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AN OVERVIEW ON CATHODIC SHIELDING PRODUCED BY DISBONDED COATINGS

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SUMMARY: Over the past decade, the shielding of cathodic protection (CP) produced by disbonded coatings, commonly referred to as cathodic shielding, has gained significant attention in the pipeline industry. Problems such as stress corrosion cracking (SCC), pitting or crevice corrosion, as well as microbial induced corrosion (MIC) have been reported to be associated with the coatings’ shielding effect. Non-shielding coatings are often defined as coatings that allow current permeation through them when a disbondment occurs and as a consequence, a protective high pH environment can develop under the disbonded coating. According to this definition, pipeline coatings have been frequently classified as per CP shielding or non-shielding, based upon field observations of corrosion features and the in-situ checking of pH beneath the coating. The validity of this classification may be subjective not only to the accuracy of the operator’s field observation, but also to the reliability of the method used for providing a genuine indication of the non-shielding ability of a coating. Currently, there is scarce information in the literature on understanding the actual contribution of different coating systems to the corrosion problems beneath disbonded coatings. This work provides an overview and brief discussion on the current understanding of cathodic shielding and non-shielding coatings, and the possible contributions of disbonded coatings to corrosion. It also presents a critical analysis of the key factors that need to be addressed in order to clearly interpret cathodic shielding and to determine coatings and CP compatibility in coating disbondment scenario.

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

1. INTRODUCTION

The protection against corrosion of buried structures such as steel pipelines is usually provided by external coatings in conjunction with cathodic protection (CP). The accepted protection criterion consists of setting the metal to a potential of \(-850 \text{ mV}\) respect to the Cu|CuSO\(_4\) reference electrode. Such electrochemical polarisation would effectively reduce the steel corrosion rate\(^1\). Nonetheless, the efficiency of the CP protection system can be compromised when coating disbondment occurs.

Coating disbondment is recognised in the field to be one of the highest risk failure mechanisms of pipeline coatings\(^2,3\).

Figure 1 shows some cases of a coal tar coating disbondment observed by the first author of this work in a reparation campaign of an Australian gas pipeline. The corrosion issues that were observed under those disbonded coatings included several morphologies of localized corrosion and stress corrosion cracking (SCC).
Figure 1. Disbonded coal tar wrap in an Australian pipeline, 2016.

When a coating disbondment occurs, the coating separates from the pipe surface, forming a crevice. Electrolytes from the soil and oxygen are able to access the crevice and accumulate at the metal/coating interface. Even though the CP system may be able to impose a protection potential that prevents corrosion at the opening of a disbondment and its surroundings, the protection may decrease when moving away from the holiday. Supporting this hypothesis, the polarisation potentials have been reported to suffer an exponential shift to less cathodic values towards the crevice closed end.7–10 In a similar way, the cathodic current density has also been observed to exhibit an exponential decrease towards the crevice bottom.11,12 Given the highly effective insulating nature of the protective coatings, the access of currents from the cathodic protection system is believed to be limited. As a result, there would be regions under the disbonded coating where the CP cannot penetrate and the metal would be unprotected. This phenomenon is known as coatings’ CP shielding. A schematic of a coating CP shielding situation is shown in Figure 2 in which the CP currents can only polarise the metal close to the holiday area.

Figure 2. CP shielding under disbonded coating.

In many instances, the particular conditions developed within the crevice under a disbonded coating have been reported to jeopardize the integrity of pipelines. Because of water accumulation, a micro-environment can develop under the disbonded coating resulting in a significantly different chemistry to that of the external soil environment. It has been mentioned that this local environment promotes corrosion problems such as SCC,2,3,5,13,14 pitting,4,5,15 and microbial induced corrosion (MIC).6,16,17 Moreover, it has been mentioned that the environment produced in the crevice not only affects corrosion but it could also promote further delamination of the coatings if high pH environments are developed.18,19

Currently there is no suitable technique that allows monitoring of corrosion under disbonded coatings in the field.20 Therefore, it is necessary to understand the evolution of the environmental conditions under disbonded coating in order to predict corrosion risks. A coating’ shielding or non-shielding behaviour could potentially change the local environment. Consequently, it is of interest to study and quantify such effects and to understand which coatings will perform better in preventing corrosion when disbondments take place.

2. CURRENT UNDERSTANDING OF NON CP-SHIELDING COATINGS

Industry observations of different coatings after several years of operation would suggest some coatings may perform better than others in regard to cathodic shielding behaviour when they are disbonded. Frequently, a
coating is said to be “non-shielding” to CP if it allows CP currents to permeate, even though a disbondment occurs. A schematic of this behaviour is illustrated in Figure 3. This definition usually leads to confusion because coatings are designed to have a high electrolytic resistance and they would be expected to shield the CP currents. Moreover, Wong affirms that a new coating will not allow enough CP currents permeation in order to achieve a protective level on the metal under disbondment.

A schematic of this behaviour is illustrated in Figure 3. This definition usually leads to confusion because coatings are designed to have a high electrolytic resistance and they would be expected to shield the CP currents. Moreover, Wong affirms that a new coating will not allow enough CP currents permeation in order to achieve a protective level on the metal under disbondment.

Figure 3. Non shielding coating schematic

Often, when a disbonded coating is found in reparation campaigns, a visual inspection is conducted to determine the condition of the coating and the corrosion morphologies underneath. In several cases the pH values of the liquid trapped under the disbonded coating are recorded too. Alkaline pH levels indicate that, preferentially, cathodic reactions have taken place over the steel surface thanks to the CP system. If those situations are achieved, a coating would be classified as “non-shielding.” In general terms, several authors support the observation that slight signs of corrosion and a high pH under disbonded coating are the typical behaviour of non-shielding coatings. However, there is not an absolute agreement about the classification criteria and the shielding behaviour of coatings. The lack of agreement is mainly due to lack of solid evidence that could be used to elucidate the phenomenon. The prime reason for this situation is that currently, there is not a methodology to quantify the parameters related to the phenomenon. Table 1 summarises the typical reported behaviour of different coatings in presence of CP. The categories presented are “shielding,” “non-shielding” and “potentially non-shielding,” for the cases where evidence of non-shielding behaviour was observed by some of the authors.

Table 1-Coatings shielding behaviour according to industry operators. Ref. 22,24-28

<table>
<thead>
<tr>
<th>Shielding</th>
<th>Non-shielding</th>
<th>Potentially non-shielding</th>
</tr>
</thead>
<tbody>
<tr>
<td>3LPO (three layer poly-olefins)</td>
<td>FBE (fusion bonded epoxy)</td>
<td>Asphalt enamel</td>
</tr>
<tr>
<td>HSS (Heat shrinkable sleeves), poly-olefins based</td>
<td>Mesh backed tapes</td>
<td>Coal Tar enamel</td>
</tr>
<tr>
<td>Solid film backed tapes, poly-olefins based</td>
<td></td>
<td>Two-part-epoxies</td>
</tr>
</tbody>
</table>

2.1 Does a high pH under disbonded coating indicate that the coating is non CP-shielding?

Steel corrosion in an aqueous solution is represented by the anodic reaction:

$$Fe \leftrightarrow Fe^{2+} + 2e^- \ (1)$$

Simultaneously, the cathodic reactions of hydrogen evolution and oxygen reduction would consume the electrons provided by the steel corrosion, as indicated per the following reactions:

$$2H_2O + 2e^- \leftrightarrow H_2 + 2OH^- \ (2)$$
If the coating allows the permeation of CP currents, the potential of the steel surface would shift from the corrosion potential towards more cathodic values. Consequently, the rate of iron dissolution process indicated by Eqn (1) would decrease. The reaction (2) would be possible for a wide range of potentials and pH values at which water is thermodynamically unstable. The reaction (3) would be maintained as long as there is oxygen under the disbonded coating. Both cathodic reactions would produce an increment in the hydroxyl ion concentration. In other words, the pH of the solution under the disbonded coating would increase. At a certain time, the final pH value would depend upon the amount of currents that the coating allowed to permeate and also the oxygen level that was available in the solution. At low cathodic polarisation levels, oxygen reduction would be the main cathodic reaction taking place. If the oxygen were consumed and the CP potentials were negative enough, the reduction of water, reaction (2), could still occur. In conclusion, an increase of the pH would be expected under disbonded, non-shielding coatings. However, there could be another reason why high pH values under disbonded coating could develop. Several researchers who have studied corrosion under simulated disbonded coatings have observed the development of highly alkaline environments. The experimental setup (Figure 4) that was used consisted of a rectangular crevice with a holiday where CP was applied, a plastic cover on the top that simulated the coating and had no contact with solution, and, several pH monitoring ports. Since the plastic cover did not allow CP current permeation, it represented the opposite behaviour of a non-shielding coating. However, the solution inside the crevice was reported as highly alkaline. The pH at and near the crevice opening was between 9 and 12, and a decrease was observed with increasing distance along the crevice from the holiday.

Based on the discussion presented above, it can be inferred that a high pH value achieved at the interface of the coating/steel disbonded area could not be sufficient to reveal the shielding behaviour of coatings.

3. ELECTROLYTIC RESISTANCE OF COATINGS AND ITS RELATIONSHIP WITH THE SHIELDING EFFECT

The resistance value of a coating in an aqueous environment, also called electrolytic resistance, indicates how effectively a coating acts as a barrier against water and ion penetration. Bacon et al. measured the DC resistance of more than 300 coating systems and classified their corrosion protection performance. Coatings offering a resistance higher than $10^6 \, \Omega \cdot \text{cm}^2$ were classified as good barriers, those having values between $10^4 \, \Omega \cdot \text{cm}^2$ and $10^6 \, \Omega \cdot \text{cm}^2$ had an acceptable performance and the ones below $10^4 \, \Omega \cdot \text{cm}^2$ presented poor corrosion.

\[ O_2 + 2H_2O + 4e^- \rightarrow 4OH^- (3) \]
protection properties. Alternatively, the electrochemical impedance spectroscopy (EIS) technique has been used to measure the electrolytic resistance and to determine the long-term performance of coatings.\textsuperscript{35-37}

If a disbonded coating has a high electrolytic resistance, it would be expected to shield the cathodic currents. In other words, it would not allow ions, driven by the CP, to permeate through them. However, several coatings have been shown\textsuperscript{38-45} to decrease their electrolytic resistance with time of exposure to water and CP. Table 2 presents a compilation of several authors’ measurements of changes in the electrolytic resistance of pipeline coatings. The table also presents results of net current related to currents’ permeation. This aspect will be discussed in the next section.

The absorption of water lowers the protective properties of coatings.\textsuperscript{44,46-48} Water absorption occurs first at the coating’s hydrophilic regions of low molecular weight and low crosslinking. Then, it produces hydrolysis and dissolution of the polymer and finally creates localised conductive pathways for the species to permeate. These localised conductive areas in a polymer have been mentioned by several researchers as D type areas.\textsuperscript{39,49-52} D type areas present a low resistance, which is proportional to the resistance of the electrolyte that is in contact with them. Once conductive pathways are formed, ions in their hydrated forms would be able to permeate.\textsuperscript{49,53,54}

Recently, Buchanan et al\textsuperscript{40} have explained the non-shielding behaviour of epoxy coatings based on the reduction of the electrolytic resistance value of epoxies over time. The non-uniform nature of polymer networks could possibly play a role in this aspect. Whether or not a certain reduction of the electrolytic resistance would allow enough CP current to permeate through the coatings and protect the steel underneath has not been yet quantified nor well understood.

3.1 CP current permeation through coatings

Some researchers have observed the permeation of currents through pipeline coatings.\textsuperscript{15,42,44,55} In these experiments, ionic CP currents managed to permeate through the coating and reach the steel, therefore, a net cathodic current was measured. Such net cathodic current indicates that the rate of cathodic reactions surpasses the rate of anodic reactions that correspond to the corrosion of the metal. However, this result does not imply that an effective cathodic protection was achieved. In addition, an increment in the pH of the solution would be expected.

Ruschau et al\textsuperscript{42} measured the current permeation and the change of the electrolytic resistance on plates coated with several polymers. The epoxy, fusion bonded epoxy (FBE) and polyurethane coated plates experienced a decrease of several orders of magnitude in the resistance value over a period of six months. This change allowed some currents to permeate through the coatings, e.g. up to 2.5 µA/cm\textsuperscript{2} for the polyurethane coating. In contrast, a polyethylene shrink sleeve maintained its electrolytic resistance during the experiment, without showing any permeation of current.

Fu et al\textsuperscript{44} studied the same parameters than Ruschau et al on membranes of medium-density polyethylene (MDPE), FBE and high performance powder coating (HPPC). The experimental setup consisted of a double cell that simulated a disbondment, where coating membranes with no apparent defects were placed in between the cells. Both the FBE and the MDPE experienced currents’ permeation of the order of 1 µA/cm\textsuperscript{2}. Additionally, the coatings suffered a drop of one to two orders of magnitude in the impedance values which were attributed to water absorption.

Kuang et al\textsuperscript{55} conducted a similar experiment as Fu et al, in which the pH under disbonded coating and the polarisation potential were measured. The authors affirmed that a 250 µm FBE coating was partially permeable to CP current, since it allowed current permeation less than 2 µA/cm\textsuperscript{2}. Despite the small current density, the pH beneath the coating was raised above 9 after 25 days. In contrast, an 850 µm high-density polyethylene (HDPE) did not allow any currents to pass through. However, a small pH increment to the value of 8 was observed under the HDPE membrane. This result would not be expected for a coating that shields the cathodic currents and it is not well understood.
Perdomo et al. used a 30 year old and, aged in-service asphalt enamel coating that presented cracks over its surface. The values of currents measured were about an order of magnitude bigger than the Kuang and Fu results. The presence of cracks could have contributed to permeation of substances and would explain the larger currents measured. This result suggests that aged coatings could permeate more currents than new coatings.

The previous results show evidence of ions’ permeation leading to more negative polarisation potentials of the metal under a disbonded coating and increasing the rate of cathodic reactions. However, the true polarisation potentials of the metals were not measured and the protection status as a result of currents permeation could not be determined. If the polarisation of the steel and the pH achieved were above the immunity zone of the Pourbaix diagram the corrosion of the steel would still be possible, even though it would occur at a lower rate. Ultimately, the true polarisation of the steel achieved as a result of current permeation and changes of the pH of the environment would be necessary to characterise the non-shielding property of a coating.

Furthermore, the interpretation of the measured current values would not allow one to quantify the non-shielding effect of the different coatings since the contribution of oxygen cathodic reaction to the current is unknown. Oxygen could become available in the disbonded area by permeation through coating defects or cracks, it could access through the testing rig in the case that it was not airtight, or it could have been dissolved in the testing solution used. No information about the oxygen content in the solutions used in the experiments was provided. The uncertainty in the data does not allow one to draw conclusions based on the presented results.

**Table 2- Permeation currents and changes in the electrolytic resistance of several coatings**

| Reference       | Coating type | Thickness (µm) | Current density (µA/cm²) | Electrolytic resistance (Ω.cm²) | CP applied (mV Cu|CuSO₄) |
|-----------------|--------------|----------------|--------------------------|---------------------------------|---------------------|
|                 |              | Initial (day 1) | Final | Day of final meas. | Initial | Final | Day of final meas. |
| Beavers et al⁴³ | FBE          | n/d            | n/d  | n/d                | 1.E+10  | 1.E+08 | 450       | -1500 |
|                 | PE tape      | n/d            | n/d  | n/d                | 1.E+12  | 1.E+12 | 450       | -1500 |
|                 | Coal tar enamel | n/d           | n/d  | n/d                | 1.E+12  | 1.E+08 | 450       | -1500 |
| Perdomo et al⁴⁵ | Asphalt enamel | n/d           | -5.5 | -16.6              | 14      | n/d    | n/d       | -850  |
|                 | Epoxy        | 600            | n/d  | n/d                | 2.E+11  | 2.E+06 | 104       | -1574 |
|                 | Polyurethane | 800            | n/d  | n/d                | 2.E+10  | 9.E+05 | 104       | -1574 |
| Ruschau et al⁴⁴ | PE shrink sleeve | 1500          | 0    | 0                  | 80      | 8.E+11 | 4.E+11   | 80    | -1500 |
|                 | FBE          | 120            | 0    | 0.06               | 180     | 2.E+11 | 8.E+06   | 180   | -1500 |
|                 | Epoxy        | 120            | 0    | 1.6                | 120     | 4.E+08 | 8.E+06   | 180   | -1500 |
|                 | Polyurethane | 120            | 0    | 2.5                | 180     | 8.E+09 | 8.E+07   | 180   | -1500 |
| Fu et al⁴⁴      | HPPC         | 1100           | 0.1  | 0.1                | 32      | 6.E+10 | 5.E+10   | 32    | -1570 |
|                 | FBE          | 250            | 0    | -2                 | 32      | 7.E+07 | 3.E+05   | 32    | -1570 |
|                 | MDPE         | 850            | -0.1 | -0.7               | 32      | 4.E+06 | 8.E+05   | 32    | -1570 |
| Kuang et        | FBE          | 250            | 0.6  | -1.2               | 30      | n/d    | n/d       | -850  |
| al | HDPE | 850 | 0.18 | 0.9 | 30 | n/d | n/d | n/d | -850 |

Notes:
Data is approximated as informed by the corresponding authors.
Currents values in ref.44 correspond to absolute values
An estimated cell diameter of 10 cm was used in ref.45 for calculations of density values.

4. SUMMARY
Currently there is not a general agreement about the classification criteria with regard to the shielding behaviour of coatings. The lack of agreement is mainly due to an absence of solid evidence of the phenomenon. The primary reason for this situation is that there is not a technique to quantify the phenomenon. Major factors that have been reported in the literature affecting the cathodic shielding and corrosion under disbonded coating include: (i) the pH increment at the interface of the coating/steel under a disbonded coating; (ii) the geometry of the disbondment; (iii) the electrolytic resistance of the coating; (iv) CP currents and chemical species permeation through the coating, and, (v) the true polarisation potential achieved by the metal under disbondment.

5. ACKNOWLEDGMENTS
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7. **AUTHOR DETAILS**

Mauricio Latino, also known as Max, is a PhD Student in the Institute for Frontier Materials at Deakin University. He is working on an Energy Pipeline CRC sponsored project. His project attempts to elucidate the role of organic coatings on cathodic shielding and corrosion under disbonded coatings of underground structures.
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.