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INVESTIGATION OF BLISTER FORMED ON COATED MILD STEEL USING SCANNING KELVIN PROBE

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Abstract. The degradation of a coated metal in terms of the area underneath a blister has been studied after being immersed in 3% sodium chlorida and 3% ammonium chloride solution. Scanning Kelvin probe (SKP) was used to map electrochemical potentials, identifying anodic and cathodic regions underneath a blister and the surrounding coating. For blisters formed on coated panel immersed in sodium chlorida solution, SKP potential map reveals that the blister has formed at a cathode due to alkali but anodes form nearby (not remote). Meanwhile SKP potential map for blister formed on coated panel in 3% ammonium chloride reveals the presence of cathodic regions within the anodic areas.

Keywords: Organic coating; scanning Kelvin Probe; blister

Abstrak. Degradasi pada besi bersalut cat dari segi gelembung yang terbentuk telah dikaji selepas direndam di dalam larutan 3% natrium klorida dan 3% ammonium klorida. Imbasan probe Kelvin (SKP) telah digunakan untuk menghasilkan peta keupayaan kimia-elektro bagi mengenal pasti kawasan anod dan katod di bawah gelembung dan kawasan persekitarannya. Bagi gelembung yang terhasil pada panel yang direndam dalam larutan 3% sodium klorida, peta upaya SKP menunjukkan gelembung yang terbentuk adalah di kawasan katod yang disebabkan oleh alkali, di mana kawasan anod juga dilihat terbentuk berdekatan. Walhal bagi peta upaya SKP untuk gelembung yang terhasil pada panel yang direndam di dalam larutan 3% ammonium klorida menunjukkan kehadiran kawasan katod dikelilingi oleh kawasan anod.

Kata kunci: Cat organik; imbasan probe Kelvin; gelembung

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1.0 INTRODUCTION

One of the main significant advances of using SKP in coating studies is to better understand corrosion mechanisms under paint as well as the capability to produce maps illustrating potential and current distribution at a defect area. The mechanisms of the delamination process of organic coatings on steel have been investigated using local electrochemical and physical techniques. Stratmann *et al.* [1-11] employed a scanning Kelvin probe to measure potential distributions at a buried coating/substrate interface. Their studies were done under accelerated corrosive conditions and minimal surface treatments, therefore the prediction of delamination rate measured was far bigger than the value from commercial technical samples [12].

Reddy, Doherty and Sykes [13] have studied the mechanism of corrosion on a steel panel with a circular scribe defect painted with pigmented coating. They used SKP to examine the corrosion propagation at the defect and its periphery and discovered a reversal of anodes and cathodes at the scribe, beneath the coating. They have suggested that the reversal is due to the accumulation of the corrosion product at the defect. Potential mapping of electrochemical behaviour underneath the coating can lead to better understanding of the mechanism involved in coating breakdown.

1.1 SKP Principle

Scanning Kelvin probe (SKP) is a technique allowing a non-contact measurement of the surface of a metal giving values of corrosion potentials that can be calibrated to a standard scale [14]. The SKP uses a scanning vibrating gold tip as a quasi-reference electrode that enables it to map electrochemical potentials, even beneath a coating, thus allowing potential measurements of corrosion processes occurring in blisters and delaminated areas as well as at defects. SKP allows an image to be constructed that shows the potential distribution on the sample and identifies anodic and cathodic regions at defects and beneath the organic coating.

This technique is very useful in corrosion studies around defects as a function of time as it produces results that can be related to the mechanistic description of the process [15]. The scanning Kelvin probe is a vibrating capacitor device used to measure the work function difference between a conducting specimen and a vibrating tip. If an external electrical contact is made between the specimen and the probe, their Fermi levels equalize and the resulting flow of charge produces a potential gradient between the plates, which is equal to the difference in the electronic work function. A variable 'backing potential' applied to the circuit is recorded at the unique point where the (average) electric field between the plates vanishes, resulting in a null output signal. For corrosion studies, the scanning Kelvin probe gives the potential of the specimen at that point that can then be calibrated to a standard scale.

2.0 EXPERIMENTAL DETAILS

2.1 Exposure Test

In this work, a commercial polyamide cured epoxy; PCE coating with 75 μm thickness was tested. Coatings were applied to grit-blasted mild steel by air spraying. The edges were protected with a thick high-performance epoxy coating. Each sample was immersed either in 3% NaCl or 3% NH_4Cl solution at room temperature. Once the blister appear the sample was taken out to be measured using the scanning Kelvin probe.

2.2 SKP Technique

The KP Technology SKP system is shown in Figure 1. The SKP was operated using a circular silver tip with a 500 μm flat end. Typically, the probe was set to vibrate at frequency of 60 Hz with amplitude of 32 μm and a gradient of 300, which gave a tip-sample separation of 64 μm at closest approach. Measurements were taken using a sample backing voltage, V_b, in the range of $\pm$ 5000 mV. This instrument uses a non-null technique that calculates the null point from the AC current at two bias values. This also allows automatic height control. For an area scan, the tip starts back left and then moves in a meander pattern, whereas for a line scan the tip start back left and moves in a line until the scan is complete. The SKP data was plotted using Origin 7.0. The area maps are based on 625 measurements and are presented in terms of relative potentials (arbitrary scale).

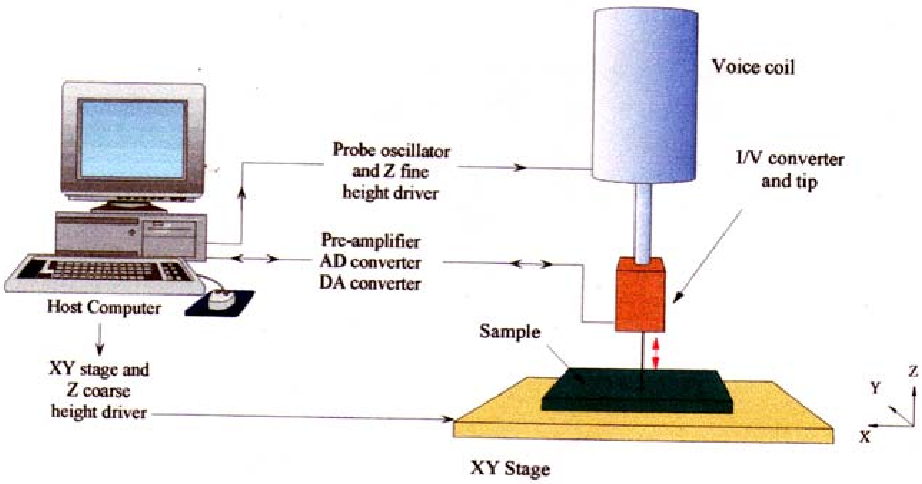

Figure 1 Schematic SKP System (After KP Technology Ltd.)

3. 0 RESULTS AND DISCUSSION

3.1 Immersion in 3% NaCl solution

3.1.1 SKP Area Scan

Figure 2a is a coated panel with blisters after 21 days exposure in 3% NaCl solution. Cathodic reduction of oxygen in a solution containing Na^+ will generate an alkaline environment therefore cathodic blistering would be expected to occur preferentially.

A SKP potential map is presented in Figure 2b for the area marked with the dashed blue box. It can be seen that the blue patch in the centre has the most positive potential and this is believed to be the blister area. In addition, orange and green areas denote the presence of anodic regions surrounding it. This result shows that the blister has formed at a cathode due to alkali but anodes form nearby (not remote). However, the area underneath the blister revealed shining bare metal without the presence of any corrosion product due to passivation in alkali as shown in Figure 3.

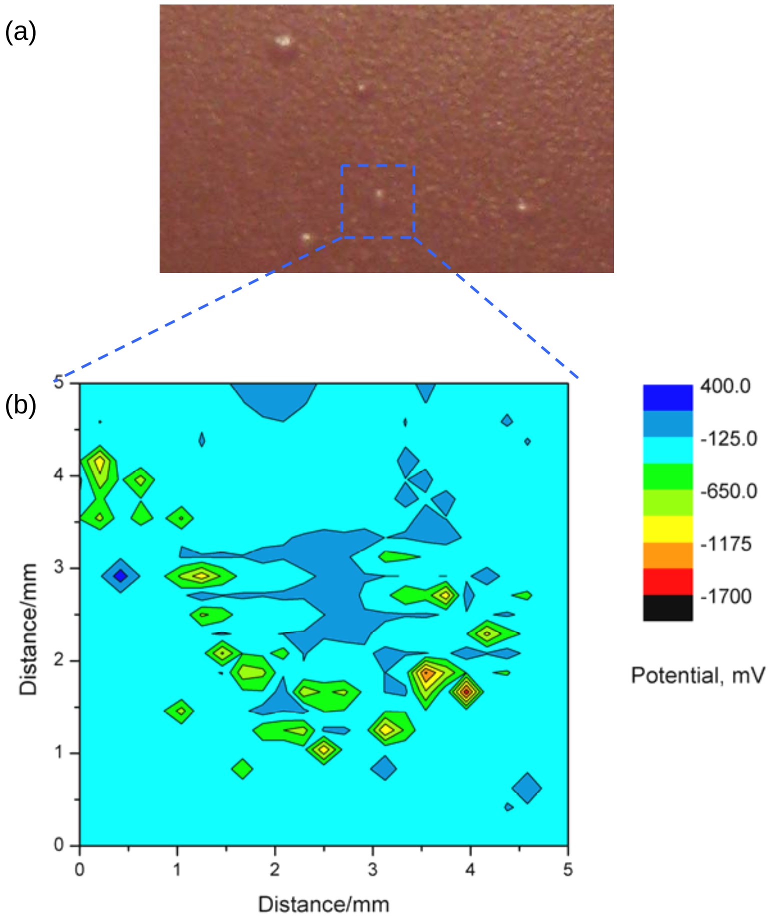

Figure 2 Blister feature and surrounding area imaged with (a) optical microscopy, (b) SKP relative potential map for PCE coating after 21 days of exposure to NaCl solution (sample area is 5mm × 5mm)

Figure 3 Image of area underneath a blister on a PCE coating exposed to NaCl solution (size 5 mm × 5 mm)

Figure 4 shows the proposed schematic representations of coated metal exposed to NaCl solution. Sodium cations migrate through the coating at cathodic areas. They carry ionic current and combine with OH^- causing NaOH to accumulate at the metal surface. The result is strongly alkaline within the cathodic area. As osmotic forces drive water through the coating to the alkaline solution, the coating is deformed upward which then generates a blister.

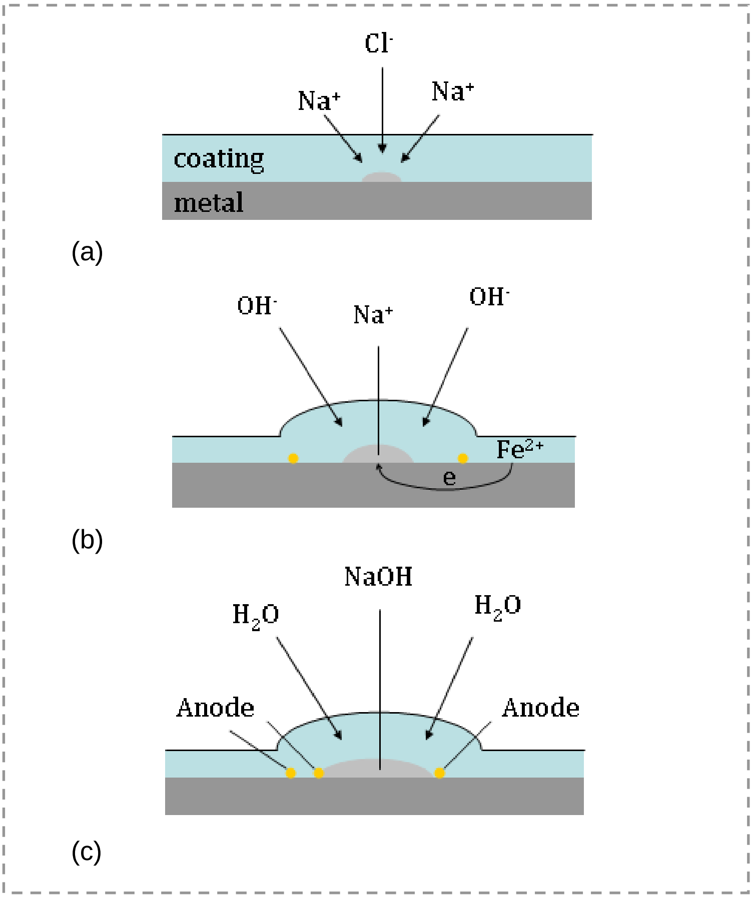

Figure 4 Schematic representations of coated metal exposed to NaCl solution (a) initially, (b) formation of alkali region and (c) blistering due to osmosis

3.1.2 SKP Line Scan

The same blister area was further investigated by using a SKP line scan. The scan was conducted based on the diagram in Figure 5. Six lines labelled A to F were scanned over the blister area with line E at the centre of the blister. The explanation given here is focusing on the area where there is an increase in blister height from the metal surface. Figure 6 shows the coating profile corresponding to the measured potentials. Notice that Linescan-E has the maximum height which confirms its position as the centre of the blister. As the line moves away from the blister centre, the height of the blister is greatly reduced. This indicates that the detachment of the coating from metal surface is lower at the edge of the blister.

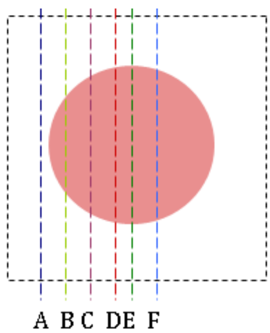

Figure 5 Position of line scan using SKP over a blister on coated panel immersed in NaCl solution (line scan length is 5 mm)

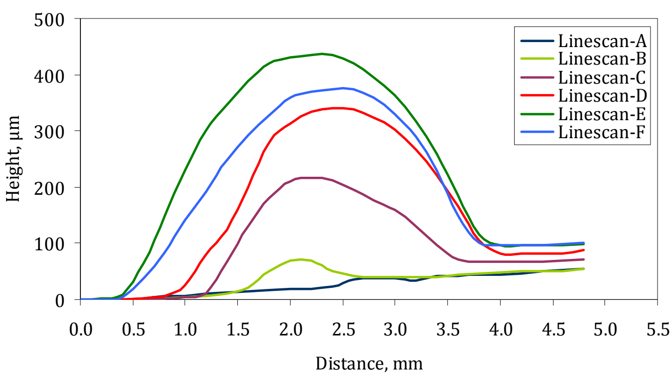

Figure 6 Blister heights according to its respective position of PCE coating exposed to NaCl solution

Figure 7 shows the potential measured for Linescan D, E and F. It can be seen that all of them show the cathodic region lying in a similar position where the blister height is at its greatest. Anodic regions were observed at specific areas surrounding the blister.

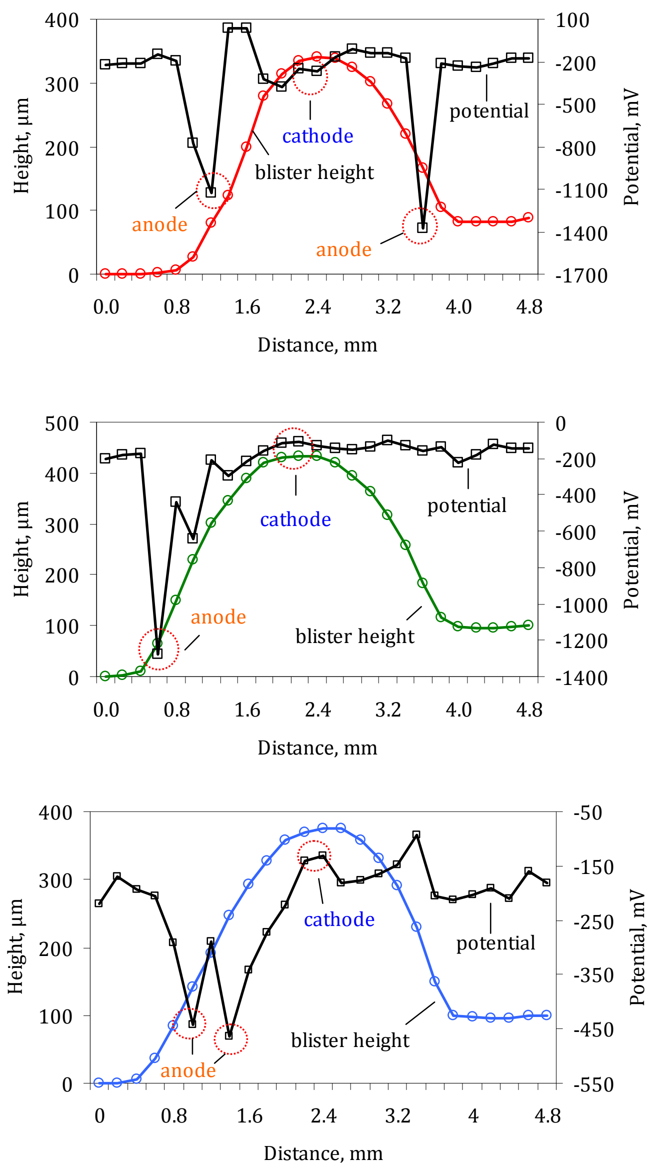

Figure 7 Blister heights and potentials measured for PCE coating exposed to NaCl solution (a) Linescan-D, (b) Linescan-E and (c) Linescan-F

3.2 Immersion In 3% NH_4Cl Solution

3.2.1 SKP Area Scan

Figure 8a is a coated panel with blisters after 13 days exposure in NH_4Cl solution. A SKP scan was conducted on the selected area as mapped out by the blue dashed box drawn on the coated panel.

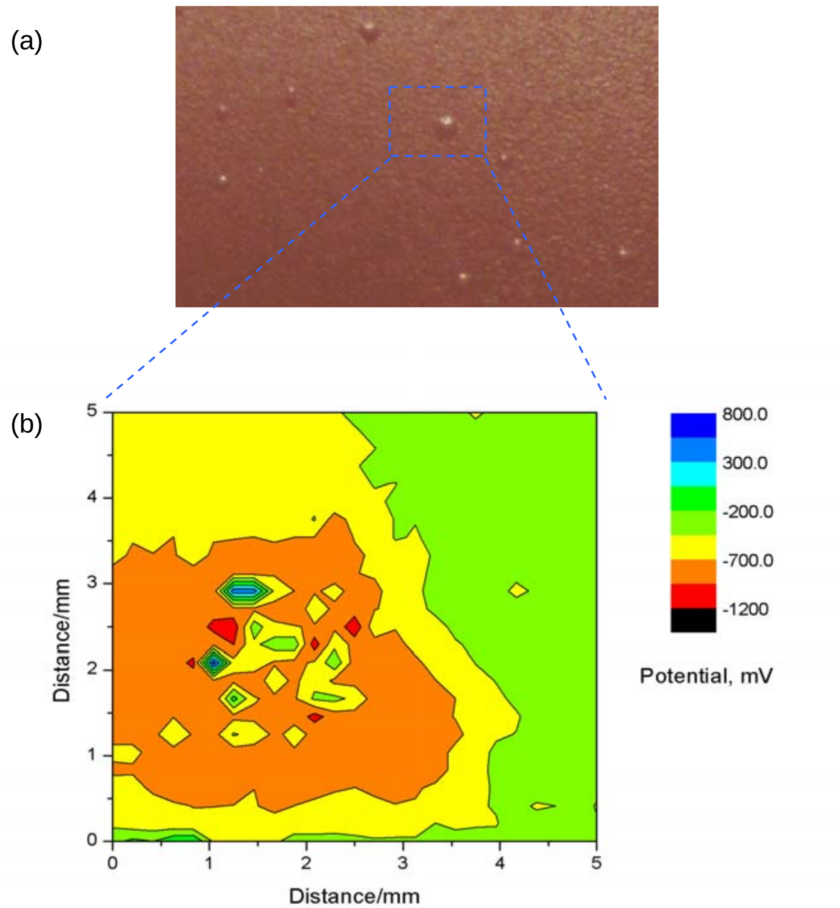

Figure 8 Blister feature and surrounding area imaged with (a) optical microscopy, (b) SKP relative potential map for PCE coating after 13 days of exposure to NH_4Cl solution (sample area is 5 mm × 5 mm)

Figure 8b shows an SKP potential map for the metal underneath the blister. The lowest (most negative) potential corresponds to areas of anodic activity (red colour). The highest (more positive) potential represents cathodic activity (blue colour). Notice the presence of orange patches in the image and small bits of red area which have the most negative potential and these correspond to the blister area. It is interesting to observe the colour changes of the area surrounding the blister. The colour changes from green towards yellow and orange which corresponds to a more negative potential as it moves towards the blister area. Notice the appearance of blue and green patches which indicate the presence of cathodic activity within the anodic region.

There is a possibility that this cathodic region may start as anodes initially. In the previous studies by Sykes and Doherty [13, 16], where a defect on a thin lacquer coating on electro-chrome coated steel was examined, they observed a gradual change from an anode region to a cathode region. They attributed this shift to the corrosion products formed in the defects becoming the cathode reactant.

Figure 9 shows the proposed schematic representations of coated metal exposed to NH_4Cl solution. Initially anodic attack on the metal produces Fe^{2+} which then combines with the chloride anion to form $FeCl_2$. As water starts coming in, $FeCl_2$ is diluted and Fe^{2+} combines with water to form iron hydroxide which is then oxidized by oxygen to rust (FeOOH). Rust becomes established on the metal surface and becomes the cathodic reactant. New anodes then develop within the blister and brown rust is gradually reduced to black magnetite. This result is confirmed when the area underneath the blister was revealed at the end of the test; it was corroded with corrosion products suggesting anodic detachment (Figure 10). Notice the presence of brown rust on top of the green rust.

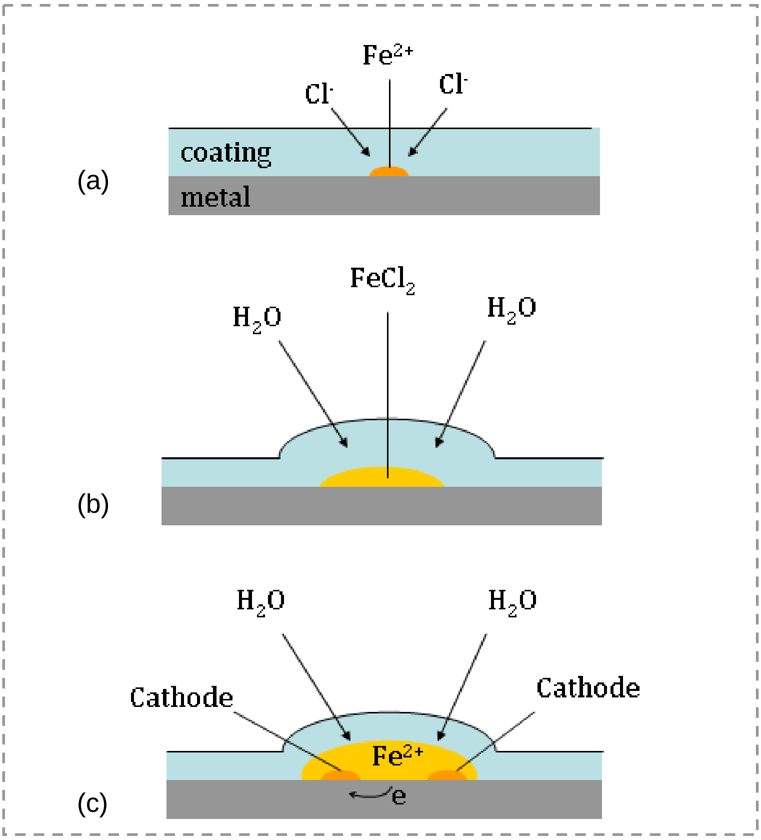

Figure 9 Schematic representations of coated metal exposed to NH_4Cl solution (a) initially, (b) corrosion initiation and (c) after blistering

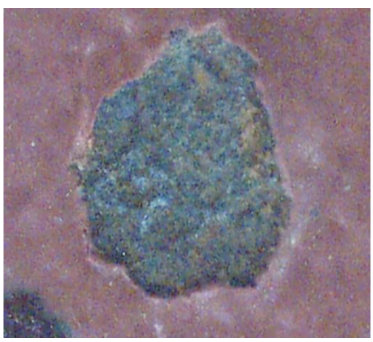

Figure 10 Corrosion products underneath the blister of PCE coating exposed to NH_4Cl solution (size 5 mm × 5 mm)

3.2.2 SKP Line Scan

The same blister area was further investigated using a SKP line scan which could provide a profile of the coating height corresponding to the potential measured on the metal surface. The scan was conducted based on the diagram in Figure 11. Five lines labelled 1 to 5 were scanned over the blister area with line 3 at the centre of the blister.

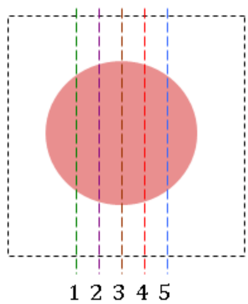

Figure 11 Schematic of the linescan position over a blister area on coated panel immersed in NH_4Cl solution (linescan length is 5 mm)

Figure 12 shows the coating height from the substrate area and corresponds to the measured potential value according to the respective line scan position. It was observed that Linescan-3 has the greatest height which confirms its position as the centre of the blister. The explanation given here is applies to the area where there is an increase in blister height from the metal surface. The potential and the measured blister height of Linescan-3 are presented in Figure 13. It can be seen that when the blister height is at its greatest, the potential is at the most negative which denotes anodic activity. Notice however the presence of a more positive cathodic region which suggests that the anode and cathode appear side by side within the blister area.

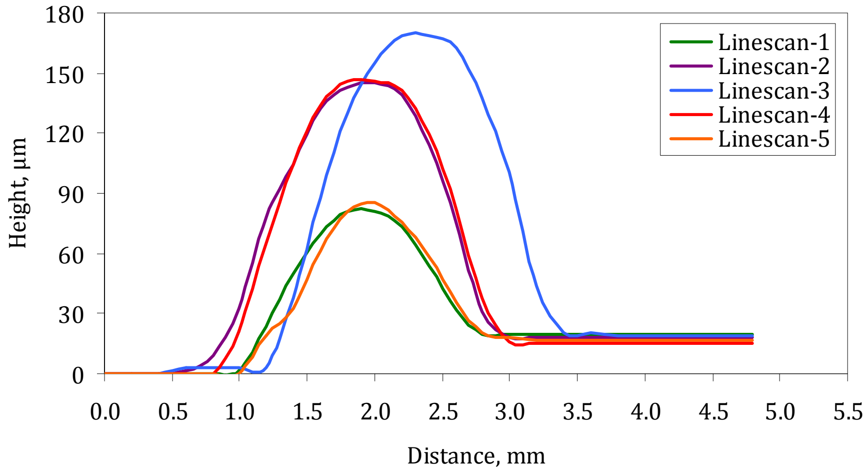

Figure 12 Blister heights according to its respective line scan position for PCE coating exposed to NH_4Cl solution

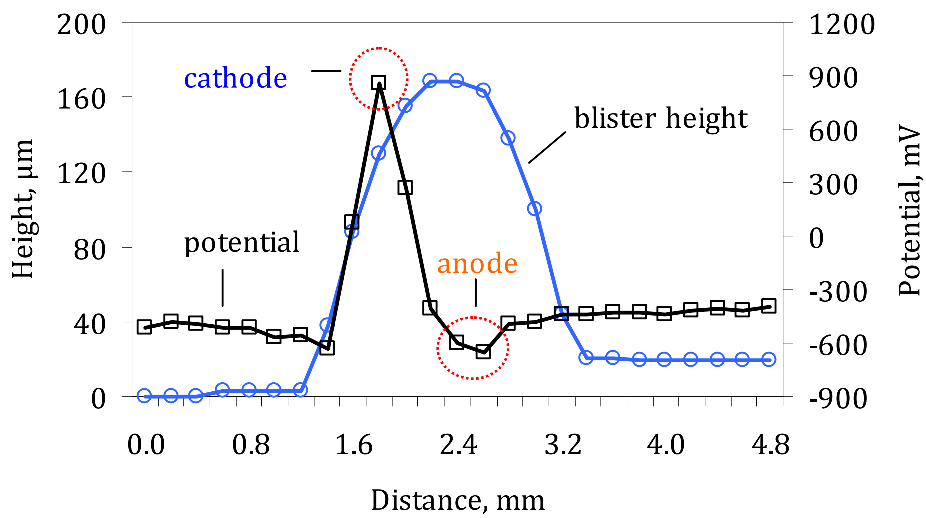

Figure 13 Blister heights and its potential for Linescan-3 of PCE coating exposed to NH_4Cl solution

According to Funke [17], the areas underneath a blister with plugged pores are anodic, with cathodic edges due to differential aeration. Similar results were observed from Linescan-2 and Linescan-4 as presented in Figure 14. Notice the anode and cathode areas appear within the same blister region which demonstrated the existence of anodic and cathodic areas on iron corroding as shown previously in the SKP area scan.

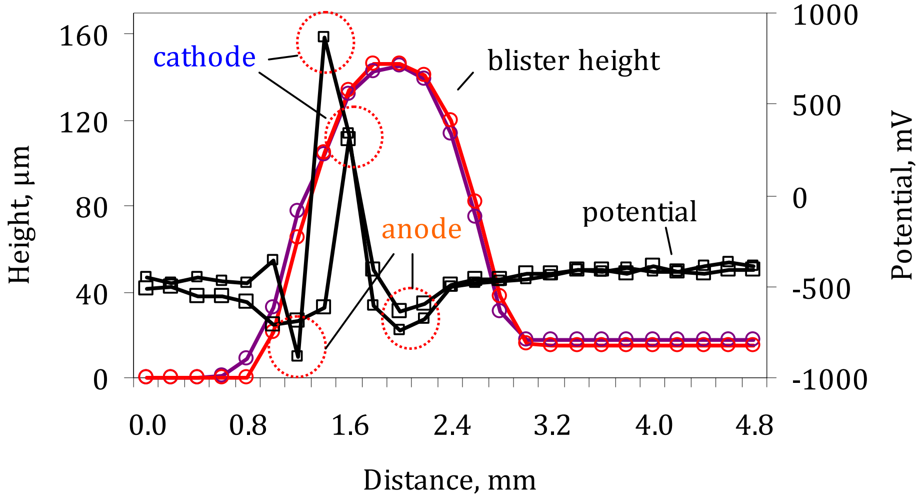

Figure 14 Blister heights and its potential for Linescan-2 and Linescan-4 of PCE coating exposed to NH_4Cl solution

4. 0 CONCLUSIONS

For polyamide cured epoxy coating on mild steel the following conclusions can be drawn from the results of this work:

(1) For blisters formed on coated panel immersed in NaCl solution, SKP potential map reveals that the blister has formed at a cathode due to alkali but anodes form nearby (not remote). This is supported by line scans which show the presence of an anode at the edge of the blister. It is possible, given that the metal underneath the blister is still bright; that the blister has began to overlap anodes formed around the edge of the blister.

(2) For immersion in NH_4Cl solution, SKP potential map on a blister forming on a coated panel reveals the presence of cathodic regions within the anodic areas. It is suggested that there is a possibility that this cathodic region may start as an anode initially, but corrosion products become the cathode reactants.

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