Evaluation of zinc-rich epoxy paint performance by electrochemical impedance spectroscopy

Nadia HAMMOUDA[a], H. Chadli [b], G. Guillemot[c], K. Belmokre [a]

[a] Laboratoire de Corrosion et Traitements de Surface, Dép. Sci. De la Matière, Université du 20 août 1955, Route d'El-Hadaiek, B.P.26, Skikda, Algérie.
[b] Laboratoire de Métallurgie et Génie des Matériaux, Université de Badji Mokhtar, B.P 12-Sidi Ammar, Annaba, 23.000-Algérie
[c] Laboratoire de Métallurgie Physique et Génie des Matériaux, école Nationale Supérieure d'Arts et Métiers de Lille, 8, boulevard Louis XIV 59046 Lille Cedex – France.
e-mail: hammoudanad@yahoo.fr

Abstract: To improve understanding of Zn-rich coatings for use in the storage reservoirs of oil, such coatings are being examined in the laboratory by the suite of testing techniques: Open Circuit Potential (OCP) (E_{cor}) measurements , exposure time to verify electrochemical cathodic protection, electrochemical Impedance Spectroscopy (EIS), Optical Microscopy, local SEM and RAMAN for Zn reaction product ID. These testing techniques are being used in conjunction with a modeling and characterization effort focused on improve understanding of the effects of the metal pigment volume concentration (PVC), particle shape and aspect ratio, particle size and size distribution, as well and particle orientation on coating performance.
The single frequency electrochemical impedance spectroscopy (EIS) measurements of impedance as a function of time for Zn-rich primers, or other active systems, gives insights into the evolution of the electrical properties .These primer coatings are usually top-coated to function optimally and have a long field lifetime. When used properly, these primers provide almost as much protection to steel as galvanizing. The coatings system of a Zn-rich primer and an exterior durable topcoat provides both barrier and damage (sacrificial/cathodic) protection to steel substrates.

Keywords: zinc-rich primer, cathodic protection, electrochemical impedance spectroscopy, corrosion mechanisms.

Introduction

The application of zinc-rich primers on ferrous substrates is a very efficient method of anticorrosion protection. They are used in many aggressive media: sea water, marine and industrial environments. It is a common fact that in order to achieve a long-life coating system, a zinc primer needs to be applied as the first coat. For solvent-based zinc-rich paints (ZRPs), it seems to be established that, at least at the beginning of immersion, zinc particles provide a cathodic protection of the steel substrate (Hare, 1998, Abreu, 1996). Then, a long term protection develops due to the formation of zinc corrosion products, reinforcing the barrier effect of the paint (Hare, 1998, Morcillo, 1990, p. 2441).

The metallic zinc content in the dry film is a very important parameter to be emphasized in the technical specifications of zinc-rich paints. However, as observed by Lindquist *et al.*, (Lindquist, 1985) this parameter is not the only factor determining the performance of this kind of paint. For exemple, Fragata (Fragata, 1987) Del Amo (Del Amo, 1990, p. 347) and Pereira (Pereira, 1990, p.1135) verified that the chemical nature of the binder and the zinc particle size are also very important.

The zinc dust (spherical or lamellar shape, or a combination of both) is dispersed in an inorganic (usually orthosilicates) or organic binder (usually epoxies) (Wicks, 1994, p.185). These particles must be in electrical contact between themselves and the metallic substrate in order to ensure a well-established electrical conduction within the coating. In such conditions of percolation, a galvanic coupling is created between zinc and the substrate (steel) which is nobler than the zinc. Then, zinc can preferentially dissolve, acting as a sacrificial pigment, and allowing a cathodic protection of the substrate. Many studies (Feliu, 1989, p.71, Pereira, 1990, p.30, Armas, 1992, p.379, Fragata, 1993, p.103, Feliu, 1993, p.438, Real, 1993, p.2029, Gervasi, 1994, Abreu, 1999, p.1173, Feliu, 2001, p.591, Vilche, 2002, p.1287) exist in literature and relate the protection mechanisms and degradation processes of such coatings.

Physico-chemical properties and corrosion resistance of solvent-based zinc-rich paints ZRPs strongly depend on pigment volume concentration (PVC), shape and size of zinc dust (Vilche, 2002, p.1287, Abreu, 1997, p.23). In common liquid ZRP, zinc is usually introduced as spherical pigments with a mean diameter ranging from 5 to 10 µm. To ensure good electrical contacts between zinc pigments and the steel substrate, a high pigment concentration is required (usually above 60 % by volume in solvent-based zinc-rich paints ZRPs) (Vilche, 2002, p.1287). A major drawback of classic solvent-based paint is the emission of volatile organic compounds (VOC), which contribute to atmospheric pollution. Since the 1970s, powder coatings are often preferred, because they are composed of dry thermosetting powders (without organic solvent) and more environmental abiding.
The aim of this work was to study the protective mechanisms of a single coat solvent-based zinc-rich paints ZRPs. Primer coating panels were applied on sandblasting steel and were studied when immersed in artificial 3% NaCl solution. Open circuit potential and electrochemical impedance spectroscopy measurements were recorded to study changes in the coating properties with the exposure time. The distribution of the zinc particles in the epoxy binder – which controls the porosity – is considered as the main factor affecting the electrolyte penetration within the coating. Moreover, Raman spectroscopy was used to analyze zinc corrosion products. This study reveals that the behavior of solvent-based zinc-rich paints ZRPs is different from powder coating. This is mainly attributed to the high porosity of solvent-based zinc-rich paints ZRPs, due to their low wetting ability, which insulates some of the zinc particles. However, cathodic protection is active and provides the sealing of the coating pores. Finally, it is found that the barrier effect is lower than the one usually observed with powder coating. S.E.M. observations have also been employed to illustrate the non-homogeneity of our paints. The main objective is to propose a model of EIS results accounting for the zinc particles distribution and mechanisms of water entrance within the coating.

Experimental part

Sample material and preparation

The metallic substrate was A283C steel (according to NF10027 standard) in conformity with the norm API (American Petroleum Industry), used in the storage reservoirs of the Algerian crude oil, the chemical composition of the tested steel is given in Table 1 . Before coating application, the metallic substrate was sandblasted to Sa 2.5 (Swedish Standard SIS 05 59 00/67) (roughness Ra 6.2 µm) or polished with emery paper up to G 400. Commercial epoxy-ZRPs were immediately applied onto steel panels using a brush or a roller (Fig. 1). Once cured, the samples were stocked in a desiccator until the moment of testing. The coating thickness was measured using an Elcometer gauge and was found around 80 µm for all panels, the composition of the coating is proprietary information.

Coated panels were cut out (100 cm×60 cm×4 cm) and an electrical wire was added in order to allow electrochemical measurements. With the aim to achieve the electrochemical measures in the best conditions it has been suited that the areas of about 15 cm^2 exposed to the electrolytic solution were sufficient. It seemed necessary to use a surface of paint relatively big in contact with electrolytic solution in order to compensate the insulating role of the sample as the thickness of the film grows. Mansfeld reports in a technical document (Mansfeld, 1981, p.237) a study of Kendig and Scully suggesting the use of samples covered with a ratio area / thickness of the coating of at least 10^4 to assure satisfactory electrochemical measurement. Samples were exposed under open circuit potential conditions in NaCl aqueous solution normally aired and none agitated whose concentration is 30 g/l for electrochemical impedance.

Electrochemical impedance spectroscopy measurements

The Electrochemical Impedance Spectroscopy (EIS) measurement is carried out in a 3% NaCl solution, using a potentiostat/galvanostat EG&G A273. A frequency response analyser Solartron FRA 1260 connected to an electrochemical interface Solartron SI 1287 was used to perform EIS measurements. A filter (Kemo VBF 8) was also employed to improve the signal to noise ratio. The frequency domain covered was 100 kHz to 10 mHz with the frequency values spaced logarithmically (five per decade). The width of the sinusoidal voltage signal applied to the system was 10 mV. All the measurements were performed at the open circuit potential and at different immersion times. The electrolyte was confined in a glass tube which was fixed to the painted surface by an O-shaped ring. The total tested area was 15 cm^2. Platinum gauze of large area was used as a counter electrode. All the potentials in the current article are referred to saturated calomel electrode (SCE). During the intervals between EIS measurements, the painted specimen was kept in the electrolyte cell without reference electrode. The cell design for EIS measurement was described in detail in a previous work (Novoa, 1989, p.223).

Characterization of wash primer coatings

FTIR analysis

The FTIR spectra of zinc rich epoxy paint were taken with SHIMATZU 8000 *série* + FTIR Spectrometer using ATR attachment in the range 4000–450 cm^{-1}.

Micro-Raman spectroscopy

Cross sections of the zinc-rich epoxy paint were polished and analyzed ex situ by micro-Raman spectroscopy after immersion. Fresh polishing with 1 µm diamond paste was performed just before Raman analysis. Fig.2 shows cross-section obtained by scanning electron microscopy of the ZRP. Only zinc particles (spherical) are observable. This figure shows that the distribution of the spherical pigments is quite inhomogeneous while zinc plates are uniformly distributed. Raman spectrophotometer (Labram from Jobin Yvon with an optical microscope from Horiba) was equipped with a HeNe laser (632.81 nm); the output power was 0.97 mW at the sample. A confocal hole set at 200 µm allowed an analyzed depth lower than 10 µm on transparent products. A 80 ULWD objective from Olympus was used to select the analyzed area. Raman spectra were only acquired on spherical zinc particle frontier.

Results and discussion

Electrochemical properties of sandblasted steel ($Sa\,2\frac{1}{2}$)

To the analysis of the curves (Fig 3), we note a continuous deterioration of the sandblasted steel to Sa 2.5 provoking a change in the state of the metallic surface. It can for example, to cover of corrosion products, weakly adhesive which provoke a stability of the free corrosion potential, the value was around -0.684 V/SCE. The diagrams of Nyquist determined to different time of immersion, in the 3% NaCl solution normally aired and non agitated are represented on the Fig. 3, the values of the different parameters are gathered in the table 2.
The values of the electrolyte resistance R_e are very weak, of the order of *14 Ωcm^2*, what shows that the middle is very conductive.

To the analysis of the impedance diagrams, since the first hours of immersion of the metallic substrate, we register a rapid evolution of the charge transfer resistance R_{ct} of the sandblasted steel, we note that at the beginning of the immersion the value of the charge transfer resistance R_{ct} only makes increase until to the fourth days of immersion (96 hours), it means that the process governing the kinetics is under control of load transfer. According to the Fig. 4 we notes that the charge transfer resistance R_{ct} evolves cyclically with time of immersion (growth then decrease) this state of fact to been signalled already by certain author (Belmokre, 1998, p.113, Kruger, p.294, Genin, 1986, p.490).

The tracing of the double layer capacitance C_{dl} curve as a function of exposure time from the values arranged in the Fig.4, show an increase of the capacity of double layer C_{dl} since the first hours of exposure. This growth is more or less important (3.810 to 4.505 $mF.cm^{-2}$) translating the deterioration of steel thus, but beyond the seventh day (168 hours) of immersion it decreases suddenly (2.892 $mF.cm^{-2}$), we think that the slowing of the decrease of the double layer capacitance C_{dl} would be due to the formation of corrosion products (Fig.4) forming a film more or less adhesive to the substrat playing the role of a gate, beyond 216 hours the capacity of double layer fluctuates weakly that we can consider like steady.

This situation has already been met, at the time of our survey with the different states of naked surface. This phenomenon observed by Duprat (Breur, 1998), has been assigned to the porous nature of corrosion products formed at the free corrosion potential and present at the metallic interface (Fig.5).
The model of equivalent circuit proposed and presented in Fig.6 could be used to represent the electrochemical behaviour of our samples after immersion in 3% NaCl solution, in this circuit R_e is the resistance of electrolyte ($\Omega.cm^2$), R_{ct} the charge transfer resistance ($\Omega.cm^2$) C_{dl} the double layer capacitance ($F.cm^{-2}$).

EIS behavior of zinc rich epoxy paint

Zinc-rich primers can only protect the steel cathodically when the zinc particles in the primer have electric contact to the steel substrate. Only the zinc particles in direct contact with the steel substrate, or connected through other zinc particles, will contribute to the cathodic protection. It is therefore necessary to have a large amount of zinc dust in the coating. The potential of ZRP is approximately −1.160 V/SCE, while the steel substrate used here has a potential of approximately −0.65 V/SCE. The measured potentials are mixed potentials between the steel substrate and the “active” zinc-pigments, and will depend on the area ratio between the two. If

only few zinc-pigments are active, the anode area will be small, and the potential will be close to that of the steel. On the other hand, if the area of active zinc particles is large, the potential will be close to that of zinc.
The Nyquist impedance diagrams for the ZRP coated panels obtained in the aerated 3% NaCl solution as a function of immersion time are shown in Fig. 7a. Two time constants (two loops) were clearly defined at the beginning of the exposure, that become more and more distinct as the immersion time increases, which corresponds well with the model shown in Fig.10 one in the high frequency range (Fig. 7b) which is related to the coating properties followed by a second one at lower frequencies which is related to the corrosion process (Deflorian, 1993, Nguyen, 1992). At high frequencies, the impedance reduces to one or two semicircles with diameters of charge transfer resistance and pore resistance. At lower frequencies, a Warburg impedance develops on the Nyquist plot by a straight line superimposed at 45° to both axes, which shows a shielding effect on mass transport of reactants and products. The shape of the impedance plot suggests that the ZRP corrosion changes from charge transfer control process to diffusion control process during time of immersion. By considering the morphology and the EIS of the ZRP, the impedance first decreased for few days showing the zinc particles activation before an increase related to the zinc corrosion products formation.

The fitting of EIS data was performed by Zview software (Scribners Associates, USA) using different electrical equivalent circuits which include two time constants (Marchebois, 2004, p.2945, Grundmeier, 2000, p.2515). Another difference with previous studies on ZRPs was found in the visual observation of panels during immersion. Usually, zinc corrosion products are clearly observed as white scale at the ZRP panel surfaces (Merowe, 2007, p.197) (Fig.8a). These new products would be maintained within the coating at the neighbourhood of the corroded zinc particles. Moreover, they could also contribute to the isolation of zinc particles as a protective barrier which reduces the corrosion rate of zinc and the coating porosity. Fig. 8b shows the visual appearance of zinc rich epoxy paint coated panel after 180 days (six months) of immersion where the whiteness related to the zinc corrosion products was not observed. It means that after zinc corroded, zinc corrosion products were not able to reach the coating/electrolyte interface, the surface appears damaged with the presence of the red rust due to a progressive attack informing on the state of steel substrat, at this stage of deterioration, the coating lost all its protective properties.

E_{cor} evolution

According to Abreu *et al.* (Abreu, 1996, p.2405), the evolution of the free corrosion potential E_{cor} allows to follow the electrochemical activity of the ZRP. It is believed that the electrochemical processes occurring in such systems are the oxidation of zinc particles fig.9 ($Zn \rightarrow Zn^{2+} + 2\grave{e}$) and the reduction of dissolved oxygen ($O_2 + 2H_2O + 4\acute{e} \rightarrow 4OH^-$). The authors reported that the E_{cor} evolution for liquid ZRP coated samples is in close relationship with the ratio of active areas (zinc/steel) and allows to define the cathodic protection (CP) duration which is the period where E_{cor} remains lower than −0.86 V/SCE, a value corresponding to the commonly accepted criterion of a maximum Fe^{2+} concentration of 10^{-6} M. In other words, the increase in this potential corresponds to the decrease of the electroactive zinc area which means the decrease of the cathodic protection intensity. This is generally attributed to the isolation of the zinc particles by the zinc corrosion products in the coating. Fig.10 shows the E_{cor} evolution with time of coated steel substrates with Zinc rich epoxy paint. It can be seen that E_{cor} was cathodic between −1.0 and −0.8 V_{SCE} during the six months of entire immersion, this result could be due to a high zinc particles amount. This shows that the zinc particles in the primers were electrochemically active with a high number of electrical contacts between zinc particles. This high percolation means that zinc pigments improve a good electrical contact which implies that the steel substrate was under a good CP. That means that a higher part of the zinc particles was involved in a percolation process.
However, as the CP duration is due to the activation of zinc particles by the electrolyte penetration, it also means that the zinc dissolution is reduced or that galvanic contact was lost after six months of immersion in 3% NaCl solution, some small spots of iron rust are detected on the film surface, indicating that the iron corrosion process started some days before. For our zinc-rich primers, it has been observed that zinc corrosion products precipitate inside the coating, around the zinc particles that originated them, blocking the pores of the coating and therefore increasing its barrier resistance (Abreu, 1996, p. 2405). After the test the latter sample was covered with red rust in a limited area. Probably the primer was very thin there, so that the zinc particles were consumed and the steel started to corrode.

Equivalent circuit for the EIS simulation

A general model of an equivalent electrical circuit from which a large number of other models can be derived (Fig. 11). This circuit is composed of the electrolyte resistance, followed by a capacitance (coating

capacitance C_c,) in parallel with a resistance (the coating or pore resistance Rp) and finally an element Z which represents the electrochemical process at the metal interface (Feliu, 1993, p.449, Miskovic-Stankovic, 1999, p.4269). It is the definition of Z which mainly distinguishes the circuits proposed in the literature. However, the model in Fig. 10 contains an important assumption: the ion flow and the corrosion process are localized under the coating and they are not homogeneous on the surface. This is because the corrosion process is presumed to be at the base of the defects in the coating, and not involving all the testing area (in this case the faradic reaction would be in series with the coating capacitance).
The diffusion process is suggested as being the controlling step and, with regard to impedance, the electrical behaviour of the interface is dominated by the Warburg element. For other authors the Warburg element does not substitute the double layer capacitance and the charge transfer resistance, but is added in series with the charge transfer resistance.

Micro-Raman spectroscopy

In order to understand the behavior of our organic coating, complementary analyzes were carried out. Raman spectroscopy analyzes were performed at the complete system. This technique allows to identify locally zinc corrosion products inside the coatings. Representative spectra obtained for the complete system sample are shown in Fig. 13. The main Raman band related to the Magnetite (Fe_3O_4) is found around 667 cm^{-1} (Tzolov, 2000). The band centered at 543 cm^{-1} was attributed to a non-stoichiometric oxide $Zn_{1+x}O$ (Cachet, 2002, p.3409, Ligier, 1999, p. 1164).

For all formulations, three kinds of zinc corrosion products were found depending on immersion duration and depth probed: zinc oxide ($Zn_{1+x}O$), simonkolleïte ($4Zn(OH)_2 \cdot ZnCl_2 \cdot H_2O$) . The oxidized forms were first observed at the solution/ coating interface and progressed towards the steel substrate as the immersion duration increased. Since $Zn_{1+x}O$ forms when zinc particles are in contact with electrolytic solution, one can then assume that the formation of $Zn_{1+x}O$ inside the coating allows to follow the progression of the solution through the paint.

FTIR spectral characterization

The FTIR spectrum of the zinc rich epoxy paint is shown in Fig. 13. The peaks around 850 cm^{-1}, 1250 cm^{-1}, 1510 cm^{-1}, 1600 cm^{-1} and 1460 cm^{-1} are due to the resin epoxy. The film is found to be hydrated by the presence of peak at 3400 cm^{-1} due to O–H absorption band. From FTIR spectra result, it can be concluded that the synthesised zinc rich epoxy paint was under a conductive form, which is represented in the Fig.14.

SEM analysis

Cross section S.E.M. micrographs of several ZRP samples exposed to the electrolyte for different time are shown in Fig.15. It was clearly observed that the coating presented zones which did not contain zinc particles. Moreover, it can be seen that the zinc particle shape varied significantly from spherical to elongated forms. Most of the zinc particles were not in direct contact with the substrate. These observations about the zinc particles distribution were considered to analyse EIS spectra.
Fig .15a and b represents a testing panel covered with the oxidation products after exposure to 3% NaCl solution. The oxidation of zinc in the coating creates the so-called “white corrosion”; the shapes of damage were under Cracks and scaling damage. Sealing of pores in a spherical zinc-pigmented coating. Which is necessary to secure the barrier protection of the substrate. The scheme outlines the possible reactions at the appearance of oxidation zinc products; these products are of alkaline nature and can manifest themselves in the neutralization protection mechanism (Kalendová, 2000, p.199, Kalenda, 1993, p.173).

Conclusion

- There is no doubt that zinc-rich primers offer a very efficient method of anticorrosion protection .Zinc offers threefold protection since it seals the underlying metal from contact with its corrosive environment, provides galvanic protection and “repairs” minor damage in a coating forming a barrier to further electrochemical action .
- Corrosion protection properties of zinc-rich epoxy primer coated carbon steel was studied and characterised in 3% NaCl solution. The EIS diagrams showed clearly two capacitive loops, however, classical equivalent circuits used to monitor coating degradation were unable to provide satisfying fitting results. It was found that the

cathodic protection was maintained for six months, due to a low percolation process combined to a low porosity, the reason is high zinc content and poor weldability.

- The good performance of ZRP coatings during immersion can also be explained by the retention of zinc corrosion products into the coating which allow improving barrier properties. However, it is important to remember that the zinc-rich paint effectiveness does not depend solely on electrochemical factors. There are other factors such as mechanical properties (cohesion, adhesion to Sa 2.5, flexibility, etc) that are very important. So, the addition of auxiliary pigments should be controlled carefully in order not to impair the film's physical and chemical characteristics.

Table 1. Chemical composition of A283C steel (% in weight)

C	Mn	S	P	Cu	Si
0.24	0.9	0.04	0.035	0.2	0.4

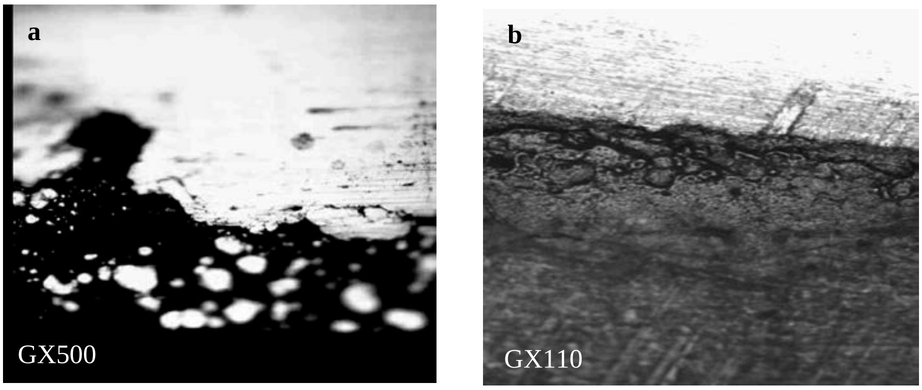

Figure 1: Cross-section of the studied ZRP. (a) Prior to exposition. The observed white particles are due to the spherical zinc particles. (b) After 360 days of immersion in NaCl 3%. Substrate steel is seen as the white region at the top of micrography.

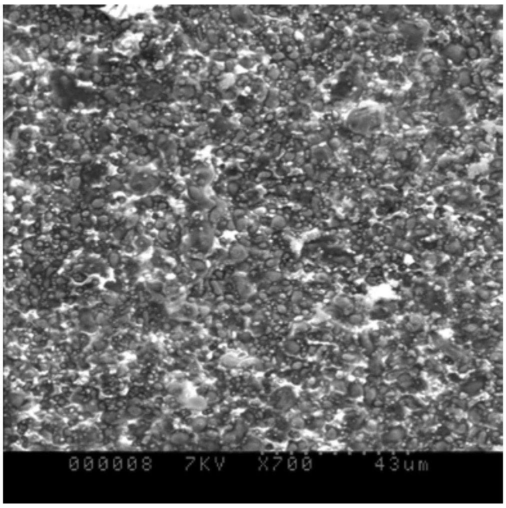

Figure 2 : Cross section SEM micrography of the coating where spherical zinc particle are visible.

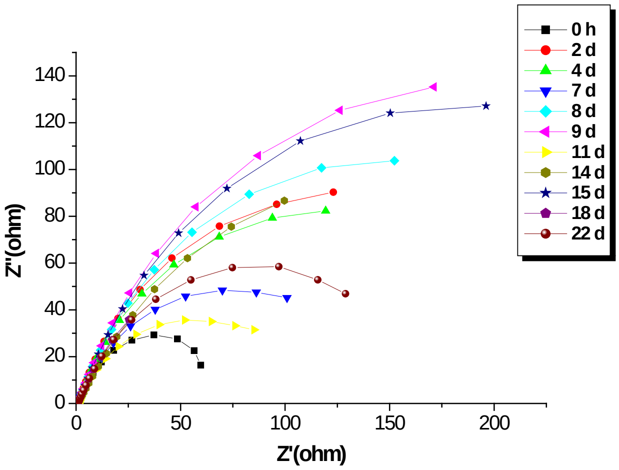

Figure 3: Evolution of Nyquist diagrams as a function of immersion time in 3% NaCl solution for the sandblasted steel (Sa 2.5).

Table 2. Parameters values extracted from the fitting procedure.

Time (days)	R_e *(Ω.cm²)*	R_{ct} *(KΩ.cm²)*	C_{dl} *(mF/cm²)*
0 h	17.97	1.044	3.810
2	13.53	3.804	4.183
4	13.14	3.532	4.505
7	13.77	2.201	2.892
8	14.53	4.460	3.568
9	14.51	5.877	2.707
11	13.65	1.706	2.331
14	14.67	2.991	2.218
15	14.95	5.532	2.876
18	14.28	2.597	2.450
22	16.02	2.546	2.500

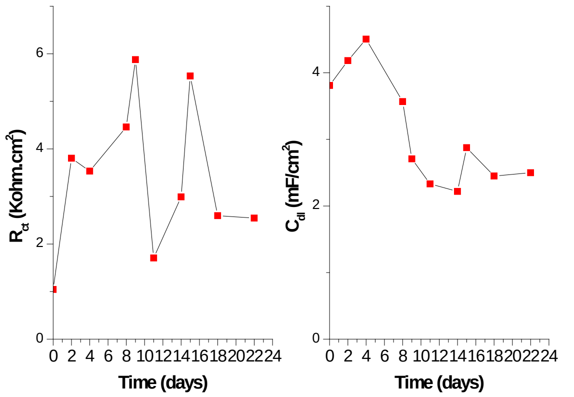

Figure 4: Variation of R_{ct} and C_{dl} with time of exposure.

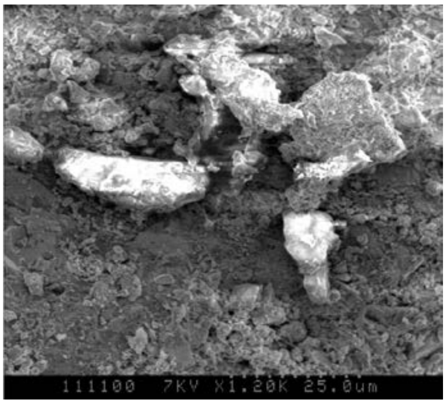

Figure 5: Cross section SEM micrograph on sandblasted steel (Sa2.5).

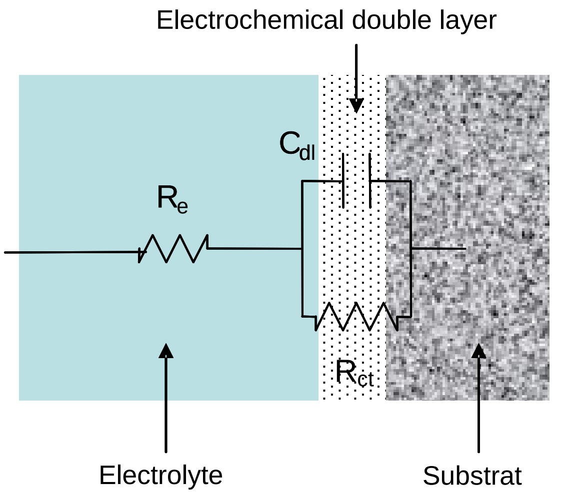

Figure 6: Equivalent circuit used to model sandblasted steel (Sa 2.5) during immersion in 3% NaCl solution.

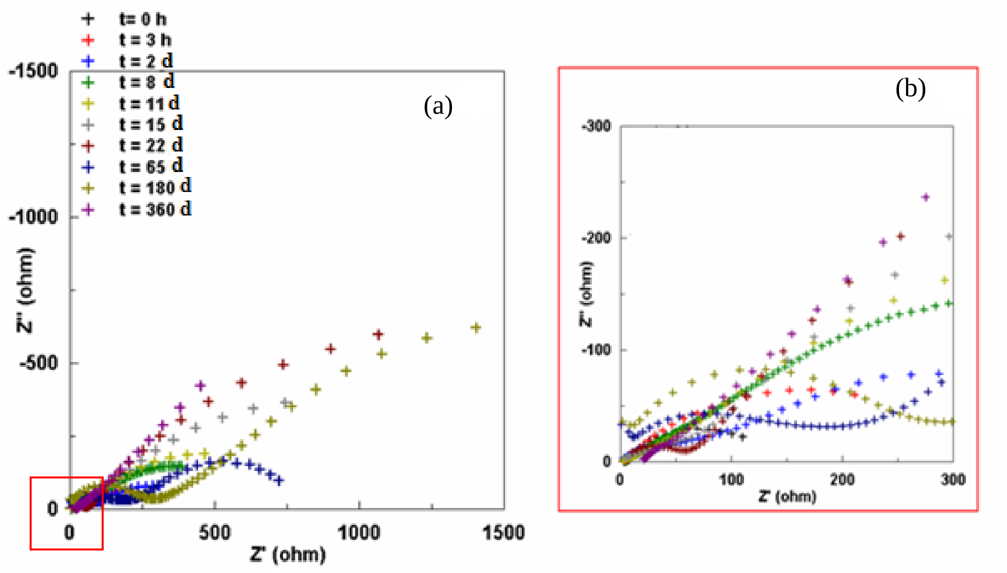

Figure 7: Electrochemical impedance spectroscopy diagrams for ZRP as a function of immersion time in aerated 3% NaCl solution.

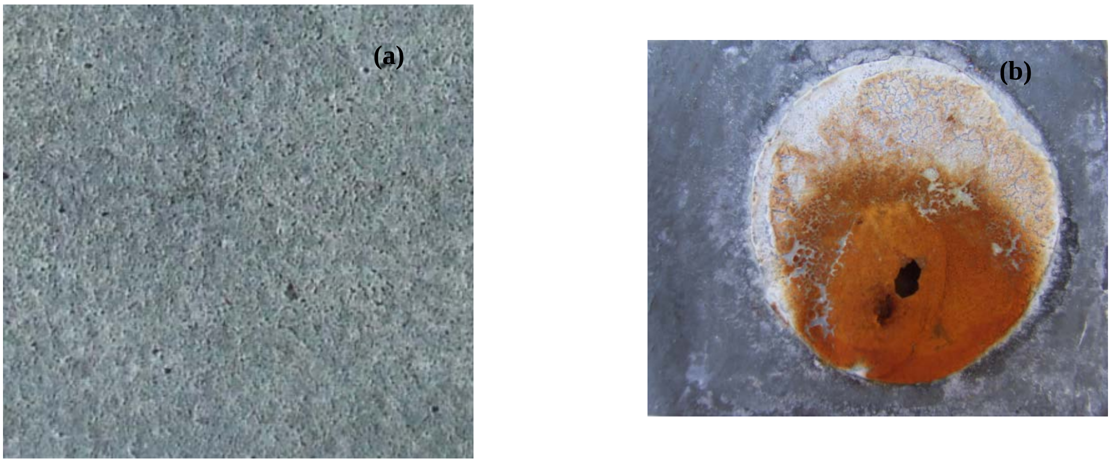

Figure 8: Visual aspect of zinc rich epoxy paint after six months of immersion in 3% NaCl solution.

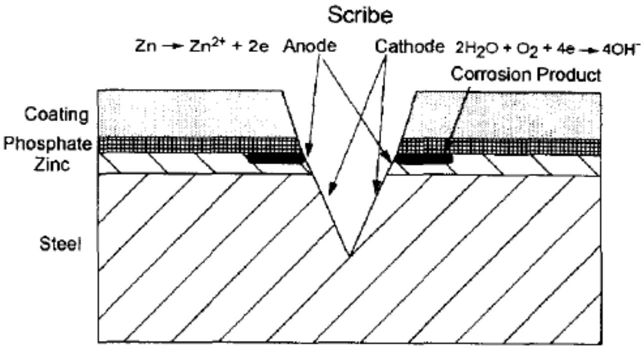

Figure 9: Corrosion process in EIS test.

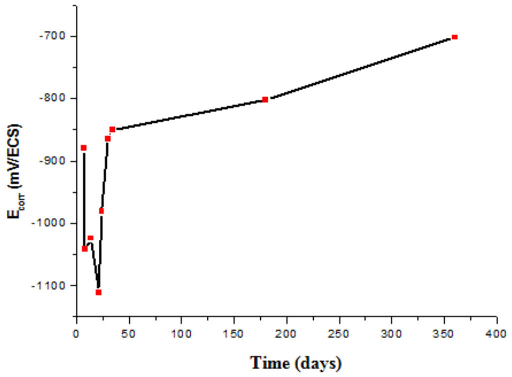

Figure 10: Variations in corrosion potential with time for ZRP exposed in 3% NaCl solution at ambient temperature.

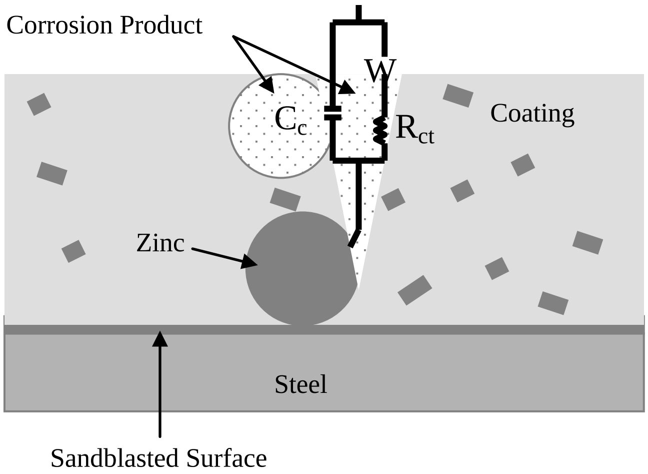

Figure 11: Electrical circuits used to simulate the EIS results.

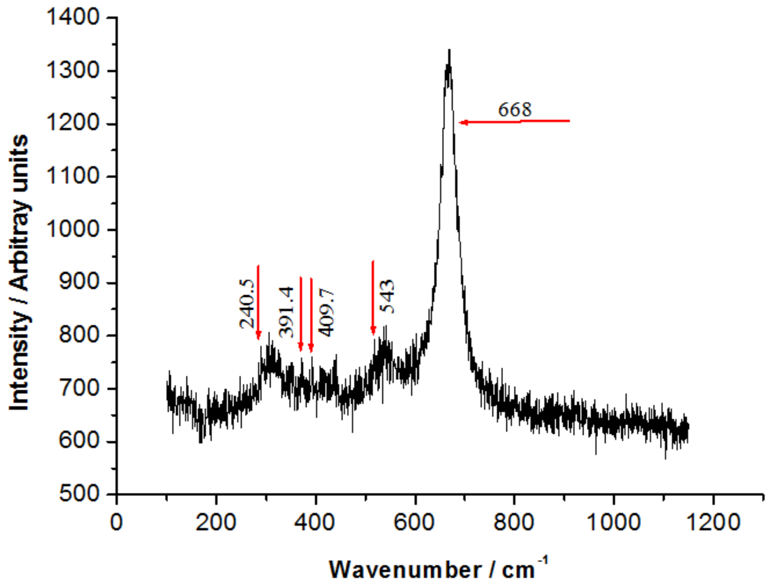

Figure 12: Raman spectrum of zinc particles near the interface film/electrolyte after six months of immersion in 3% NaCl solution.

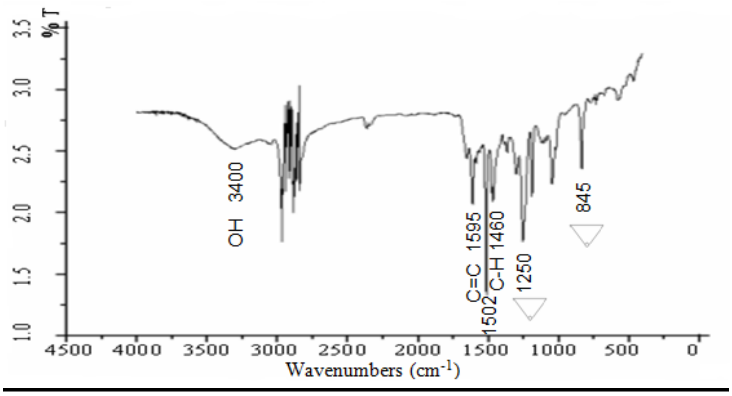

Figure 13: FTIR spectra of zinc rich epoxy paint (ZRP).

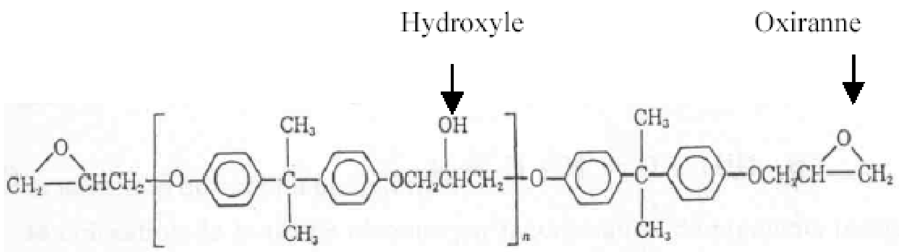

Figure 14: Structural formula of the zinc rich epoxy paint.