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New Electrochemical Methods for Visualizing Dynamic Corrosion and Coating Disbondment Processes on Simulated Pipeline Conditions

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1. Introduction

Protective coatings and cathodic protection (CP) are widely applied as the principal means of protecting buried steel pipeline from soil corrosion. Unfortunately under some complex environmental conditions the effectiveness of these methods could not be ensured, and therefore techniques are needed to monitor and evaluate their performance [1,2]. For instance, the potential of a buried steel pipeline could be diverted from the standard ‘safe’ CP level (i.e. -850 mV vs copper/copper sulphate reference electrode) due to various reasons such as stray currents, flawed CP design or faulty CP control, leading to insufficient CP (in cases of anodic potential excursions) and over-protection (in cases of excessive negative potential excursions). Some forms of potential excursions are known to be harmful to buried steel pipelines; however currently the exact effects of potential excursions on CP efficiency and corrosion have not been sufficiently understood primarily due to difficulties in measuring these effects [3,4]. Over-protection is known to cause cathodic disbondment of pipeline coatings [5,6]. However traditional methods of evaluating cathodic disbondment based on visual inspection of pipeline conditions and laboratory testing of cathodic disbondment resistance have many limitations in quantitatively and instantaneously measuring and monitoring disbondment of thick pipeline coatings [6]. There is a need for the development of new methods that are able to perform in-situ and quantitative measurements of stray current corrosion and cathodic disbondment of pipeline coatings.

On the other hand, structural health monitoring and life prediction tools are needed to provide long-term remnant pipeline life prediction and in-situ pipeline condition monitoring. A critical step in pipeline structural health monitoring is the enhancement of technological capabilities that are required for quantifying the effects of key factors influencing buried pipeline corrosion and environmentally assisted materials degradation, and the development of condition monitoring technologies that are able to provide in-situ monitoring and site-specific warning of pipeline damage [1,2]. The concept of in-situ monitoring and site-specific warning of pipeline corrosion is illustrated by a case of monitoring localised corrosion under disbonded coatings using a new corrosion monitoring probe [7-10]. A basic principle that underpins the use of sensors or probes to monitor localised corrosion has been presented: Localised corrosion and coating failure are not an accidental occurrence, but result from fundamental thermodynamic instability of a metal exposed to a specific environment. Therefore corrosion and coating disbondment occurring on a pipeline will also occur on a sensor or a probe made of the same material and exposed to the same environment as a pipeline [2]. Although the exact location of localised corrosion or coating disbondment could be difficult to pinpoint along the length of a buried pipeline, the ‘worst-case scenario’ and high risk pipeline sections and sites are predictable. Sensors can be embedded at these strategic sites to collect data that contain ‘predictor features’ signifying the occurrence of localised corrosion, CP failure, coating disbondment and degradation. Information from these sensors would enable pipeline owners to prioritise site survey and inspection operations, and to develop a maintenance strategy to manage aged pipelines, rather than replace them.

In this work, advantage was taken of the high temporal and spatial resolution of an electrochemically integrated multi-electrode array, often referred to as the Wire Beam Electrode (WBE) method, for probing localised electrode processes evolving dynamically and propagating freely on a steel electrode surface under the effect of cathodic protection and anodic transients. This paper provides an overview of our new approaches aimed at developing new probes for monitoring, categorising and quantifying the level and nature of external pipeline and coating damages under the combined effects of various inter-related variables and processes such as cathodic shielding, stray current corrosion, coating disbondment and localised corrosion [11-13].

2. Experimental Details

Figure 1 illustrates a typical experimental configuration using an electrochemically integrated multi-electrode array based sensor to facilitate the in-situ monitoring and visualisation of electrochemical processes occurring on buried steel surfaces under CP and anodic transient conditions [12]. The WBE sensor used in this work consists of 100 closely packed but isolated square shaped carbon steel electrodes (e.g. 2.44 mm x 2.44 mm) embedded in epoxy resin. The gaps between neighbouring electrodes were kept small (e.g. 0.10 ± 0.05 mm). After grinding using SiC 600 grit paper, the sensor was installed in a specifically designed sandy soil box cell [4,12] that facilitates the effective simulation and control of CP testing conditions. Washed fine sand with a typical resistivity of 1000 Ohm.cm was used in the sand box cell, and the resistivity was adjusted using a 3% NaCl solution. The sand box cell was sealed to prevent evaporation. A potentiostat (Bio-Logic Science Instrument) was used to apply CP and anodic transient signals on the sensor surface under potentiostatic control. Similar electrochemical cells and experimental setup were used in experiments for studying various inter-related processes such as cathodic shielding and localised corrosion [11], coating damage and disbondment [13]. More details on the experimental and data analysis methods can be found elsewhere [11-13].

Figure 1. A typical experimental configuration for performing in-situ monitoring of electrochemical processes occurring on a WBE sensor surface buried in a soil cell under CP and anodic transient conditions [11].
3. Results and Discussion

3.1 Case 1: The monitoring of localised corrosion processes under simulated disbonded coatings

The monitoring of localised corrosion processes under a dynamically changing electrochemical environment under disbonded coatings is a technical challenge. Cathodic disbondment is a major form of electrochemically induced coating failure that frequently takes place at the metal/coating interface on cathodically protected steel infrastructure such as pipelines. Disbonded coatings are believed to shield CP current, and therefore localised corrosion frequently occurs under disbonded coatings. Currently there is no technique that can be used to perform in-situ monitoring of its occurrence in the field. Electrochemical techniques such as conventional electrochemical impedance spectroscopy (EIS), localised electrochemical impedance spectroscopy (LEIS), scanning Kelvin probe and scanning vibrating electrode techniques (SVET) have been employed to measure coating disbondment in the laboratory; however, there are significant obstacles for these techniques being practically used to monitor in-situ cathodic disbondment of thick pipeline coatings (e.g. 1000 μm in thickness) [7-9]. Currently detecting corrosion under disbonded coatings, especially at pipeline joints, relies heavily on periodic time based routine inspections using pipeline condition assessment methods including in-line inspection tools (intelligent pigs) and historical excavations. These methods are useful for detecting and locating big defects on the pipeline and for assessing the operation of CP systems, however they are often expensive and therefore are performed only on a periodic basis (usually every 5-15 years for intelligent pigs).

Another approach that should be useful for pipeline corrosion management is the use of corrosion monitoring and warning sensors. Currently the most widely adopted corrosion monitoring sensors in the pipeline industry are steel coupons and electrical resistance probes (ER probes). Steel coupons buried next to the pipe and electrically connected to it are used to assess the operation of CP systems; however conventional weight-loss measurement can be difficult for buried structures because of practical difficulties in coupon installation and excavation. ER probes, often referred to as ‘intelligent’ weight-loss coupons, are used to detect corrosion by monitoring the electrical resistance between the ends of an elongated coupon of constant cross-section subjected to the corrosive environment. The ER coupon can be electrically connected to the 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 detection of localised corrosion such as corrosion under disbonded coatings, because an ER probe may not be able to simulate corrosion under disbonded coatings, and also because localised damages may not lead to any significant change in electrical resistance detectable by an ER probe. Although corrosion monitoring has been widely applied to many industrial structures such as chemical plants, practical application of existing corrosion monitoring techniques to buried structures such as a steel pipeline has been limited probably due to unavailability of suitable sensors [2].

A new sensor [9-11] has been designed to measure the distribution of electrochemical currents over an electrode array surface partially covered by a crevice that simulates a disbonded coating. The sensor has been evaluated using immersion tests at open circuit potential (OCP) and under CP conditions. A typical series of results are shown in Figure 2. Under both OCP and CP conditions, anodic as well as cathodic current densities were detected within the crevice. Corrosion patterns were estimated based on the current density distributions from two different methods [9-11]. The acceptable level of correlation with the corrosion damage observed at the array surface at the end of the tests suggests that the sensor surface has the potential to monitor localised corrosion under disbonded coatings. Using sensors 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.

3.2 Case 2: The monitoring of the effects of various forms of stray currents

Significant efforts have been made to systematically categorise and quantify the level and nature of damage to a pipeline as a result of CP excursions, however there are still major difficulties in drawing decisive conclusions because of the complexity of the electrochemical corrosion processes occurring at the complicated soil/buried steel interface. Technological difficulties in measuring buried steel corrosion under CP are believed to be the prime reason responsible for the lack of conclusions on the exact effects of CP excursions on pipeline corrosion. Currently potential recording is the most commonly used method for inspecting stray current activities in the pipeline industry; however potential recording does not provide sufficient information about corrosion rates and patterns. Weight-loss coupons have been used to determine corrosion rates of steel buried in soil, however weight-loss coupons are unable to provide in situ corrosion rate data required for quantifying the effects of relatively short duration CP potential excursions.

A major difficulty in stray current corrosion research is the lack of reliable and reproducible experimental methodologies that are able to systematically categorise and quantify the level and nature of damage as a result of various modes of CP excursions. In this work, the WBE method has been applied for the first time as a new sensor for detecting localised corrosion initiation under various dynamic anodic transient influences. Experiments have been carried out for measuring the effect of an anodic transient on the corrosion of a steel WBE sensor in a soil corrosion cell [12]. A typical series of results are shown in Figure 3. A common phenomenon that was observed from these tests is that shortly after an anodic transient was applied to a CP protected steel surface, anodic current and corrosion activity dropped dramatically from an initial anodic current peak value. This has been explained by the passivity of steel under CP induced high pH condition. Another phenomenon observed by inspecting the occurrence of local anodic currents in WBE maps was that localised corrosion initiation occurred after a critical duration. This critical duration could be explained by the breakdown of passivity under the effects of anodic transient induced pH and surface chemistry changes. This work suggests that the WBE sensor could be used as an effective tool for studying localised corrosion initiation under the effect of complex factors, as well as for the in-situ monitoring of stray current corrosion of buried steel structures.

3.3 Case 3: The monitoring of cathodic disbondment of coatings

Cathodic disbondment is a major form of electrochemically induced coating failure that frequently takes place at the metal/coating interface on cathodically protected steel infrastructure such as pipelines. Extensive research over the past decades has developed a good understanding of the phenomenon, however currently there is no technique that can be used to perform in-situ monitoring of its occurrence in the field. Traditional methods of evaluating cathodic disbondment of pipeline coatings are based on ex-situ visual

Figure 2. Under both OCP and CP conditions, anodic as well as cathodic current densities were detected within the crevice. Corrosion patterns were estimated based on the current density distributions from two different methods [9-11]. The acceptable level of correlation with the corrosion damage observed at the array surface at the end of the tests suggests that the sensor surface has the potential to monitor localised corrosion under disbonded coatings. Using sensors 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.

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inspection of excavated pipes. Electrochemical techniques such as conventional electrochemical impedance spectroscopy, localised electrochemical impedance spectroscopy, scanning Kelvin probe and scanning vibrating electrode techniques (SVET) have been employed to measure coating disbondment in the laboratory; however, there are significant obstacles for these techniques being practically used to monitor in-situ cathodic disbondment of thick pipeline coatings (e.g. 1000μm in thickness). A thick coating would ‘shield’ the current from reaching the disbonded area, especially far away from the original defect, and therefore the measurements are more likely to be dominated by the lower impedance present at the coating defect areas. Under these conditions, little information can be obtained from higher impedance regions deep in the disbonded area. Indeed, in a previous study the authors have found that conventional EIS loses sensitivity in detecting cathodic disbondment propagation due to such limitations [6]. The electrode array [14] is a method that has been applied to measure local direct currents for evaluating the cathodic disbondment of defective thin coatings (< 100 micron) by Le Thu et al. [15] and Wang et al. [16]. However, there is little evidence to show that direct current mapping is sensitive enough to detect coating disbondment, especially at its propagation stage. This is a concern because a resistive coating film could ‘shield’ the direct current from flowing into the disbonded coating area. Here we describe a new approach to measuring coating disbondment based on local AC impedance measurement using the electrode array and assess the viability of different approaches. Previously Kong et al. [17] measured the EIS of individually selected steel electrodes in an electrode array; however the purpose of their measurement was for assessing the degradation of intact coatings (100 micron), not for monitoring coating disbondment.

Figure 4 shows typical maps of local impedance amplitude (|Z| at 300 MHz) and a direct current map measured after different periods of exposure of the sensor to the test solution under CP potential of -1.40 V Ag/AgCl or -0.95 V Ag/AgCl. It is clearly shown in maps (a) - (f) that, under a CP potential of -1.40 V Ag/AgCl, the impedance of electrodes surrounding the defect area continuously decreased (to less than 10$^5$ ohm) over the 624 hours (26 days) exposure period. These low impedance...
areas expanded with the increasing exposure time, while electrodes located far away the defect area maintained a high impedance of larger than $10^7$ ohm after 624 hours. These maps clearly indicate coating disbondment due to permeation of the test solution along the disbonded coating/metal interface gap rather than absorption of the solution by the coating. After 624 hours, as shown in Figure 4(f), the majority of electrodes on the sensor were disbonded. Direct current maps measured at $-1.40 \text{ V}_{\text{Ag/AgCl}}$ (not shown here) also show similar coating disbondment processes and behaviour. However, when the CP potential was reduced from $-1.40 \text{ V}_{\text{Ag/AgCl}}$ to $-0.95 \text{ V}_{\text{Ag/AgCl}}$, as shown in Figure 4(g) and Figure 4(h), the impedance map still clearly shows the disbonded area, while the direct current map, on the other hand, lost sensitivity and this coating disbonded area was not visible, as seen in Figure 4(h). This may explain a result reported by Le Thu et al. [15] that, in a previous attempt to measure coating disbondment using array electrodes (coating thickness $60 \mu m$) under a CP potential of $-1.5 \text{ V}_{\text{Ag/CSE}}$, no significant coating disbondment was observed on direct current maps over a 336 hour exposure period [15]. This is clearly a major limitation of the direct current measurement technique given that a CP potential of $-0.95 \text{ V}_{\text{Ag/AgCl}}$ is close to industry standard CP criteria for practical, coated pipeline.

These results illustrate that local electrochemical impedance measurements using an electrode array sensor have significantly improved sensitivity for monitoring the propagation of cathodic disbondment of defective coatings compared with the conventional overall electrochemical impedance and local current measurements approaches. This new approach also provides the opportunity of eliminating the effects of the low impedance coating defect regions on the visibility of higher impedance regions deep in the disbond coating, facilitating the probing of electrode processes and mechanisms in selected regions of heterogeneous electrode surfaces.

Figure 4. Typical maps of impedance amplitude ($|Z|$) at $300 \text{ MHz}$ and direct currents measured over a coated sensor after various periods of exposure and under different CP potential.
4. Conclusions
Sensors designed using an electrochemically integrated multi-electrode array have been successfully employed for (i) monitoring localised corrosion under the dynamically changing electrochemical environment under a simulated coating disbondment; (ii) visualising passivity and its breakdown and localised corrosion under the effect of dynamic anodic transients; and (iv) detecting coating disbondment under excessive cathodic protection conditions by measuring local electrochemical impedance.

5. Acknowledgments
This work was funded by the Energy Pipelines CRC, supported through the Australian Government’s Cooperative Research Centres Program. The funding and in-kind support from the APGA RSC is gratefully acknowledged.

6. References


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