure saturation and simulate the wet season. After 24 hours, the soil was allowed to become non-saturated by allowing electrolyte to gradually leave the soil from the bottom of the cell, simulating the transition of wet and dry seasons. A CP potential of -850mV_{CSE} was applied to the specially designed array probes, simulating CP protected pipeline with coating defects and disbonded coatings. Figure 4 shows typical
results obtained from repeated testing of simulated coating disbondments with different gap sizes (0.25mm, 1mm and 2mm).

The behaviour of CUD was found to be distinctively different in coating disbondments of different gap sizes and in saturated and non-saturated soils [7]. In saturated soil, CUD behaved similarly as it usually does in electrolyte solutions, where CUD is mitigated by a cathodic protection induced high pH environment and a concentration polarisation mechanism. In non-saturated soil, CUD behaviour changed significantly with coating disbondment gap size. These results demonstrate that the disbondment geometry can significantly influence the corrosion process within the disbonded coatings in soil with varying wet/dry conditions, which is in agreement with observations in the field: CUD was not normally observed if the coating-disbonded region is tightly bound to a steel pipe (It could be similar with the case that the gap size was 0.25mm) while localised corrosion under disbonded coating was observed if the disbonded coating is loosely bound on a pipe (It could be similar with the case that the gap size was 1mm). Moreover, the results here indicated CUD would not occur when the gap size of disbondment region increased to 2mm. This may be similar to the case that when coating is totally loose when disbonded, e.g. coal tar epoxy coatings, corrosion may not occur. It should be noted, however, that these industry experiences are not quantitative and therefore they could not be used for direct comparison with results reported here. These results also have implications for designing probes for monitoring corrosion in soil. It is clear that the crevice geometry should be considered to let the corrosion probes experience the maximum corrosion rate in order to provide early warning of the underground infrastructure system. These observations have been explained by solution/soil distribution models proposed for coating disbondment of different geometries. More details regarding this work can be found in references [7,8].

![Corrosion morphologies and current density distribution results from repeated tests obtained from simulated coating disbondments with different gap sizes (0.25mm, 1mm and 2mm).](image)

Figure 3. Typical corrosion morphologies and current density distribution results from repeated tests obtained from simulated coating disbondments with different gap sizes (0.25mm, 1mm and 2mm).
3.2 The Effects of coating shielding properties on CUD

Another mystery in the coating and pipeline industries is possible differences in the permeability of CP current through different types of coatings, especially when a disbonded coating film is aged. It is believed that CP currents through a coating film would affect the local environment in the coating disbondment crevice in contact with the steel pipeline, however little direct evidence is available to verify these. Extensive experimental studies have been carried out using an experimental setup shown in Fig. 2, with an aim to provide better understanding of possible corrosion mitigation under disbonded so-called ‘non-CP-shielding’ coatings. The key tool used for this study is an enhanced-accuracy method to measure small currents through pipeline coatings [5]. The experimental setup consisted of a glass cell where with several chambers with electrodes, filled with 0.1 M NaCl aqueous solution and separated by thin films.

Figure 4 shows typical results on the effect of ageing on cathodic protection shielding by fusion bonded epoxy coatings. The CP current permeability of fusion bonded epoxy (FBE) coatings in as new condition was evaluated and found to be very low (see Figure 4(a)). In order to explore the possible effects of ageing and, in particular, water uptake on CP current permeability, FBE films were hydrothermally aged for up to 7 months. Hydrothermal ageing of FBE films was conducted at 85 °C for several months to study the conduction of CP current and its ability to modify the local environment under disbonded coating. The ageing treatment resulted in degradation of FBE films promoting a significant amount of water uptake by FBE films. Water uptake was found to increase drastically over the first three months and then reach a plateau. CP current permeability of aged FBE coatings had a significant increase in relation to unaged samples, as show in Figure 4 that presents the ionic current flow through aged FBE films, and theoretical and measured pH values at the cathode chamber. The ageing treatment allowed for ionic transport through FBE films. Currents larger than the technique's accuracy were captured with a high sensitivity potentiostat. This result varied from that obtained for the unaged or starting material (Figure 4(a)). However, experiments also suggested that the current was unable to produce the high pH environment required for steel passivation. Measured pH values in the cathode-chamber for all aged samples maintained near-neutral values during the tests. No significant alkalinisation resulted because of CP application. This indicates that CP current conducted through FBE coatings as a result of ageing is not the likely cause for the distinctive non-corrosion under disbonded FBE coating behaviour observed in the pipeline industry. The cause for this behaviour is most likely due to the effects of pinholes developed in service on the CP current permeability FBE coatings. It was found that the CP current permeation increased drastically on FBE films with pinholes, allowing increase of pH to values sufficient for steel passivation. More details have been contained in reference [4,11].

4. CONCLUSIONS

Progresses made using innovative corrosion probes and devices have been successfully employed for monitoring localised corrosion under the dynamically changing electrochemical environment under a simulated coating disbondment, as well as CP current permeability of selected coatings. Disbondment geometry, pH and soil saturation status have been shown to be key parameters affecting CUD. For instance, in non-saturated soil CUD behaviour changed significantly with coating disbondment gap size. All commercial coatings tested were found to shield CP current. Although it has been found that some coatings allow some CP current penetration and that a slight increment of CP current through the coating was observed with ageing of coatings, unfortunately for the types of coating assessed none was able to create a high pH condition sufficient to protect the pipeline steel surface under disbonded coatings.

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Figure 4. Current through 280 µm FBE films with different ageing periods under CP equivalent to -850 mV versus Cu|CuSO₄, cathode-chamber in-situ pH measurement and theoretical pH calculation (considering cathodic current only).

6. REFERENCES


7. AUTHOR DETAILS

Mike Yongjun Tan is a Professor in Applied Electrochemistry and Corrosion Technologies at Deakin University in Australia. He is also a Research Program Leader of the Energy Pipelines Cooperative Research Centre. Dr Tan’s principal teaching and research interests are in corrosion science and engineering and their applications for enhancing the reliability and durability of civil and industrial infrastructures. He contributed to electrochemical methods for corrosion testing, monitoring and prediction and corrosion inhibitor and anti-corrosion coating research. He is the author of some 200 publications and a book entitled ‘Heterogeneous Electrode Processes and Localised Corrosion’ (2012 John Wiley & Sons).

Facundo Varela, also known as Bob, is a Research Fellow in the Institute for Frontier Materials at Deakin University, working on an Energy Pipeline CRC sponsored project. He completed his PhD studies on corrosion sensors at Deakin University in 2016. His PhD project was on the development of new corrosion monitoring technologies to measure corrosion rates under disbonded coatings in underground structures. His completed materials engineering studies with honours in the Instituto de Tecnología Jorge A. Sábato in 2009. As bachelor final year project, he joined Professor Maria Forsyth’s Group at Monash University where he worked on the Inhibition of Stress Corrosion Cracking in aluminium 7075.