

Impedance Measurements of Polyester-Coated Galvanised Mild Steel in 10xAcid Rainwater After an Accelerated Wet-Dry Test

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The variation of defective polyester-coated performance with time in 10xacid rain solution was investigated using electrochemical impedance spectroscopy. Measurements were carried out on samples after an accelerated atmospheric corrosion test. The impedance diagrams (Nyquist plots) were simulated using the EQUIVCRT program which was elaborated by Boukamp and the semi-ellipse model which was developed by Erbil. It has been shown that the defective coating resistance changes with time for the samples subjected to acid rainwater. The corrosion rate of coated metal also changes with time.

Key Words: EIS, coating, defect, corrosion, equivalent circuit, accelerated test.

Introduction

Paints, and in the last decade, plastic coatings, are the most widely used methods of protection against atmospheric corrosion of metals. The paint film is a barrier against aggressive species such as some ions, water and oxygen. However, all paints are more or less permeable to these species and their presence at the metal/coating interface. The resistance of coatings decreases by corrosion or delamination. The evolution of hydrogen or oxygen at the metal /coating interface is very dangerous for blistering. An important question which allows a better understanding of the performance of a coating is the study of the behaviour of painted metals after the imposition of some complex combination of stresses. The prediction of the corrosion resistance of stressed painted galvanised steel coils is relevant in the assessment of the quality of such materials frequently used in industrial applications.

Electrochemical impedance spectroscopy (EIS) has proven to be a valuable test method for the electrochemical characterisation of the protective organic coating on metals¹⁻⁹. The system, which consists of a metal covered by an organic film, is generally quite complex and it may consider a large number of different situations. From the complex situation previously described about organic coatings and metal, it clearly emerges that such electrical equivalent circuits will be different with different materials. One of the first works on the EIS characterisation of organic coatings was published by Mansfeld et al¹⁰., which suggested a general model of an electrical equivalent circuit from which a large number of other models

can be derived. The electrical equivalent circuits for intact and defective organic-coated metals, which are generally reported in the literature, are shown in Fig.1.

This equivalent circuit, in Fig. 1a. is composed of the electrolyte resistance, followed by the coating capacitance (C_{pf}) in parallel with a coating resistance (R_{pf}) and finally an element Z which represents the electrochemical process at the metal/solution interface. In Fig. 1b. C_{pf} is the coating capacitance, R_{pf} the coating resistance, and C_{dl} and R_{ct} are the double - layer capacitance and charge transfer resistance respectively. Recently a new electrical equivalent circuit model has been suggested for defective organic-coated materials¹¹. The term differential capacitance is proposed and a charge transfer resistance (R_{ct}) is redefined in this model in Figure 2.,

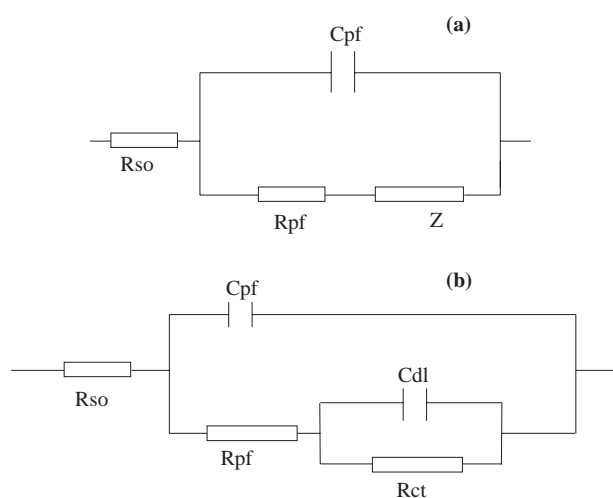


Figure 1. Electrical equivalent circuit for (a) intact (b) defective organic-coated metals as generally reported in the literature^{1,2,5}.

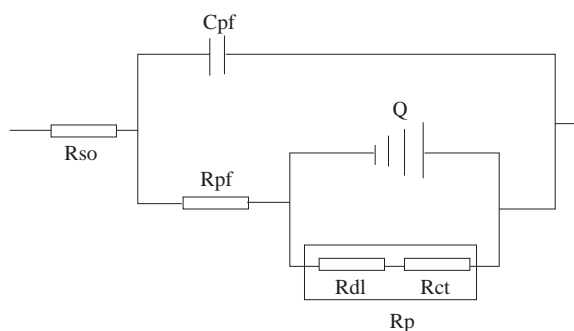


Figure 2. The envisaged electrical equivalent circuit model for defective organic-coated metals in literature¹¹.

where polarisation resistance R_p , is used instead of R_{ct} in Figure 1b. It has been reported that R_p should contain charge transfer resistance (R_{ct}) and diffuse layer resistance (R_{dl}) in serial. The corroded metals represent a general behaviour where the double layer on the interface of the metal/electrolyte does not behave as a real condenser. On the metal side of the double layer, electrons control the charge distribution, whereas on the solution side it is controlled by ions. Since the ions are much larger than the electrons, the equivalent ions to the charge on the metal will occupy quite a large volume on the solution side of the double layer. The constant phase element (Q_{dl}) has been defined as differential capacitance by authors. Q_{dl} represents all the frequency-dependent electrochemical phenomena, namely double-layer capacitance and the diffusion process. The polarisation resistance has been divided into diffuse layer resistance (R_{dl}) and charge transfer resistance (R_{ct}).

The aim of this work was to determine the protective performance of polyester coating against 10xacid rainwater after defect formation by accelerated atmospheric corrosion tests.

Experimental

The corrosion tests were performed on 20 μm hot deep galvanised steel, chromate epoxy primer and 20 μm polyester top coat. The samples were exposed to 10 times artificial acid rain (pH 3.5) in a wet/dry test chamber. Artificial acid rain solution has been reported recently¹². The test conditions were 30 minutes wet, 2.5 hours dry. The acid rain solution temperature was 25 °C and drying cycle was 35 °C. After 26 days the samples were taken out of the chamber for electrochemical impedance measurement. A 3.08 cm² PVC tube was placed on the sample. The 10 times artificial acidrain solution filled into the tube.

All measurements were carried out at ambient temperature. The temperature was 20 ± 2 °C for 50 days. Impedance data were obtained 1, 10, 30 and 50 days after applying the solution, at the corrosion potential in the 10 kHz-10 mHz frequency range using a Solartron Schlumberger 1250 Frequency Response Analyser connected to ACM potentiostat. The amplitude of sinusoidal voltage was 10 mV. Potentials were measured versus saturated calomel electrode. All the impedance measurements were carried out with a two-electrode system. Platinum wire was used as the counter electrode. The experimental impedance spectra were interpreted on the basis of equivalent electrical circuits using fitting software (EQUIVCRT) elaborated by Boukamp¹³ and the semi-ellipse model described by Erbil^{14,15}.

Results and Discussion

The simulated Nyquist plots of polyester-coated galvanised mild steel after defect formation on the sample via accelerated atmospheric wet/dry test are given in Fig. 3 for the 1st day, in Fig. 4 after 10 days, in Fig. 5 after 30 days and in Fig. 6 after 50 days.

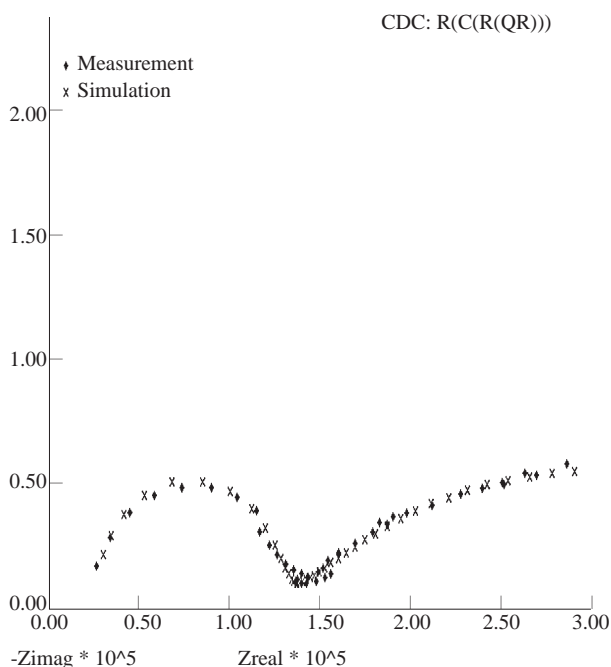


Figure 3. Simulated Nyquist plot for polyester-coated galvanised mild steel in 10xacid rain solution 1 day after being exposed to the solution.

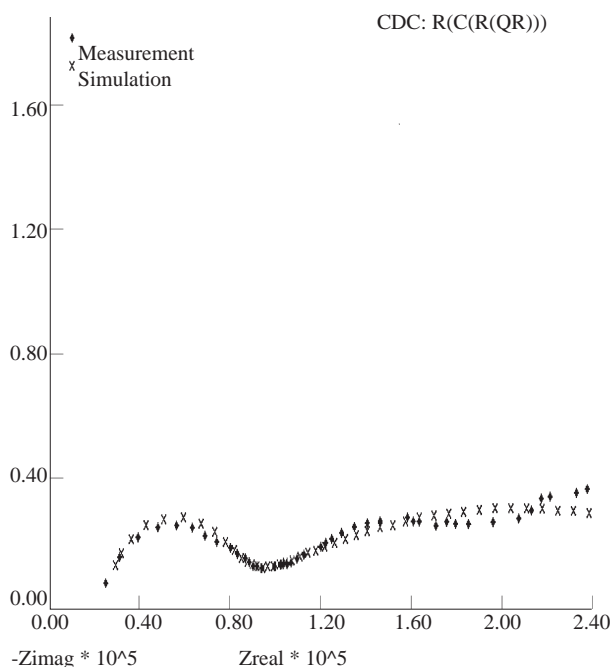


Figure 4. Simulated Nyquist plot for polyester-coated galvanised mild steel in 10xacid rain solution 10 days after being exposed to the solution.

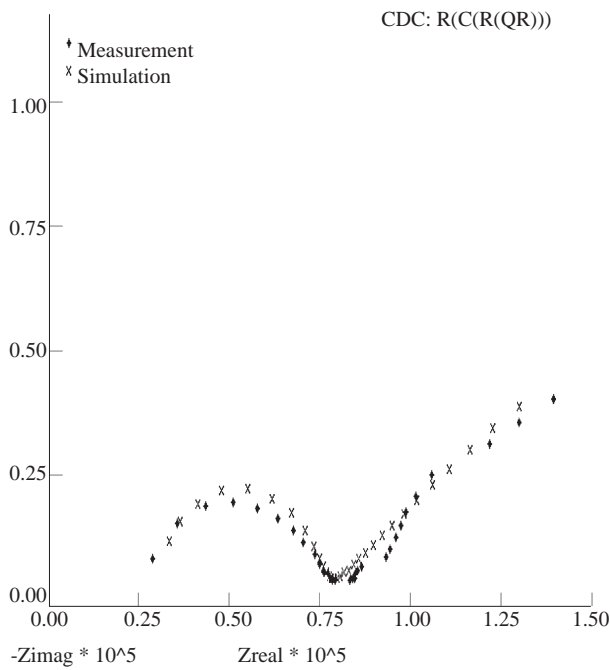


Figure 5. Simulated Nyquist plot for polyester-coated galvanised mild steel in 10xacid rain solution 30 days after being exposed to the solution.

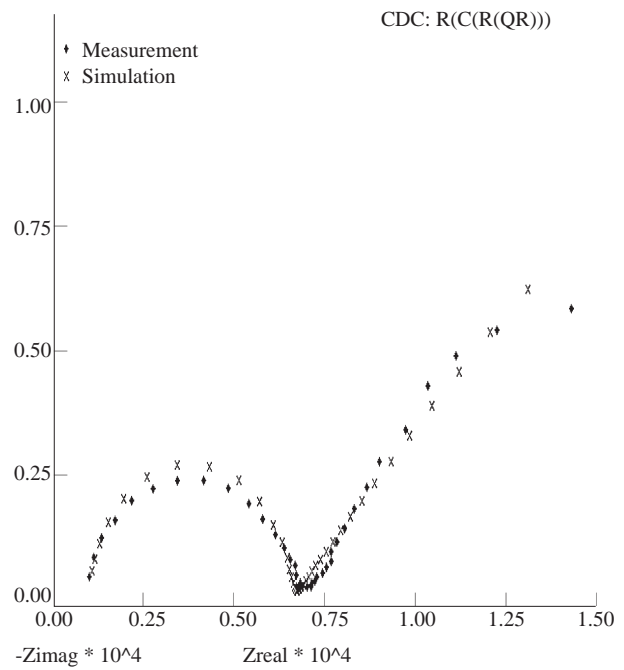


Figure 6. Simulated Nyquist plot for polyester-coated galvanised mild steel in 10xacid rain solution 50 days after being exposed to the solution.

The equivalent electrical circuit, which is proposed for the defected organically coated metal specimens tested in the present study, is shown in Fig. 1b. This electrical equivalent circuit, with appropriate values for each circuit element, gives good simulations of the experimental data by using EQUIVCRT program where the constant phase element Qdl is used instead of Cdl. The equivalent circuit with two time constants, shown in Fig. 1b, appears to be the most suitable simulation for all time measurements. Rpf, Rct, Qdl and Ecor values obtained by the EQUIVCRT program are given in Table 1.

Table 1. The variation of equivalent circuit elements values as a function of time obtained by the EQUIVCRT program for defective polyester-coated galvanised mild steel in 10 times artificial acid rain solution.

Time (days)	Ecor (V)	Rpf (ohm)	Cpf (F)	Rct (ohm)	Qdl (F)
1	-0.870	$1.02 \cdot 10^5$	$7.50 \cdot 10^{-10}$	$3.45 \cdot 10^5$	$6.88 \cdot 10^{-6}$
10	-0.908	$4.77 \cdot 10^4$	$1.24 \cdot 10^{-9}$	$2.69 \cdot 10^5$	$5.75 \cdot 10^{-6}$
30	-0.950	$4.54 \cdot 10^4$	$1.27 \cdot 10^{-9}$	$1.21 \cdot 10^5$	$9.66 \cdot 10^{-5}$
50	-0,982	$5.58 \cdot 10^3$	$2.30 \cdot 10^{-8}$	$9.70 \cdot 10^4$	$3.10 \cdot 10^{-4}$

The Rpf values were $1.02 \cdot 10^5$ ohms on the first day, and $4.77 \cdot 10^4$ ohms, $4.54 \cdot 10^4$ ohms and $5.58 \cdot 10^3$ ohms on the 10th, 30th and 50th days respectively. The Cpf values increased with time (Table 1). These results indicate that the coating protective performance changes with time. Rpf values on the first and fifth days clearly show that the coating lost about 18% resistance in 50 days. Ecor values decreased with time. This means that the corrosion process continues without corrosion products. Coating permeability increases with time and corrosion products, which decrease the corrosion rate, do not form on the metal surface. According

to the semi-ellipse model, the R_{ct} which is obtained by the EQUIVCRT program is not the charge transfer resistance but the polarisation resistance. The polarisation resistance includes charge transfer resistance and diffuses layer resistance (Figure 2). R_{pf} , C_{pf} , R_{ct} , double-layer differential capacitance (Q_{dl}) and E_{cor} values are given in Table 2.

Table 2. The variation of equivalent circuit elements values as a function of time obtained by the semi-ellipse model for defective polyester-coated galvanised mild steel in 10 times artificial acid rain solution.

Time (day)	E_{cor} (V)	R_{pf} (ohm)	C_{pf} (F)	R_p (ohm)	R_{dl} (ohm)	R_{ct} (ohm)	Q_{dl} (F)
1	-0.870	$1.20 \cdot 10^5$	$7.50 \cdot 10^{-10}$	$2.10 \cdot 10^5$	$1.88 \cdot 10^5$	$2.20 \cdot 10^4$	$6.88 \cdot 10^{-6}$
10	-0.908	$7.12 \cdot 10^4$	$1.24 \cdot 10^{-9}$	$1.13 \cdot 10^5$	$1.03 \cdot 10^5$	$9.75 \cdot 10^3$	$5.75 \cdot 10^{-6}$
30	-0.950	$5.73 \cdot 10^4$	$1.27 \cdot 10^{-9}$	$8.24 \cdot 10^4$	$6.34 \cdot 10^4$	$1.90 \cdot 10^4$	$9.66 \cdot 10^{-5}$
50	-0.982	$1.53 \cdot 10^3$	$2.30 \cdot 10^{-8}$	$1.15 \cdot 10^4$	$7.73 \cdot 10^3$	$3.77 \cdot 10^3$	$3.10 \cdot 10^{-4}$

The R_{pf} values calculated by the EQUIVCRT program are lower than those calculated by the semi-ellipse model. However, the R_{ct} values obtained from the EQUIVCRT program are higher than the R_p values of the semi-ellipse model, which correspond to R_{ct} in the EQUIVCRT program. In order to decide which model is more accurate, the differences between the models should be compared. According to experimental results the most suitable electrical equivalent circuit in the EQUIVCRT program was determined as $R(C(R(QR)))$. This electrical equivalent circuit shows that first time constants which belong to the coating were assumed to be a real condenser circuit. Thus, the time constant was assumed and interpreted as a semi-circle. In contrast to the EQUIVCRT program, in the semi-ellipse model, defected coating is permeable and not assumed to be a real condenser. In an impedance diagram:

For semi-circle: $r = R_p/2$

For semi-ellipse: $a = R_p/2$ and $b = Z''_{max}$

An evaluation of an impedance diagram based on the semi-ellipse model is illustrated in Figure 7¹⁴.

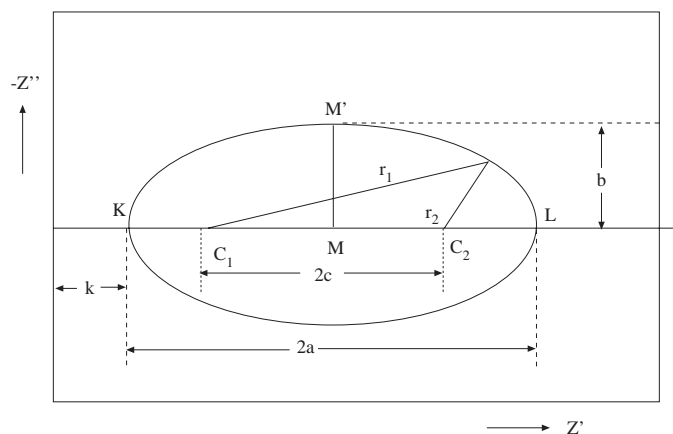


Figure 7. The semi-ellipse model diagram.

In an ellipse $r_1 + r_2 = 2a$ (constant), $KL = 2a$, $MM' = b$, $MC_1 = MC_2 = c$, $a^2 - b^2 = c^2$ and the equation of ellipse as follows:

$$\frac{(Z' - (a + k))^2}{a^2} + \frac{(-Z'')^2}{b^2} = 1$$

R_p , R_{dl} and R_{ct} equations derived from Figure 7 are given as follows^{11,14}:

$$R_{dl} = 2[(R_p/2)^2 - (Z''_{\max})^2]^{1/2} \quad (1)$$

$$R_{ct} = R_p - 2[(R_p/2)^2 - (Z''_{\max})^2]^{1/2} \quad (2)$$

$$R_p = R_{dl} + R_{ct} \quad (3)$$

In a real corrosion system, time constants are like a semi-ellipse rather than a semi-circle¹⁴. Therefore, it can be said that the equivalent circuit element values obtained from the semi-ellipse model are more accurate.

Conclusion

1. The acid rainwater is very effective on the performance of the defective polyester coating resistance and also the corrosion of the metal under the coating.
2. It has been shown that the corrosion process continues without corrosion products accumulating on the metal surface under the coating.
3. The most probable equivalent circuit, with appropriate values for each equivalent circuit element, has been identified for polyester-coated galvanised steel at all time measurements after exposure to a cyclic wet/dry atmospheric corrosion test.

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