

Electrolytic stabilisation of a marine composite porthole and its framework

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Abstract

Often the treatment of a composite metal artefact that cannot be dismantled requires a compromise as regards the conservation of all the materials involved. While treating one material it is difficult to assure that the others are not affected. With this paper we propose a methodology for the safe electrolytic stabilisation of a marine composite metal artefact (a porthole and its framework) constituted mainly of graphitized grey cast iron elements associated with other materials such as copper, glass, rubber and paint. The methodology comprises the determination of the parameters of treatment with metal coupons simulating the behaviour of real artefacts, together with the use of basic electrolytic equipments that are normally available in a conservation laboratory.

After the description and condition survey of the artefact, the coupons are used to determine the ranges of electrolytic parameters that are suitable for the stabilisation of the artefact in a non buffered 1% (w/v) NaNO₃ solution. Emphasis is put on the stability of the pH during the stabilisation process to assure the protection of all the materials.

Keywords: Composite metal artefacts, electrolytic techniques, stabilisation in neutral solution, monitoring of parameters, transfer of knowledge

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1. Introduction

This project started while the two authors were both staying in Finland, at the Conservation Department of EVTEK, Institute of Art and Design, Vantaa. This institute had previously established a Master's degree in the conservation of marine artefacts, and during that period a conservation laboratory had been specifically equipped to treat artefacts recovered from the sea.

One aspect of the project consisted in a transfer of knowledge on electrolytic techniques used for the conservation of metal artefacts. Some artefacts could be easily treated since protocols already existed (stabilisation of iron or copper based artefacts). Others needed a new approach that required the participation of both a conservator and a conservation scientist. Composite artefacts are typical of these complex objects that raise either ethical issues such as the need to treat the artefact as a whole (without dismantling it) and/or technical ones such as the conservation of the original materials (that might get damaged during the treatment). The porthole and its framework provided to the institute by Mr. Mika Pohjonen, private diver, were challenging enough to be considered as case studies within this transfer of knowledge exercise. To date only a few composite artefacts have been treated

with electrolytic techniques (Degrigny 2001, Monluçon & Lacoudre 1988). Most of the time these composites contain waterlogged organic materials and specific protocols have to be developed (Degrigny & Guilminot 98, Guilminot 2000). In this project we wanted to concentrate on non-waterlogged materials for which the literature is more scarce.

1.1 Description of the artefact

The object was raised out of *the Rhein* shipwreck, which had sunk in 1958 in the Baltic Sea near Utó (West-coast of Finland), and was left exposed outdoors for some years without any treatment. The object is made of two parts. A round porthole and its round framework consisting mainly of grey cast iron. In the porthole broken pieces of the glass window are held in their original position in between the cast iron frame and a cast copper based alloy rim that are screwed together. A rubber isolating ring is located in a channel of the cast iron porthole, next to the rim. White paint is evident on the grey cast iron elements of the porthole under the powdery orange-brown crust and the copper based alloy rim is covered with a black paint. Both the porthole and its framework have two closing systems and a hinge. Parts of these closing systems are made of a copper based alloy. Figure 1 shows the front and rear of the porthole with all the different elements mentioned above.



Figure 1: General view of the porthole (a/ front side and b/ rear)

1.2 Condition report

When they were transferred to the conservation laboratory the two artefacts were covered with a very thin marine crust. The grey cast iron elements were heavily graphitized. The graphitization phenomenon corresponds to the corrosion of the metal that leaves behind a material that respects the original shape of the artefact but is made of iron corrosion products maintained together by graphite lamellas. Some fragments came off and many cracks were visible. The “weeping” phenomenon that is characteristic of active corrosion (Selwyn 1999) could be observed on the surface of iron based elements. The extent of the corrosion on some elements had provoked the breakage of the hinge and fastening systems. Abrasion in the marine environment further eroded the surface of artefacts. Copper based alloy elements in contact with iron elements were in a good condition due to the cathodic protection provided by the iron. The white paint covering some grey cast iron elements was loose due to past and current corrosion processes (during immersion in the sea and after exposure to the atmosphere). The rubber on the porthole was cracked due to its storage outdoors. UV-light, oxygen and ozone favour the deterioration of rubber (Lemaire 1993). The glass on the

porthole was broken in its whole thickness. Only the edge was preserved. This condition survey clearly shows that the artefacts had suffered not only during their immersion of 40 years in the sea but after their recovery as well due to the exposure to new environmental conditions that accelerated further the alteration processes (North and MacLeod 1987, North 1987).

1.3 The research methodology

Both the porthole and its framework are composite materials that cannot be dismantled without damage. These artefacts had then to be treated as a whole. Due to their long exposure to the marine environment and the sensitivity of iron artefacts to chlorides we suspected the presence of aggressive chloride species within their structure. The observation of the “weeping” phenomenon on the surface of the grey cast iron confirmed this hypothesis. Exposing the porthole and its framework to a humidity chamber could be used to check whether these chlorides were active but since the risk of further damage was very high we decided to perform stabilisation treatment immediately.

Simple immersion of the artefacts can be used to extract aggressive chloride species, however, electrolytic processes are much more efficient (Degrigny & Lacoudre 1999). This is particularly interesting in the case of composite artefacts where associated materials such as glass, rubber and paint might get damaged during the process. Basic electrolytic equipments (power supplies, voltmeters and reference electrodes) available in the marine conservation laboratory at EVTEK, Institute of Art and Design were considered. Alkaline solutions (pH>9) used commonly to stabilise iron based materials could not be considered since the silica network of the glass may be damaged (Newton 1997), and paint layers are very sensitive to high pH. A neutral and safe solution for the associated materials had to be considered. The use of a buffer is a common practice to maintain a stable pH. Since we wanted to prevent any electrochemical activity that we would not be able to control we decided to use a non-buffered solution, with a chemical that had a minimal electrochemical activity. A preliminary study was needed to see how the system would react with time while applying a cathodic potential to the object in the selected neutral solution .

2. Experimental conditions

The treatment parameters were first determined using sacrificial coupons. Historic wrought iron nails (19th–20th century) were used because their microstructure made of ferrite is much simpler than the one of grey cast iron. To study the effect of different surface conditions on the electrolytic parameters the nails were either completely stripped of corrosion products (“bare” nails thoroughly polished), slightly cleaned (“slightly polished” nails where the powdery corrosion products were removed by polishing, leaving behind the magnetite (Fe₃O₄) layer), or left untouched (“corroded” nails presenting a double layer of red-brown and powdery oxyhydroxide (FeO(OH)) and black magnetite). No metallographic study of the nails was performed since historic wrought nails are usually made of ferrite and the amount of slag inclusions is rather low.

The nails were connected to the negative terminal of a power supply (Mascot, type 719) while a 316 stainless steel grid anode was connected to the positive terminal. A 1% (w/v) NaNO₃ neutral solution (pH=6.5-7) was chosen as an electrolyte because it is not active electrochemically in the range of potentials between the hydrogen bubbling on the cathode and oxygen bubbling on the anode. Furthermore, it should not have any effect on the associated materials. We tried in each experiment to expose a similar metal surface to the volume of solution considered (300ml). Velleman DVM 92 multimeters and an Ag-AgCl

Metrohm reference electrode (200 mV/SHE) were used to measure cathodic and anodic potentials and an Ecoscan pH-electrode to measure the pH.

Each experiment started by the monitoring of E_{corr} of iron nails in the NaNO_3 solution. Once E_{corr} value was stable the polarization could start. The surface of the nails changed during polarization and the “bare” and “slightly polished” nails had to be re-polished before each new experiment to recover the original appearance and obtain reproducible conditions. The “corroded” nails were only used once. Stainless steel anodes were cleaned before each polarization by immersion of a few hours in a 7% (v/v) HNO_3 solution.

Both the anodic and cathodic potentials were measured during the polarization and monitored with time. The monitoring of the anodic potential is rather unusual but since the stainless steel was systematically cleaned after each experiment we could use it as a reference material compared to the cathode that presented a different surface in each case. Measurements of the anodic and cathodic potentials were performed before measuring the pH. When using a non-buffered solution, stirring is needed to have a correct pH value but stirring modifies cathodic and anodic readings and when performed manually makes their monitoring with time rather difficult.

Experiments were performed on a 24 hour basis. This long period was chosen to simulate the treatment of real artefacts when treatment would proceed during days (where intervention is possible) and nights (where no intervention is possible). When an increase of pH was noted diluted HNO_3 (3.5 or 7% (v/v)) drops were added to recover a neutral pH. Therefore only the concentration of nitrates was increased. When a decrease of pH was measured diluted NaOH (10% (w/v)) drops were added increasing the concentration of the non active sodium cation.

Once the influence of the electrolytic parameters was better understood we could start the electrolytic stabilisation of the porthole and its framework and monitor the same electrolytic parameters as before with time.

3. Results

3.1 Simple immersion of iron coupons in neutral solution

Figure 2 shows E_{corr} measurements for all wrought iron nails whatever the surface preparation. The decrease of E_{corr} versus time occurs systematically and indicates the corrosion of the “bare” metal combined (or not) with the transformation of the corrosion layers (“slightly polished” or “corroded” nails). This experiment clearly shows that without any cathodic polarization iron artefacts, with or without corrosion layers, do corrode in a neutral 1% (w/v) NaNO_3 solution.

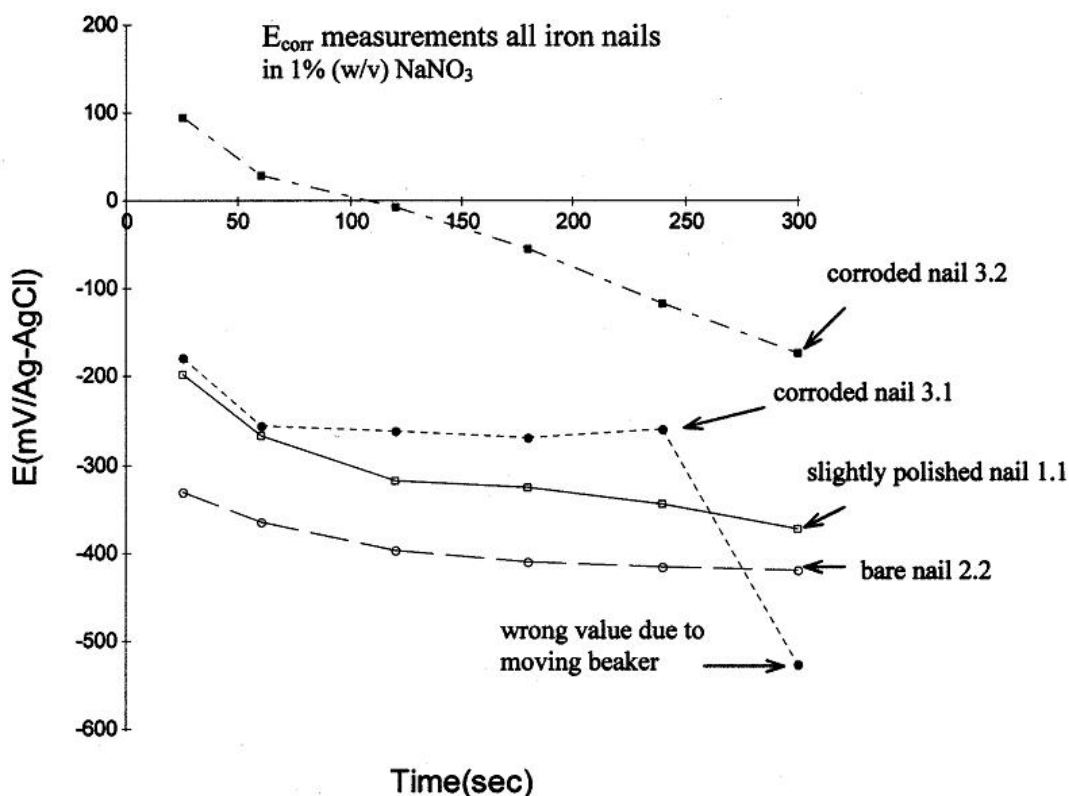


Figure 2: E_{corr} monitoring for “bare”, “slightly polished” and “corroded” iron nails in 1% (w/v) NaNO_3 solution

“Corroded” nails have the higher initial potentials due to the presence of a thick corrosion layer that passivates the surface. The potentials obtained after five minutes of immersion (0 to -250 mV/SHE, Standard Hydrogen Electrode=0V) and inserted in a simplified Pourbaix diagram for Fe, confirm that in the present conditions the coupons should corrode (Figure 3). The stabilisation of iron based materials in neutral solution requires cathodic polarization to work.

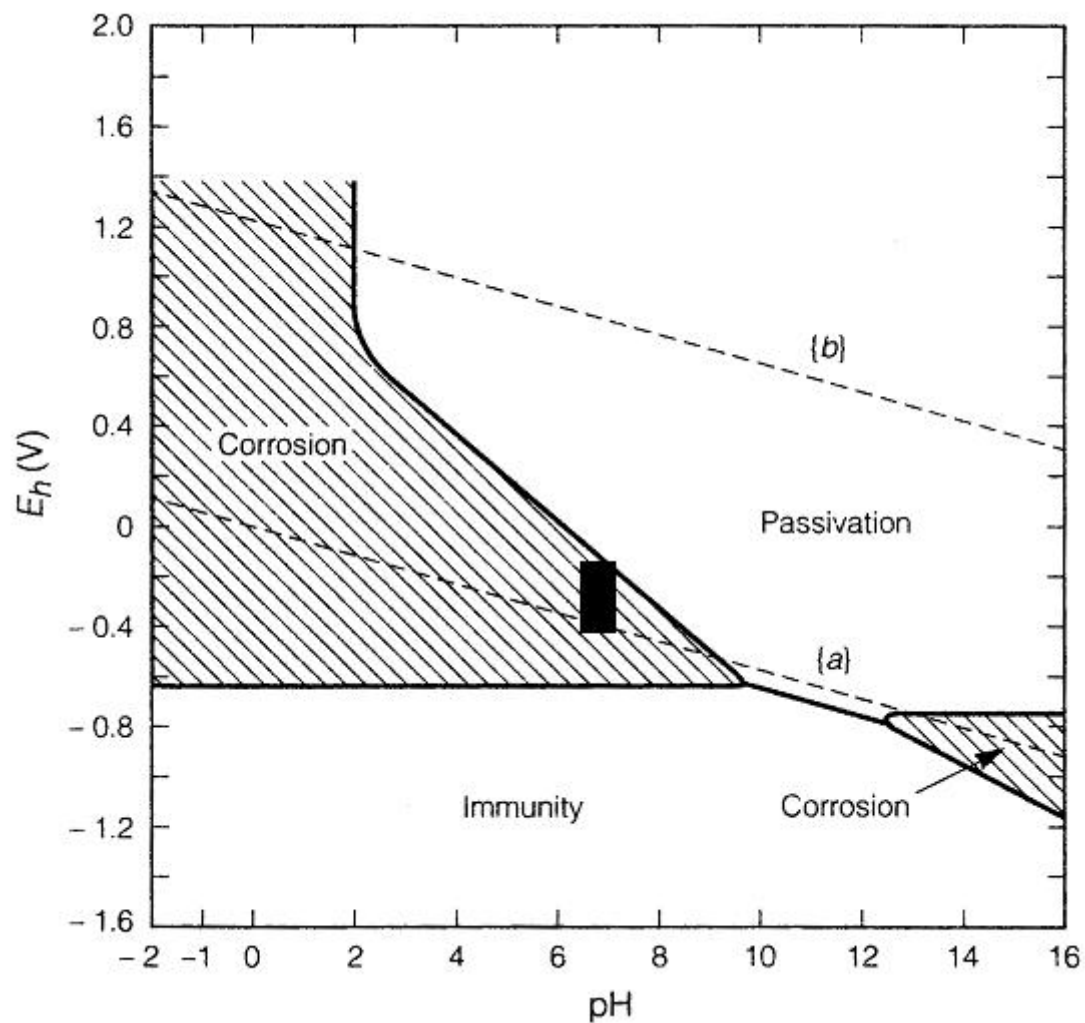


Figure 3: Simplified Pourbaix diagram for iron (concentration of Fe species $<10^{-6}$ M) (from Pourbaix 1963). The black area corresponds to the E_{corr} values for “bare”, “slightly polished” and “corroded” iron nails after five minutes of immersion in a neutral 1% (w/v) NaNO_3 solution

3.2 Polarization on artificial coupons

Polarization was started on “bare” nails at a cathodic potential of $-1000 \text{ mV}_{/\text{Ag-Ag/Cl}}$ ($E_{\text{Ag-AgCl}}=0.2\text{V/SHE}$) (Figure 4). This potential is close to the one used for the treatment of another composite artefact in a neutral KNO_3 solution (Degriigny 2001).

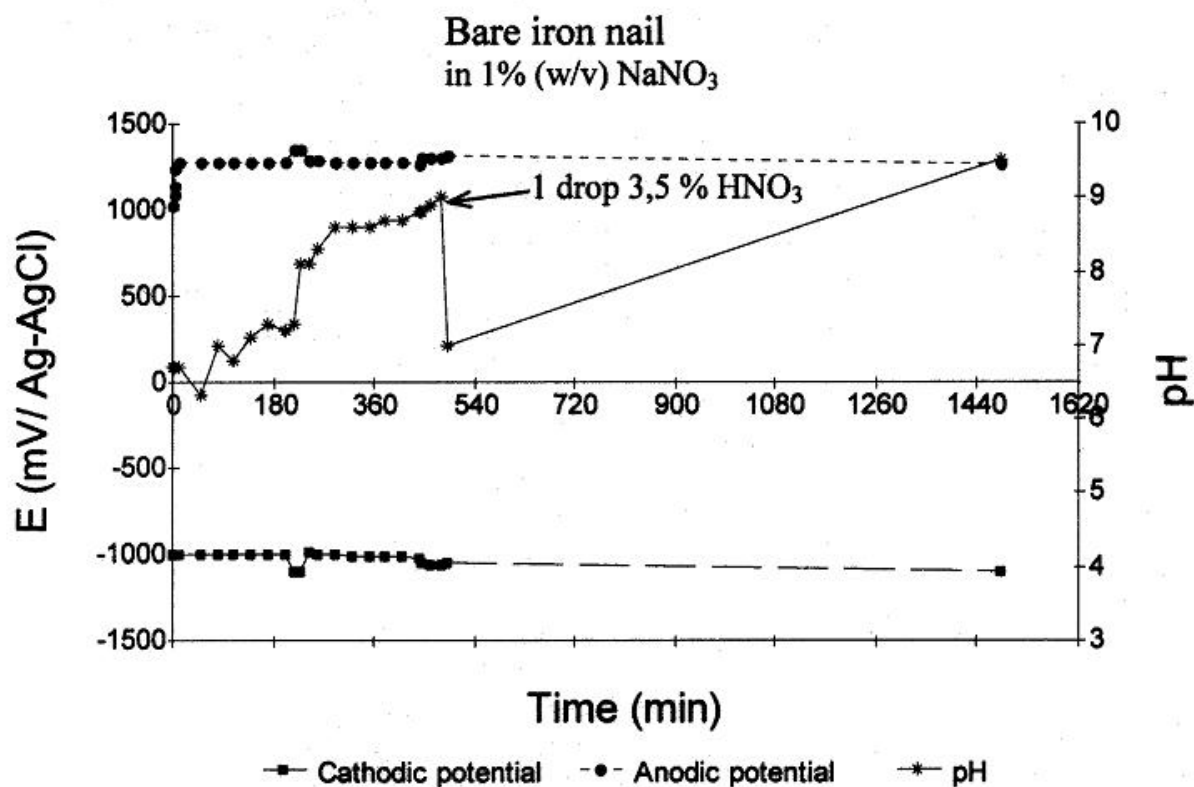


Figure4: Polarization of a “bare” iron nail at $-1000 \text{ mV}/_{\text{Ag-AgCl}}$ in 1% (w/v) NaNO₃ solution. A drop of HNO₃ 3.5%(v/v) is added after eight hours. No modification of the solution could be performed afterwards (night)

Values indicated in Figure 4 are average values (around $1300 \text{ mV}/_{\text{Ag-AgCl}}$ at the anode). The pH increases slowly but constantly during the first three hours of the experiment. During two short periods while applying a more negative cathodic potential of $-1100 \text{ mV}/_{\text{Ag-AgCl}}$ (after 215 minutes) and $-1050 \text{ mV}/_{\text{Ag-AgCl}}$ (after 445 minutes) the pH increased faster than during polarization at $-1000 \text{ mV}/_{\text{Ag-AgCl}}$. A decrease in the cathodic potential has a direct influence on the anodic potential (immediate increase). Because the pH had increased to 9.0 after eight hours a drop of HNO₃ (3.5% (v/v)) was added to recover a neutral pH of 7.0. During the night when the system cannot be modified and drops cannot be added the pH increased again and the next morning a pH of 9.5 was measured.

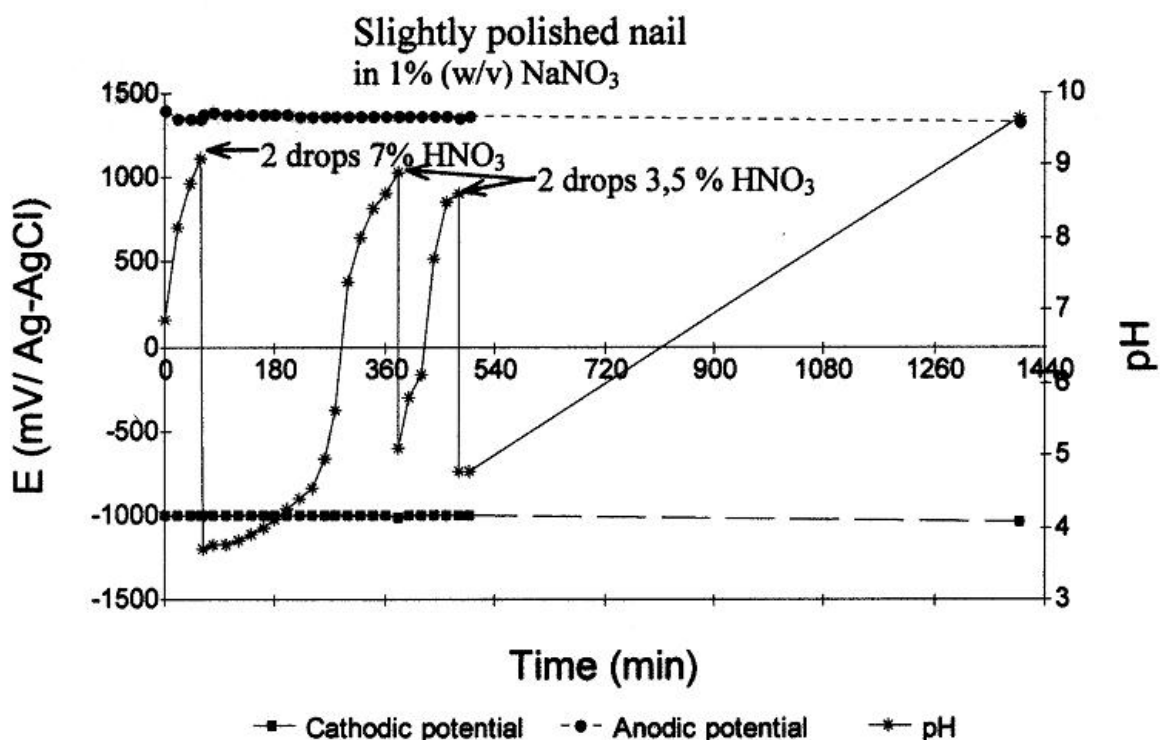


Figure 5: Polarization of a “slightly polished” iron nail at $-1000 \text{ mV}/_{\text{Ag-AgCl}}$ in 1% (w/v) NaNO₃ solution

When moving from the “bare” nails to the “slightly polished” ones, similar results were obtained although the increase of pH was much faster (Figure 5). Drops of HNO₃ (even more concentrated than before) had to be added three times in eight hours to recover a neutral pH. Although the cathodic potential is the same as in the previous experiment the anodic potential was a bit higher, around $+1400 \text{ mV}/_{\text{Ag-AgCl}}$. The application of a lower cathodic potential (around $-800\text{-}900 \text{ mV}/_{\text{Ag-AgCl}}$) tended to slow down the increase of pH as indicated on Figure 6 but the extraction of chlorides is then less effective. Another way to monitor the treatment was by applying a constant anodic potential. This approach seems to be much more reliable practically, since the stainless steel is clean of any corrosion product and the surface is reproducible from one experiment to another.

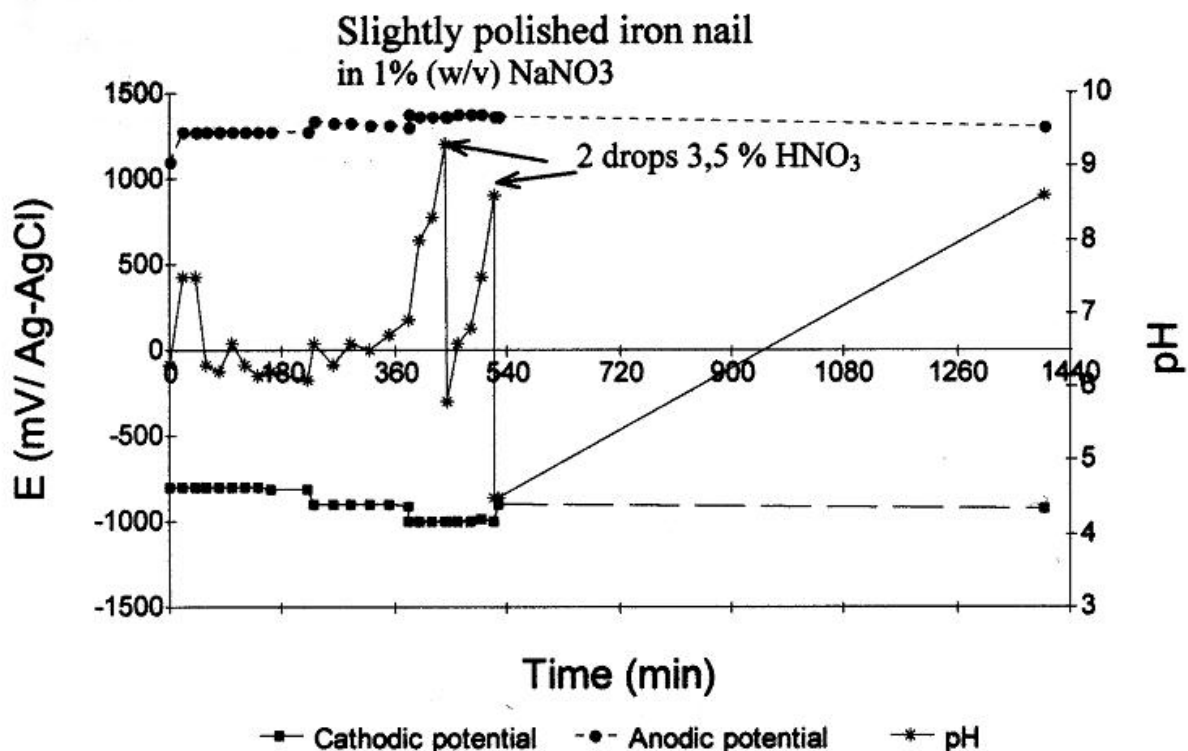


Figure 6: Polarization at different cathodic potentials and effect on the pH values in 1% (w/v) NaNO₃ solution

Based on the previous observation, preliminary experiments on the “corroded” nails were performed at $-850 \text{ mV}_{/\text{Ag-AgCl}}$ (Figure 7). The anodic potential increased during the day from $+695 \text{ mV}_{/\text{Ag-AgCl}}$ to $+1000 \text{ mV}_{/\text{Ag-AgCl}}$. This value is much less positive than the one obtained with a “slightly polished” nail (Figures 4 and 5). There was no modification of pH during the first day and night. The cathodic potential was then decreased until bubbling of Hydrogen could be observed ($-1465 \text{ mV}_{/\text{Ag-AgCl}}$). Hydrogen bubbling can damage the object and must always be avoided. At that value the anodic potential was around $+1300 \text{ mV}_{/\text{Ag-AgCl}}$. By decreasing the cathodic potential back to $-1100 \text{ mV}_{/\text{Ag-AgCl}}$ (anodic potential of $1200 \text{ mV}_{/\text{Ag-AgCl}}$) the pH remained stable. A stable pH at this cathodic potential was not observed with the “bare” and “slightly polished” nails.

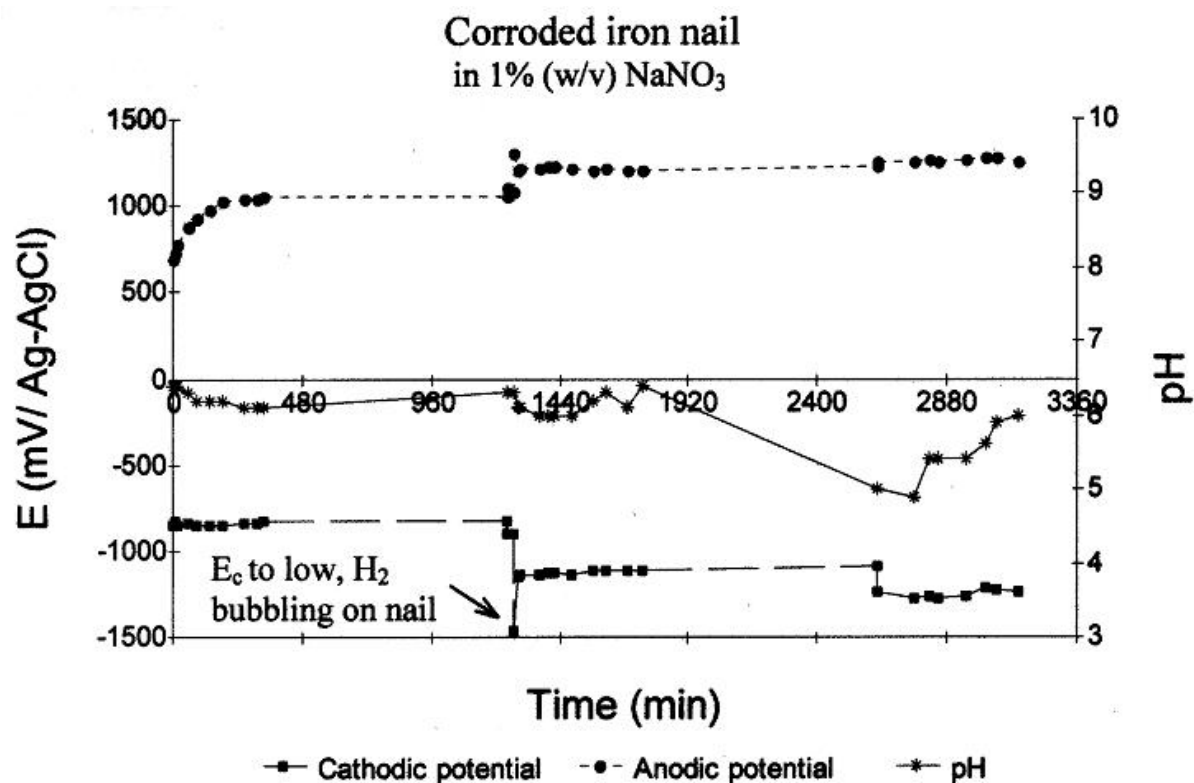


Figure 7: Polarization of a “corroded” iron nail at $-850 \text{ mV}_{/\text{Ag-AgCl}}$ in 1% (w/v) NaNO_3 solution and effect of a modification of the cathodic potential on the other electrolytic parameters

The experiment was left for another night during which the pH decreased from 6.4 to 5.0. The decrease of pH can be as dangerous for the object as the increase of pH. The next morning the anodic potential was increased from $+1200 \text{ mV}_{/\text{Ag-AgCl}}$ to $+1250 \text{ mV}_{/\text{Ag-AgCl}}$. As expected from the previous experiments the pH increased slowly during the day from 5.0 to pH 6.0. The cathodic potential was around $-1200 \text{ mV}_{/\text{Ag-AgCl}}$.

As a conclusion from these preliminary tests, the “corroded” nail reacted differently than the “bare” and the “slightly polished” iron nails. With the “bare” and “slightly polished” nails the pH increased when decreasing the cathodic potential below a certain value (around -800 - $850 \text{ mV}_{/\text{Ag-AgCl}}$). With the “corroded” nail a decrease of pH was observed in the same range of potentials (at least down to $-1100 \text{ mV}_{/\text{Ag-AgCl}}$). The use of a non-buffered solution implies the requirement of constant correction of the pH either with drops of diluted HNO_3 or NaOH solutions. During the night when the system cannot be modified a less negative cathodic potential (and as a consequence a less positive anodic potential) should be applied to maintain the pH constant, or at least limit its modification. Finally the monitoring of the polarization through the anodic potential appears as an interesting approach when dealing with corroded artefacts.

Without plotting voltammetric curves ($I=f(E)$) both on the nails and the stainless steel it is difficult to tell which electrochemical reactions are really occurring when the potential of the nails is decreased or the potential of the stainless steel grid increased, and to find an explanation for the modification of pH. Hypothesis might be made as regards the reactions that are favoured. For “bare” and “slightly polished” nails the reduction of oxygen

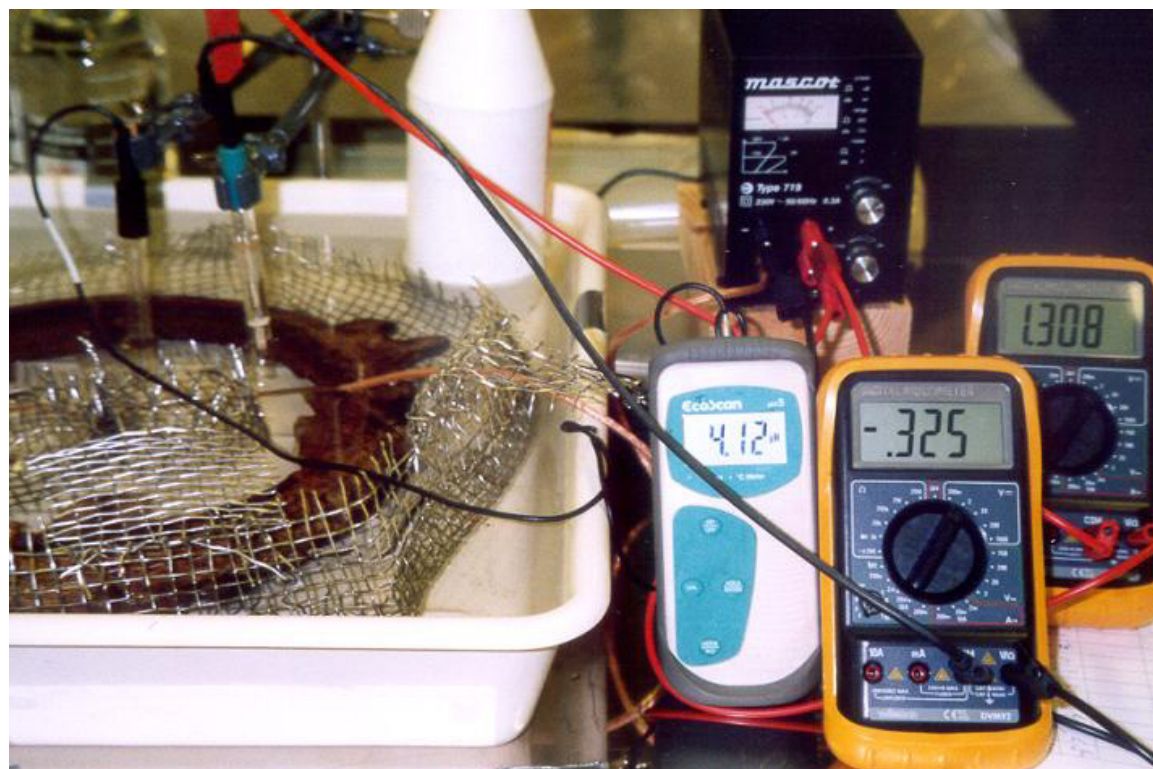
dissolved in the solution ($2\text{H}_2\text{O} + \text{O}_{2d} + 4\text{e}^- \rightarrow 4\text{OH}^-$) accompanied by the reduction of oxyhydroxide and Oxide layers ($3\text{FeO}(\text{OH}) + \text{e}^- \rightarrow \text{Fe}_3\text{O}_4 + \text{H}_2\text{O} + \text{OH}^-$ and $\text{Fe}_3\text{O}_4 + 4\text{H}_2\text{O} + 8\text{e}^- \rightarrow 3\text{Fe} + 8\text{OH}^-$) are obviously favoured and this is reflected by the pH increase. Further investigation are required to find a reason for the decrease of pH when corroded nails are polarized.

3.3 Stabilisation of the porthole and its framework

Since similar stabilisation treatments were applied on the two artefacts only the porthole will be described in the following.

The treatment started by a mechanical cleaning of the corrosion layers on the grey cast iron elements. The objective was to remove any physical barrier to the extraction of chloride species. It was performed both with a scalpel and a hand held rotary drill with a soft abrasive wheel. Powdery oxyhydroxides layers could be removed but attention was paid not to damage the remaining, but loose, white paint covering the graphitized surface of the grey cast iron elements. No consolidation of the paint was performed at that stage.

Due to the extensive corrosion of the cast iron elements the electrical contact was made on the copper based rim. The wire was attached on a pre-polished area with “Araldite” rapid set epoxy adhesive. Stainless steel grids were placed in and outside the porthole. Through a bridge a good connection was made between the inner and the outside anode. The object together with the anode were placed in a plastic tank. To limit the volume of electrolyte to the minimum (to be able to better follow up the extraction of chlorides) spare containers were placed in the tank. The porthole was connected to the negative (-) terminal of the power supply and the stainless steel anode to the positive (+) terminal. The 1% (w/v) NaNO_3 solution was prepared with deionised water and to avoid its evaporation and pollution a plastic sheet covered the tank. The pH of the electrolyte at the beginning of the stabilisation treatment was 6.2 (the device is shown in Figure 8).



a/ monitoring of the electrolytic parameters



b/ covering of the tank with a polyethene sheet. Note the presence of spare containers in the tank to limit to the minimum the volume of the electrolyte

Figure 8: General device for the cathodic polarization of the porthole.

Based on the results obtained with “corroded nails”, an anodic potential value of $+1300 \text{ mV}_{/\text{Ag-AgCl}}$ was applied at the anode (Figure 9). The cathodic potential measured on the porthole was less negative than with the iron nail experiments: $-300 \text{ mV}_{/\text{Ag-AgCl}}$. The penetration of the solution within the graphitic corrosion layer expelled air bubbles that were trapped on the metal surface. These were not hydrogen bubbles since the applied cathodic potential was too low. The pH decreased very fast, in one hour from 6.2 to 4.8. No increase of pH could be obtained by increasing the anodic potential (to $+1400 \text{ mV}_{/\text{Ag-AgCl}}$). The contrary happened: the pH became even lower; it decreased from 4.8 to 4.1. So the anodic potential was left at $+1300 \text{ mV}_{/\text{Ag-AgCl}}$. The next morning the pH was 4.0 and the cathodic potential was $-371 \text{ mV}_{/\text{Ag-AgCl}}$. In order to speed up the chloride extraction, the anodic potential was once again increased to $+1400 \text{ mV}_{/\text{Ag-AgCl}}$ but both the cathodic potential and the pH decreased, the latter from 4.0 to 3.6.

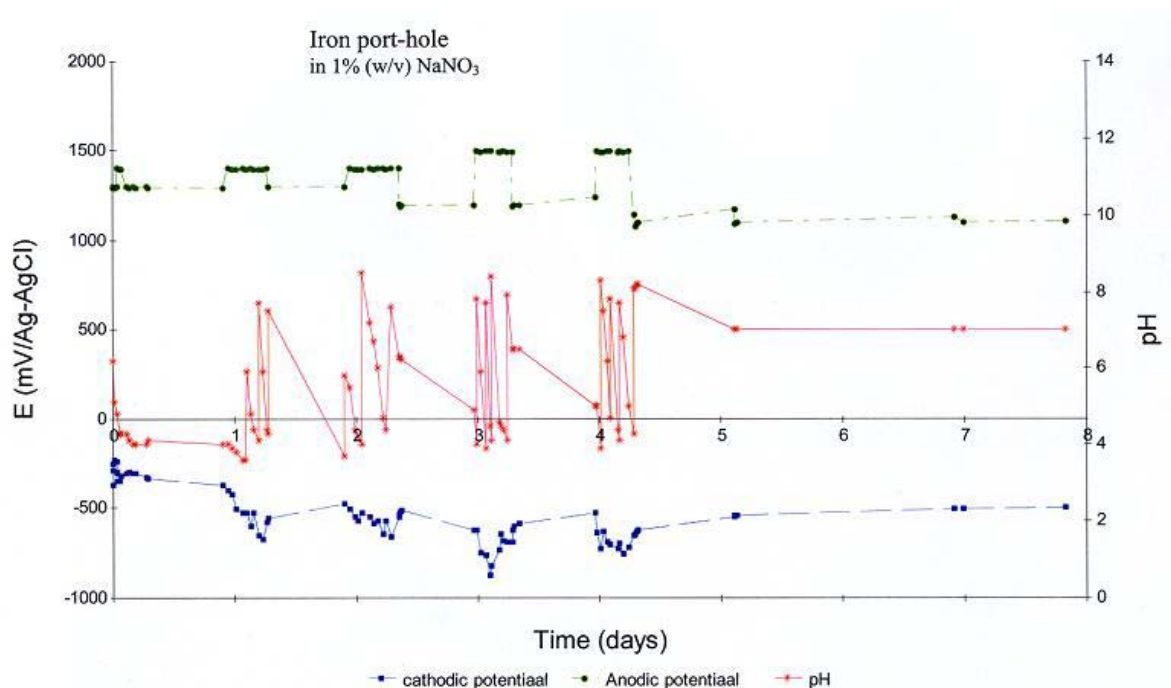
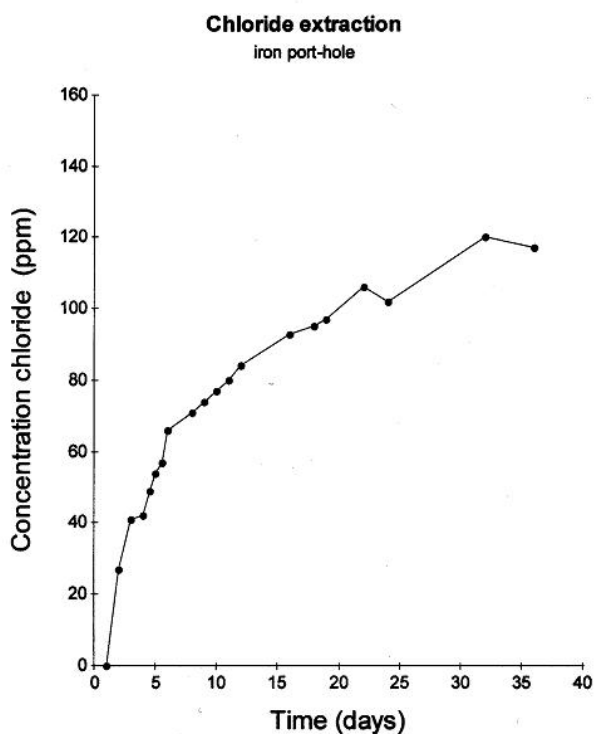


Figure 9: Monitoring of the electrolytic parameters during the cathodic polarization of the porthole in neutral NaNO_3 solution.. Drops of NaOH were constantly added during days 2, 3, 4 and 5 to maintain a constant neutral pH

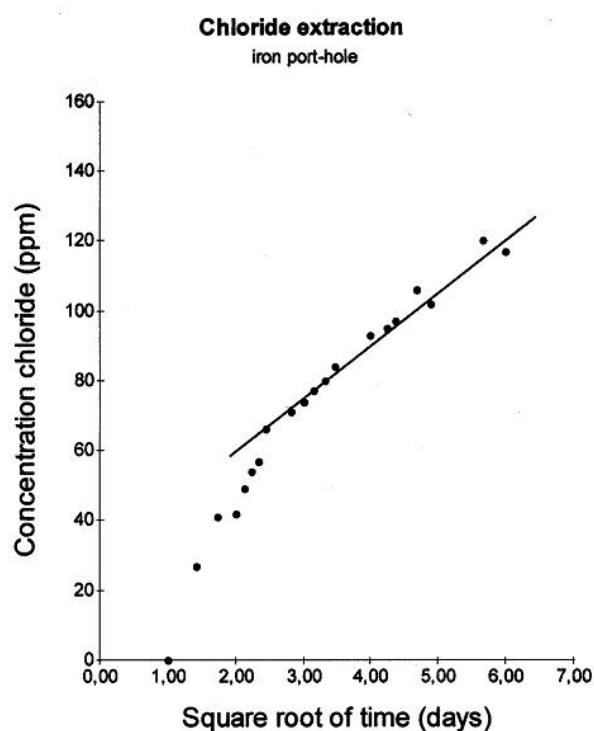
The solution had turned yellow due to the corrosion of the stainless steel, and iron species formed deposits at the bottom of the tank. Some also formed on the artefact but could be easily brushed away. Three millilitres of diluted NaOH solution (10%) was added to increase the pH from 3.6 to 5.9. Stirring is very important while adding NaOH to obtain an equal pH for the whole electrolyte. The process of adding NaOH was repeated every two hours during the day. The volume of NaOH that was needed to get a higher pH was different each time. Before we left the object during the night we decreased the anodic potential to $+1300 \text{ mV}_{/\text{Ag-AgCl}}$.

The process of increasing the anodic potential to a more positive value during the day, decreasing the anodic potential to a less positive value during the night and controlling the pH by adding a few millilitres of NaOH was repeated during the next five days. Since the increase of the anodic potential did not increase the pH it was decided to decrease the anodic potential to see how the pH would react. The first two nights an anodic potential of $+1300 \text{ mV}_{/\text{Ag-AgCl}}$ was applied. The third and the fourth night an anodic potential of $+1200 \text{ mV}_{/\text{Ag-AgCl}}$. During the fifth night an anodic potential of $+1100 \text{ mV}_{/\text{Ag-AgCl}}$ was applied and a stable pH was finally obtained.

Adding a few millilitres of NaOH every two hours is time consuming and therefore not a realistic way to treat an artefact in a conservation laboratory. Also it is unknown whether this rapid fluctuation of pH (between 4 and 8) can damage the object as well. Therefore it was decided to continue the treatment at an anodic potential of $+1100 \text{ mV}_{/\text{Ag-AgCl}}$ for which the cathodic potential measured on the porthole was $-500 \text{ mV}_{/\text{Ag-AgCl}}$.



a/



b/

Figure 10: Monitoring of the extraction of chlorides versus time (days) (a/) and the square room of time (b/) for the porthole, under cathodic polarization in neutral NaNO_3 solution

During the treatment the extraction of chlorides was monitored. The extraction was faster during the first six days as can be seen in Figure 10a, when the applied cathodic potential was more negative. When plotting the values versus the square root of the time (Figure 10b) we realised that the values obtained were eventually on a straight line. The extraction of chlorides appears to be following a diffusion law.

Due to the sudden closure of the conservation laboratory, the treatment had unfortunately to be interrupted and we did not have the chance to follow up the end of the stabilisation process.

4. Conclusion

We have shown through this project that it is possible to stabilise a marine metal composite artefact constituted mainly of grey cast iron, in a neutral and non-buffered solution with basic electrolytic equipment: a power supply, a reference and pH electrodes, two voltmeters and a pH meter.

Preliminary experiments were performed on iron nails covered (or not) with corrosion layers, to determine the safest electrolytic parameters. The study of "corroded" nails was particularly interesting since we found out that their electrochemical behaviour is different from the one of "bare" or "slightly polished" nails.

While polarizing the highly graphitized porthole, we decided to work under constant anodic potential conditions and to monitor the cathodic potential measured on the artefact. Although the behaviour of the latter seemed to be similar to the one of "corroded" nails, we had to adapt the parameters in a way to protect the artefact (by maintaining a constant and neutral pH) but obtain too the most efficient extraction of chlorides.

The methodology followed has shown its limits. We now need to plot voltammetric curves to understand the electrochemical reactions involved during the polarization process. Still, we have now some ideas of the range of cathodic potentials that are suitable for such a treatment.

Acknowledgments

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