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Protection of reinforcement steel corrosion by phenylphosphonic acid pre-treatment PART II: Tests in mortar medium

N. Etteyeb^{a,b*}, L. Dhouibi^b, H. Takenouti^{c,d}, E. Triki^b

^a *Institut Supérieur de Biologie Appliquée de Médenine, Université de Gabes,
km 22,5; Route el Jorf, 4111 Médenine, Tunisie*

^b *Laboratoire de Mécanique Appliquée et Ingénierie, Equipe « COPROMET », Ecole Nationale
d'ingénieurs de Tunis, Univ. Tunis El Manar, BP37, Le Belvédère 1002, Tunis, Tunisia.*

^c *CNRS, UMR 8235, Laboratoire Interfaces et Systèmes Electrochimiques (LISE),
Case 133, 4 Place Jussieu, 75252 Paris Cedex 05, France.*

^d *Sorbonne Universités, UMR 8235, LISE, Case 133, 4 Place Jussieu, 75252 Paris Cedex 05, France.*

Abstract

A pre-treatment of steel reinforcement in mortar by a 72 hours immersion in 0.1 M phenylphosphonic acid ($C_6H_5P(O)(OH)_2$; PPA) was investigated. Then effectiveness of this procedure for protection against the corrosion of steel bars embedded in pre- or post-addition of sodium chloride mortar was evaluated by electrochemical impedance spectroscopy, visual inspection, SEM, and EDS analyses.

The results showed that for non-treated steel reinforcement, the charge transfer resistance (R_t) decreases considerably with time indicating a very advanced state of corrosion after 54 months corrosion test. In contrast, for pre-treated steel rebar, this resistance remains high reflecting the effectiveness of the pre-treatment method against corrosion. The corrosion rate evaluated from the charge transfer resistance at 54 months corrosion in chloride containing medium was $0.5 \mu\text{m year}^{-1}$.

Key words: Pre-treatment, Phenylphosphonic acid, Mortar, Electrochemical Impedance Spectroscopy, Sodium chloride.

* Corresponding author. naceur.etteyeb@gmail.com;

Phone: +216-97-208-278; Fax: +216-75-633-918.

1 Introduction

The high alkalinity of the concrete ensures chemical protection by the formation of protective passive layer on the reinforcements. However, in the presence of water, of oxygen, and various aggressive agents such as chlorides and carbon dioxide, this film will be damaged. Corrosion process thus starts, and as consequences in one hand the formation of expansive corrosion products leading to the loss of adherence to the concrete, and on the one hand, the reduction of the steel reinforcements sections is resulting in a loss of mechanical resistance. The former will involve the cracking of the concrete and will accelerate thus the process of corrosion by facilitating the diffusion of oxygen and the corrosive species.

Several methods are used to mitigate the corrosion effect of the reinforcements in the concrete; they include cathodic protection [1], metallic, inorganic, or organic coatings, and addition of inhibitors to the freshly mixed concrete like additives [2] as preventive methods, or by surface impregnation on hardened concrete [3] as curative application.

The calcium nitrites as additives in the concrete was proposed as the first inhibitors [4], and revealed a significant decrease of the corrosion rate of the steel reinforcements. However, their toxicity led several researchers to propose other inhibitors innocuous and friendly to the environments [5].

The use of the phosphates ($\text{Na}_2\text{PO}_3\text{F}$ [6-9], Na_3PO_4 [10-13]), recognized not toxic, gave promising results. They indeed showed, a remarkable effectiveness in alkaline medium simulating the interstitial solution of the concrete. However, its efficiency is partially lost in concrete [12]. The loss of efficiency of these compounds when added to fresh concrete is attributed to the reaction with Ca forming $\text{Ca}_3(\text{PO}_4)_2$ that precipitates in the pores reducing the content of soluble PO_4^{3-} in the pore solution able to actuate as inhibitor, as happens with $\text{Na}_2\text{PO}_3\text{F}$ [6-9].

Phosphonates are molecules that contain one or more groups $R-PO(OH)_2$. Their good chemical stability and solubility in water make possible their use in oil production, in the formulation of detergents, and in the inhibition of corrosion and scale formation [14]. Among all these properties, their ability to form strong complexes with metals plays a very important role in the rate of transports of these compounds in the environment.

The use of phosphonic acids to protect carbon steel against corrosion was studied by various work [15–24]. In part I of the present paper [25], Etteyeb et al. reported the viability of the pre-treatment of carbon steel in phenylphosphonic acid solution, against the corrosion in alkaline chloride solution. Moreover, they showed that the protective film formed by the pre-treatment procedure is stable in air. In this paper, authors will investigate the long-term effectiveness of the pre-treatment against the corrosion of reinforcement steel when embedded in mortars, especially by Electrochemical Impedance Spectroscopy (EIS) because this method is considered as no-invasive. Indeed, in the last decades, several authors have studied the reinforcement corrosion activity in concrete by Electrochemical Impedance Spectroscopy [26–29].

2 Experimental conditions

2.1 Mortar specimens

For this study, to ensure uniform distribution of electric field, cylindrical mortar specimens, 70 mm in height and 46 mm in diameter, were prepared. The overall aspect and the dimension of mortar specimen are presented in Fig. 1. The mortar was fabricated with Ordinary Portland Cement (OPC). A cement/sand (c/s) ratio of 1/3 and water/cement (w/c) ratio of 1/2 was used [30, 31]. The steel reinforcement was set at the centre of the mortar cylinder. The steel reinforcement was made of a plain carbon steel rod of 6 mm in diameter and 70 mm in length. The bars were chemically cleaned, then rinsed with acetone and distilled water. The test

specimens were prepared with non-treated steel rebars and with steel rebars treated by continuous immersion in 0.1 M Phenylphosphonic acid (PPA) solution during 72 hours.

<Fig. 1>

Each rebar had a protruding part in the specimen for electrical connection. To minimize differential aeration and also to determine the exposed area, the top and bottom parts of the rebar were covered with an insulating tape. The upper part, that is, the cover mortar thickness was 2 cm. The length of rebar exposed to the mortar was of 3 cm in length thus having an area of 5.7 cm². The specimens were cured in a humidity box at 100% RH and 20 ± 2 °C for 7 days before any experiments. Three replica measurements were carried out for each series to check the reproducibility of results.

Mortar tests were divided into two groups:

2.1.1 Group I:

In this group, 1 % NaCl by weight of cement was added to the mixing water. These specimens were prepared with untreated steel rebars (reference specimens) or with steel rebars treated as indicated above. This group is called hereby as “pre-chlorinated mortar”. Between two collections of impedance spectra, the mortar samples were left in a humidity box. Fig. 2 illustrates the humidity box used for the ageing of pre-chlorinated mortar specimens. The specimens were set on a perforated plastic plate and the water filled in the bottom of the box to insure the humidity in the tightly covered plastic box.

<Fig. 2>

2.1.2 Group II:

Mortar specimens without chloride were prepared with untreated or treated steel bars. After a curing period, the samples were submitted to alternative cycles of immersion and emersion, (2 days drying and 1-day immersion in 0.5 M NaCl solution, thus 3 days for one cycle). This system will be called “post-chlorinated mortar”.

For the former group, the aggressive chloride ions were present initially by adding NaCl in the mortar whereas for the second group, the chloride ions were brought by immersion in NaCl solution. The alternative cycles between immersion and emersion enhanced the penetration of chloride ions inside the mortar matrix.

2.2 *Electrochemical measurements*

The experiments were performed to follow the time-change of the electrochemical impedance spectrum. Fig. 3 shows the electrochemical cell layout used for these measurements.

<Fig. 3>

The electrochemical impedance spectra (EIS) were collected with a Gamry potentiostat (model PC4/300) using a 10mVrms ac-signal at the open circuit corrosion potential (E_{oc}) from 100 kHz to 10 mHz with 5 points per decade.

The saturated calomel electrode (SCE) was used as reference and in fixed at the upper part of the mortar cylinder. The electrical contact to the mortar that consists of the electrolyte was ensured with a tiny wet synthetic sponge. The counter electrode was stainless steel wire of 0.5 mm in diameter surrounding the lateral part of the mortar cylinder. A wet synthetic sponge surrounding the lateral part of mortar cylinder and its bottom allows also the electrical contact with the counter electrode and also avoids the drying of mortar specimens during impedance measurements. After these measurements, the mortar specimens were transferred to a humidity box or an immersion – emersion cell for the next impedance measurements.

2.3 *Characterization of steel-mortar interface*

At the end of the test, specimens were broken and the surface state of steel and mortar were examined visually.

This examination made possible the characterization of the corrosion pattern. The corrosion products and steel–mortar interface were then analyzed with Energy Dispersive Spectrometry (EDS) coupled with Scanning Electron Microscopy (SEM). First, visual inspection gives a

global overview of the interface between steel and mortar. By using SEM with EDS analyses chemical composition of the corrosion products can be determined.

3 Results and discussion

3.1 Electrochemical Impedance Spectroscopy (EIS)

3.1.1 Pre-chlorinated mortar

The variation of electrochemical impedance spectra (EIS) with ageing period at 1, 3, 9, and 54 months for untreated specimens is presented in Fig. 4.

<Fig. 4>

In the absence of pre-treatment (Fig. 4), all of the impedance spectra are formed of a single capacitive loop. A decrease in the value of the total impedance, with respect to the ageing time in humidity box was observed reflecting an acceleration of the corrosion.

The experimental diagrams were modelled using an equivalent electric circuit, which comprises an electrolyte resistance (R_e), a charge transfer resistance (R_t) in parallel with the capacitance (C_d) relative to the double layer as illustrated in Fig. 4. The impedance modulus remains almost constant in high frequency domain whereas a small increase of phase shift was observed for the frequencies above several kHz. By comparison with treated specimen (Figs. 5 and 7), this behaviour was allocated to the mortar phase itself [32], and not to the steel reinforcement. A depressed feature of the impedance diagram in Nyquist plot was expressed by a Cole-Cole type distribution of time constant:

$$Z = R_e + \frac{R_t}{1 + (j \cdot \omega \cdot R_t \cdot C)^\alpha} \quad (1)$$

The variable α is a coefficient reproducing a depressed feature.

For the regression calculation however, a parallel connexion of R and C circuit was added in series for the mortar phase behaviour. The impedance at very high frequency domain was not

analysed in this paper because this part does not concern the characterization of corrosion behaviour of reinforcement steel.

With pre-treated steel rebar (Fig. 5), the appearance of another loop in higher frequencies is observed. Its capacitance values is in the order of several nF cm^{-2} , and thus attributed to a surface film formed by the pre-treatment. To meet this new feature, the impedance spectra were modelled with an electrical circuit with two hierarchical connections of R and C circuits as illustrated in the right hand. The experimental and calculated spectra overlaps well in the whole frequency domain, thus corroborates the adequacy of the equivalent circuit adopted.

<Fig. 5>

Fig. 6 shows the evolution of the equivalent circuit elements R_t and C_d for untreated and pre-treated reinforcement steel. In the absence of pre-treatment, the charge transfer resistance R_t (Fig. 6a) is high at the beginning of the test. This can be explained by the formation of a passive film on the metal surface due to the high alkalinity of the medium (the pH of the mortar pore solution is in the order of 13). However, R_t decreased then significantly with ageing time and simultaneously C_d increased. These variations can be explained by an increase of the active surface area induced by the corrosion.

In the presence of pre-treatment, it appears that the charge transfer resistance R_t is more than two times greater at the beginning, and then it keeps almost constant during 15 months, then it decreases with ageing time. At 54 months ageing, R_t value is still greater than that obtained at the beginning of untreated specimen. This can be explained, probably, by the reaction of phosphate film formed on steel rebar surface with calcium of mortar. A higher value of R_t all through this experiments, shows the effectiveness of the pre-treatment against corrosion of steel rebars embedded in chlorinated mortar.

<Fig. 6>

3.1.2 Post-chlorinated mortar

Fig. 7 presents the impedance spectra obtained after 1, 3, 9 and 54 months in immersion - emersion cycles of reinforced mortar specimens made with untreated steel rebars. No chloride was added in the mortar at the preparation (Group II) but chloride ions were brought by immersion-emersion cycles.

<Fig. 7>

In these diagrams, two capacitive loops can be observed. However, we note:

- A marked decrease of the high frequency loop beyond 9 months.
- The diameter of the low frequency loop decreased with ageing time.

The capacitive loop observed at high frequency domain was allocated to the mortar behaviour as it was the case for untreated rebars embedded in the pre-chlorinated mortar (Fig. 4).

With the pre-treated rebars (Fig. 8), two capacitive loops were observed, as it was the case with pre-chlorinated mortar. With pre-chlorinated mortar, the high frequency capacitive loop was observed even up to 54th month, in contrast this loop was vanished at 54 months ageing in alternative immersion – emersion cycles. As for the corrosion test method, the post-chlorinate mortar by immersion - emersion ageing can be considered more aggressive, since the protective film seems to be disappeared in a shorter test period compared with the pre-chlorinated mortar at 1 % NaCl.

<Fig. 8>

Figure 9 depicts the time change of R_t and C_d under immersion - emersion cycles without or with pre-treatment. The features of these variations are similar to that shown in Fig. 6.

As for the R_t change, as can be seen in Fig. 9a, for untreated steel rebars, it decrease steeply with ageing period. It decayed to ca. one fifth at 9 month corrosion test. For the pre-treated specimens, the impedance modulus is much higher at the beginning, almost twice as high, and decreases much slowly as it was observed for pre-chlorinated mortar. After 31 months exposure in the post-chlorinated mortar, R_t decreases by less than 10 %.

<Fig. 9>

For untreated steel rebars, the double layer capacitance (Fig. 9b) increases steeply for the first ten months then it increases much slowly. The decreases of R_t and the increase of C_d are closely correlated, and may be explained by the augmentation of the active surface area induced by the corrosion process as this is the case for the pre-chlorinated mortar. For pre-treated specimens, the double layer capacitance is similar at the early stage of corrosion test, but increases much slowly. The pre-treatment is thus found to be very efficient.

These results showed clearly that the protective film formed on the steel rebars surface by pre-treatment in 0.1 M PPA constitutes an efficient barrier against the invasion of aggressive ions (Cl⁻) as well for pre-chlorinated as post-chlorinated mortars.

For pre-treated rebars for both mortar systems, R_t was ca. $800 \text{ k}\Omega \text{ cm}^2$ at the end of the ageing tests. By using Stern – Geary relationship [33] with its coefficient equal 0.052 V [34] and the dissolution valence of three, since the steel remained in the passive state, one gets the loss of steel thickness equal to $0.5 \mu\text{m year}^{-1}$ by considering the generalized corrosion. This corrosion rate is sufficiently small to ensure the durability of the concrete structure.

3.2 Characterization of corrosion pattern

At the end of each test, the reinforced mortar specimen was broken. It is important to notice that the top and the bottom of steel rebars covered by insulating tape are not suffered of the corrosion. Its protection, as often reported in the literature, is easy to apply and sufficiently efficient. The surface state of the steel rebar was then observed first visually then by SEM and analysed by EDS. From visual inspection (Fig. 10a), it appears that, in the absence of pre-treatment, the steel surface exhibited a marked corrosion pattern. That is, in the case of untreated steel rebar, there is a formation of non-protective corrosion products through two main stages according to the literature. In a first step, transient products, called green rust, should be formed [35, 36]. Then, in the absence of oxygen, they may transform into

magnetite. However, in most cases, oxygen is present and these products become FeOOH (lepidocrocite, akageneite, etc.). This process agrees well with the observation, which shows that corrosion products of iron in chlorinated environment include Fe^{2+} and Fe^{3+} [37–39]. The EDS analyses show the presence of the iron element mainly as attested by SEM and EDS analysis (Fig. 11).

<Fig. 10>

<Fig. 11>

The specimens with pre-treated steel, in contrast, did not show any degraded areas visible by the naked eye (Fig. 10b and 10c) and the surface remained bright metallic aspect as prepared by chemical cleaning. Thus, we can conclude that the specimens with pre-treated steel rebar provided a good protection to the embedded steel against corrosion. SEM picture shows the presence of a protective film. From EDS analyses, it appears the presence of the phosphor element (Fig. 12 and 13), but with a small amount. This can be explained partly by its reaction with calcium to form a complex as $\text{Ca}_3(\text{PO}_4)_2$ and also partly by the fact that surface film obtained by pre-treatment was too thin to be analyzed quantitatively.

<Fig. 12>

<Fig. 13>

4 Conclusion

The aim of the present investigation was to evaluate the long-term efficiency of the pre-treatment of steel rebars, by immersion in 0.1M PPA solution during 72 hours, against the corrosion in pre-chlorinated and post-chlorinated mortar,.

The electrochemical impedance spectroscopy for steel rebars embedded in pre- or post-chlorinated mortar showed that corrosion resistance remained high even after 4.5 years of ageing in immersion – emersion cycles in 0.5 M NaCl solution. The surface film formed on the steel rebar surface during the pre-treatment, plays an efficient barrier layer against the aggression of chloride ions, and offers a noticeable mitigation against corrosion.

The visual inspection and SEM pictures corroborate these results.

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FIGURE CAPTIONS:

- Fig. 1. Photograph of the reinforced mortar test specimens employed (a) overall view (b) the dimension
- Fig. 2: Humidity box in plastic vat for ageing of pre-chlorinated mortar specimens
- Fig. 3. Electrochemical cell layout for electrochemical impedance spectroscopy measurements
- Fig. 4: Evolution of the electrochemical impedance spectra with respect to ageing time of untreated steel rebar embedded in pre-chlorinated mortar. Ageing in a humidity box.
- Fig. 5: Time evolution of the electrochemical impedance spectra of pre-treated steel rebars in 0.1M $C_6H_5PO_3H_2$ embedded in pre-chlorinated mortar spectra ($c/s = 1/3$, $w/c = 1/2$, 1% NaCl). Ageing in a humidity box.
- Fig. 6: Time dependence of charge transfer resistance, R_t (A) and double layer capacitance, C_d (B) of steel rebars without and with treatment before embedding in the pre-chlorinated mortar. Between two impedance measurements, the mortar specimens were left in a humidity box.
- Fig. 7: Evolution of the impedance spectra of untreated steel rebars embedded in post-chlorinated mortar ($c / s = 1/3$, $e / c = 1/2$). Ageing by alternative immersion - emersion cycles: 1 day immersion in 0.5 M NaCl solution and 2 days drying in ambient air.
- Fig. 8: Evolution of the electrochemical impedance spectra with ageing time of pre-treated steel rebars embedded in post-chlorinated mortar. Ageing by immersion - emersion cycles.
- Fig. 9: Time variation of the charge transfer resistance, R_t (A) and the double layer capacitance, C_d (B) of untreated and pre-treated steel rebars with respect to the immersion / drying ageing period with post-chlorinated mortar.
- Fig. 10: surface state of steel rebars after 54 months ageing by immersion – drying cycles in 0.5 M NaCl (a) without pre-treatment (b) with pre-treatment for Group I and (c) with pre-treatment for Group II.
- Fig. 11: Characterization of non-treated steel/mortar interface by SEM and surface analysis by EDS.

Fig. 12: Characterization of pre-treated steel/mortar interface by SEM and surface analysis by EDS for specimens of Group I.

Fig. 13: Characterization of pre-treated steel/mortar interface by SEM and surface analysis by EDS for specimens of Group II.

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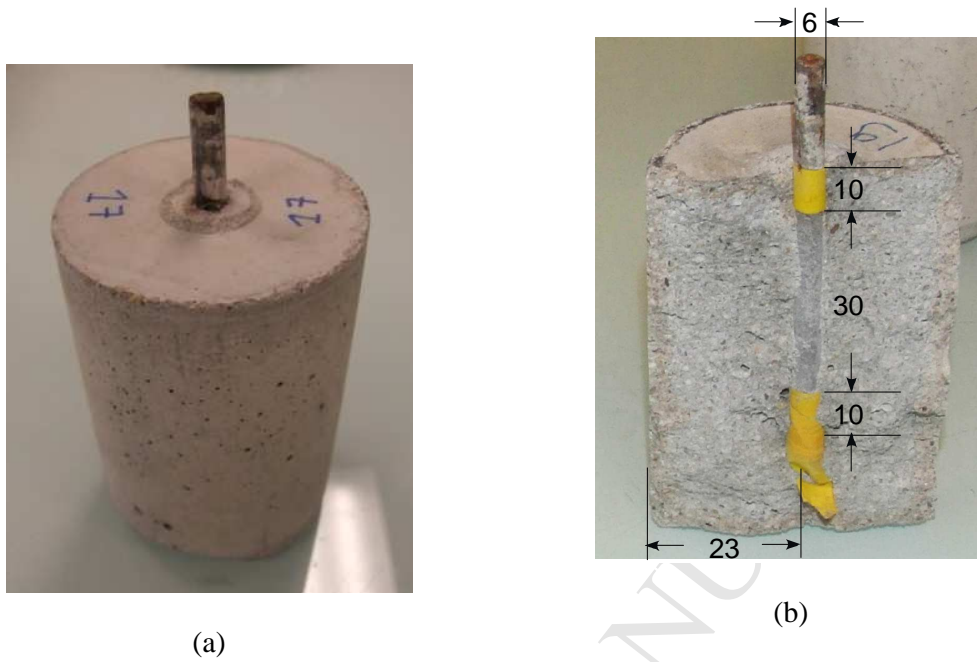


Fig. 1.

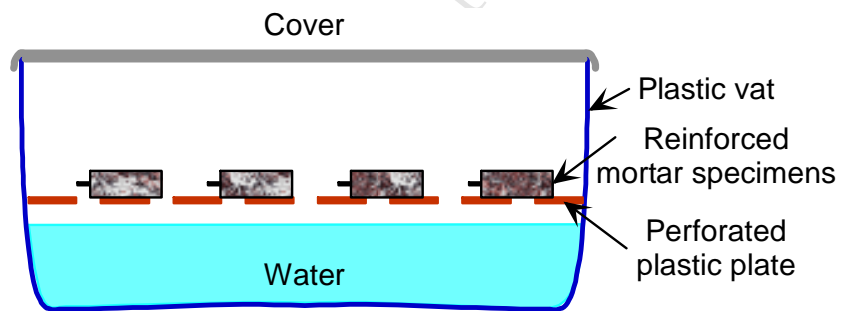


Fig. 2.

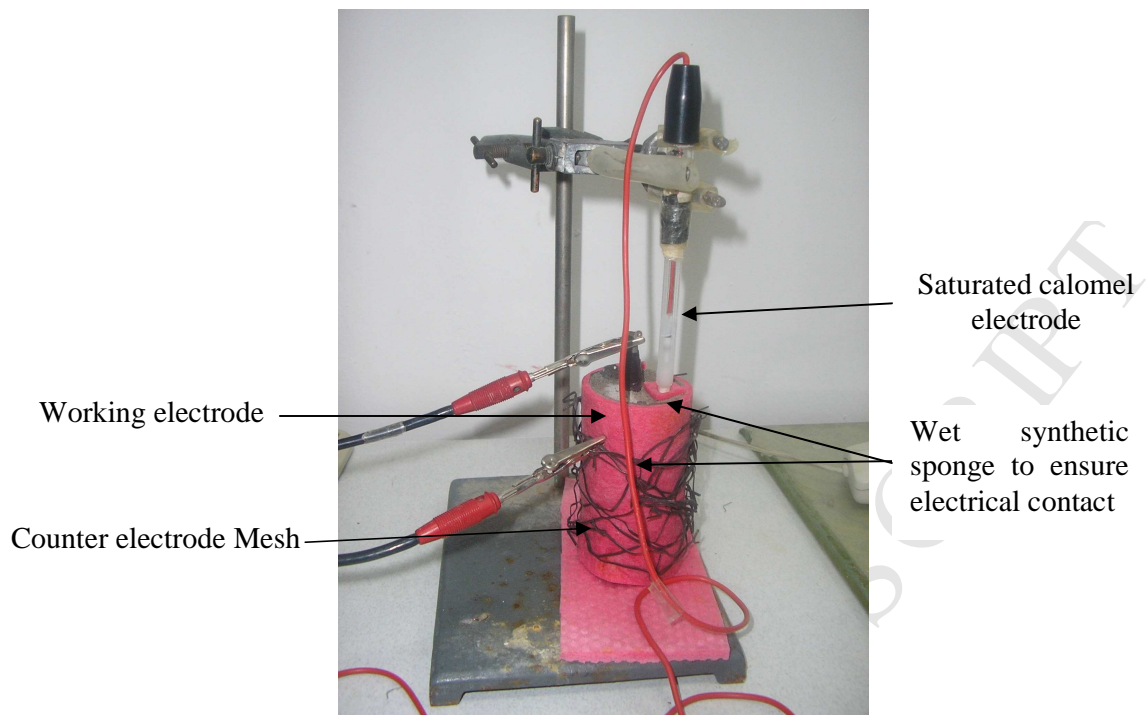


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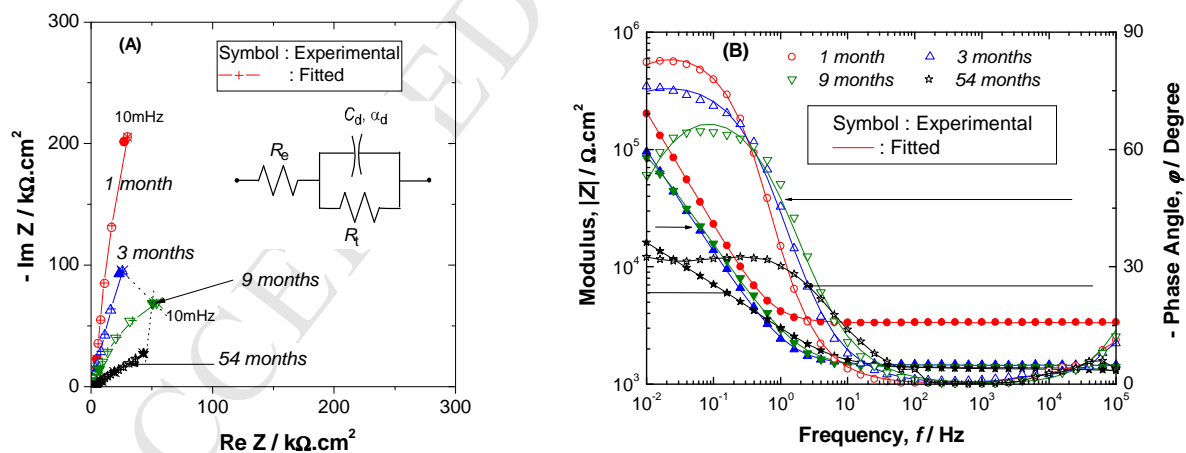


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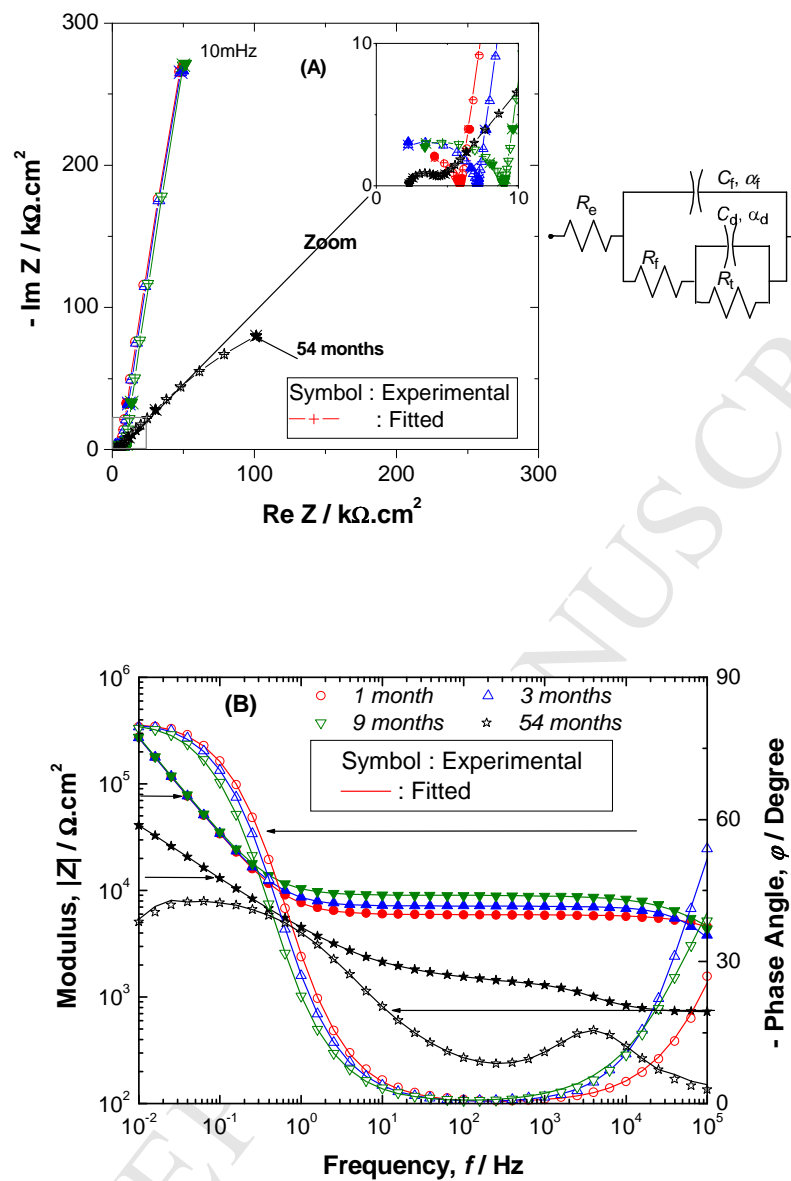


Fig. 5.

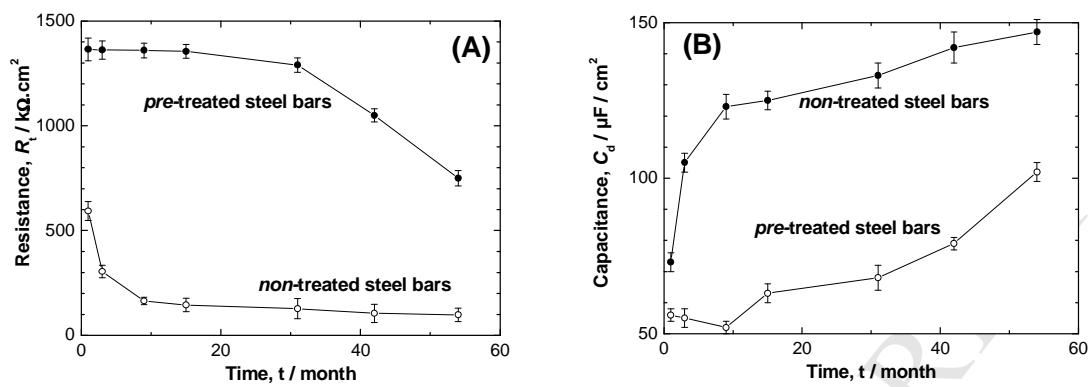


Fig. 6.

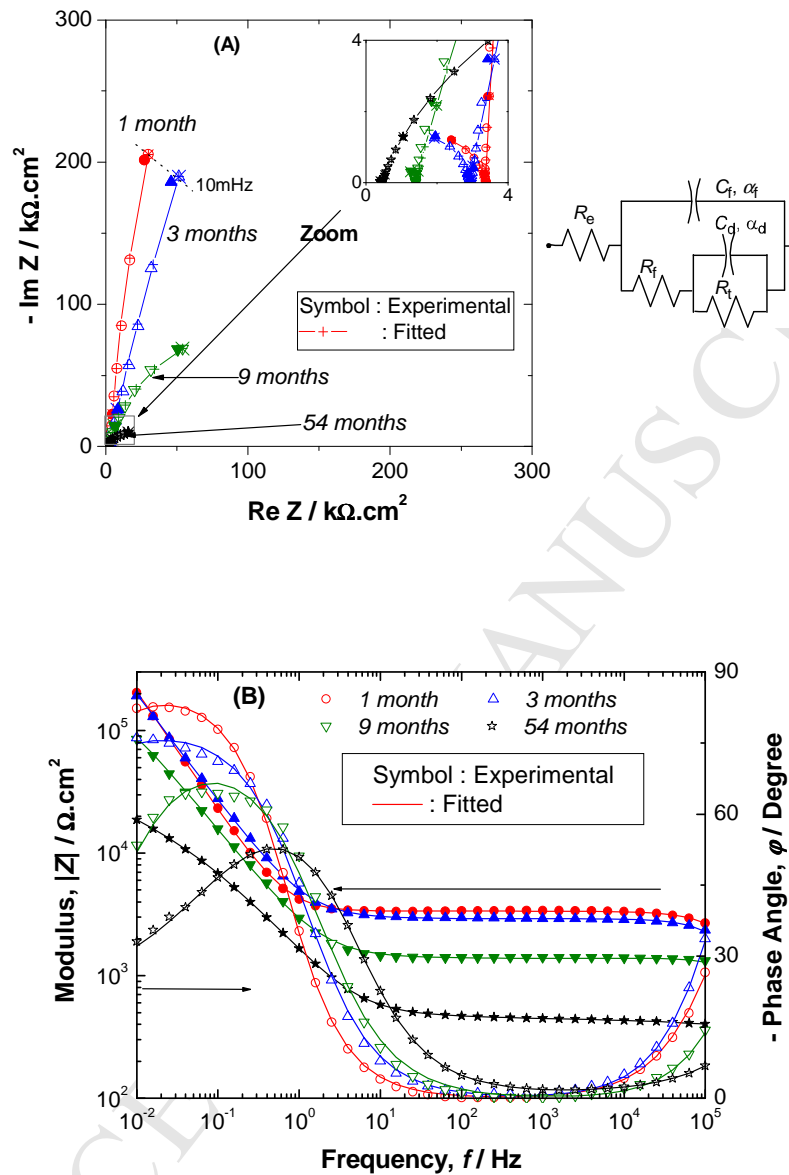


Fig. 7.

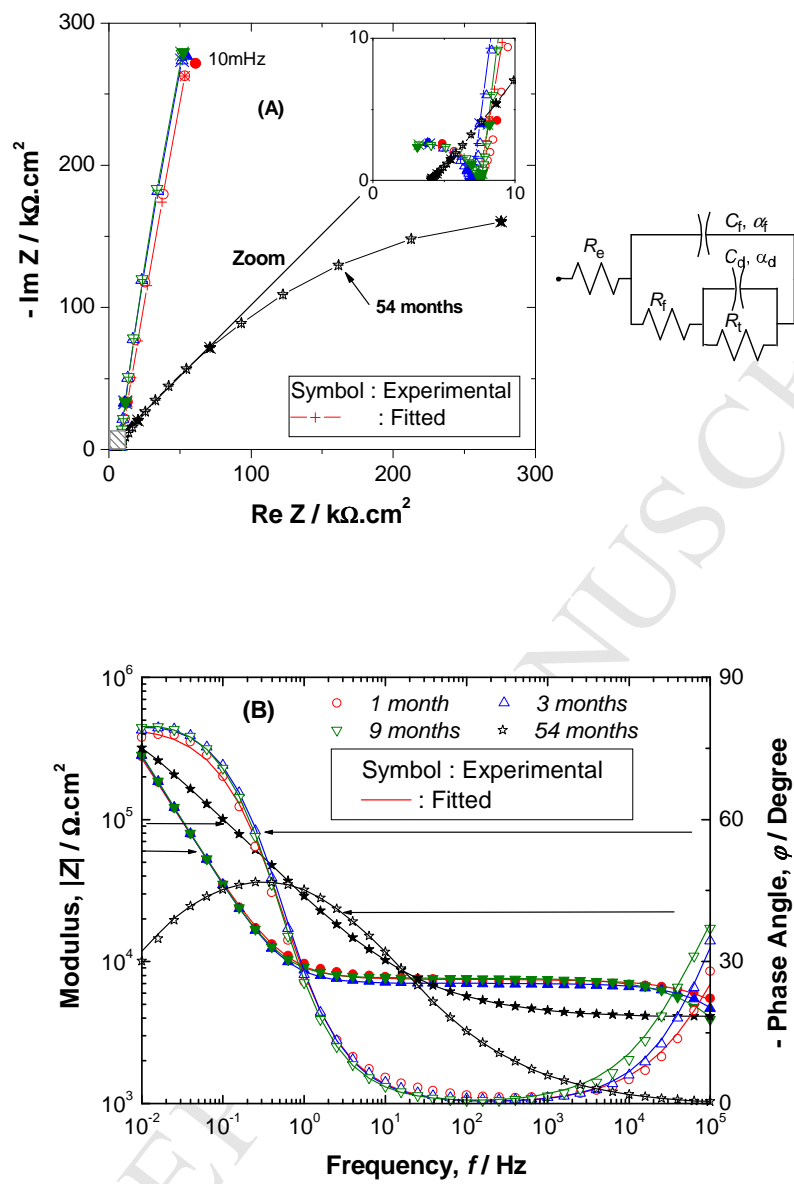


Fig. 8.

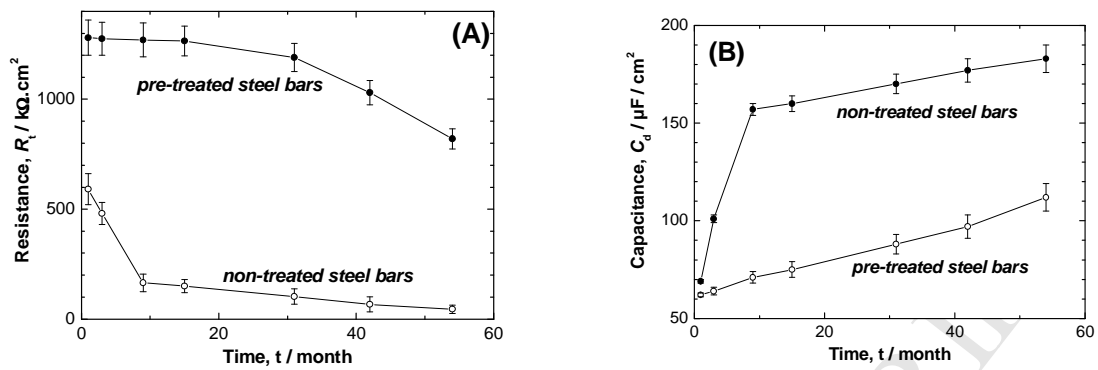


Fig. 9.

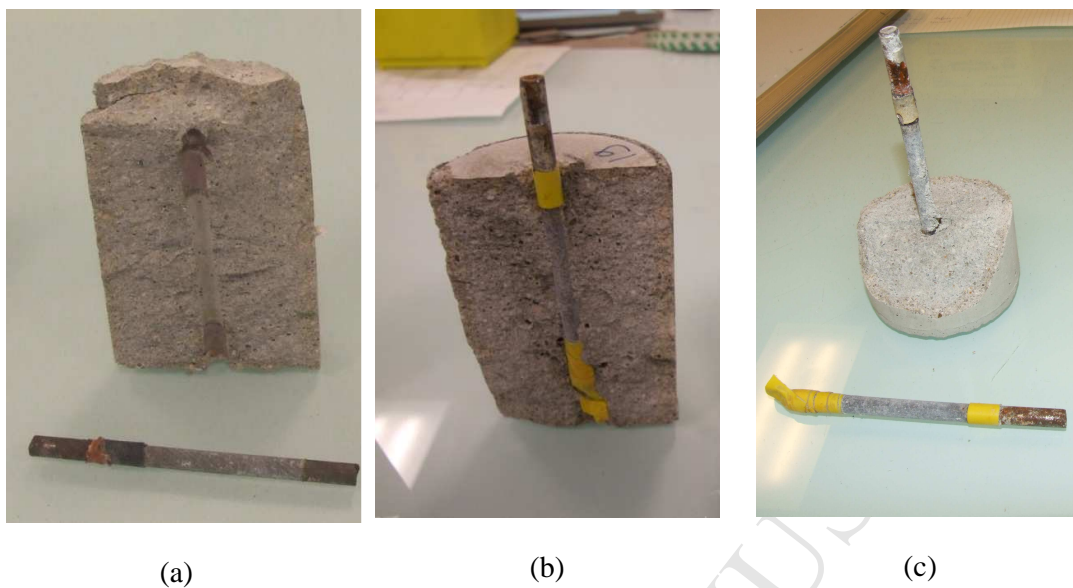


Fig. 10.

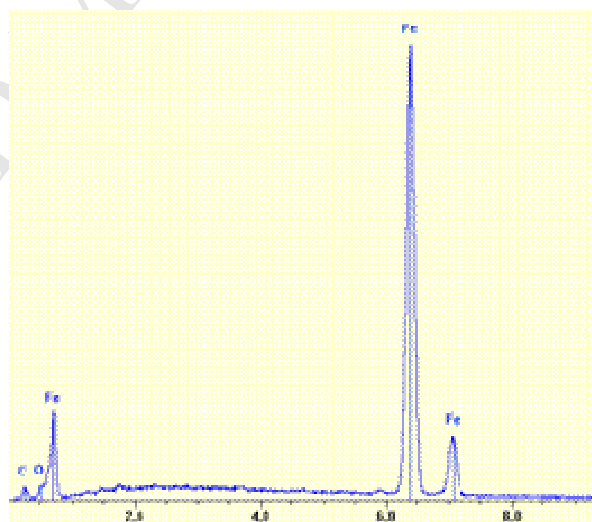
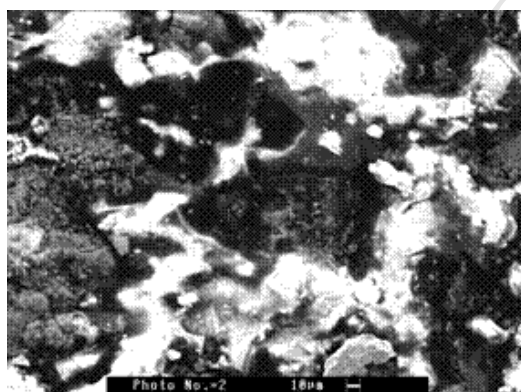


Fig. 11.

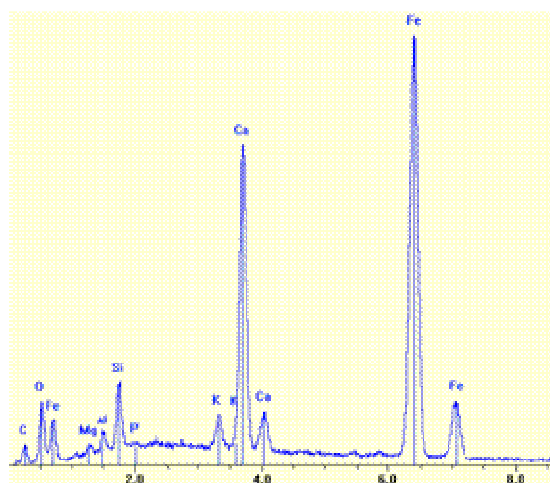
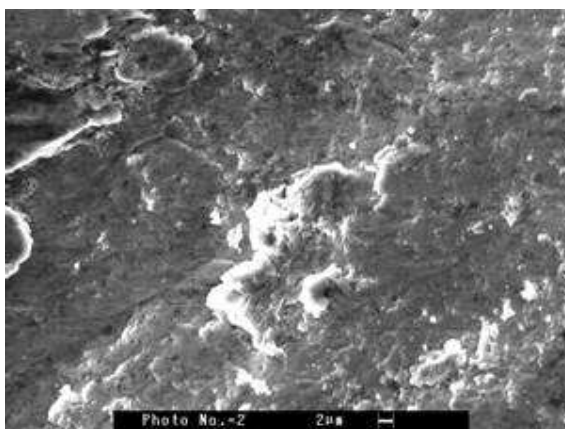


Fig. 12.

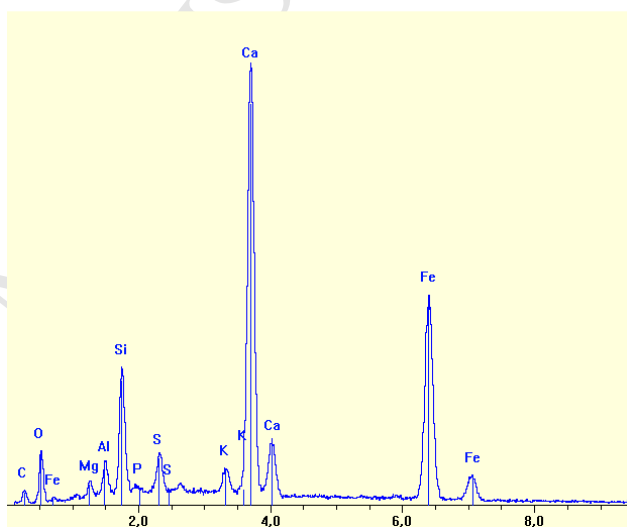
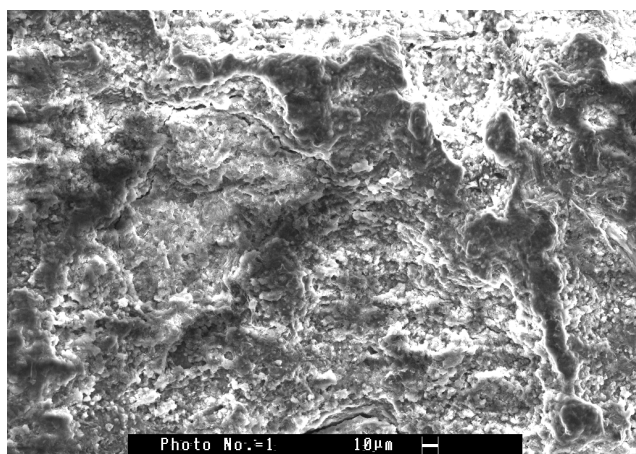


Fig. 13.