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CP PERMEABLE COATING AND CORROSION UNDER DISBONDED COATINGS

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SUMMARY:

Corrosion under disbonded coatings is generally considered a 'worst case scenario' corrosion condition in the pipeline industry. Severe cases of localized corrosion issues including pitting, microbiological induced corrosion and stress corrosion cracking have often been linked to environments that are typically developed under disbonded coatings that shield cathodic protection (CP). It is believed in the industry that some coatings are partially permeable to CP currents, usually referred to as non-CP-shielding coatings, offering protection in case of coating disbondment allegedly by increasing the alkalinity of the local solution in contact with steel. However, this effect is not well understood and evidence on the matter is limited. In the present work, we aim to link the CP currents passing through coatings to the understand their actual effect on the polarisation of pipeline steel and the pH developed under disbonded coatings. Tests on selected coating and CP levels show that the magnitude of currents able to pass through coatings was insufficient to both polarise significantly the steel and generate a protective elevated pH environment. Therefore, we have not be able to identify an obvious advantage in corrosion protection provided by a coating permeable to CP.

Keywords: Pipeline coating, Cathodic protection, Cathodic shielding, Epoxy coating, Disbonded coating

1. INTRODUCTION

Corrosion under disbonded coatings is generally considered a "worst case scenario" in the pipeline industry. Severe cases of localized corrosion issues including pitting [1-3], microbiological induced corrosion [4, 5] and stress corrosion cracking [3, 6, 7] have been often linked to environments that are typically developed under disbonded coatings in presence of cathodic protection (CP) and a CP-shielding coating. However, for reasons such as water absorption and in-service ageing, coatings could become partially permeable to CP (non-CP-shielding coatings), developing local conditions that may offer a performance advantage in protection against corrosion. Linking the currents through coatings with the local conditions can have important consequences in coating selection for new pipelines and provide a better understanding of protection against corrosion in the long run.

Extensive research on corrosion under disbonded coatings simulated experimentally elongated crevice geometries with a macroscopic opening or defect and using plastic covers that avoided the passage of ions through them [1, 8-16]. Works provided a good understanding of the effects of CP currents through a macroscopic opening creating a local high pH and polarisation of the metal, with these effects becoming less important far away from the defect. However, these experiments do not allow to predict the conditions when coatings allow conduction of CP currents through. For this, the coating's contribution to changes in the local environment as per conduction of very small CP currents passage needs to be isolated and studied separately.

Recently, we developed an enhanced-accuracy method to measure small currents through pipeline coatings. This work focused with a great level of detail on the contributions of coatings to changing the pH as per the conduction of ionic CP currents through them. Currents through epoxy coatings demonstrated to be able to promote a substantial increase of the local environment's alkalinity [17]. However, the methodology required a major simplification from the real case scenario by means of using an inert electrode, and it is still unknown how to interpret the effect currents through coatings in a more complex steel system and if they would be sufficient to provide protection against corrosion or not.

Protection of steel under disbonded coatings could be achieved by two possible pathways. The first would be through direct protection; this occurs when the CP current through the coating is sufficient to polarise the metal to reduce or stop corrosion [18]. Alternatively, currents through the coatings could provide indirect protection by generating changes in the local environment. Cathodic reactions under disbonded coatings resulting in

alkalinisation could lead to negligible corrosion rates of the metal [19] and, ultimately, to passivation of the metal [1]. Reactions that consume or remove hydroxyl ions in the iron system may play a key role in this protection mechanism as they could also affect the local pH.

Unfortunately, there is not enough evidence on the actual role of CP-permeable coatings in allowing either direct or indirect protection of the pipe.

This research aims to provide a better understanding of corrosion mitigation under disbonded non-CP-shielding coatings. We study how the currents through an epoxy coating film may affect directly and indirectly the corrosion of steel under disbonded coating. For this, the true polarisation of steel and the local pH are continuously monitored. Complex variables studied include different CP polarisation levels.

2. EXPERIMENTAL DETAILS

The experimental setup consisted of a glass double-chamber cell with electrodes, filled with 0,1 M NaCl aqueous solution and separated by thin films. A schematic of the setup is shown in Figure 1. A cathode-chamber of 30 ml 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/KCl (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. 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 cold mounting epoxy resin. The surface of the electrode was sanded with a 220 grit paper and rinsed with ethanol.

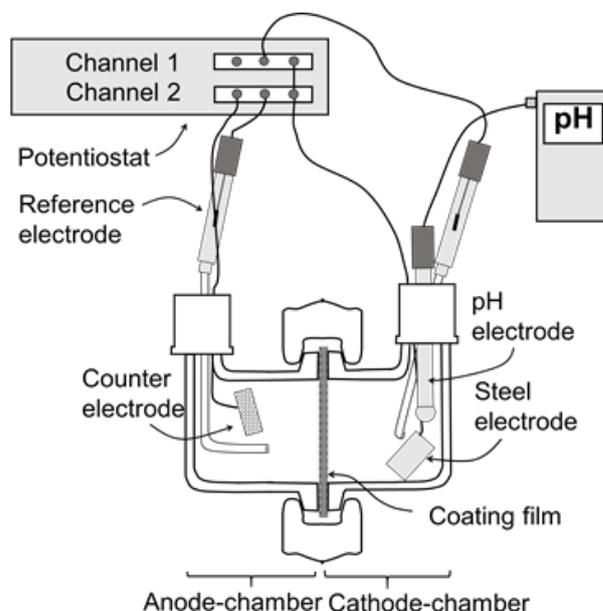


Figure 1 Schematic cross sectional view of the experimental setup

The counter electrode contained in the anode-chamber was made of a titanium mix-oxide and had an area of approximately 1 cm². Tests were conducted open to air to simulate a condition where the testing solution has oxygen availability in a consistent way during the test duration.

A high sensitivity potentiostat and a Faraday cage were used for the experiments. A three-electrode configuration was selected for the application of CP and measurement of current through the coating using "Channel 2" as shown in Figure 1. Constant CP potentials equivalent to -850 mV, -1050 mV and -1250 mV vs. Cu|CuSO₄ were applied during the tests for the periods of time indicated alternating with periods of open circuit potential (OCP). The true polarisation of the steel electrode was continuously measured with an independent potentiostat, named as per "Channel 1" in Figure 1.

2.1 Test without coating

A control experiment was performed by applying alternating periods of OCP and CP application equal to -850 mV and -1050 mV vs. Cu|CuSO₄ over a steel electrode without the presence of a coating barrier using the experimental arrangement described above. Current density and local pH in the cathode cell were measured for several hours.

2.2 Materials

The coating films tested consisted of a commercially available two parts epoxy used frequently as a field joint coating. This coating was selected for the present study based on a previous results that indicated its permeability towards CP [17]. Thin films of approximately 250 μm were prepared. The epoxy consisted of a bisphenol-F-epoxy amine-hardener based system and was obtained by mixing three volume parts base resin with one-part hardener. Then it was applied over aluminium foil using a drag-down film applicator and once hardened they were manually peeled off and visually inspected for the presence of pinholes or macroscopic defects. Coatings films were cured for at least two weeks at room temperature.

3. RESULTS

Measurements of current densities and pH for alternated periods of OCP and CP application on a steel electrode in a testing cell without a coating film are shown in Figure 2. Current densities are in the range of $20 \mu\text{A}/\text{cm}^2$ and $40 \mu\text{A}/\text{cm}^2$ for CP equal to -850 mV and -1050 mV , respectively. The pH in the neighbourhood of the steel cathode increases above nine units upon CP application; this value is maintained for about five hours and then the pH quickly returns to a near neutral value in the next five hours.

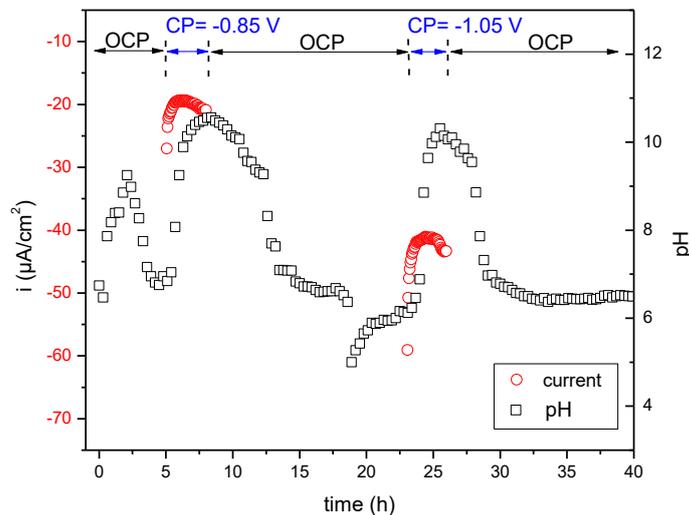


Figure 2 - current density and local pH measurements for a cell in absence of a coating barrier

Results of the current conducted through epoxy coatings for different CP potentials, and local pH in the cathode chamber are shown in Figure 3 (left). The cathodic current densities measured through the coatings are smaller than $1 \mu\text{A}/\text{cm}^2$ during the first day slightly exceeding this value when CP is increased to -1.25 V . The pH in the cathode cell does not exhibit a notorious last-standing increase during the test. Only short periods of alkalinity increase to values around eight pH units were observed upon CP application quickly returning to near neutral pH values. The true polarisation of the steel electrode in the cathode chamber is presented in Figure 3 (right). No apparent instant polarisation shifts were observed when applying different CP potentials or when CP was disconnected. After finalising the experiment, a CP of -850 mV was applied over a week. Corrosion products became noticeable after a few days testing. As an example, Figure 4 shows the presence of reddish corrosion products suspended in solution and on the steel electrode's surface after a week of CP application of -850 mV .

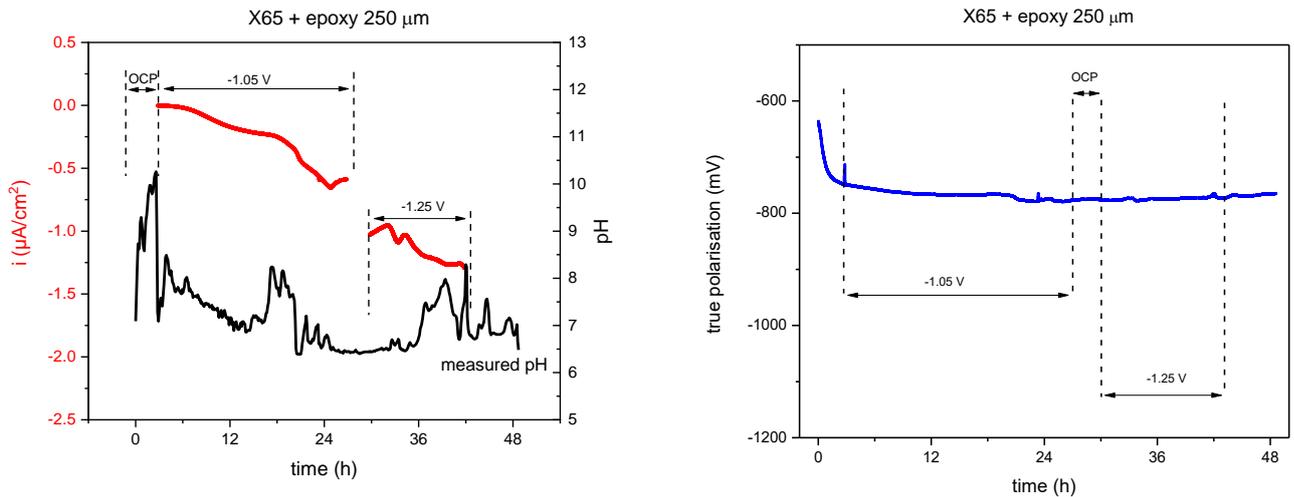


Figure 3 - Experiments for steel cathode subjected to alternated cycles of OCP, CP= -1.05 V vs. Cu|CuSO₄ and CP= -1.25 V vs. Cu|CuSO₄. Left: current density conducted through a 250 μm field joint epoxy coating and local pH under simulated disbonded coating. Right: true polarisation of X65 under simulated disbonded coating.

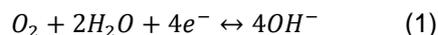


Figure 4 – appearance of a cathode chamber after one week testing under CP= -0.85 V

4. DISCUSSION

Results in Figure 3 indicate that direct protection by polarisation to the desired potential of -850 mV vs. Cu|CuSO₄ was not achieved efficiently. Applying a CP potential of -1.25 V did not affect significantly the true polarisation of the steel. The reason for this is that, despite the coating allows conduction of CP current, it still represents a physical barrier limiting the amount of ions passage. This can also be inferred when comparing the small current measured through coating with the current necessary to polarise a steel electrode up to the desired potentials in Figure 2. While the current necessary to polarise the steel electrode to approximately -1.05 V would be of about -40 μA/cm², the presence of a coating barrier limits the transported current to a fraction of a μA/cm². Therefore, such magnitude of current would be insufficient to effectively counteract the anodic reactions happening on the steel surface and the metal would consequently corrode. These results suggest that even though the thin coating allowed the conduction of CP, the amount of currents conducted upon the different CP levels applied would be insufficient to protect effectively the underlying metal by electrochemical polarisation.

The current conducted through the coatings was not able to affect the pH significantly. Final pH values measured were only between seven and eight pH units. Oxygen reduction (Eqn 1) is expected to be the main cathodic reaction occurring based on the true polarisation potentials measured and oxygen availability.



This reaction in Eqn 1 could lead to alkalinisation of the solution due to the generation of hydroxyl ions. This was the case observed in previously conducted research [17] when using an inert cathode such as titanium-mix-oxide. Previous results reproduced in Figure 5 show a significant alkalinisation in the cell simulating the coating disbondment mainly because the cathode would not present anodic reactions and the measured current would translate into generation of hydroxyl ions. However, when the cathode is made of steel, the pH is maintained around near neutral values. A plausible explanation for the near neutral pH values observed in the experiment in Figure 3 could be due to the complex formation of iron corrosion products that follow a non-stoichiometric relationship with OH⁻ consumption. Such products would remove hydroxyl ions from the environment in contact

with the metal and decrease the pH. The presence of orange-reddish precipitates shown in Figure 4 indicates the formation of iron products, which would support the latter statement.

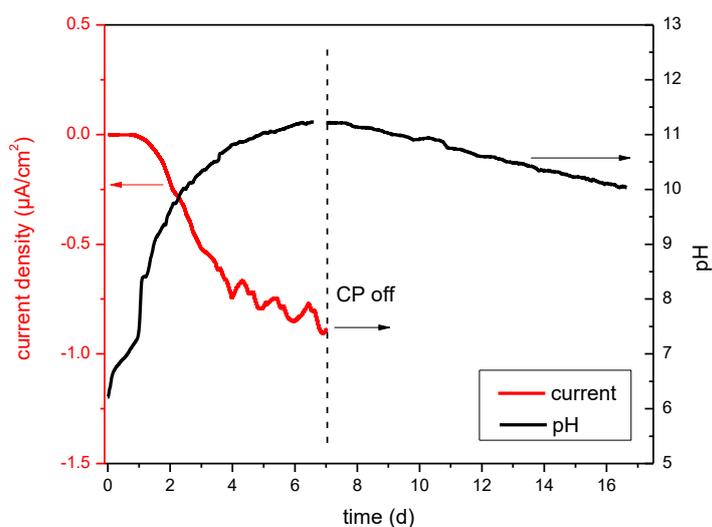


Figure 5 – pH and current through a 280 μm field joint epoxy under CP of -850 mV vs. Cu|CuSO₄ using an inert cathode. Data was extracted from [17]

It would be natural to think that hydroxyl ions movement through a semipermeable coating could also lower the pH. However, the test using an inert cathode in Figure 5 demonstrated that the coating would be able to retain a high pH environment after disconnection of CP, i.e. only a decrease of less than a pH unit was observed after seven days without CP. This slight decrease in pH in the cathode chamber may be explained as per either inwards diffusion of protons or outwards diffusion of hydroxyl ions, or both. Although this effect was noticeable, it demonstrated to be second order of importance in comparison with consumption of hydroxyl ions as per reactions discussed above.

Findings above indicate that reactions consuming hydroxyl ions would significantly oppose to the increase of pH created by CP currents through the coating and that the small currents through the coating would not be sufficient to offer protection by local alkalinisation for large disbondments in presence of oxygen.

5. CONCLUSIONS

- The possible alterations to the local environment under disbonded coating produced by a field epoxy film partially permeable to CP current were tested.
- The cathodic currents measured through epoxy coatings under different CP levels demonstrated to be insufficient to polarise effectively the steel to the desired potential. Increasing the CP level did not change this result significantly.
- The cathodic currents through the coating did not significantly elevate the local pH in contact with steel. The alkali concentration may be highly attenuated by hydroxyl ion consuming reactions typical of the iron system.
- Corrosion products were observed despite the conduction of cathodic currents through the tests.

6. ACKNOWLEDGMENTS

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8. AUTHORS DETAILS



Mauricio Latino, also known as Max, is completing PhD research in the Institute for Frontier Materials at Deakin University. As part of an Energy Pipeline CRC sponsored project, he has been investigating the role of organic coatings on cathodic shielding and corrosion under disbonded coatings of underground structures. Max professional interests are focused in developing suitable energy materials and solutions for a fast-evolving society.



Facundo Varela, also known as Bob, is a research fellow at the Institute for Frontier Materials at Deakin University. He has recently completed his PhD project that focused on new electrochemical methods for monitoring localized corrosion under cathodic protection. As a research fellow, Bob is working on an Energy Pipeline CRC sponsored project aiming to perform field trials of the sensors developed during his PhD.



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 150 publications and a book entitled 'Heterogeneous Electrode Processes and Localised Corrosion' (2012 John Wiley & Sons).



Professor Maria Forsyth completed her PhD in January 1990 at Monash University and moved to Northwestern University to take up a Fulbright Fellowship in the area of solid electrolytes for lithium batteries. On her return to Melbourne she worked at DSTO for a year before joining the Department of Materials Engineering as a Lecturer in 1993. In 2001 she was awarded an ARC Professorial Fellowship and is currently the Chair in Electromaterials and Corrosion Sciences at Deakin University, within the Institute for Technology Research and Innovation (ITRI). She is co-author of over 280 refereed journal papers, has delivered over twenty invited talks in the last 5 years and has over 7000 citations at present.