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ORIGINAL PAPER

Electrochemical assessment of the restoration and conservation of a heavily corroded archaeological iron artifact

M. Hernandez-Escampa · J. Gonzalez ·
J. Uruchurtu-Chavarin

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Abstract This study proposes an electrochemical conservation routine applicable to iron archaeological artifacts extracted from their archaeological context and later exposed to a marine atmosphere. The case of study consisted of a Nineteenth Century anchor safeguarded in the Mexican City of Campeche. Metallurgical characterization and electrochemical studies were used to evaluate and assess the conservation process (electrochemical free chloride removal and species reduction, passivation and coating treatment evaluation) and to quantify their effectiveness. Additionally, archaeological information regarding the manufacture process was obtained. The techniques used include potential measurement, potentiodynamic polarization (polarization curves), potentiostatic measurements, electrochemical impedance spectroscopy, electrochemical noise measurements, as well as metallography studies. The method here proposed can then be used in analogous set up as a guideline example for evaluation and assessment purposes during similar procedures.

Keywords Iron conservation · Archaeological anchor · Chloride removal · Heritage conservation · Archaeometallurgy · Electrochemical assessment

1 Introduction

Archaeological metal artifacts call for special attention from the conservational point of view. Additionally, after excavation, stabilization, restoration, and conservation, some of these artifacts are exposed and exhibited to highly corrosive atmospheres, resulting in the deterioration and consequent loss of valuable social and cultural information. This is the case of iron anchors, cannons, and cannon balls, exhibited in public places in the fortified Mexican City of Campeche. This coastal city located in the Yucatan peninsula is considered World Heritage site according to the United Nations and its collection of historical artifacts range from pre-Columbian times to the Nineteenth Century.

Over many years, the stabilization of excavated archaeological iron artifacts has presented serious problems for conservators, which are associated with the nature of the artifacts and the limitations imposed by the desired final state, as well as exhibition conditions [1]. The structure and composition of excavated archaeological iron artifacts are well characterized [2–7]. The metal core is typically covered by several millimeters of dense (predominantly magnetite) corrosion products overlain by a looser FeOOH and soil aggregate layer. The latter is comparatively easily removed by mechanical means (done during this work), but the inner layer contains the original shape of the artifact [1]. Thus, complete oxide removal is not appropriate and efforts must be made to stabilize the oxide covered surface. The solution included within the pores of the corrosion products contains significant ferrous and chloride ion concentrations.

M. Hernandez-Escampa (✉) · J. Uruchurtu-Chavarin
Universidad Autónoma del Estado de Morelos, CIICAP,
Avenida Universidad No. 1001, Colonia Chamilpa, CP 62210
Cuernavaca, Morelos, Mexico
e-mail: marhea62@hotmail.com

M. Hernandez-Escampa
Centro de Investigación y Docencia en Humanidades del Estado
de Morelos (CIDHEM), Av. Morelos Sur 154 esq. Amates,
Col. Las Palmas, CP 62050 Cuernavaca, Morelos, Mexico

J. Gonzalez
Universidad Autónoma del Estado de Campeche, CICORR,
Avenida Agustín Melgar s/n entre Calle 20 y Juan de la Barrera,
Colonia Buena Vista, CP 24039 Campeche, Campeche, Mexico

Depending on the anions present in the archaeological matrix under the seabed or soil, there might also be other solid ferrous compounds (phosphate, carbonate, etc.) [1].

With untreated artifacts the initial rapid deterioration processes after excavation are predominantly due to oxidation of included ferrous ion by air [8, 9]. This results in the formation of FeOOH, generally γ-FeOOH due to the presence of chloride in the pore solution) and local acidification to pH as low as 1. These conditions also result in the formation of beta β-$Fe^{3+}O(OH, Cl)$ (akaganeite). The volume expansion due to oxide formation, possibly aided by magnetite dissolution that forms because of the acidity, causes the spalling of the oxide layer. Concurrently, but slower, and continuing from the initial oxidation stage, corrosion of the base metal leads to deterioration.

The possibility of these processes depends in the ambient relative humidity and they occur rapidly above 45% relative humidity (RH), determined by the critical humidity for the dissolution of ferrous chloride, although much slower reaction rates have been observed down to 20% RH in the presence of ferrous chloride and metallic iron [8]. The objective of stabilization treatments could then be defined being able to raise the critical relative humidity below the level in which no deterioration occurs [10].

Most low temperature *stabilization* treatments are described as chloride removal methods although the preceding discussion indicates that ferrous ion removal is equally, if not more, important [11, 12]. However, removal of cations implies anion removal. This desalination treatment can be attempted in various ways, of which a simple immersion treatment is the most common. Numerous solutions have been used, including sodium hydroxide, alkaline sulphite, sodium sesquicarbonate, and alcoholic hydroxides [13–16]. At the present, there is no consensus as to the optimum treatment and one reason for this appears to be that there is no reliable method of assessing the ongoing processes during treatment or the stability of treated artifacts, except the potentially destructive exposure to high humidity. Corrosion potentials during treatments were measured, but almost none electrochemical rate measurements on such artifacts have been published [4].

This article presents results of electrochemical monitoring studies and assessment of the behavior of archaeological iron artifacts, focusing on the case of an Nineteenth Century iron anchor during stabilization and conservation procedure that can be applied to heavily corroded iron surfaces to be exposed and exhibited in the atmosphere of the city. The techniques applied include dc and ac electrochemical methods, and the results from artifacts are compared to the simpler responses obtained with clean and artificially precorroded modern steel surfaces.

2 Experimental procedure

2.1 Metal sampling

Figure 1 shows the graphic description of the artifact under study. No sampling from the main body of the anchor was allowed due to legal restrictions. However, during rescue the stock of the anchor was broken. This situation justified obtaining a transversal section (1.0 cm) from the broken stock. This main sample was cut to obtain a limited number of 1 cm cubic coupons. Therefore, some of the archaeological coupons presented a surface with the corrosion products

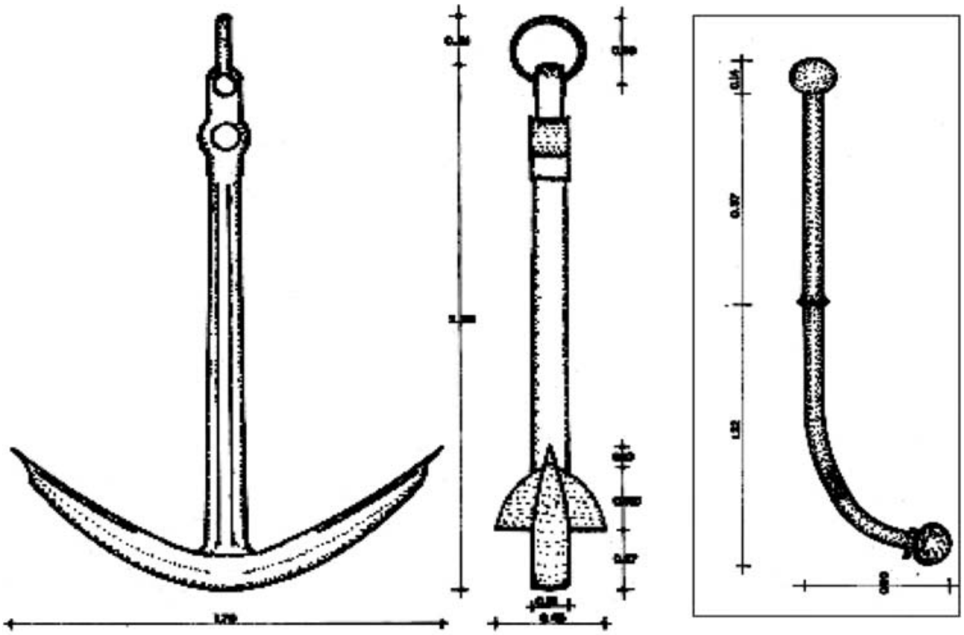


Fig. 1 Nineteenth century anchor and stock. Maximum dimensions of the anchor are 2.59 m in height and 1.79 m in width. The stock is a separate piece with irregular diameter due to corrosion but averaging 10 cm. The maximum dimension of the stock is 2.33 m. The stock was broken due to manipulation and this event allowed sampling. (Drawings provided by Centro INAH Campeche)

while others corresponded to the metallic core only. Due to the limited amount of disposable archaeological samples, it was decided in most experiments to first test modern material samples (blank) polished or artificially pre-corroded, instead of the actual archaeological material. Unlike modern iron, ancient wrought iron has low carbon content. In this sense, low carbon steel has a reasonably near composition to wrought iron. That is why the chosen blank was ASTM 615 Grade 40. The composition of the blank samples is: 0.31% max C, 0.15–0.30% Si, 0.70–1.10% Mn, 0.45% max P, 0.45% max S, and 0.012% max N. The use of blank samples was not intended to replicate the ancient wrought iron material. Instead, blank samples provided a preliminary test before risking the valuable archaeological coupons.

Therefore, four main kinds of samples were used in the different experiments: modern polished (blank), modern precorroded, archaeological polished, and archaeological with corrosion products. According to their characteristics, samples were cleaned in the standard way. Electrical connections to the electrodes were achieved by soldering to the tip after corrosion products were ground off. The exposed metal and surrounding area was sealed off with a thick layer of epoxy resin. Afterward, they were stored over silica gel prior to use. In the case of the precorroded samples, this was achieved by hanging them above a 10% HCl solution for 2 weeks, simulating marine atmosphere conditions.

2.2 Metallography

The archaeological coupons were embedded in Bakelite and polished with 600, 800, and 1,200 papers. The coupons were attacked with *Nital* solution (10% HNO_3 and 90% methanol) during 30 s. The attacked coupons were observed using optical microscopy (5×, 10×, 50×). Since these coupons belong to the stock and not to the body of the anchor, in situ metallography of the main body was performed, in order to compare both metallic cores and determine if they were equal or not. This was done by polishing a 1 cm^2 surface in the main body, attacking it with the Nital solution and then obtaining the print using acetone and an acetate paper.

2.3 Measurements

All measurements reported here were made using a three-electrode arrangement, and potentials were quoted versus saturated copper sulphate reference electrode. The potential of a $Cu/CuSO_4$ electrode is +0.314 with respect of the Standard Hydrogen Electrode (SHE). Electrochemical values are all corrected for the area of the working electrode, although the areas of the archaeological electrodes were estimated from the apparent surface, the true surface of the electrode being unknown.

2.3.1 *Potential measurement*

Modern coupons were prepared and used in two ways: polished surface and precorroded surface. Precorrosion was meant to simulate the marine corrosion products of the actual archaeological material. Therefore, these coupons were pre-corroded with HCl vapors for 2 weeks. Both kinds of coupons were immersed in unstirred saturated alkaline solutions (NaOH, KOH, and Na_2CO_3). A fourth saturated solution of sodium sesquicarbonate ($Na_2CO_3 \cdot NaHCO_3$ equimolar) was also tested. The high concentrations in the solutions provided alkaline conditions which are known to give protection to the ferrous materials. Potential measurements as a function of time were made for 60 days or more.

2.3.2 *Polarization*

Electrochemical polarization curve measurements were made with a scan rate of 10 mV min^{-1}. Pre-corroded and polished modern coupons were immersed in each of the four unstirred solutions. The stabilization period before polarization was 60 min. Cathodic branch was performed first starting from the rest potential down to a cathodic potential of −1,200 mV. The aim of this experiment was to establish the cathodic reduction regions in the pre-corroded coupons. After this, the anodic branch was performed starting from the rest potential and up to approximately to an anodic potential of 1,200 mV. Passivation regions and passive current were expected to be established with this procedure. After testing the modern coupons, the electrochemical behavior of a polished archaeological sample and a modern polished sample were compared in a similar way.

In order to remove free chlorides from corrosion products present in the surface, consecutive potentiostatic cathodic polarization was performed and cathodic reduction current as a function of time was obtained for both, modern pre-corroded and archaeological samples. Samples were immersed in sesquicarbonate saturated solution and polarized at −1,300 mV which is the reduction potential established from polarization curves. During this period AC impedance measurements and solution conductivity measurements as a function of time were obtained. This was done to remove free chlorides and the reduction of some species [17]. The reduction current of a modern polished sample was established, and afterwards reduction current measurements as a function of time were performed in precorroded and archaeological samples till reaching the established cathodic reduction current for the modern polished sample.

After the chlorides removal was done, a passive layer was formed. The samples were immersed in KOH solution and potentiostatic anodic polarization was performed at the passive potential previously established through the polarization curves (480 mV). Passive current as a function of time was obtained until the passive current diminished to a minimum steady passive state.

2.3.3 *AC impedance*

The electrochemical impedance spectroscopy (EIS) used a sine wave. Classical three-electrode arrangement experimental set-up was used for EIS tests. The electrochemical signals were monitored by AC Gill potentiostat connected to a personal computer. The equipment was previously calibrated in accordance with the standard [18]. An alternating current (AC) signal, with a 20 mV amplitude signal, was applied in the frequency range of 50 mHz to 10 kHz, every day for several days. Immediately, the specimens were immersed to the solution in the glass cell. A copper/copper sulphate electrode connected through a lugging probe was used as a reference electrode and graphite as counter electrode. These measurements were performed during chloride removal, passivation tests and to evaluate different conservation measurements and their evolution in time.

2.3.4 *Electrochemical noise*

The experimental set up used for electrochemical noise data recording, consists of a working electrode, the tip of a platinum wire and the reference electrode. The potential and current electrochemical noise fluctuations were obtained at a sampling rate of 1 point per second for 2,048 s every day, for several (50) days using an auto-ZRA ACM instrument connected to a personal computer. Electrochemical potential and current noise measurements were recorded simultaneously. Removal of the DC trend from the raw noise data was the first step in the noise analysis. To accomplish this, a least squared fitting was used. The DC trend has to be eliminated because this could originate large distortions in subsequent statistical noise data processing [19].

The noise resistance (R_{noise}) was obtained by statistical analysis of voltage and current noise records as follows:

$$R_{\text{noise}} = \frac{\sigma[V(\Delta t)]}{\sigma[i(\Delta t)]} \qquad (1)$$

where $\sigma[V(\Delta t)]$ is the standard deviation of voltage noise in time interval Δt and $\sigma[i(\Delta t)]$ is the standard deviation of current noise in the same time interval Δt. The noise resistance as a function of time was obtained and presented. These measurements were performed to evaluate different conservation measurements and their evolution in time.

2.4 Conservation measures and evaluation

2.4.1 *Rust converter and coating evaluation*

After the electrochemical chloride removal and passivation procedures, a conservation oriented experiment was designed. The goal was to create coupons subject to different treatments or combination of treatments to compare their protective capacity. Besides the electrochemical treatments (dechlorination and passivation), two standard conservation procedures were introduced in the experiments: Rust converters and use of coatings.

2.4.1.1 Rust converters Atmospheric corrosion studies evaluating rust converters established experimentally that a solution of H_3PO_4 38.6% (w–w) saturated with $Al(OH)_3$ can reduce corrosion rate in two to four decades as rust converter pretreatment, prior to coating application. Optimal rust conversion conditions were reached after 5 months [20, 21]. This solution was prepared and the rust converter procedure applied to an archaeological sample with original corrosion products layer.

2.4.1.2 Coating Some coupons were covered with a commercial polyurethane aliphatic coating. This coating was chosen because it is transparent, colorless, and recommended for iron and steel protection. A single application was performed. It is important to clarify that the intention was not to evaluate the coating itself, but its interaction with other previous treatments was examined.

Table 1 summarizes the different combinations of treatments performed for the creation of coupons with several conditions as follows:

Table 1 Description of treatments for each kind of coupon

Coupons	Electrochemical dechlorination	Electrochemical passivation	Rust converter treatment	Polyurethane aliphatic coating
A			¤	
B	¤	¤		
C				¤
D	¤	¤		¤
E			¤	¤

A. Treated with rust converter. Only rust converter treatment is employed. Partial dechlorination was done by rinsing in water. This simulates one of the average conservation protocols usually practiced for major artifacts in the field.
B. Electrochemically passivated in KOH. Only electrochemical procedures are employed. This was done to evaluate the protective capacity of the passivation layer created previously through electrochemical techniques.
C. Untreated and polyurethane coating. Once again, a conservation procedure in field conditions is reproduced. Partial dechlorination was done rinsing in water.
D. Electrochemically passivated in KOH and polyurethane coating. This combination employed the proposed improved conservation method combining electrochemical procedures and standard coating.
E. Treated with rust converter and polyurethane coating. This is a second proposed conservation improvement method employing rust converter and standard coating.

All the coupons were immersed in Na_2SO_4 1 M and 3% in weight of sodium chloride solution to simulate aggressive environment during 45 days. Electrochemical Impedance Spectroscopy and Electrochemical Noise measurements were performed to determine resistance to corrosion.

3 Results and discussion

3.1 Metallography

Figure 2 shows the metallography of the archaeological iron from the stock. The microstructure corresponds to that of a wrought iron: a continual phase of ferrite grains, with non-metallic inclusions, and elongated slag fibers following the direction of the deformation. The same microstructure was observed in the main body of the anchor. Afterwards, electrochemical procedures and evaluation were applied to both stock and main body.

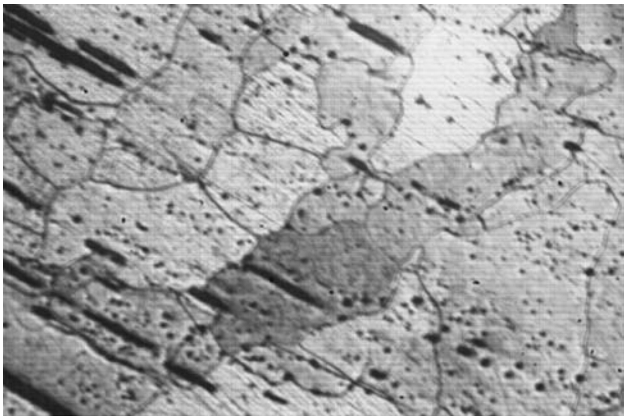


Fig. 2 Metallography of the case study ×10. Absences of deformation lines in both structures suggest that the material was heated above 800 °C and shaped mechanically

3.2 Electrochemical tests

Figure 3 presents the free corrosion potential as a function of time for polished samples (blank) and pre-corroded modern samples simulating the archaeological anchor material immersed under the sea or in the seabed. These samples were immersed in different solutions to establish the behavior of the material and to observe the ennoblement of the free corrosion potential. It can be seen in Fig. 3 that the noblest potential obtained corresponds to the KOH solution, also observed in the blank sample. This suggests that under this immersion condition the iron samples develop a passivation film over the surface, in accordance with the potential-pH diagram for alkaline conditions. Similar behaviors were observed for the blank sample and the pre-corroded sample immersed in different solutions. Because of these values, both KOH and sesquicarbonate solutions were expected to bring adequate protection as it was confirmed in further tests.

Figure 4a and b shows the polarization curves for the different modern samples (polished and precorroded) immersed in different proposed electrolytes, namely; sesquicarbonate, KOH, NaOH, and Na_2CO3 solutions.

Once again, from Fig. 4a, KOH and sesquicarbonate solutions showed more protective values both for pre-corroded and polished coupons. Reduction region was established at −1,300 mV and passive regions were clearly observed in both solutions.

To establish the electrochemical parameters, especially the passive region, Fig. 4 presents the polarization curves for the polished blank sample and the polished archaeological sample immersed in KOH (pH > 12). This assures the passivating conditions for iron according to pH-potential diagrams [22]. The similarity in the electrochemical behavior of both materials can be observed. The corrosion potential is around −500 mV and the anodic region is followed by a passive region which decreases the current density as the potential becomes more positive up to 500 mV. The archaeological sample showed a slightly higher passive current but the general behavior was considered similar. This reasonably general equivalent electrochemical behavior validated the further use of a modern material, despite the obvious metallurgical differences. It is important to establish that this comparison is not considered a replication of archaeological material. It only means that general mechanisms were tested in the blank coupons instead of risking the limited archaeological material (Fig. 5).

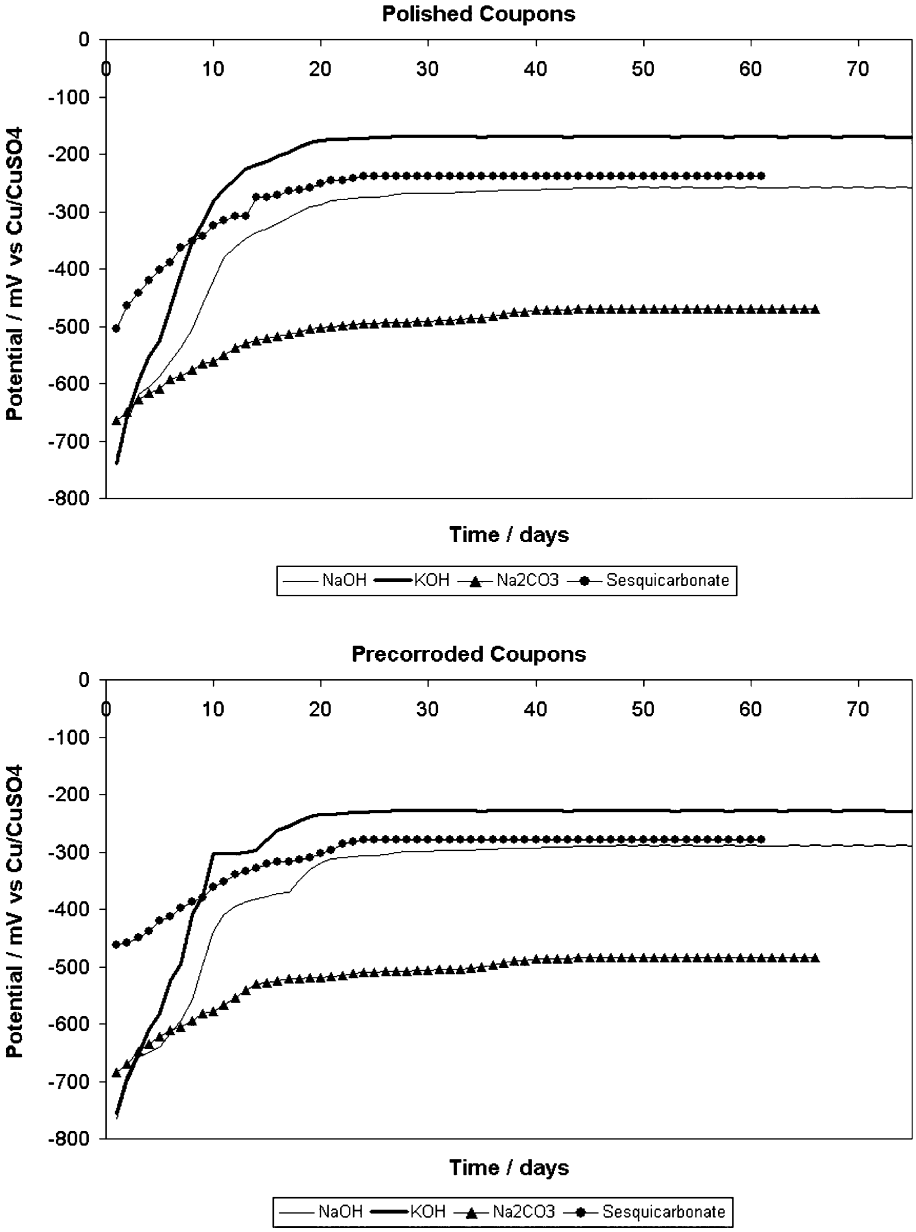


Fig. 3 Free corrosion potential vs time showing higher protective values for KOH saturated solution both in polished and pre-corroded modern coupons

In order to remove chloride ions from the corrosion products and to favor their reduction process it was decided to polarize cathodically the iron samples in sesquicarbonate solution as suggested in the literature [12]. To follow the process as a function of immersion time, electrochemical spectroscopy impedance technique was used and compared to conductivity solution measurements made during the test. This experiment was done using a polished blank sample as reference. A pre-corroded modern steel coupon was compared with an archaeological sample with original corrosion products.

Figure 6 presents the solution resistance obtained from electrochemical impedance measurements under cathodic reduction potential (−1,300 mV) in the current limit region. The measurements were taken every 3 h for 36 h. A cathodic impedance reduction was observed. For the polished blank sample, the solution resistance remained almost the same since chloride species are not available. In both samples, pre-corroded modern steel and archaeological, the solution resistance decreased its value suggesting that free chloride ions were moved into the solution due to cathodic polarization. The solution resistance for the pre-corroded modern coupon changed from 8.14 to 7.57 Ω cm^2 while the solution resistance for the archaeological sample changed from 9.67 to 5.82 Ω cm^2. The greater change observed for the archaeological coupon is easily explained due to the thicker corrosion products layer prone to accumulate more chlorides. Figure 7 presents the conductivity solution measurements in sesquicarbonate solution, where an increase in the solution conductivity measured was

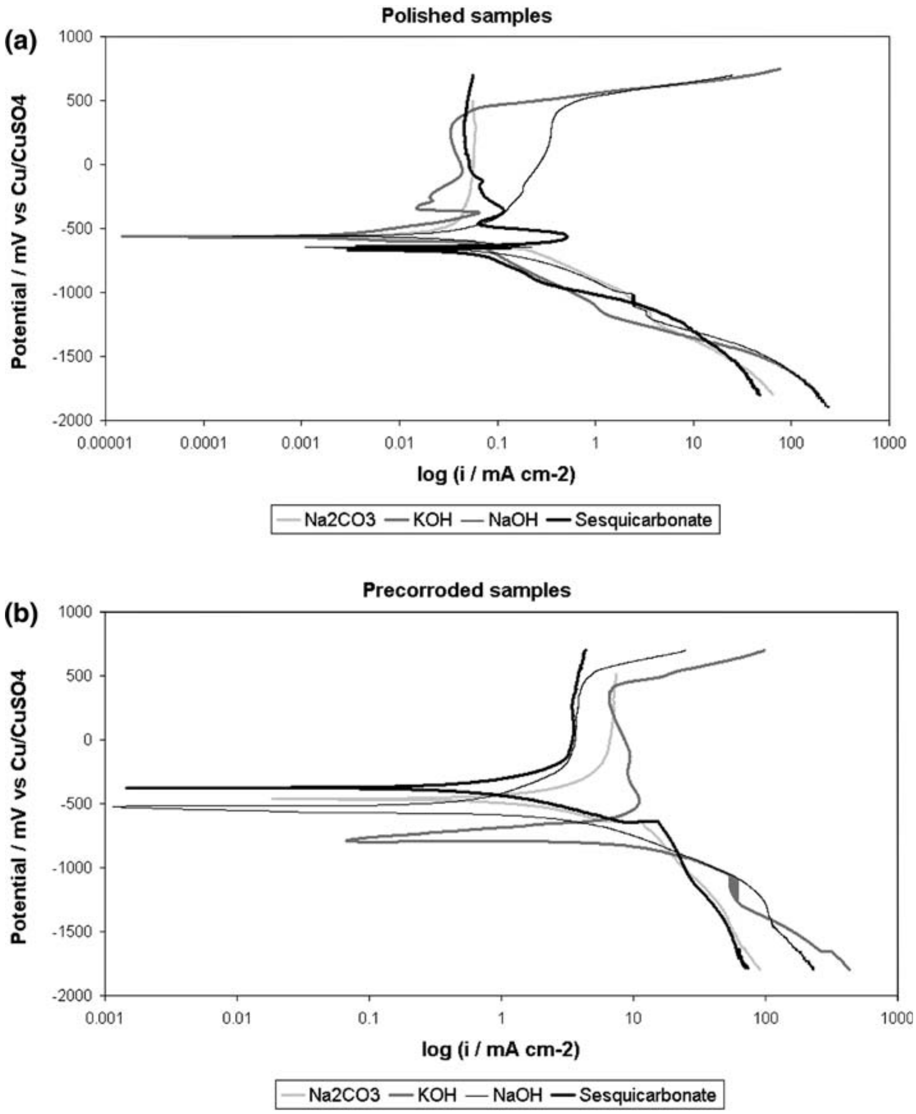


Fig. 4 Polarization curves for blank and precorroded modern steel samples in saturated sesquicarbonate solution

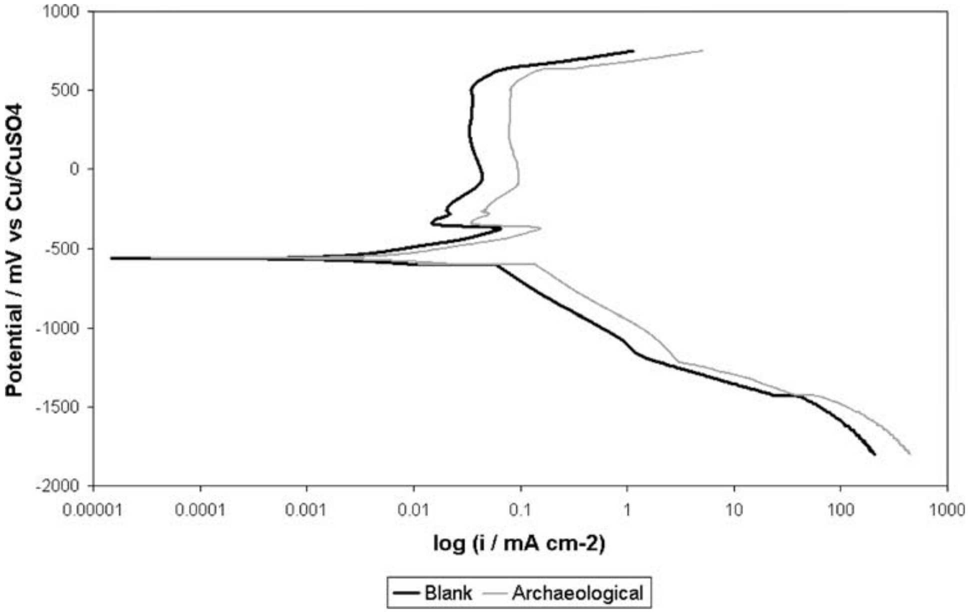


Fig. 5 Polarization curves for modern (*blank*) and archaeological polished steel samples in KOH saturated aqueous solution. General electrochemical behavior was considered reasonably equivalent

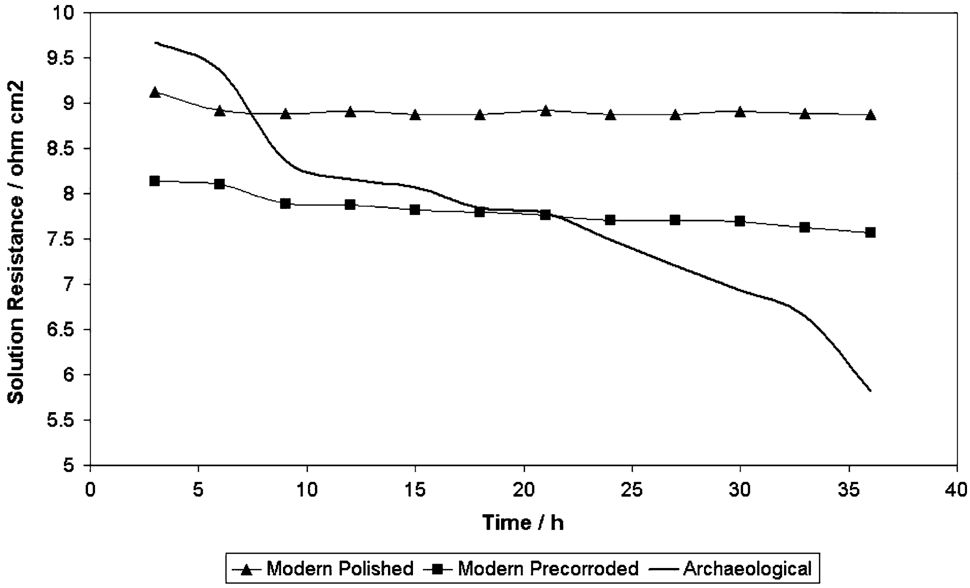


Fig. 6 Solution resistance obtained from electrochemical impedance under cathodic polarization (−1,300 mV vs. Cu/$CuSO_4$) in sodium sesquicarbonate saturated solution. The archaeological sample showed the major change in time compared to modern coupons

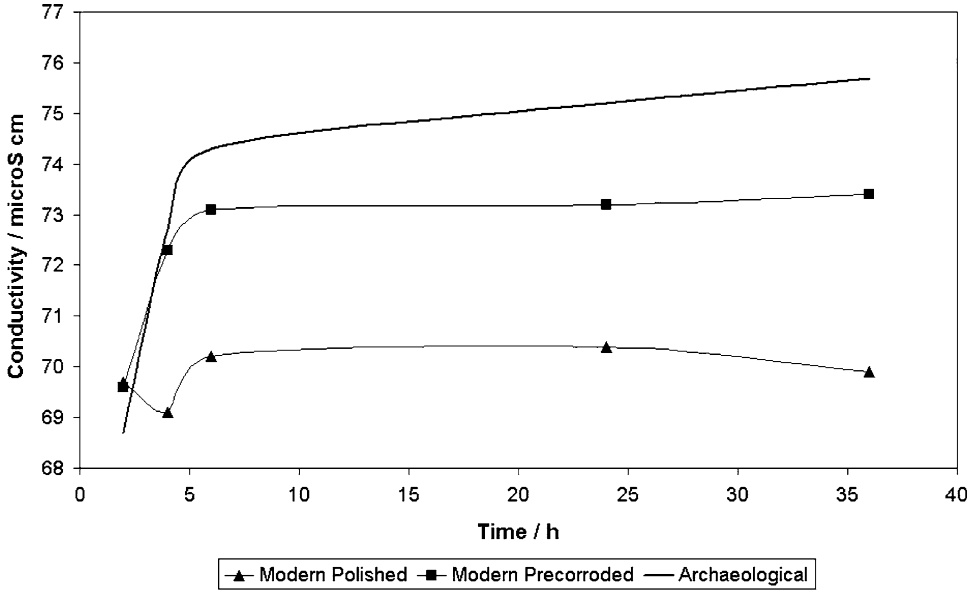


Fig. 7 Solution conductivity increasing as chlorides was removed. Measurements made in sodium sesquicarbonate saturated solution during 36 h

observed. These values are coherent with the impedance results obtained, during the 36 h of the test. Also, the cathodic current density as a function of time under potentiostatic conditions were obtained, and presented in Fig. 8. After a few hours the current density diminished and reached the steady state conditions, comparable to the one obtained for the blank sample. The interrelated results of the three tests suggest that some species were reduced and free chlorides were expelled from the surface, as expected.

In order to passivate the samples after corrosion products reduction and chloride removal, the coupons were polarized in the passive corrosion potential region (480 mV vs. Cu/$CuSO_4$) in KOH during 48 h. Figure 9 presents the passive current density as a function of time for all the samples. It can be seen that the passive current density decreases as a function of time as the passive layer was formed. The passive current density tends to reach similar values obtained from the polarization curves for the passive region. The archaeological coupon resulted very active and formed a passive layer that diminished the current values notoriously compared with the modern coupons. This behavior can be interpreted as positive in conservation terms.

3.3 Rust converter and coating evaluation

After 5 months, the untreated archaeological sample was compared with a treated with rust converter one using optical microscopy. This visual examination showed that color changed from reddish to black as seen in Fig. 10. The

Fig. 8 Current density as a function of time under cathodic polarization (−1,300 mV Cu/$CuSO_4$) in sodium sesquicarbonate saturated solution; 36 h

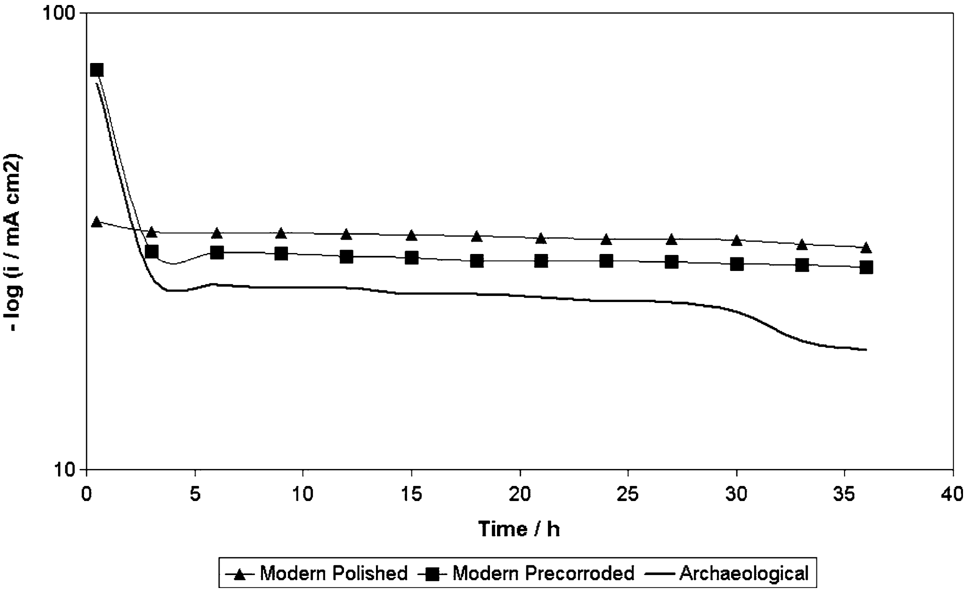


Fig. 9 Passivation current density (mA cm^{-2})

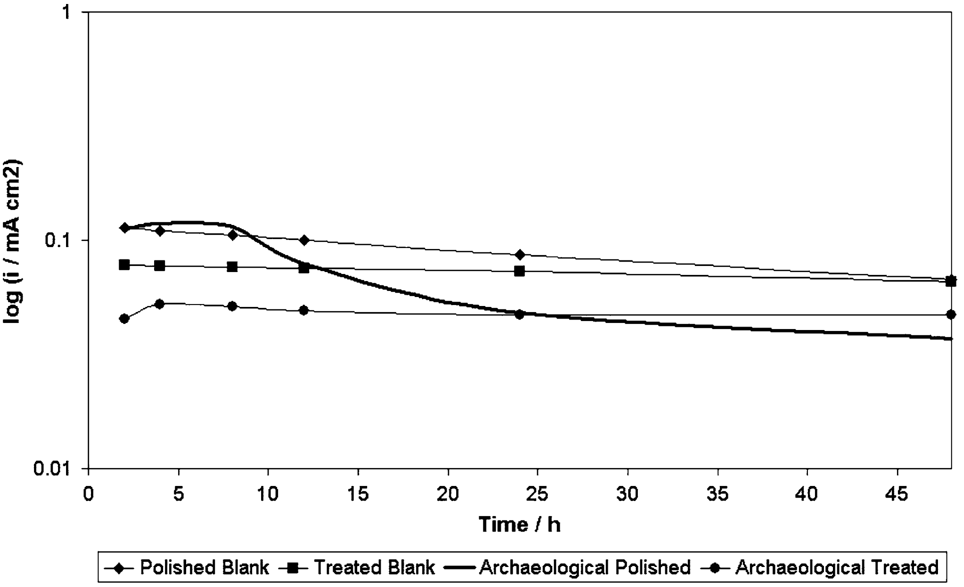
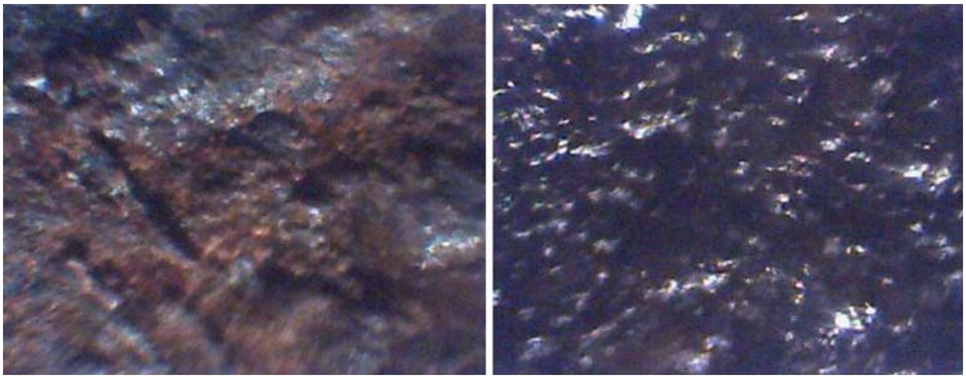


Fig. 10 Untreated corrosion products (*left*) compared with corrosion products treated with rust converter during 5 months (*right*) ×10



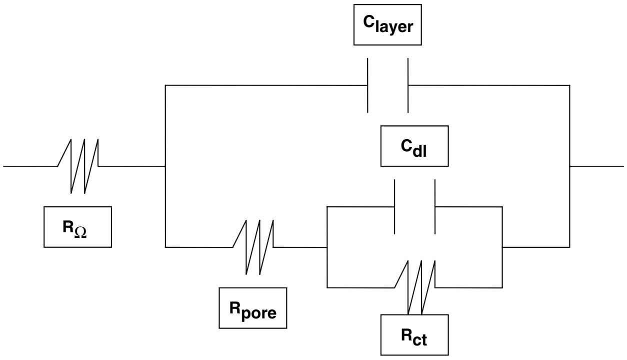


Fig. 11 Equivalent circuit of the system. R_Ω represents the resistance of the solution. R_{pore} is the corrosion products layer resistance and represents the resistance of areas in the corrosion products layer with more rapid solution uptake. R_{ct} is the charge transfer resistance representing the corrosion resistance of the metal which is in parallel to the capacitance of the double layer C_{dl}. C_{layer} is the capacitance of the corrosion products layer

treated corrosion products also became more adherent to the metallic surface. From an aesthetical point of view, the treated surface presented a more uniform aspect.

The corrosion behavior of all the archaeological coupons designed with different surface treatments were analyzed through Electrochemical Impedance Spectroscopy and Electrochemical Noise. Figure 11 shows the equivalent circuit used for modeling the obtained behavior. In this way despite that some coupons actually present one interface (metal-corrosion products) and some present two (metal-corrosion products—and corrosion products-coating), all of them were evaluated as a metal-treatment system electrical circuit [23]. The Nyquist plots present a capacitive charge transfer semicircle and a low frequency diffusion/mass transfer type behavior controlling the reaction kinetics. As time of immersion increases, the semicircle changes its diameter and the low frequency region bends toward the real axis, suggesting a change from diffusion process to mass transfer adsorption reaction through the corrosion products and/or coating layers (see Fig. 12; Table 2).

As a resume, Fig. 13 shows Rp values obtained from impedance as function of time, reflecting the different degree of protection obtained under each condition. The Rp values were obtained from the Nyquist diagrams using geometry of the second semicircle. The data was compared with the plateau values from the Bode diagrams using the value of the low frequency plateau minus the value of the other plateaus [$\mathrm{Rp} = Z_t - (R_\Omega + R_{pore})$]. It is clear that coupons without polyurethane coating (passivated and rust conversion treatment) corroded more than those with coating. Even more important, the electrochemically treated and the rust converter treated samples with coating, clearly resisted more than the average conservation procedure observed in the locality, represented by the untreated with polyurethane coating sample. Therefore, it is possible to suggest the effectiveness of the proposed treatments for conservation purposes. Corrosion rates were calculated using the Rp values and the Stern–Geary equation. The constant B was obtained with the values of Tafel slopes from potentiodynamic polarization. The results are shown in Table 3.

Table 2 Main frequencies for Nyquist diagrams

Nyquist diagram	R_Ω (kHz)	$R_\Omega + R_{pore}$ (kHz)	$R_\Omega + R_{pore} + R_{ct}$ (Hz)
3 days	10	5	50
24 days	10	2	150
45 days	10	3	300

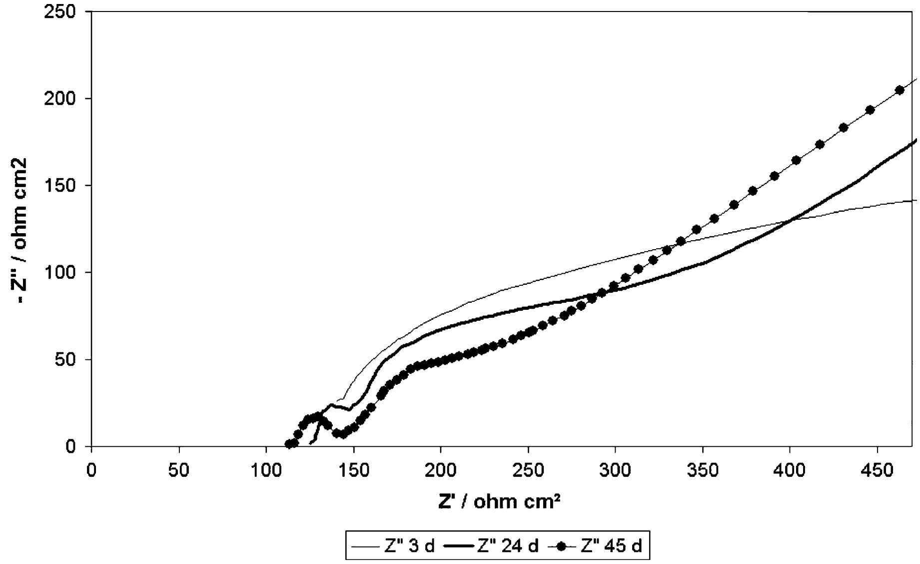


Fig. 12 Nyquist diagrams for untreated with coating sample

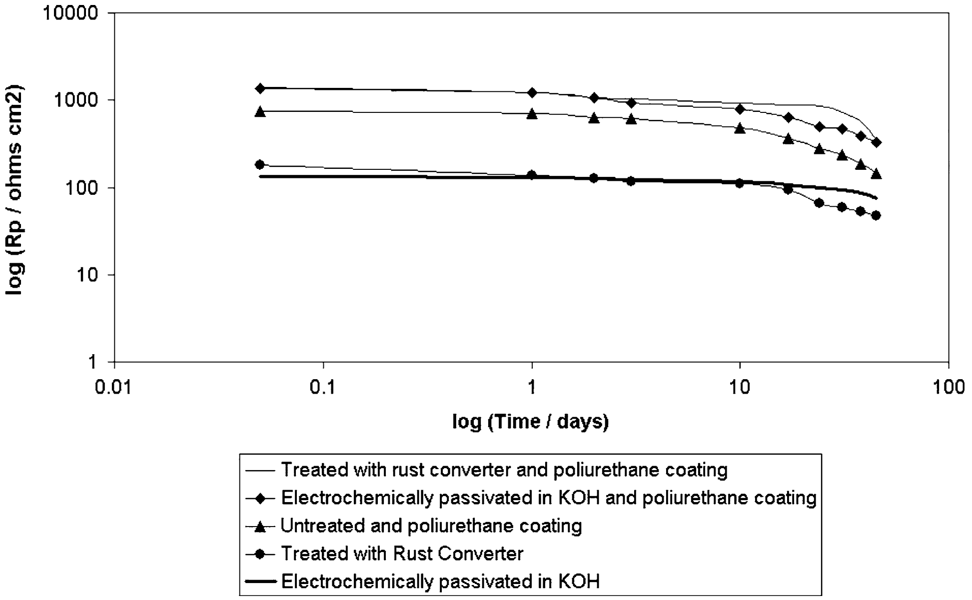


Fig. 13 Rp obtained with electrochemical impedance spectroscopy

Table 3 Corrosion rates obtained by EIS

Time (days) – corrosion rate (mm year^{-1})	Treated with rust converter and polyurethane coating	Electrochemically passivated in KOH and polyurethane coating	Untreated and polyurethane coating	Treated with rust converter	Electrochemically passivated in KOH
0.04	0.013	0.019	0.013	0.027	0.007
1	0.042	0.023	0.113	0.087	0.008
2	0.048	0.033	0.118	0.108	0.056
3	0.052	0.068	0.127	0.115	0.138
10	0.123	0.080	0.147	0.182	0.145
17	0.216	0.090	0.172	0.249	0.159
24	0.218	0.119	0.290	0.450	0.490
31	0.220	0.190	0.393	0.648	0.817
38	0.230	0.230	0.450	1.100	0.870
45	0.249	0.247	0.509	1.545	0.926

Finally, Fig. 14 presents the noise resistance Rn as a function of time, obtained from electrochemical noise measurements. The values obtained present similar trends as the total impedance values, corroborating the electrochemical impedance values observed and presented before, where the highest noise resistance values obtained, ranked the samples with coatings on top.

4 Conclusions

Metallographic characterization showed that both, anchor body and stock were manufactured with the same material, namely typical Nineteenth Century wrought iron. No deformation lines were observed suggesting shaping at high temperatures. In archaeological terms, a manufacture process has been identified. Additionally, these materials characterizations represent information which can be compared with those from other artifacts and eventually broaden the comprehension of metallurgy evolution.

The free corrosion potential test showed that the materials, modern and archaeological, present a more noble potential immersed in KOH and sesquicarbonate compared to other solutions. This implies that both solutions provide more protection in conservation terms. This was corroborated by potentiostatic polarization (polarization curves). Additionally, the materials clearly showed passivation zones in the anodic region. Reduction zone was established at −1,300 mV.

Cathodical polarization near the limit current value (−1,300 mV) in KOH and sesquicarbonate removed free chlorides and reduce some species ions according to impedance and conductivity measures. At the same time, this process cleaned the surfaces which were passivated

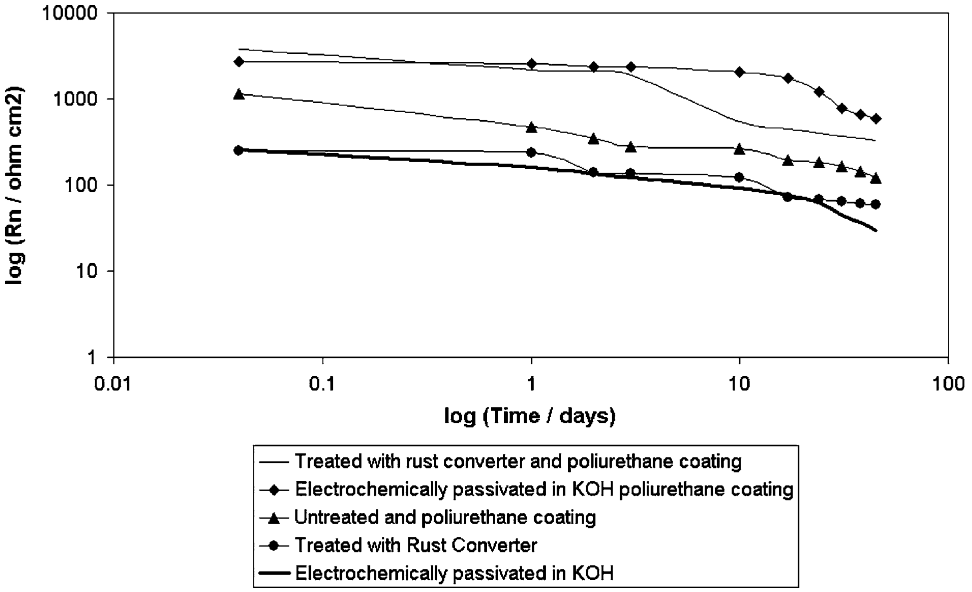


Fig. 14 Rn obtained with electrochemical noise

with a film created through anodic polarization in KOH. Coating performance was improved preparing the surface through electrochemical techniques as well as by using a rust converter.

In methodological conservation terms and according to the aim of this work, a routine can be proposed for iron archaeological artifacts extracted from the seabed and/or exposed to marine atmosphere. Artifacts can be cleaned and freed from chlorides by immersion in sesquicarbonate solution and cathodically polarized at −1,300 mV. The needed time may vary from artifact to artifact, however, stabilization of current density values becomes a parameter to establish duration of treatment. After this, an acceptable efficient protective film can be produced polarizing anodically in the passivation zone. This surface preparation improves the further performances of coatings. However, the exact values and times may change according to each case. Similar modern materials may be used at blank before treating the actual artifacts.

References

1. Hjelm-Hansen N, Van Lanschot J, Szalakay CD, Turgoose S (1993) Corros Sci 35:767
2. Turgoose S (1982) Conservation of Iron. National Maritime Museum Monograph No. 53:1
3. MacLeod ID (1981) Electroanal Chem 118:291
4. North NA (1982) Stud Conserv 27:75
5. North NA (1976) Int J Naut Archaeol 5:253
6. Argo J (1981) Stud Conserv 26:42
7. Gilberg MR, Seeley NJ (1981) Stud Conserv 26:50
8. Turgoose S (1982) Stud Conserv 27:97
9. Knight B (1982) Conservation of Iron. National Maritime Museum Monograph No. 53:50
10. Morcillo M (1999) Progr Org Coat 36:137
11. Castellote M, Andrade C, Alonso C (2000) Cem Concr Res 30:615
12. Andrade C, Castellote M, Sarría J, Alonso C (1999) Mater Struct 32:427
13. Rinuy A and Schweizer F (1982) Conservation of Iron. National Maritime Museum Monograph No. 53:44
14. North NA and Pearson C (1975) ICOM Committee for Conservation, 4th Triennial Meeting, 75/13/3:1
15. Gilberg MR, Seeley NJ (1982) Stud Conserv 27:180
16. Oddy WA, Hughes MJ (1970) Stud Conserv 15:83
17. Andrade C, Díaz I, Helene P, Romero de Carruyo A, Tronconis de Rincón O (1998) Manual de inspección, evaluación y diagnóstico de corrosión en estructuras de hormigón armado. CYTED, Venezuela
18. ASTM G 106 – 89 (2004) Standard practice for verification of algorithm and equipment for electrochemical impedance measurements
19. Uruchurtu-Chavarín J, Malo M (1997) Trends Corros Res 2:49
20. Almeida E, Santos D, Uruchurtu J (1999) Progr Org Coat 37:131
21. Almeida E, Mariaca L, Rodriguez A, Uruchurtu-Chavarín J, Veloz MA (1996) In: Kearns JR, Scully JR, Roberge PR et al (eds) Electrochemical noise measurements for corrosion applications. American Society for Testing and Materials Publication, Montreal Quebec
22. Pourbaix M (1966) Atlas of electrochemical equilibria in aqueous solution. Pergamon Press, Lomdon
23. Murray JN, Hack HP (1991) Corrosion 47:480