Proceedings of Metal 2004 National Museum of Australia Canberra ACT 4–8 October 2004
ABN 70 592 297 967

Electrochemical monitoring of marine iron artefacts during their storage / stabilisation in alkaline solutions

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Abstract

Removing the protective crust that covers marine iron artefacts can lead to accelerated corrosion processes. To prevent this further damage the immediate storage of the artefacts in appropriate solutions is required. The additional analysis of chlorides extracted can even assure the monitoring of the stabilisation process.
After a thorough literature survey that presents these different aspects, this paper develops a new approach to monitor the storage / stabilisation of marine iron artefacts in alkaline solutions through the measurement of their corrosion potential, E_{corr} versus time. Preliminary investigations are performed on non-corroded and corroded steel plates in diluted KOH solutions and are followed by experiments in real conditions. Three steps are commonly observed when monitoring E_{corr}: first an abrupt decrease that is followed by a period where E_{corr} remains constant and a final phase where E_{corr} tends to increase again. Possible explanations for these behaviours are given according to the nature of the corrosion layer as well as suggestions to speed up the stabilisation process while monitoring both the amount of chlorides extracted and E_{corr}.

Keywords
Storage / stabilisation; marine iron artefacts; electrochemical monitoring; alkaline solutions

1. Introduction

Marine iron artefacts recovered from the sea are usually covered with a protective crust (concretion) that should be preserved until their transfer to conservation laboratories. When no budget for treatment is immediately available a simple immersion of the encrusted artefact in tap water is normally conducted. If left to dry the crust becomes so hard that during its mechanical removal some damage of the fragile altered artefacts might occur.
Unfortunately marine iron artefacts are often cleaned from their crust by their discovers and conservation professionals have no option than to immerse them in an appropriate storage / stabilisation solution that requires a thorough monitoring. With experience we have learnt that the short storage conditions expected initially (before a budget is allocated to the conservation treatment) become eventually long storage conditions. Because stabilisation treatments are time consuming processes, it seems logical to start the treatment straight away.

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The stabilisation process is monitored through the regular analysis of chlorides extracted in the storage / stabilisation solution. Other options have been suggested recently such as the monitoring of the corrosion potential of the artefact under treatment with time. It is the objective of this paper to investigate more thoroughly the information provided by this parameter and to see how its monitoring relates to the stabilisation process.

2. Scientific Background

2.1. Specificity of the corrosion of iron artefacts in seawater

The corrosion of iron artefacts in seawater is dominated by the formation of massive crusts which completely cover the metal surface. Marine crusts form a more or less protective barrier between the artefact and the surrounding environment. If it is compact corrosion processes slow down rapidly and the metal is well preserved underneath. If it is porous corrosion activity is maintained at the metal surface and thick corrosion layers are progressively formed (North 1976 and North & Pearson 1987).

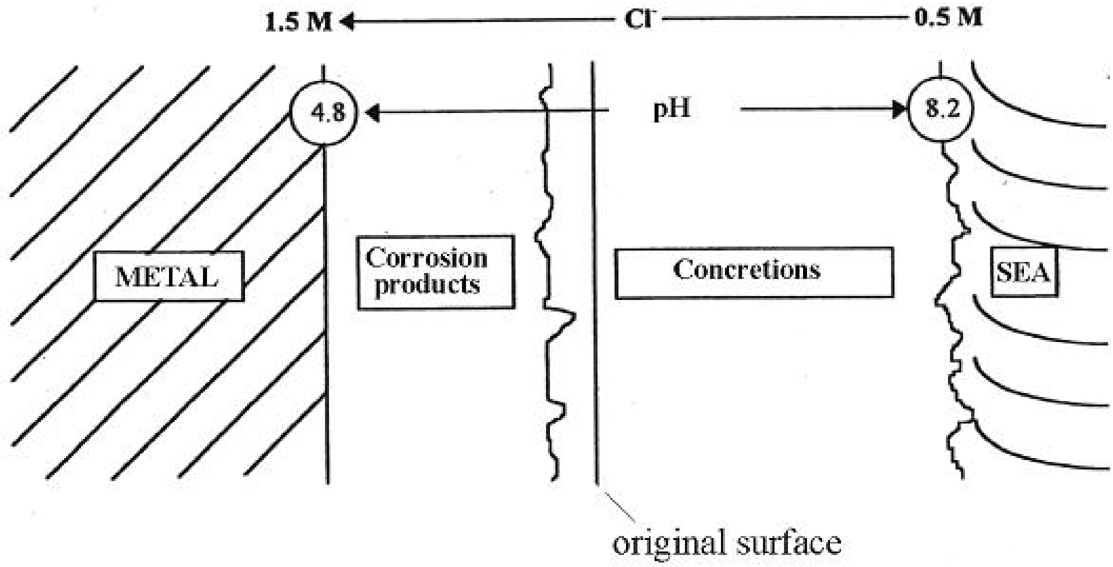

Figure 1 : Cross-section on a wrought iron exposed to seawater. The original surface is lost in the concretions (from (MacLeod 1989))

The composition of iron affects the way the corrosion proceeds. Wrought iron contains slag inclusions which provoke galvanic corrosion and allow the penetration of water deep into the metal (North & MacLeod 1987). Corrosion occurs then inside the metal resulting in a wood grain appearance with the details and form of the original surface being lost (Figure 1) (MacLeod 1989).

The corrosion of grey cast iron is much more complicated as it contains different solid phases rich in carbon. In addition to the principal phases, which are ferrite, pearlite, cementite and graphite, grey cast iron often contains varying amounts of phosphorus, silicon and sulphur. Of these different phases only the graphite lamellas remain unaffected by the corrosion. They form a three-dimensional network, which tracks the iron corrosion products and so retains the original shape and the surface details (Figure 2) (North 1976). The resulting corrosion layer is called the "graphitic corrosion layer".

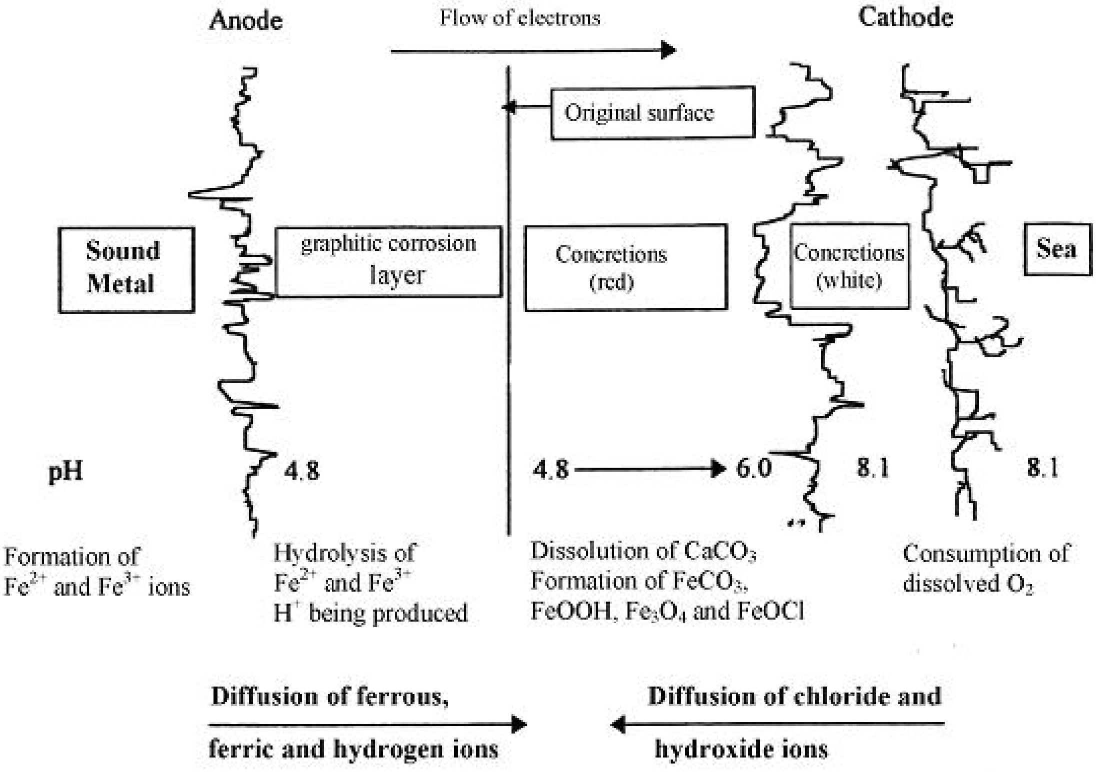

Figure 2 : Cross-section of a cast iron exposed to seawater. The original surface is preserved above the graphitic corrosion layer (from North 1976)

It is commonly agreed that the chloride ions in archaeological iron are situated at the metal / corrosion layer interface. However, the nature of the compounds containing them is still under research. Ferrous chloride ($FeCl_2$) has been suggested (North & Pearson 1977), although according to Turgoose its formation is not likely to occur thermodynamically (Turgoose 1982a and 1982b). Also iron oxychloride (FeOCl) has been detected, especially on marine archaeological iron artefacts (North & Pearson 1977). The corrosion layer itself is made both for grey cast iron and wrought iron of a mixture of magnetite, oxyhydroxides (lepidocrocite and goethite) and iron sulphides, although magnetite is the main iron oxide component due to the low oxygen content under the crust (North & MacLeod 1987).

2.2. Post-recovery corrosion

If cleaned from their marine crust and left to dry out the iron objects are exposed to a rapid oxidation. Corrosion layers crack allowing more oxygen to reach the metal surface. According to Turgoose (Turgoose 1982a) this oxidation causes the formation of solid iron oxyhydroxides and can be described by the reaction :

$$4Fe^{2+} + O_2 + 6H_2O \rightarrow 4FeOOH + 8H^+$$

There are several forms of iron oxyhydroxides. Their precipitation damages the corrosion layer as the formation of any of them results in an increase in its volume. At high chloride concentrations it is normally akaganeite (β-FeOOH) that is being formed. It appears underneath the upper corrosion layers introducing stresses to the object. Akaganeite is known to contain variable amounts of chloride ions in its tunnel structure (Schwertmann 1991).

Akaganeite is often accompanied by droplets of yellow solution which contains mainly ferrous (Fe^{2+}) and chloride ions but also some ferric ions (Fe^{3+}). The appearance of the solution on the surface of an iron object is called "weeping" and it is caused by the dissolution of iron oxyhydroxides in acidic environment (Selwyn 1999).

2.3. Storage / stabilisation of marine iron artefacts

As chloride ions are known to accelerate the corrosion of iron, marine iron artefacts cleared from their marine crust have to be conserved in solution before a proper conservation treatment is started. The Pourbaix diagram (Pourbaix 1963) for iron indicates that in strong alkaline solutions ($pH \geq 10$) the metal surface is passivated (figure 3). For that reason marine iron artefacts are often stored in NaOH, Na_2CO_3, or sodium sesquicarbonate solutions (Pearson 1987).

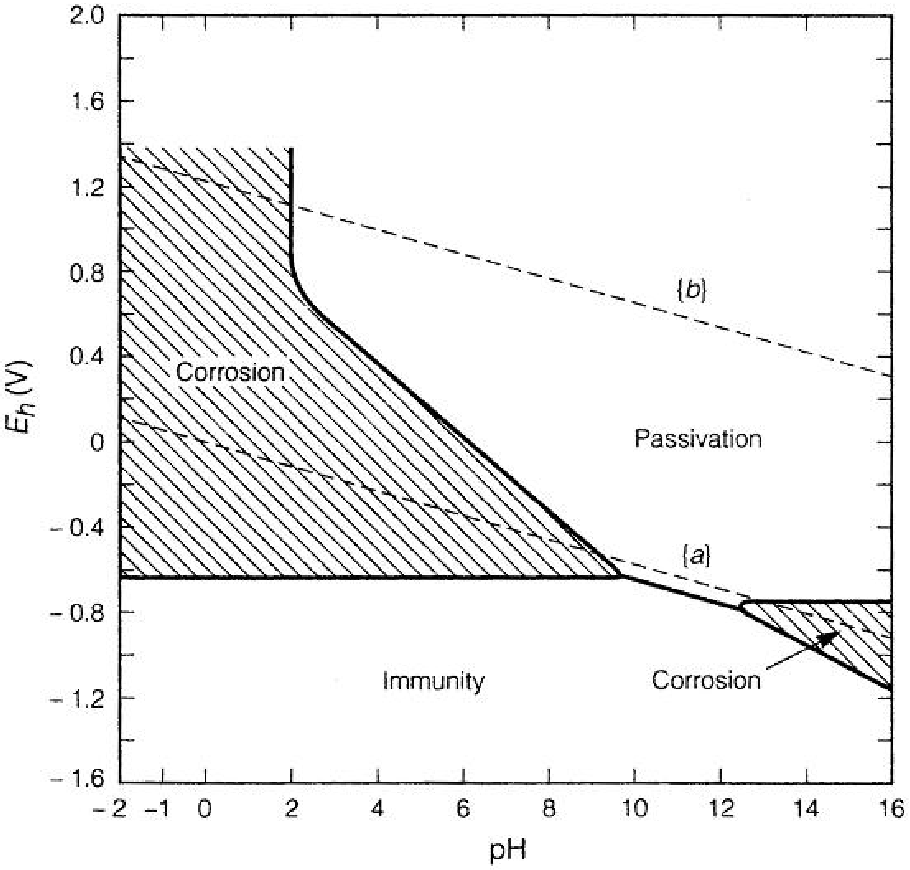

Figure 3 : Simplified Pourbaix diagram for iron.(concentration of Fe species ($<10^{-6}$ M)) (from Pourbaix 1963).

Due to lack of budget, this storage step can sometimes lasts longer than initially planned. It is worth then starting the stabilisation process at once since the chemicals commonly used for the stabilisation of archaeological iron are the same as the ones mentioned above (North & Pearson 1978). The main difference between the storage and the stabilisation steps is that the stabilisation requires a thorough monitoring of the extraction of chlorides in the solution. The mechanisms by which chlorides are extracted from marine iron artefacts in basic solutions have been studied by North and Pearson (1976) and the extraction rate was found to be controlled by a diffusion law.

The quantity of chlorides released during the early stage of washing is after some time proportional to the square root of the total washing time (Figure 4). Plots of the chloride concentration versus the square root of time are then useful tools to monitor the stabilisation process. Deviations from linearity occurs only when the amount of chlorides extracted is equal to the chloride concentration of the iron corrosion products and the remaining metal.

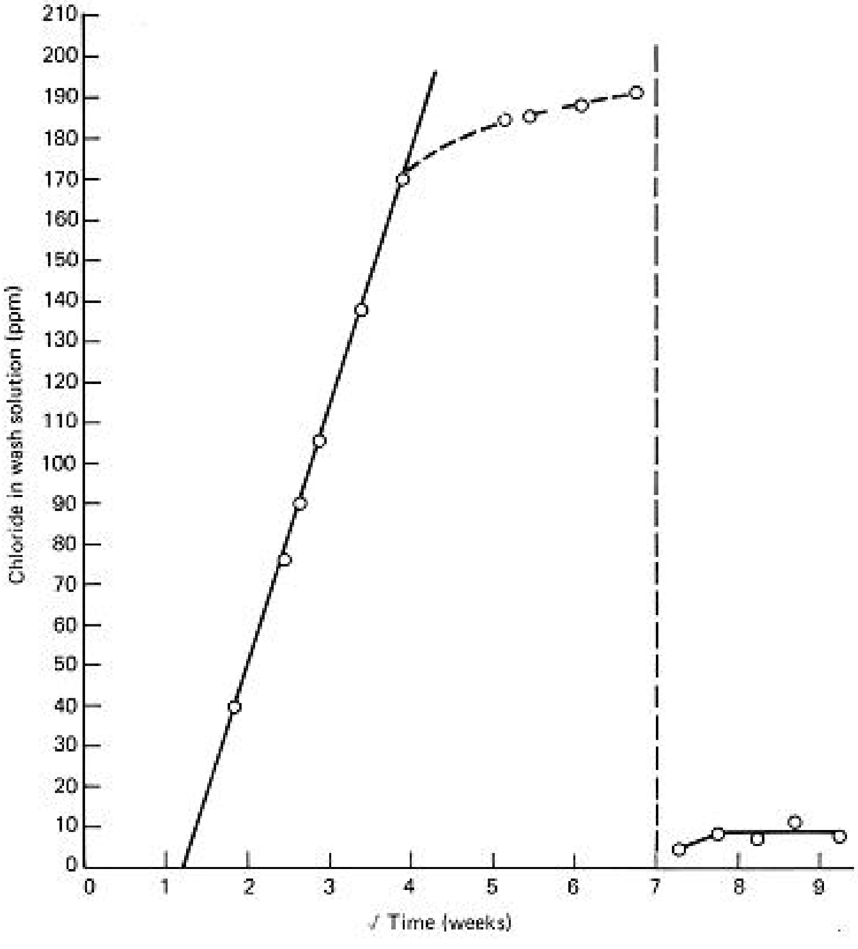

Figure 4 : A typical plot of C_{Cl}- =(√t, t in weeks) for a cast iron artefact pretreated by hydrogen reduction (North 1987)

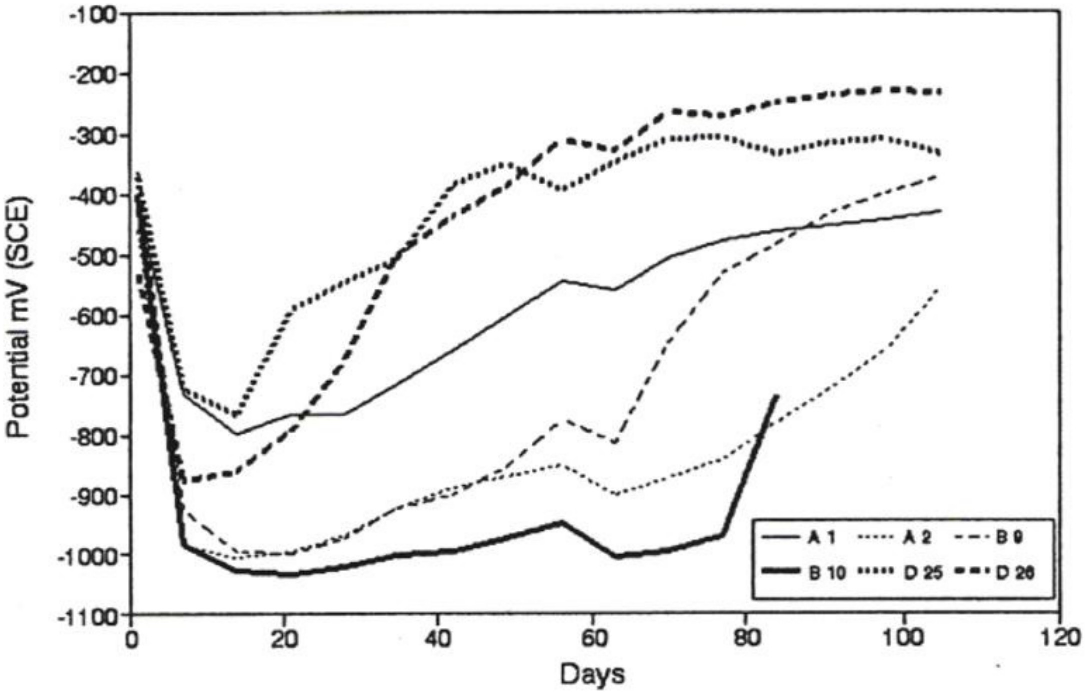

Figure 5 : E_{corr} (SCE) vs. time for iron archaeological artefacts immersed in 0.5 M sodium hydroxide (Hjelm-Hansen 1992)

The electrochemical monitoring of artefacts during storage (or stabilisation) is rarely mentioned in the literature. Only Hjelm-Hansen et al. reported results on several archaeological iron objects treated by immersion in sodium hydroxide and sodium sesquicarbonate (Hjelm-Hansen 1992). The objects came from four different Danish terrestrial sites with different post-excavation history and condition. A common behaviour of the objects immersed in sodium hydroxide was observed (Figure 5). The corrosion potential (E_{corr}) decreased to a very low value (-0.8 to –1.0 V/SCE, Saturated Calomel Electrode (SCE)=0.242V/SHE, Standard Hydrogen Electrode (SHE)=0V) soon after immersion, remained at this potential for a time depending on the object (a few days to 80 days), and then rose towards –0.2-0.3V/SCE (-0.058 to 0.042V/SHE). The same trends were observed for artificially precorroded mild steel plates. The extent of corrosion was noticed to affect the time scale in which the metal artefacts reached –0.2-0.3V/SCE corresponding to the passivation process. A much longer time was required for the archaeological artefacts with thick corrosion products (A2, A1 and B10) than for those with thin ones (D25 and D26) and the precorroded mild steel plates.

Therefore these experiments suggested that rapid electrochemical processes are taking place during immersion in alkaline solution. These processes are likely to cause irreversible changes in the corrosion product layers, which should be realised when considering the use of these solutions. On the other hand the effectiveness of the stabilisation may be associated with these changes.

3. Experiments and results

3.1. On artificial coupons

Several experiments were performed on artificial coupons simulating the behaviour of real artefacts to study the reactions taking place when they are immersed in alkaline solutions such as potassium hydroxide (KOH). A preliminary exercise consisted in immersing un-corroded steel plates E24-2 in 1% (w/v) KOH solutions and to monitor the corrosion potential (E_{corr}) with time. The curve obtained for one of these plates clearly shows an increase of E_{corr} which corresponds to a passivation phenomenon (figure 6). The potential gets stable after one hour and the value obtained is –0.660 V/HSE (or roughly 0V/SHE, Mercury Sulphate Reference Electrode (HSE)=0.658V/SHE). Note that this value is very close to the final value of the monitoring experiments performed by Hjelm-Hansen (see figure 5).

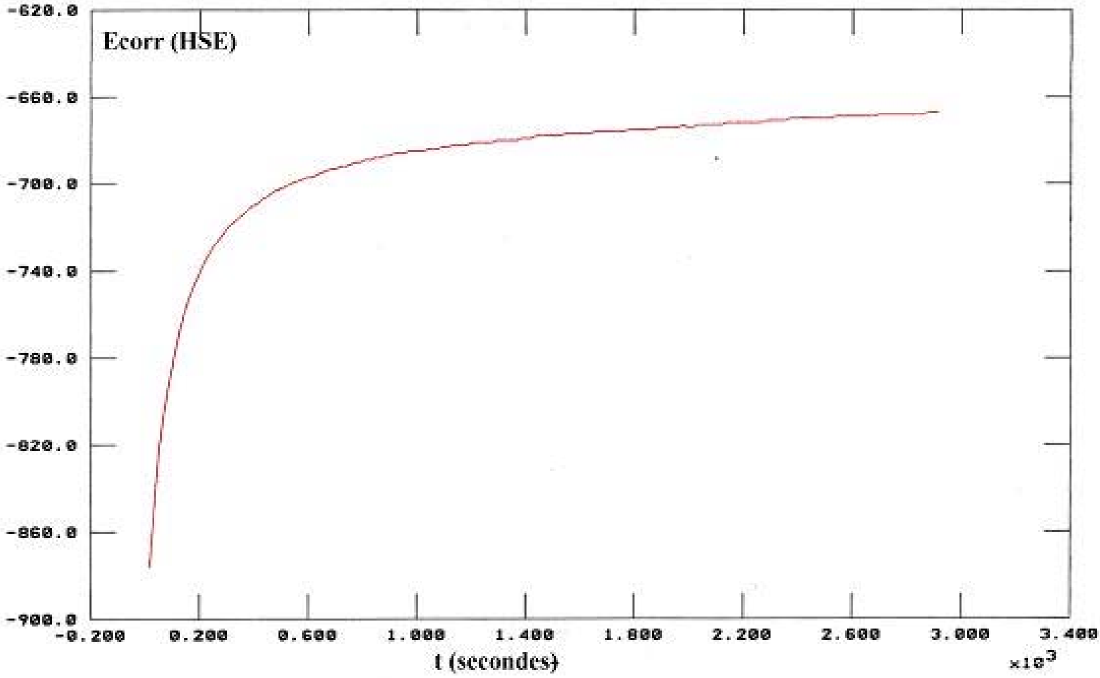

Figure 6 : Monitoring of E_{corr} versus time for an un-corroded steel plates E24-2 in 1% KOH solution. The potential is given versus the mercury sulphate electrode (HSE : 0.658V/SHE)

These steel plates were corroded artificially to simulate the behaviour of real artefacts. Four different preparation surfaces were considered (blasted with grey cast iron particles, just degreased, abraded and polished with 240 SiC paper) and the steel plates were then immersed 22 days in a $FeCl_2$ solution to form akaganeite and exposed 45 days vertically in a climatic chamber to the following conditions:
- 24 hours (30°C – 100% RH)
- 24 hours (20°C – 50% RH)

to form a double layer of corrosion products (magnetite and oxyhydroxides).

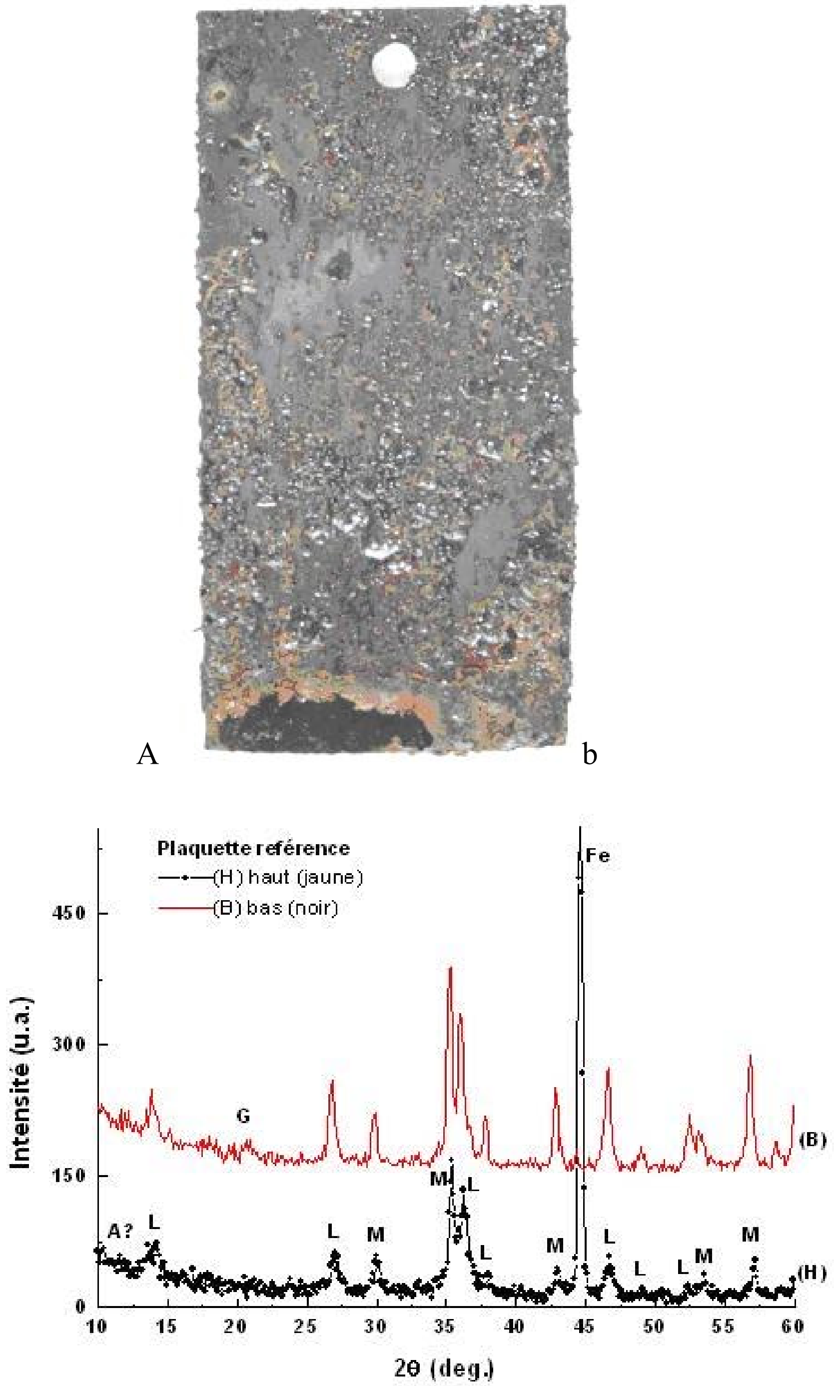

Figure 7: Degreased E24-2 steel plate after 22 days immersion in $FeCl_2$ and 45 days exposure in a climatic chamber (a/) and XRD analysis of the corrosion products, at the top (H) and the bottom (B) of the plate (b/). M (magnetite), L (Lepidocrocite) and G (goethite), A (akaganeite)

Figure 7a shows the visual appearance of one of the plates (degreased) after the ageing process. Corrosion layers do not depend on the surface preparation and observation on cross-sections indicate that they form a thin and multilayered film that is adherent to the metal surface. XRD analysis reveals the presence of lepidocrocite (γFeOOH) and magnetite (Chevalier 2001 – Figure 7b). Both observation and analysis of the corrosion layers show that the artificial coupons can be used to simulate the behaviour of real artefacts.

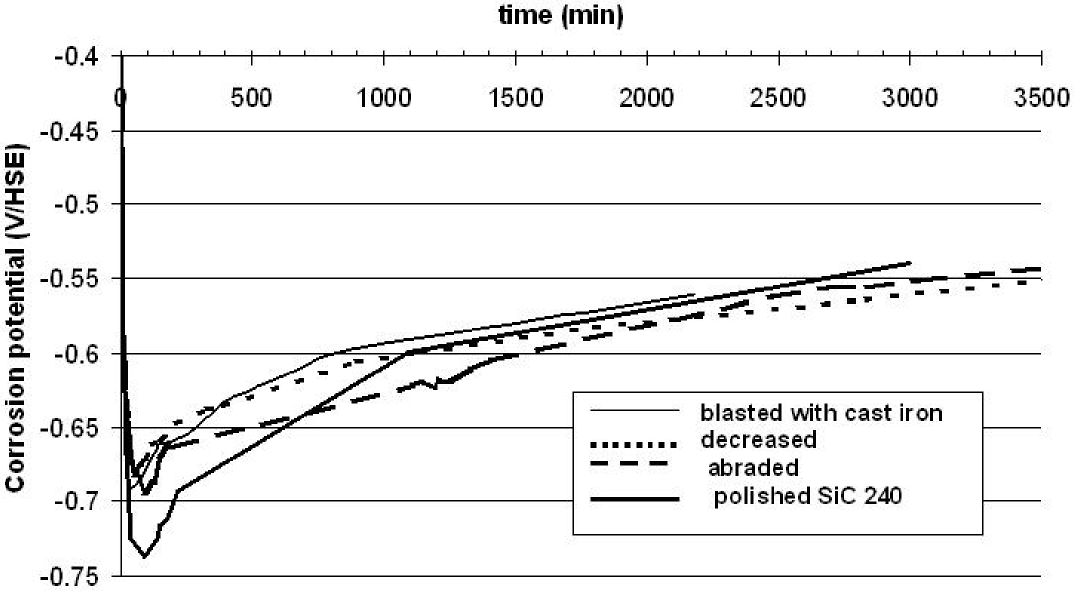

Figure 8 : Influence of the surface treatment of steel plates on the E_{corr} measurements with time in 1% KOH solution

These corroded steel plates were immersed then in 1% (w/v) KOH solutions and figure 8 shows that whatever the surface preparation of the steel plates is the corrosion potential E_{corr} decreases immediately to reach a stable value after less than 2 hours. The values obtained at that stage depend on the thickness of the corrosion layer but are comprised between –0.7 and –0.75 V/HSE (or –0.05 to –0.1V/SHE). These are much higher than the ones obtained by Hjelm-Hansen (figure 5) because of the thin corrosion layers present on the artificial coupons. E_{corr} increases progressively afterwards to reach a value close to –0.5V/HSE (or roughly 0.16V/SHE) which is quite a similar value than the ones obtained on figure 5. When comparing the monitoring of both E_{corr} and the concentration of chlorides in solution versus time we observe that a large amount of chlorides is extracted during the decrease of E_{corr} step (Figure 9). Electrochemical reactions conduct then to the transformation of the corrosion layers that permit the dissolution of chloride species. When the alkaline solution reaches the metal surface on the whole plate E_{corr} starts increasing (passivation effect).

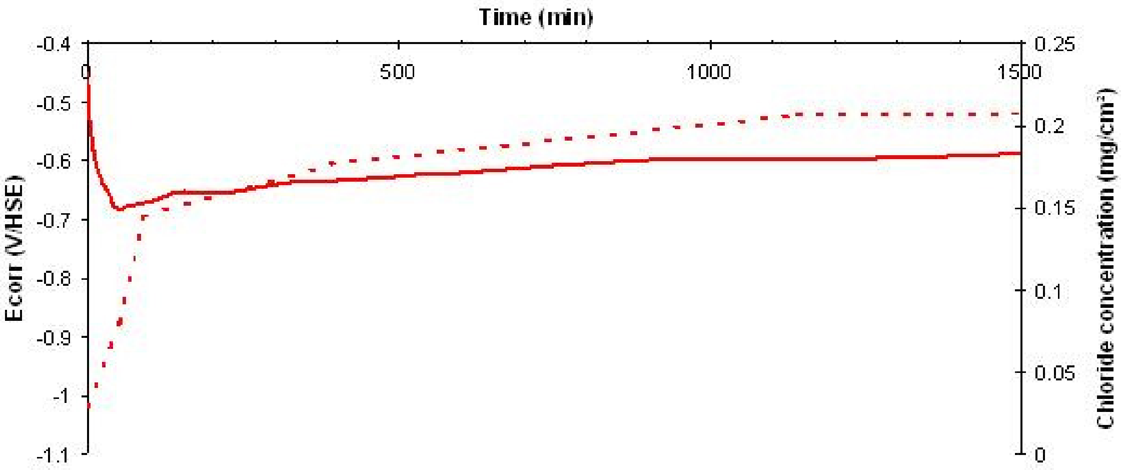

Figure 9 : Comparison between the E_{corr} (—) and concentration of chlorides (---) monitoring versus time for a steel plate corroded artificially and immersed in 1% KOH solution

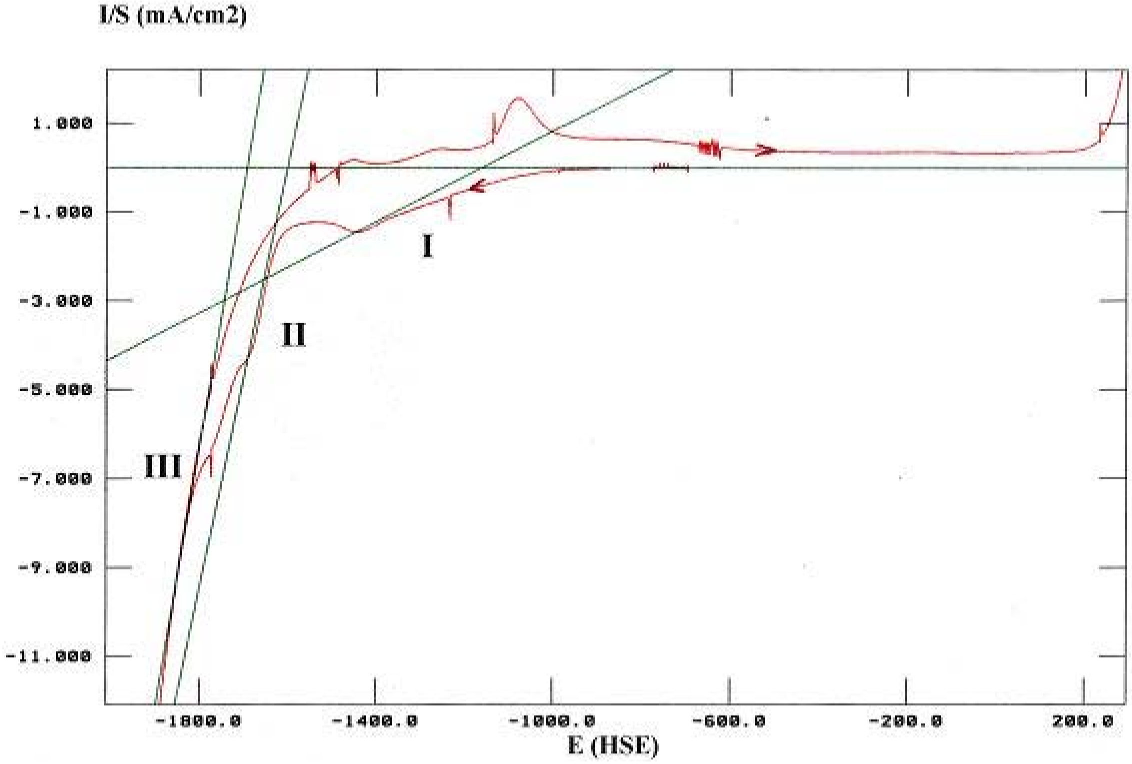

Figure 10: Voltammetric curve showing the behaviour of mild steel in 1% KOH solution when polarised cathodically from E_{corr} and then anodically (scanning rate=30mV/s), the counter electrode being a platinum grid. Reaction I corresponds to: $Fe^{3+} \rightarrow Fe^{2+}$ and reaction II to: $Fe^{2+} \rightarrow Fe$

Figure 10 shows the voltammetric I=f(E) curve obtained for a corroded steel plate in 1% (w/v) KOH solution from E_{corr} to –2V/HSE (cathodic part) and then back to 0.2V/HSE (anodic part). Two reduction peaks are obtained in the cathodic part. The first one corresponds to the reduction of Fe^{3+} in Fe^{2+} at the approximate potential of –1.15V/HSE

(-0.49V/SHE) and the second one to the reduction of Fe^{2+} in iron occurring at –1.6V/HSE (or –0.94V/SHE). This curve clearly indicates that none of these reactions occur during the immersion of the corroded plate in 1% KOH solution since the lower potential we could get is –0.75V/HSE (or –0.1V/SHE). The extraction of chlorides is not provoked then by the reduction of the oxyhydroxides.

Looking back at Hjelm-Hansen results (Figure 5) it seems though that E_{corr} measured on some artefacts can go as low as –1V/SCE (-0.758V/SHE), a potential for which the reduction of Fe^{3+} in Fe^{2+} is possible. In these cases the transformation of corrosion layers through reduction processes might occur.

3.2. On artefacts

Monitoring of the corrosion potential was performed on some marine artefacts that had been cleaned from their crust and were stored / stabilised afterwards in 1% (w/v) KOH or NaOH solutions.

3.3. Storage of *Saintes-Maries-de-la-Mer* iron ingots

These iron ingots were recovered in the Mediterranean Sea in 1996 from two different ancient Roman wrecks discovered and surveyed by the DRASSM (Département des Recherches Archéologiques Subaquatiques et Sous-Marines) (Baudat 1997).

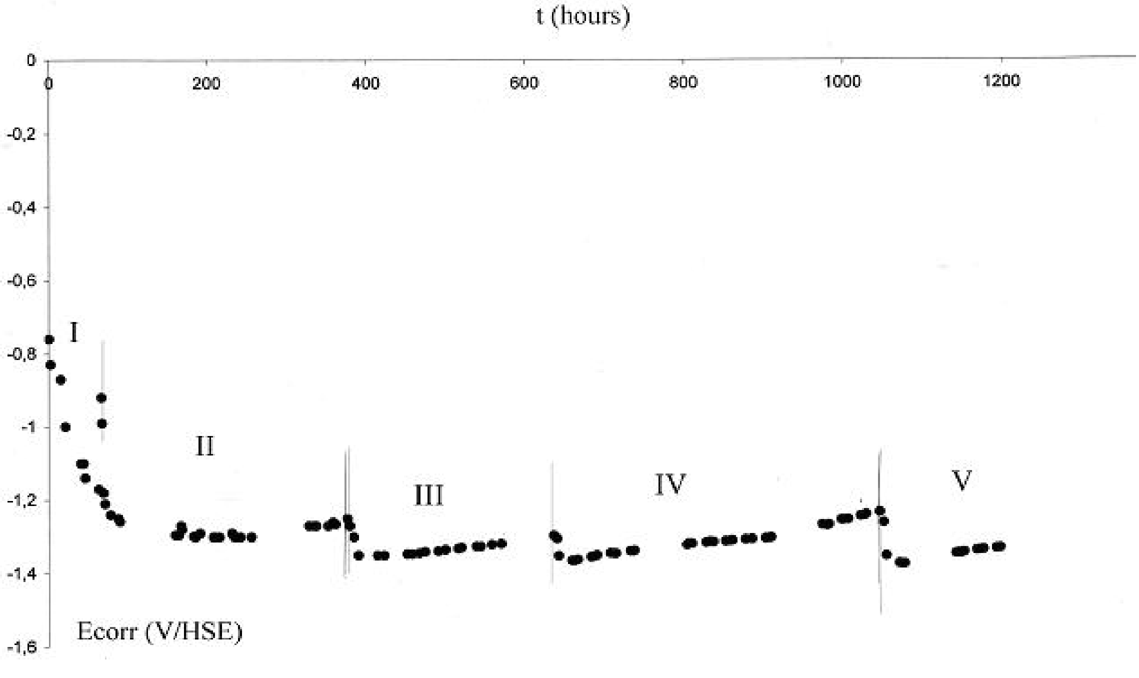

Figure 11 : Monitoring of E_{corr} versus time for one of the *Ste-Marie-de-la-Mer* iron ingot immersed in 1% KOH solution. Phases I to V correspond to the change of solution

Some of them were transferred for investigation and conservation to the conservation Laboratory Arc'Antique, France and were immediately immersed in KOH 1% (w/v) solution. The investigation of one ingot on cross-sections revealed that it was made of ferrite (αFe) and perlite (αFe + Fe_3C) and that the superficial corrosion layer was quite thin. Seawater had penetrated though in the metal structure through cracks and large amount of chlorides were expected. The monitoring of E_{corr} with time indicated three steps (figure 11). First an abrupt decrease of E_{corr} to values as low as –1.3V/HSE (-0.642V/SHE) followed by a step where E_{corr} remained stable. Later on the corrosion potential increased again but very slowly. The difference phases I to V correspond to regular changes of the solution when the amount of chlorides extracted started to reach a constant value. Large amount of chlorides were actually extracted. Note that the final potential (phase V) was still quite low although the stabilisation process was apparently finalised (only low amount of chlorides were obtained at that stage).

3.4. Stabilisation of a two arms iron anchor

This wrought iron anchor of the Admiralty type (shank with a movable iron stock) was found in the Baltic Sea in a depth of 17 m East West from Helsinki and brought dry to the conservation laboratory at the EVTEK, Institute of Art and Design clean of marine crust. The metal was directly apparent and most of the original surface was lost.

No active corrosion could be noticed on the metal surface (even after the humid chamber test). It was decided though to immerse the artefact in a 1% (w/v) KOH solution to check whether chlorides could be extracted from the internal structure.

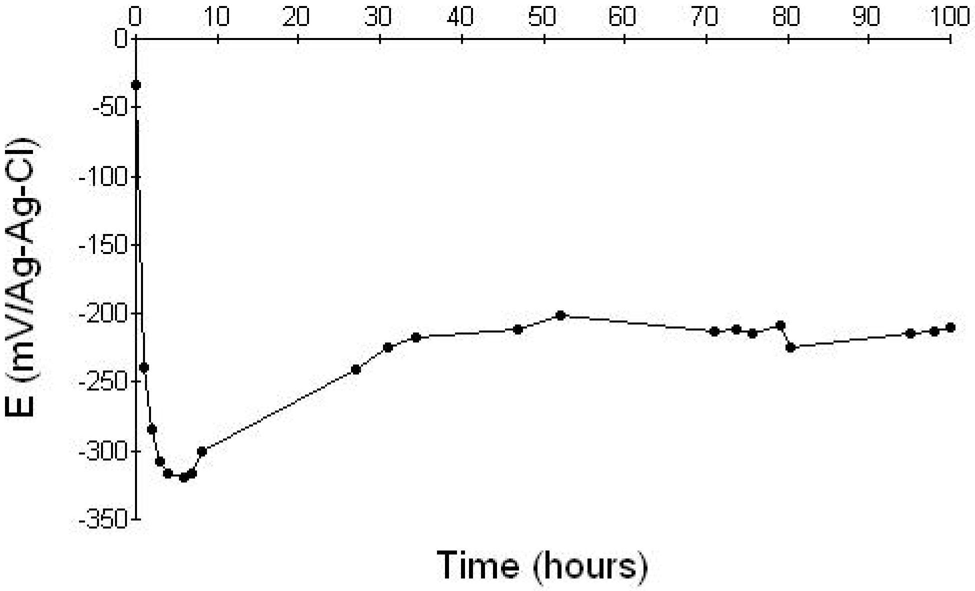

Figure 12: E_{corr} versus time for a wrought iron anchor immersed in 1% KOH solution

The monitoring of E_{corr} with time is given on figure 12. Although the common behaviour is obtained (preliminary decrease of E_{corr} followed by a short time where it remains stable followed itself by a re-increase of E_{corr}) the lower values obtained (-0.325V/Ag-AgCl or –0.125V/SHE) did not permit any reduction of Fe^{3+} in Fe^{2+}. The potentials measured here are quite similar to the ones obtained on artificial coupons, indicating then the presence of a thin corrosion layer which is confirmed by the metallic appearance of the artefact.

Noteworthy no chloride extraction was observed during this experiment.

3.5. Storage / Stabilisation of an iron based swivel gun

This breach loading swivel gun was recovered from the sea around Malta some years ago (June 2000) and will be exhibited at the Malta Maritime Museum. It seems to be made of a grey cast iron body with the swivel and the tiller made of wrought iron. The grey cast iron is heavily graphitised but the wrought iron elements are very well preserved. After been mechanically cleaned from its crust the swivel gun was conserved in a sodium carbonate solution that was changed every 2 months. The artefact was brought to the Malta Centre for Restoration for stabilisation and was immediately immersed in a 1% (w/v) NaOH solution (NaOH was used instead of KOH because of the presence of large quantities of chlorides in the KOH brand available in Malta). Figure 13 shows how the reading of E_{corr} were performed during the stabilisation process and figure 14 gives both the follow up of E_{corr} and the extraction of chlorides with time.

Figure 13: Principle of the measurement of E_{corr} with a reference electrode. The artefact is an iron based swivel gun immersed in 1% NaOH solution (credit: D. Vella)

Like in the examples above the common behaviour was once again obtained but the lower potentials measured were this time quite similar to the ones given by the iron ingots: -0.92V/Ag-AgCl (around –0.72V/SHE) indicating then that reduction reactions might have occurred. Like for the ingots the potentials did not re-increase straight away but only after more than 30 days. Large amount of chlorides were measured too in that case. These chlorides were obviously extracted from the body made in grey cast iron.

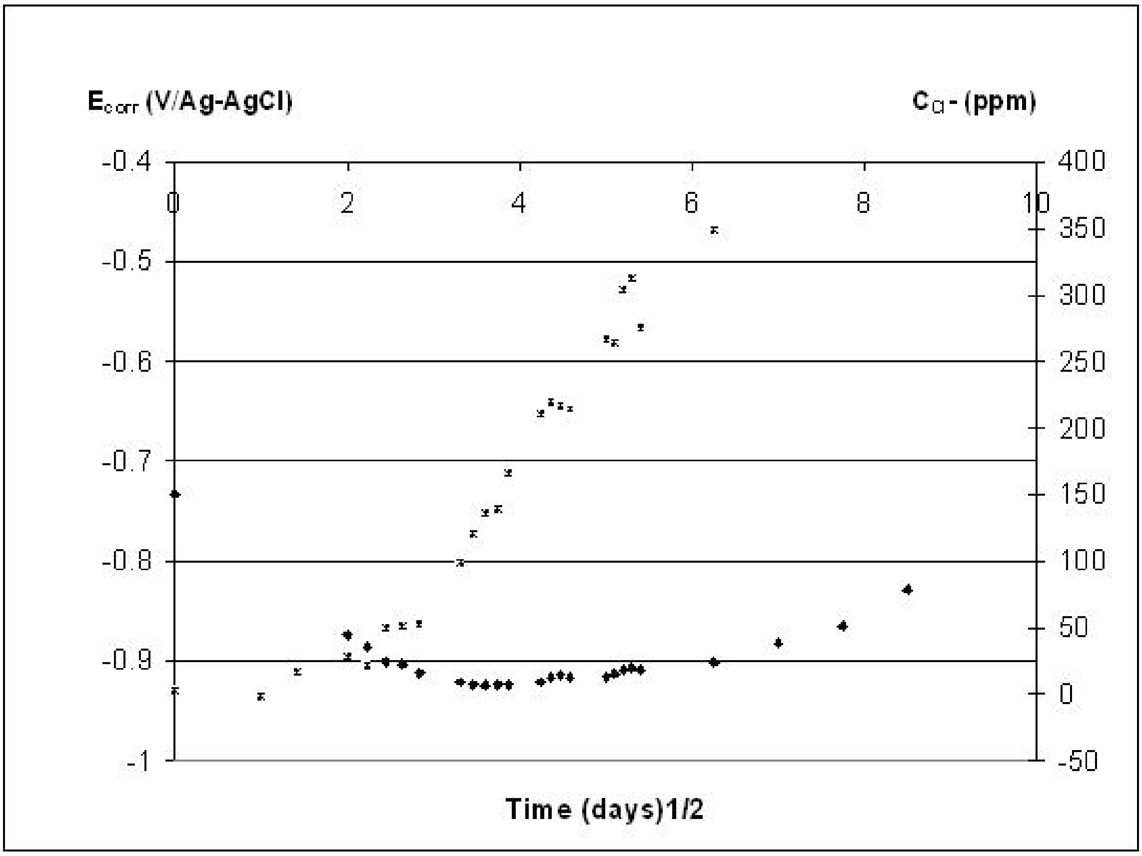

Figure 14: E_{corr} (♦) and concentration of chlorides extracted (✱) versus time for an iron based swivel gun immersed in 1% NaOH solution

4. Discussion

All our results show that the electrochemical behaviour of iron artefacts covered with corrosion layers and immersed in strong alkaline solutions given by Hjelm-Hansen (1992) is correct. Their corrosion potential first decreases abruptly to reach a value which depends on the nature of the corrosion layers. For archaeological artefacts covered with thick and compact corrosion layers this potential is comprised between –0.75 and -0.65V/SHE. For thin and/or porous corrosion layers this potential is closer to –0.1V/SHE. Voltammetric curves for iron in KOH solutions show that the reduction of Fe^{3+} in Fe^{2+} is possible below –0.49V/SHE. We can suspect then that some reduction reactions are taking place in the corrosion layers covering archaeological artefacts immersed in KOH but not on artefacts covered with thin corrosion layers.

Chlorides are either present at the interface remaining metal / corrosion layer as $FeCl_2$, FeOCl or at the surface of the artefact as βFeOOH. For thin and porous corrosion products most of the chlorides are released almost immediately. For archaeological artefacts covered with thick corrosion layers this extraction takes more time due to the slow penetration of alkaline solutions through the corrosion layers (through existing cracks or by decomposition/reduction of some of the corrosion products (oxyhydroxides mainly)).

The re-increase of E_{corr} corresponds to the normal behaviour of iron in alkaline solutions (either KOH or NaOH). It indicates that the solution has penetrated the corrosion layers and that the hydroxide anions are now passivating the metal underneath. Figures 5, 8 and 12 show that this phenomenon occurs quite rapidly when the corrosion layer is thin and/or the concentration of chlorides to extract is quite small. This process takes much more time when corrosion layers are very thick and the quantity of chlorides to extract is quite important. In the former case the hydroxide anions will take more time to reach the metal surface. In the latter chloride and hydroxide anions might compete and prevent any passivation phenomenon to occur. It is necessary then to change the solution for a new one to protect the material and to increase the efficiency of the stabilisation process.

5. Conclusion

E_{corr} measurements during the storage / stabilisation of marine iron artefacts in diluted NaOH and KOH solutions are an important addition to the monitoring of the treatment via the regular analysis of chloride extracted. The latter approach will tell us when the extraction becomes less effective and the solution has to be changed or when the stabilisation is over. E_{corr} measurements are related to the behaviour of the surface of the metal artefacts. Corrosion potentials give us information on the thickness of the corrosion layer and the accessibility of chlorides species. They tell us whether the passivation of the remaining metal finally occurs not preventing though the extraction of chlorides. E_{corr} measurements alone cannot replace though the follow up of the storage / stabilisation process via the analysis of the chlorides extracted.

The monitoring of E_{corr} versus time offers a simple and safe way to store and stabilise iron metal artefacts in NaOH and KOH solutions but further research has to be performed to explain the way the corrosion products are really affected by the hydroxide anions and chlorides are then released. This knowledge could contribute to the optimisation of the stabilisation process.

Acknowledgements

The authors would like to thank Ms Saila Sorsa, objects conservator, for the information on the conservation of the ingots from Saintes-Maries-de-la-Mer, Ms Ilonne de Groot, private objects conservator, for providing similar information on the Admiralty anchor treated in the Marine conservation laboratory at EVTEK, Institute of Art and Design, Vantaa (Finland) and Mr Emmanuel Magro Conti, Curator of the Malta Maritime Museum, for the technical information on the breached loading swivel gun. Thanks should also go to Heritage Malta for its kind collaboration.

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