

The effects of zinc ions on the performance of epoxy coated mild steel under cathodic protection (CP)

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ABSTRACT

This work aimed to address the issues that arise when cathodic protection is applied to a coated structure. The use of zinc chloride (ZnCl_2) as a corrosion inhibitor was suggested; the idea was to bridge the weakly cross linked areas on the coating by depositing a film of zinc compounds in order to seal them from the corrosive environment.

It was shown that the addition of 300 ppm ZnCl_2 to 0.6 M KCl has an impact on the performance of the coating under the two different levels of potential that were used (-0.78 V and -1.1 V SCE) by maintaining the resistance of the coating above the border line between fair and poor coating for a period of 35 days; this was attributed to the deposition of zinc oxide (ZnO) at the base of the weakly cross linked areas.

EDAX examination has confirmed the presence of zinc ions on the metal surface after immersion; this result was supported by the detection of ZnO using XRD technique.

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1. Introduction

One of the problems face the pipeline industry is that most external corrosion of pipe lines is caused by disbonded coatings which shield CP, not lack of CP, because CP is effective when there is a route to the pipe structure. Therefore, without understanding the relationship between CP and coatings, external corrosion problems cannot be resolved.

It is widely accepted that the application of cathodic protection to a bare structure requires large amount of cathodic protection current which is very expensive. At the same time coating on its own cannot provide full protection as it usually contain pin holes, pores, and defects resulted from the application process, transportation, mechanical damages, and exposure to UV, etc. [1]. The defected areas may introduce direct pathways for different corrosion species to reach the metal surface resulting in localised loss of coating barrier properties. The corrosion of exposed areas on the coating film can be prevented by applying cathodic protection. Based on this argument the combination of organic coatings and cathodic protection is considered to be the best option to protect steel structures. However, many coatings have been observed to separate from the metal surface as a result of the formation of

alkaline environment at the metal coating interface. Consequently, further reduction in the coating barrier properties will take place [2].

In the first two papers in this series [3,4], it was demonstrated that, the application of negative potential has affected the protective properties of the epoxy coating in three different solutions namely 0.6 M KCl, NaCl, and CaCl_2 due to enhanced water and ion penetration. Coated specimens immersed in CaCl_2 had shown the best protective properties due to the slow movement of Ca^{2+} , and its inability to form alkaline solution at the metal coating interface. It was also demonstrated that epoxy coated specimens immersed in KCl solution has shown the least protective properties with coating resistance fell below $1 \times 10^5 \Omega \text{cm}^2$ within 15 days of immersion. The deterioration of the coating was attributed to the fast movement of potassium cations under the influence of the negative potential. The use of EDAX had confirmed the presence of dense areas of potassium ions on the metal surface, whereas on the surface of specimens which were immersed in NaCl solution, sodium ions were detected. When CaCl_2 was used no calcium ions were detected on the metal surface. Based on this, it was considered important to investigate the deterioration of the coating in KCl solution further by adding ZnCl_2 as a corrosion inhibitor and this is the main aim of this paper in the series.

ZnO is a well known protective corrosion product which behaves as a good barrier to corrosion [5,6]. It is also well known that the high corrosion resistance of zinc in atmospheric and

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other environments gives rise to its extensive use in the corrosion protection of steel. Almost half of all zinc produced is used in corrosion protection [6]. This study will look at the impact of the addition of $ZnCl_2$ on the performance of epoxy coated mild steel under two different levels of cathodic protection.

2. Experimental procedure

2.1. Materials and sample preparation

The samples used were cold rolled mild steel panels measuring $15\text{ cm} \times 10\text{ cm} \times 0.12\text{ cm}$ and supplied by Q Panel Company. The epoxy coating used was manufactured by HMG Paints Ltd., Manchester, and supplied in two parts a clear epoxy top resin and a hardener. The epoxy top coat contains bis-phenol and epichlorohydrine (xylene mix), the hardener was an amine based 3,6-diaz octane thylene diamine, xylene mix.

The coating was mixed according to the manufacture's specification of one part hardener to three parts epoxy top coat by weight and stirred thoroughly to ensure complete homogeneity of the paint. It was then thinned with a manufacturer recommended thinner. Coating was then stirred thoroughly by a mixer between 5 and 10 min to ensure complete mixing of the thinner and the coating. The epoxy coating mixture was then allowed to stand in a dust free room to remove any air bubbles that might be present.

Prior to the application of epoxy coating mixture, the test panels were washed with detergent in hot water and rinsed with deionised water followed by degreasing in acetone solution. Samples were then dried and stored in a desiccator containing silica gel. Epoxy coating mixture was applied to the mild steel panels using a spray technique with compressed air. After the coating process, coated panels were kept in a dust free room for 3 h at ambient temperature to dry. Samples were then transferred to an oven at 65°C for a period of 24 h to cure.

The coating thickness was measured using an Elcometer 256 instrument. Coating thickness of $50 \pm 10\ \mu\text{m}$ was measured and used for all experiments. Coated samples were then waxed using a heated mixture of Beeswax and a colophony resin supplied by BDH Ltd. in the proportion of three parts to one part respectively. The reason for using the beeswax was to cover the uncoated parts of the samples and the edges in order to avoid any interference with the EIS measurements. The wax was applied to cover the uncoated side of the samples as well as the edges using a brush. Waxed areas were checked thoroughly using a magnifier to make sure that there were no defects.

2.2. Electrochemical Impedance Spectroscopy (EIS) and UTHSCSA Image Tool software

A three electrode cell was used, the three electrodes being the coated specimen as working electrode, saturated calomel reference electrode, and a platinum counter electrode. 0.6 M KCl solution was prepared before 300 ppm $ZnCl_2$ added. The solution was then stirred thoroughly and the specimens were immersed in the solution. Impedance measurements were made using ACM (GILL AC) version 5 consisting of potentiostat and a frequency response analyser build up into the machine. Measurements were carried out on a set of three different replicate specimens. The following is the parameters which were used to run the EIS (Table 1).

Table 1
Parameters used to run the EIS.

Frequency	10 kHz–0.1 Hz
Amplitude	20 mV
Exposed area	25 cm^2

Experiments were conducted at room temperature which was approximately $(23 \pm 1^\circ\text{C})$ for a period of 35 days. Cathodic protection was applied at -0.78 V , and -1.1 V vs. SCE between days 3 and 35 of immersion, the reason for applying it at this time was to simulate a real situation where cathodic protection is applied to a coated structure at a later stage. The impedance spectra were analysed using a suitable fitting procedure to the Nyquist plot. Z view was also employed to confirm the fitting of the impedance data by transferring the impedance data from the ACM machine to Z view.

The specimen's surfaces were visually monitored by looking at them at different immersion times. UTHSCSA Image Tool software was employed to numerically estimate the percentage of corroded areas on the coated samples after immersion. Pictures were taken for the coated specimens using a digital camera before being transferred to the software. The software displayed the corroded areas as dark areas and the intact coating film which suffered no corrosion as white areas.

2.3. EDAX examination

After the immersion period, the coated specimens were washed thoroughly with deionised water in order to remove any salts that may be present on the upper side of the coating film. Small samples ($3 \times 3\text{ cm}$) were cut out of the large coated samples before layer of gold was sputtered on the top of the coating film. Samples were then glued to an aluminium stub using carbon tape. The coated specimens were examined using EVO 60 machine which is manufactured by Oxford instruments analytical company. The coating film was also peeled off of the surface manually and the metal surface was examined using the same machine, the reason for that was to find any trace of zinc that may be present on the metal surface.

2.4. XRD examination

The coated specimens were guillotined into small shapes; they were then washed thoroughly with deionised water and dried before being examined by Philips xpert machine which is manufactured by Philips analytical X-ray.

3. Results and discussion

3.1. Specimens tested under CP -0.78 V (SCE)

After running the impedance for 35 days, the coating resistance values were extracted from the impedance Nyquist plots using a suitable fitting procedure as mentioned in Section 2.2, the extracted data was then plotted in Fig. 1. As can be seen, the coating resistance for specimens that were immersed in 0.6 M KCl solution under CP (-0.78 V) was in the order of $10^9\ \Omega\text{ cm}^2$ in the first 6 days of

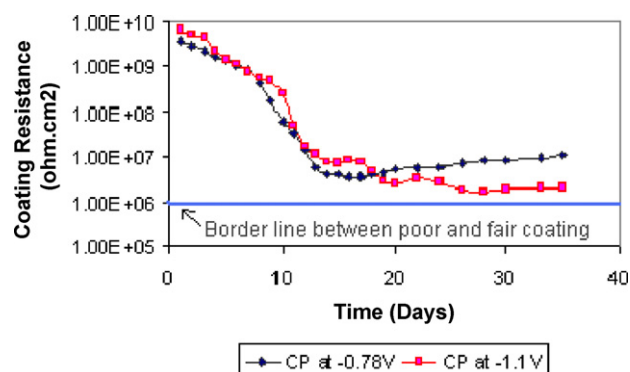


Fig. 1. Time dependence of coating resistance for specimens immersed in 0.6 M KCl with the addition of 300 ppm $ZnCl_2$ under CP (-0.78 V and -1.1 V).

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