

New Corrosion Inhibitor Containing *Opuntia ficus indica* Seed Extract For Bronze and Iron-based Artefacts

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Most archaeological objects made of iron or copper are exposed to corrosive agents, such as pollutants, fluctuating humidity, etc, and are slowly lost in Museums. In our laboratory, we have tested formulation (OTH) on an uncorroded surface of iron and bronze Cu-8Sn, in 3% sodium chloride solution. The inhibiting effect of this formulation was investigated by electrochemical measurements. The obtained results indicate that this formulation acts as good corrosion inhibitor. In the present work, the formulation (OTH) was tested as an atmospheric corrosion inhibitor on corroded surface of iron and bronze coupons. The artificially aged coupons have a similar composition to archaeological and historical objects. The state of coupons surfaces was carried out by visual observations, and recorded by digital photographs, examination with a Scanning Electron Microscope (SEM) coupled to Energy Dispersive Spectrometry (EDS). Electrochemical measurements were carried out in the case of bronze coupons. From all experiments, (OTH) is a good inhibitor of historical iron and bronze against atmospheric corrosion and also in 3% NaCl corrosive medium.

Keywords: *Opuntia ficus indica*, atmospheric corrosion, steel, bronze, artefacts, corrosion inhibitor

1. INTRODUCTION

The corrosion is a damage caused to a metal by chemical, electrochemical or even biological reactions between the metal and the surrounding medium. Most human activities are victims of this phenomenon, considering the use of metals and their alloys in all domains.

The knowledge of the causes of corrosion is essential to develop a control technology and to improve the means of protection.

Among several protection means, those called “corrosion inhibitors”, which are substances, when added in small quantity can delay effectively or even cancel the corrosion process of the metal in contact with a corrosive medium. The protection systems against corrosion are more important, when the main aim is to protect metallic archaeological objects, which represent a cultural and historical richness of a culture.

For a very long time, effective products were developed to protect the vulnerable metallic systems against corrosion. However the majority of these corrosion inhibitors are not environmentally friendly, and are highly toxic. They may cause harmful effects on the organisms, some of them are suspected as cancer agents [1,2]. These facts call for a research of cheap, safe, and environmentally friendly corrosion inhibitors.

Several tests and studies deal with the problem of iron and copper corrosion [3-5], and recent scientific research tries to develop new and safe corrosion inhibitors. Vegetal

is a rich source of active molecules, some plant extracts have been tested as metals corrosion inhibitors [6,7], with a good inhibition efficiency. This work is a trial to test a new formulation containing *opuntia ficus indica* seed extract as corrosion inhibitor of pre-corroded bronze and steel coupons.

The *Opuntia ficus indica* originates from Mexico, and is very widespread in Morocco, and is a highly productive cactus, which is cultivated as a food source for both human and animals. Also, it plays an important ecological part in combating erosion, and it is adapted and integrates in the agricultural production system of arid and semi-arid zones in Morocco. In our laboratory, extracts of this cactus have been developed as corrosion inhibitors. The inhibitive action of the *Opuntia* stems extract was tested against corrosion of iron in 3% NaCl solution using polarisation technique and electrochemical impedance spectroscopy measurements. The extract examined leads to important inhibition efficiency around 86% [6].

The aim of the present work is to study the corrosion inhibition effect of a new formulation (OTH) containing *opuntia ficus indica* seed extract on the behaviour of artificially aged steel and bronze coupons. The monitoring of the study was carried out by surface analysis with SEM-EDS for coupons exposed one month to the laboratory atmosphere. Furthermore, monitoring of coupons was recorded by digital photographs after various times (10 days and 3 months) of exposure to atmospheric corrosion.

For the artificially aged bronze coupons, the electro-

chemical properties have been characterized by electrochemical impedance spectroscopy measurements in 3% sodium chloride solution in the presence and absence of the inhibitor.

2. EXPERIMENTAL PROCEDURE

2.1 Material

This work was carried out as part of PROMET project; all experiments used the PROMET coupons, which simulate the behaviour of historical and archaeological metal artefacts.

Steel coupons were corroded artificially in an accelerated corrosion chamber (RH 100%), the typology of corrosion formed through the accelerated process is pitting [8].

The bronze coupons were artificially covered with patina layer and corroded inside a corrosion chamber [9].

The dimensions of each coupon are as follows: (50×75×(2-3)) mm, which composition is presented in Tables 1 and 2 for steel and bronze coupons respectively.

Elm	Si	Mn	C	Fe
Wt%	0.201	0.519	0.157	Balance

Table 1: artificially aged steel coupons composition [8].

Elm	Cu	Zn	Sn	Pb
At%	85	5	5	5

Table 2: bronze composition [9]

2.2 Atmospheric exposure

Metallic coupons were exposed to atmospheric corrosion in our laboratory characterized essentially by relative humidity values of about 63-68 %. These conditions are similar to Rabat Museum atmosphere.

2.3 Inhibitor

This work is novel in terms of the application of cactus extract as a new and environmentally friendly corrosion inhibitor. The *Opuntia ficus indica* seed extract used in this work is essentially based on fatty acids [10-12]. The formulation preparation called OTH contains *Opuntia* fatty acid, triethanolamine, and KOH. OTH is easy to apply on metallic surfaces; and it is totally reversible in ethanol.



Figure 1 - photographs of *Opuntia ficus indica* plant (left) and its fruit seed (right)

The inhibitor was applied by immersion of the coupons during one hour in a solution containing 0.02% OTH inhibitor in pure ethanol.

2.4 Material characterisation

The micrographic negatives have been taken using SEM (HV 16 KeV for steel coupons and 5 KeV for bronze coupons), equipped by EDS (elemental dispersion analysis using X-ray) (ZAF quantification standard less).

SEM/ EDS was carried out for the coupons with and without inhibitor after one month of exposure to atmospheric corrosion. Digital photographs were taken before exposure to a laboratory atmospheric corrosion, after 10 days and after 3 months of exposure.

2.5 Electrochemical measurements

The corrosion tests were performed with classic 3-electrode configuration: a Platinum grid as a counter electrode, a Ag-AgCl as a reference electrode (Figure 2). The working electrode was a bronze sample (25 cm²) immersed in 0.02% solution of ethanol/formulation OTH for 1 hour before each experiment (Figure 3). The electrolytic solution used was 3% NaCl solution.

The impedance data were collected at the open -circuit potential over a frequency range between 100 KHz and 10 mHz using EG&G apparatus M6310.

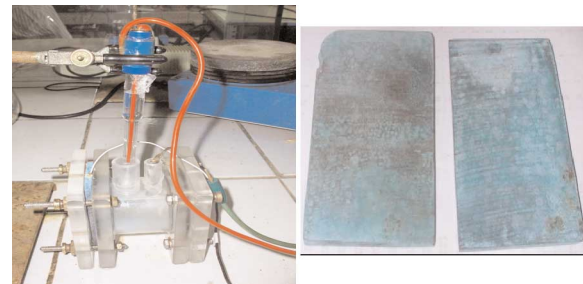


Figure 2 - Electrochemical cell Figure 3 - Bronze coupons

3. RESULTS AND DISCUSSION

Figures 4, 5, 6 and 7 gives SEM photographs coupled with EDS results on steel with and without corrosion inhibitor, along, with digital photographs for different exposure times of steel coupons with and without corrosion inhibitor.

3.1 Case of artificially aged steel coupons

3.1.1 SEM/ EDS analysis

3.1.1.a without inhibitor

Figure 4 shows the SEM picture steel coupon analysed in the absence of the inhibitor.

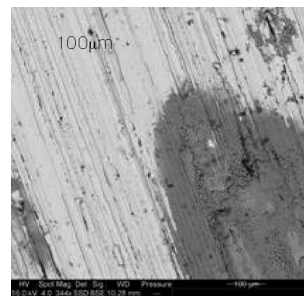


Figure 4 - SEM micrographic of artificially aged steel coupons

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From this Figure, one clearly distinguishes two main zones, the white zone which may correspond to the part of coupon where the metal surface is not corroded, even if new and very small pitting are developing due to the atmospheric exposure. The black zone may correspond

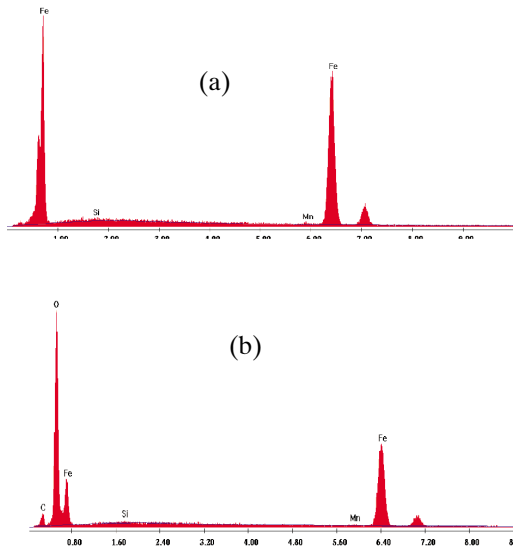


Figure 5: EDS spectra realized on black and white zones of a reference steel surface. (a): in white zone; (b) in black zone

to a corroded zone of steel surface with pitting corrosion, which was already present on the coupon surface. These pits developed after one month of exposure to atmospheric corrosion. EDS analyses were carried out for both zones, as given in Figure 5.

The EDS analysis corresponding to these zones reported in Fig.5 (a) and (b) reveal differences between the two zones:

The white section where the metal is not corroded contains essentially Fe (98%), in association with Si and Mn, but at less percentage as shown in Table 3 (a). The absence of oxygen confirms the absence of iron oxides and the corresponding zone is not corroded under exposition time.

At black zone, the concentration of oxygen is high (50%), with (16%) of carbon as shown in Table 3 (b). The percentage of iron is less compared to value obtained in white zone. The presence of oxygen is due to iron oxide formation resulting from process of artificially corrosion in an accelerated corrosion chamber; where the R_H is about 100%, and also the ambient humidity during exposure in our laboratory, thus this zone is rich on corrosion products.

(a) white zone

Element	Si	Mn	Fe
At %	0,85	1,05	98,10

(b) black zone

Element	C	O	Si	Mn	Fe
At %	15,91	50,46	0,29	0,41	32,92

Table 3 - Elements composition corresponding to the two zones shown in figure 4, and issued from EDS spectra

3.1.1. b In the presence of inhibitor

Figure 6 shows the SEM photo of the steel coupon with the presence of OTH inhibitor. The inhibition test was carried out with the immersion of coupon in the formulation solution. With the presence of OTH, one observes from the coupon general view that corrosion does not appear on sample area. The pitting corrosion is less developed compared to the reference sample after one month of exposure time to atmospheric corrosion.

The EDS analysis given in Figure 7, corresponds to spectra obtained by analysing black and white zones of iron coupon treated with inhibitor formulation. These spectra reveal the presence of oxygen, nitrogen, carbon and potassium in the white zone, compared to the reference sample. The presence of these elements were absent in the blank essay. This gives evidence to the presence of inhibitor on the coupon surface.

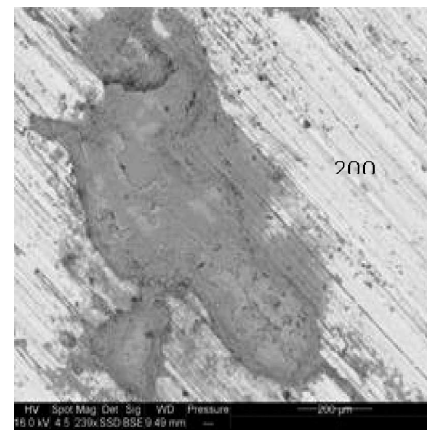


Figure 6: SEM micrograph of artificially aged steel surface with OTH corrosion inhibitor after one month of exposure to atmospheric corrosion.

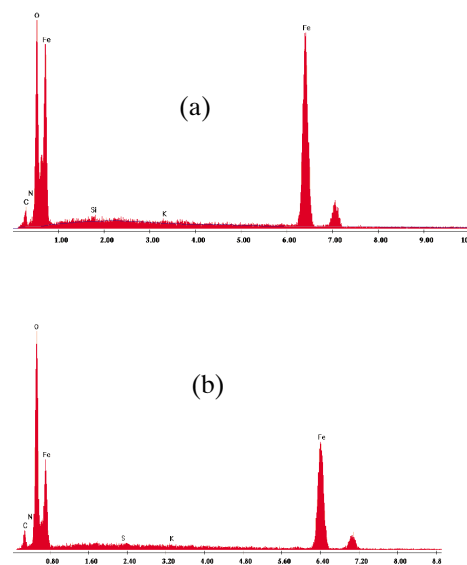


Figure 7 - EDS spectra obtained on black (b) and white (a) zones of iron surface with OTH inhibitor treatment

In black zone: the EDS analysis reveals the presence of sulphur and potassium compared to the reference where these elements were absent Table 4 (b). This may mean that S and K and N elements come from inhibitor present on steel surface. The corrosion inhibition may be also characterised by a decrease of oxygen percentage from 50 to 44%.

(a)

Element	C	N	O	K	Fe
At%	15.54	4.01	33.23	0.27	46.96

(b)

Element	C	N	O	S	K	Fe
At %	18.09	3.4	44.02	0.19	0.16	34.14

Table 4 - values of element percentage determined by EDS analysis on white (a) and black (b) zone of steel surface protected with OTH applied by immersion

The effect of inhibitor is also marked by the absence of a new corrosion pits on the level of white sites, which keeps its metal brightness compared to the state of coupons before experiments, and its capacity to limit the development of pitting corrosion when compared to the reference sample.

Visual inspection of the artificially aged steel coupons surface shows clearly that application of OTH by immersion method for 1 hour in ethanol/ OTH formulation protects the metal surface against further atmospheric corrosion.

The observations propose an establishment of inhibitor thin film, which may protect the metal surface against atmospheric corrosion.

3.1.2 Digital photographs

The condition of coupons surfaces were recorded by digital photographs shown in Figure 8, in order to show the protective effect of the inhibitor on samples treated by immersion compared to the references ones exposed to atmospheric corrosion after 3 months

Photographs below represent the coupons surface before exposure, after 10 days and after 3 months of exposure to atmospheric corrosion in our laboratory.

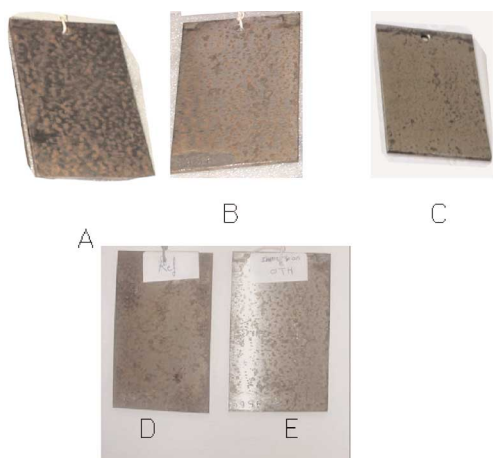


Figure 8 - Digital photographs of steel samples exposed to atmospheric corrosion for different exposure times

A: Photography of artificially aged steel coupon before exposure to atmospheric corrosion:

Steel coupon artificially corroded presents corrosion pits distributed on surface, with some intact zones.

B.C: Photography of steel coupons after 10 days of exposure to atmospheric corrosion,

After 10 days there is not a visual change on the coupons surface either for reference sample (B) and he treated one (C). Metallic coupons must be exposed for a longer period.

D.E: Photography of steel coupons after 3 months of exposure to atmospheric corrosion:

After 3 months, the corrosion is well developed in many pits of the reference sample without corrosion inhibitor essentially in the sides of the coupon (D).

The coupon treated with the inhibitor (E) kept its initial aspect and its brightness.

3.2 Bronze samples

As for the steel coupons, the bronze coupons were prepared by PROMET partner [9]. The patina layer was formed artificially under special conditions by this partner. Our study was to apply the OTH corrosion inhibitor for analysing its behaviour for bronze in laboratory atmospheric conditions as described for steel coupons.

Bronze samples with a composition analogous to that of archaeological and historical metal objects were artificially aged in a climatic chamber with moist air containing sulphur dioxide. The patina formed on the surface was investigated by SEM / EDS in the presence and absence of OTH formulation applied by immersion.

The electrochemical reactivity of patina will be determined by EIS experiments.

3.2.1 SEM/ EDS analysis

This technique has also been applied to compare the bronze coupons varying condition after exposure with and without corrosion inhibitor.

3.2.1. a. Reference sample

Figure 9 shows a bronze reference state of coupon covered with patina layer. The examination of this Figure shows a heterogeneous surface with green and brown sites. The patina layer is discontinuous, which affects the corrosion resistance of this metal.

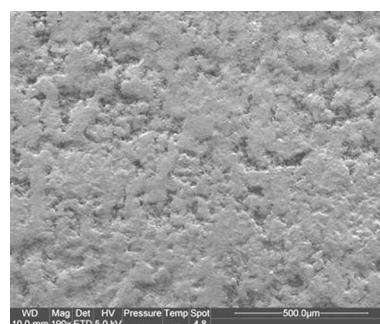


Figure 9 - SEM picture of bronze covered with patina layer, before its exposition to laboratory atmosphere

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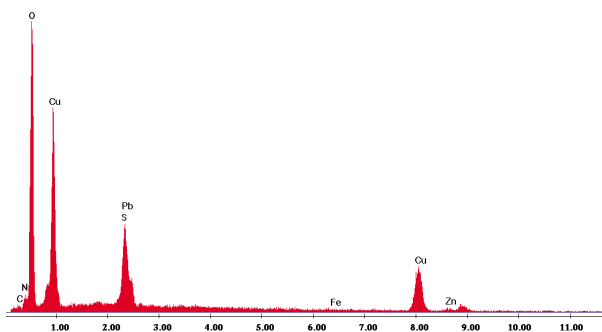


Figure 10 - EDS spectra of patina layer that makes up the bronze coupon sample

The analyzed values of constituent elements are shown in Table 5

Element	C	N	O	S	Pb	Fe	Cu	Zn
At %	5.69	8.92	58.13	4.29	1.52	0.15	19.86	1.44

Table 5 - Percentage of elements in patina layer of bronze coupon

This table shows basic elements of the bronze metal Cu, Zn and Pb, and the other elements: carbon, nitrogen, oxygen that also make up the patina layer. The sulphur atom presence may be attributed to the medium of patina formation.

3.2.1. b. Examination of OTH formulation effect on patina behaviour

The bronze patina was immersed in OTH inhibitor formulation and exposed to a laboratory atmosphere. The general view of sample area is shown in Figure 11.

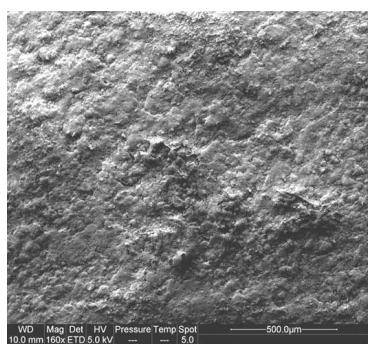


Figure 11 - patina layer after immersion in inhibitor formulation

Our visual inspection, after immersion of the coupon in the inhibitor solution, found that the initial colour of the patina did not change. This first result is an important character for the OTH application on real archaeological objects exposed in a museum environment.

The comparison of SEM picture between the reference sample and the treated one with OTH inhibitor by immersion show that the general aspect of patina change, when the inhibitor is added leading to homogeneous and com-

pact patina layer. The use of inhibitor favours the corrosion resistance of bronze metal coupon.

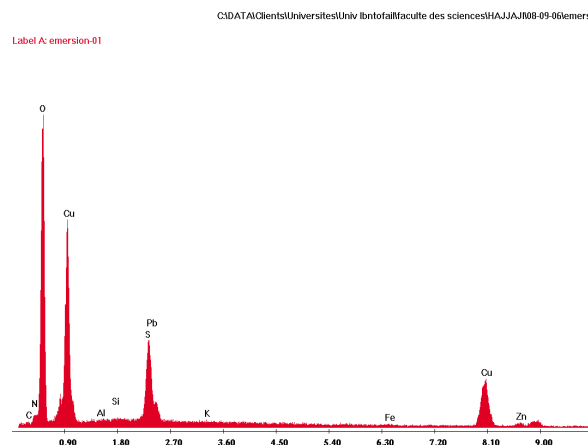


Figure 12 - EDS spectra of patina layer immersed in inhibitor formulation

The EDS analysis of patina layer in presence of inhibitor formulation is illustrated by Fig. 12, and Table 6.

Element	C	N	O	Al	Si	S	Pb	K	Cu	Zn
At %	4.68	7.56	58.89	0.16	0.14	4.83	1.05	0.07	20.63	1.78

Table 6 - Composition of patina layer protected by OTH

These results lead us to note that there are not significantly differences between a reference sample and the treated one with OTH; they present roughly the same composition, except for potassium due to the presence of the inhibitor on the patina surface.

The bronze sample was immersed for one hour in the inhibitor solution (ethanol/0.02% OTH), but this may not be enough time for the inhibitor to be completely adsorbed on the patina layer. In order to have more information about the action mechanism of our inhibitor, this work was completed by electrochemical measurements whose results are presented below.

3.3 Electrochemical impedance experiments

Figure 13 shows the impedance spectra (Nyquist plots) of inhibitor-free sample measured at open-circuit potential and recorded after different immersion times 2h to 168h. The capacitive behaviour is represented by one time constant, which has 1200 Ωcm² of resistance after 2 hours of immersion in 3% sodium chloride solution. This resistance increases with time, after 72 hours. The corresponding value is around 3700 Ωcm².

At higher time, 120 hours, the resistance value of patina layer tends to be stabilized towards 5900 Ω.cm².

However, in Figure 13 one notes at low frequencies, the start of a second time constant, which is not well distinguished.

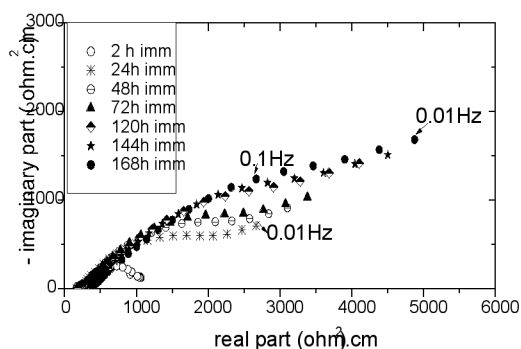


Figure 13 - Impedance spectra for bronze sample without inhibitor in 3% sodium chloride at different immersion times

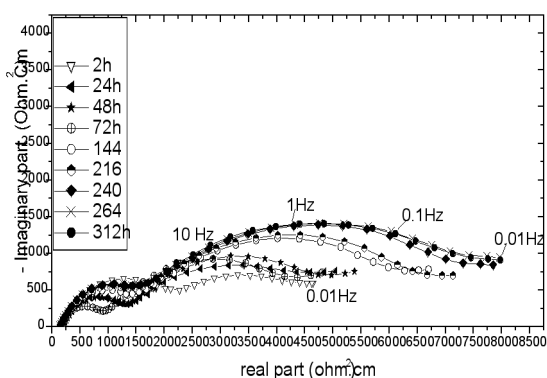


Figure 14 - Impedance spectra of bronze sample protected by (0.02%) of inhibitor in 3% (w/v) sodium chloride at different immersion times

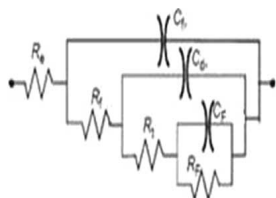


Figure 15 - Electrical equivalent circuit used to simulate EIS data for the bronze corrosion in 3% NaCl with inhibitor

As can be seen in Figure 14, in the presence of inhibitor on the metal surface, one notes that the impedance changes in shape and size. There are two semicircles detected for all immersion times of bronze sample with inhibitor. The shape and size of impedance spectra in the presence of OTH inhibitor tends to stabilize after 144h of immersion. In high frequency (HF) range, the characteristic frequency f_c , at the maximum of the imaginary part is 631Hz. However, it is only about 0.63Hz for the low frequency semicircle (LF).

In the presence of inhibitor, the first semicircle located at high frequencies range may be associated to the inhibitor film. The second semicircle may be attributed to the charge transfer at the interface patina/3% NaCl.

The capacity value of a high frequencies for 144h hours of immersion is about $0.13 \mu\text{F}/\text{cm}^2$ (the value of the associated capacity was calculated from the relation $C = (2\pi fR)^{-1}$, (where “f” is the characteristic frequency in the maximum of the semicircle and R is its diameter). This semicircle has a very low capacity, lower than $1 \mu\text{F}/\text{cm}^2$ justifying its attribution to a thick and compact film as shown elsewhere [13]. The protective character of the inhibitor is improving with time by corrosion products.

However, these diagrams cannot be explained with only two R and C circuits, a third process seems to start. The electrical equivalent circuit used to simulate EIS data is shown in Figure 15, which is in agreement with results presented in references [14-16], the R-C couples may be attributed to following contributions:

The high frequency contribution (C_f - R_f) is attributed to the dielectric character of the corrosion products (C_f) due to the formation of surface film that is reinforced by the presence of the inhibitor and by the ionic conduction through the pores of the film (R_f). The medium frequency contribution is attributed to the double layer capacitance (C_d) at the electrolyte/bronze interface at the bottom of the pores coupled with the charge transfer resistance (R_t), whereas the low frequency elements are related to the oxidation-reduction contribution of the corrosion products (R_F - C_F).

4. CONCLUSION

The obtained results using digital and SEM surface observations, coupled with EDS spectra lead us to propose that OTH natural inhibitor formulation applied by immersion method on the artificially aged steel surface, acts as a good atmospheric corrosion inhibitor. The corrosion inhibition efficiency is clearly marked after 3 months of exposure. This inhibiting effect may correspond to an establishment of inhibitor film on metal surface.

For bronze coupons, surface analysis and visual inspection, confirm the presence of inhibitor on the surface, this was justified by electrochemical impedance, which in presence of inhibitor shows a semicircle in high frequencies range.

The inhibiting film is reinforced according to the immersion time certainly by corrosion products.

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