

Original research or treatment paper

Influence of crucial parameters on the dechlorination treatments of ferrous objects from seawater

E. Guilminot¹, D. Neff², C. Rémazeilles³, S. Reguer⁴, F. Kergourlay^{3,4}, C. Pelé¹, P. Dillmann², P. Refait³, F. Nicot⁵, F. Mielcarek⁵, N. Huet⁶, J. Rebière⁵

¹EPCC Arc'Antique, Nantes, France, ²IRAMAT LMC CNRS UMR5060 and SIS2M/LAPA CEA/CNRS UMR3299, Gif sur Yvette, France, ³Laboratoire d'Etude des Matériaux en Milieux Agressifs (LEMMA), Université de la Rochelle, Bât, La Rochelle, France, ⁴Synchrotron SOLEIL, L'orme des Merisiers – Saint Aubin, Gif sur Yvette, France, ⁵Laboratoire de Conservation Restauration et Recherches (LC2R), Centre Archéologique du Var, Draguignan, France, ⁶DRASSM (Département des Recherches Archéologiques Subaquatiques et Sous-Marines), Marseille, France

This article compares chemical dechlorination treatments (immersion in sodium hydroxide or alkaline sulphite) and electrochemical treatments of iron bars from the Gallo-Roman period excavated from a marine environment. Some important parameters, such as storage before treatment, temperature, solution composition, and drying after treatment, were varied during the study to assess their influence on the chloride extraction process. The kinetics of these treatments depend mainly on chloride diffusion through the corrosion layers. The kinetics are promoted by high temperatures and, in the case of electrolysis, by the electric field effect. The reduction of corrosion products during electrolysis occurs only for objects previously stored in air. In fact, the manner in which the objects are stored before treatment is critical in the dechlorination processes. The sooner the objects are treated after excavation (with water storage), the better the removal of chloride ions, in both chemical immersion and electrolysis treatments. But if the object is stored in air, material losses occur, and only electrolysis results in complete extraction of the chlorides. These differences are due to modifications in the corrosion products during storage. Drying after treatment also has a significant impact on the composition of the corrosion layers. If the objects are dried too quickly, Fe(OH)₂ oxidizes into FeOOH, which thus forms a layer with low cohesion.

Keywords: Iron, Marine corrosion, Dechlorination, Electrolysis, Alkaline sulphite, Sodium hydroxide

Introduction

Ferrous archaeological objects excavated from the marine environment are subjected to harsh conditions and the corrosion products formed contain chloride ions. After the objects are excavated, the corrosion processes are amplified by the presence of chloride ions that can cause rapid and irreversible damage, such as cracking and swelling of the corrosion layers that can rapidly lead to the complete loss of historic artefacts (Selwyn *et al.*, 1999). It is therefore necessary to stabilize the objects by removing the chloride ions. The main dechlorination methods are chemical methods (immersion in alkaline solutions), cathodic polarization, hydrogen plasma reduction (North,

1987; Schmidt-Ott & Boissonnas, 2002), and more recently a new technique using subcritical fluids (Gonzalez *et al.*, 2007; Mardikian *et al.*, 2010; Gonzalez-Pereyra *et al.*, 2011). Currently the most commonly used stabilization techniques for ferrous objects are the chemical and electrochemical methods. There is extensive literature (North & Pearson, 1978; North, 1987; Selwyn, 2004; Mardikian *et al.*, 2010) presenting the parameters, effectiveness, and limitations of such treatments. These treatments are carried out in alkaline solutions at pH 13–14 (usually NaOH) so that iron is in its passivation zone. In immersion, the excess of OH⁻ ions is supposed to favour the extraction of Cl⁻ ions (Helm-Hansen *et al.*, 1993; Selwyn *et al.*, 2001; Selwyn, 2004; Selwyn & Argyropoulos, 2005; Gonzalez *et al.*, 2007). However, iron corrosion can still occur

Correspondence to: E. Guilminot, EPCC Arc'Antique, 26 Rue de la Haute Forêt, 44300 Nantes, France. Email: Elodie.guilminot@arcantique.org

because of the presence of dissolved oxygen. Increasing the temperature of the solution not only reduces the solubility of dissolved oxygen while promoting diffusion (Selwyn, 2004), but also increases the reaction kinetics.

Dissolved oxygen is often removed by the addition of an antioxidant such as sodium sulphite. These treatments, commonly called alkaline sulphite ($0.5 \text{ mol l}^{-1} \text{ NaOH} + 0.5 \text{ mol l}^{-1} \text{ Na}_2\text{SO}_3 - \text{pH} = 13.7$), developed by North and Pearson (1978), are inexpensive and easy to implement, which explains their success (in comparison to electrolysis treatments). The use of alkaline sulphite solutions at concentrations lower than those indicated above is just as effective (Wang *et al.*, 2008). The limitations of this method have, however, been demonstrated: despite alkaline sulphite treatment, some of the collections studied showed recurrence of corrosion after several years of exposure (Beaudoin *et al.*, 1997; Wang, 2007). For example, in the case of artefacts from English or Anglo-Saxon Roman sites, studied by Wang (2007), it was recommended to keep these objects in a dry environment. In the other case, the objects were retreated by electrolysis (Beaudoin *et al.*, 1997). This electrochemical technique was also initiated by the team of North and Pearson (1978) and then developed by the laboratory EDF-Valectra (Lacoudre *et al.*, 1991).

Iron objects immersed in an alkaline solution are protected by being cathodically polarized. The electric field promotes the extraction of chloride ions from the object to the grid acting as an anode. But the parameters of this process must be carefully defined to minimize the release of hydrogen at the surface of the object (Dalard *et al.*, 2002; Degriigny, 2004; Liu *et al.*, 2008). Although a slight release of hydrogen favours the elimination of the concretion (Lacoudre *et al.*, 1991; Degriigny, 2004), it should be avoided during stabilization because it can cause the object to become brittle and crack. Tests conducted at the Clemson Conservation Center (Gonzalez *et al.*, 2007; Mardikian *et al.*, 2010) showed that immersion in alkaline solutions and cathodic polarization can extract the same amount of chloride ions, but the extraction rate is faster with polarization. The study of the corrosion potential of an object immersed in an alkaline solution showed that two stages occur during dechlorination (Degriigny & Spiteri, 2004). The first stage corresponds to the penetration of the solution into the layers of the corrosion products, and it is only in the second stage that OH^- ions passivate the metal. The duration of each stage depends on the thickness of the corrosion layers limiting the penetration of the solution.

However, the analysis of the corrosion products of the objects treated, performed by X-ray diffraction and Mössbauer spectroscopy, did not clearly

determine the role of NaOH (Selwyn, 2004; Gonzalez *et al.*, 2007; Mardikian *et al.*, 2010). The extraction mechanisms of chloride ions are therefore still poorly understood. According to the literature, immersion methods eliminate chloride ions by diffusion while electrolysis does so by reducing the corrosion products (North & Pearson, 1978; North, 1987; Mardikian *et al.*, 2010). According to North (1987), the reduction of corrosion products increases the porosity and thus accelerates the diffusion of the chloride ions. It is generally assumed that the corrosion products (FeOOH oxyhydroxides) are reduced to magnetite (Fe_3O_4) or Fe(II)-hydroxide ($\text{Fe}(\text{OH})_2$) during cathodic polarization in the alkaline solution (Selwyn, 2004). A modification of the corrosion products is also reported during chemical treatments (Selwyn, 2004). In NaOH, the corrosion products are probably transformed into $\text{Fe}(\text{OH})_2$, and alkaline sulphite solutions may be more aggressive than sodium hydroxide solutions. Additional research is needed to understand the behaviour of the corrosion products during immersion treatment.

It is difficult to model the diffusion phenomena because many parameters are involved: cracking of the layer, transformation of corrosion products that can alter the kinetics of displacement of chlorides, etc. (Helm-Hansen *et al.*, 1993; Selwyn *et al.*, 2001; Selwyn, 2004). One reason for the difficulty in determining the mechanisms involved in dechlorination treatments is that the chloride ion distribution within the corrosion layers of ferrous objects from the marine environment is not precisely evidenced. The objects are usually covered with concretions (CaCO_3) (North, 1987; Selwyn *et al.*, 2001; Degriigny, 2004). The corrosion layers are mainly composed of iron oxides and oxyhydroxides (Fe_3O_4 , $\alpha\text{-FeOOH}$, $\gamma\text{-FeOOH}$) (Argo, 1981; Gilberg & Seeley, 1981; Selwyn *et al.*, 1999; Degriigny, 2004). The chlorinated phases identified are often akaganeite ($\beta\text{-FeOOH}$) and FeCl_2 .

A recent study on iron bars from a Gallo-Roman wreck has clarified the nature of the corrosion products and the distribution of chloride ions (Réguer *et al.*, 2007a; Guilminot *et al.*, 2008; Rémazeilles *et al.*, 2009). On these objects, akaganeite ($\beta\text{-FeOOH}$ or $\beta\text{-FeO}_{1-x}(\text{OH})_{1+x}\text{Cl}_x$) is detected, but the corrosion layers are mainly composed of ferrous hydroxychloride $\beta\text{-Fe}_2(\text{OH})_3\text{Cl}$ with a variation from 15 to 20% mass of Cl in the same zone. This ferrous hydroxychloride was identified for the first time on terrestrial ferrous archaeological objects using microanalysis (X-ray absorption spectroscopy, X-ray diffraction, and Raman spectroscopy) (Neff *et al.*, 2005; Réguer *et al.*, 2007b;). This has led to a new interpretation of the mechanisms of alteration of iron in marine environments (Rémazeilles *et al.*, 2009). The presence

of ferrous hydroxychloride and akaganeite is a characteristic of corrosion processes in a chloride medium (Rémazeilles & Refait, 2007). The hydroxychloride β -Fe₂(OH)₃Cl can form while the object lies on the seabed and is stable under anoxic conditions. In the presence of oxygen, it can oxidize into akaganeite (β -FeOOH) or goethite (α -FeOOH) (Refait & Genin, 1997; Rémazeilles *et al.*, 2009).

As part of a research programme called ODéFA (Optimisation de la Déchloruration des objets Ferreux Archéologiques), conservation-restoration workshops have joined research laboratories to bring new insight into the transformation of chlorinated corrosion products during stabilization treatments and the mechanisms involved in the extraction of chlorides. For this study, ferrous objects from the same underwater site underwent chemical or electrochemical stabilization treatments, according to protocols typically used in conservation workshops. The corrosion products of the objects were analysed before, during, and after treatment. The analytical results obtained have already been published (Réguer *et al.*, 2007a; Guilminot *et al.*, 2008; Rémazeilles *et al.*, 2009, 2010; Kergourlay *et al.*, 2010, 2011). These previous studies demonstrated that the nature of the storage protocol influences the corrosion system formed after excavation. For bars stored in tap water or in sea water the main corrosion product present is still a Fe^{II} hydroxychloride, β -Fe₂(OH)₃Cl and the original surface corresponds to a thin layer of magnetite. In tap water some akaganeite can be observed as a thin layer in the outer zone of the Fe^{II} hydroxychloride. In contrast to wet storage, storage in air caused irreparable damage to the objects: decohesion of corrosion products and significant loss of the concretion and corrosion layers including the original surface. Moreover, the chlorinated compounds are partially transformed into goethite and poorly crystallized phases such as feroxyhyte (δ -FeOOH) and ferrihydrite (Fe₂O₃·*n*H₂O) (Réguer *et al.*, 2007a; Kergourlay *et al.*, 2010). The only chlorinated phase still detected was akaganeite. This phase was located at the interface between metal and corrosion products, but also distributed in strata throughout the corrosion products, mainly in the outer layers. The storage conditions affect the corrosion pattern: the quantities of chlorides to be extracted differed and the chloride species were not present in the same form.

In the present paper, we evaluate the influence of the storage protocol on the dechlorination treatments. We focus on the treatment conditions (temperature, solution, polarization, water quality) and their impact on chloride extraction, as well as on the conservation of the objects. We do not detail the analysis of corrosion products but we use them to explain and discuss our results.

Materials and methods

Archaeological corpus

The objects studied are iron bars from a Gallo-Roman shipwreck (first-century BC) submerged off the coast of Les Saintes Maries de la Mer (Fig. 1) (Long, 2003). These bars, whose metallurgy was thoroughly studied (Pagès *et al.*, 2008), have a low carbon content. The first bars were excavated in 2005 and stored in air for one or two years, which caused significant alterations: decohesion of corrosion products and a significant loss of the original surface. The bars excavated in 2005 were cut in half to create an opportunity to test various treatment baths on identical samples. Other bars were excavated in 2006. To limit the modification of their corrosion products, they were never exposed to the atmosphere and were stored in tap water for six or nine weeks. Finally, two other bars were excavated in 2008 and stored in seawater. All the bars were covered with a thin layer of concretions. In contrast to what is usually done during dechlorination treatments of ferrous objects from the marine environment, this concretion layer was not removed in order not to disturb the stratigraphy of the corrosion products. These bars were in a very good state of conservation (thin layer of corrosion products of the order of 3–5 mm with most of interior metal core remaining). However, in some spots, the original surface had completely disappeared.

These bars underwent different dechlorination treatments, some of which were not completed so that the corrosion products could be analysed during the treatment. All the bars studied are listed in Table 1 according to the dechlorination treatment used.

Dechlorination treatments

The dechlorination treatments were performed in the conservation-restoration laboratories taking part in the ODéFA program (EPCC Arc'Antique in Nantes and LC2R in Draguignan, France) according to their usual protocols. Dechlorination treatments



Figure 1 An example of one of the iron bars from a Gallo-Roman shipwreck (first-century BC) submerged off the coast of Les Saintes Maries de la Mer (France).

Table 1 Storage, treatment, and analysis of archaeological iron bars

Storage	Bars	Treatment (days for bath1/days for bath2/.../days for bath n)						Analyses
		No Treatment	Electrolysis (KOH 1%, +1.45 V/SSE) Treatment: osmosed water except (*) rain water Rinsing: osmosed water, (P) under polarization Drying in the air		NaOH Treatment: osmosed water with 2% NaOH except (1) 1%NaOH Rinsing: osmosed water except (*) tap water Drying in the air except (E) in ethanol		Alkaline sulphite Treatment: 0.5 mol l ⁻¹ except (-) 0.1 mol l ⁻¹ NaOH + 0.05 mol l ⁻¹ Na ₂ SO ₃ Rinsing: tap water Drying in the air	
			20°C	20°C	50°C	20°C	50°C	
3 weeks in tap water (Cl 470 mg l ⁻¹) + 3 weeks in tap water (Cl 480 mg l ⁻¹)	A	X						X
	B		25					X
	C		16/26/21/28					X
	D		16/26/21/28/37/35/ 27/21/14 (P)					X
5 weeks in tap water (Cl 185 mg l ⁻¹) + 4 weeks in tap water (Cl 190 mg l ⁻¹)	E					22/7 (E)		X
	F					22/27 (E)		X
	G					22/27/29/37 (E)		X
1 year in air	H					22/27/29/37 (E)		X
	I		14/17/8 (P)					X
2 years in air	J			14/17/8 (P)				X
	K		14/17/8 (*) (P)					X
	L						14/17/8	X
	M					14/17/8 (1) (*)		X
	N					14/17/8 (1) (*)		X
	O	X						X
7 months in seawater	P		9/13/28/48/39 (P)					X
	Q						9/13/28/48/39/31/ 21/22/27 (-)	X

based on electrolysis methods on one hand and on immersion in sodium hydroxide or in alkaline sulphite on the other hand were carried out.

The protocol of the electrolysis treatment is described as follows. Each object was individually polarized at a cathodic potential (-1.45 or -0.8 V/SHE) using a stable power supply. The object acted as the cathode, and the anode consisted of a stainless-steel grid. Every treatment were realized by electrolysis except one was carried out in osmosis water. The 1% w/v KOH solution in reverse osmosis water (RO water) at room temperature was stirred regularly. In the case of bar K (Table 1), the RO water was replaced by rainwater (reclaimed water from Nantes, France). The use of tap water (especially hard water) is discouraged because it causes calcium–magnesium deposits on the objects. As the analysis of rainwater collected in Nantes showed the absence of components that can form deposits on cathodically polarized iron, we considered replacing RO water by rainwater. The results obtained with rainwater proved to be similar to those obtained with osmosis water. The electrolysis treatments, usually conducted at room temperature, were also tested at 50°C . The electrolysis solution and the alkaline sulphite were raised to 50°C using a heater thermostat with constant stirring.

As far as alkaline treatments are concerned, they are usually done by immersion in 2% w/v sodium hydroxide solutions at 50°C . The temperature of 50°C is maintained by placing the treatment tanks in an oven, and the solutions are stirred regularly. Some parameters were varied during treatment of the half-bars (I to N) in order to determine and compare their efficiency (Table 1). The concentration of sodium hydroxide in particular was set to 1% w/v in some cases. The treatments were performed at room temperature and at 50°C .

Treatment with alkaline sulphite (equimolar mixture of NaOH and Na_2SO_3 at 0.5 mol l^{-1}) was also tested, because this method is also used frequently in many conservation-restoration labs to stabilize certain ferrous objects. Bar L was treated in a 0.5 mol l^{-1} NaOH solution and a 0.5 mol l^{-1} Na_2SO_3 solution, but in light of the paper by Rimmer *et al.* (2010), the concentrations in the sulphite baths were reduced. For the treatment of bar Q, the solution consisted of 0.1 mol l^{-1} NaOH and 0.05 mol l^{-1} Na_2SO_3 . The volume of treatment solutions was calculated to maintain a constant solution volume/bar volume of 10 in the case of bars B–H and 15 for bars I–Q.

After treatment, the objects were rinsed in RO water under cathodic polarization for the objects treated by electrolysis, or under a stream of RO water for other objects. The treated objects were dried in air, except for bars E–G that were dried by being immersed in an ethanol bath. The duration of treatment depended

on the quantity of chloride ions to be extracted, and was determined through measurements taken during treatment monitoring, as described below.

Treatment monitoring

For all the objects except for bars E–G, the potential was measured by placing a non-polarized contact on the object. The measurement was taken with a high input impedance multimeter (MX53C Metrix, Annecy, France) and a reference electrode (saturated sulphate electrode (SSE) = 0.65 V/SHE (standard hydrogen electrode)). Samples of the solutions were taken to measure the pH using a glass electrode. Then these solutions were acidified to determine the concentration of chloride ions extracted by argentometry–potentiometry ($10^{-2}\text{ mol l}^{-1}$ silver nitrate) with an error of 4–10%. Each time the solutions were sampled (50–100 ml), they were stirred and topped up with RO water to compensate for losses due to evaporation. Samples were taken at least once a week. The solutions were changed when the concentration of chloride ions stopped increasing or reached approximately 2000 mg l^{-1} in the case of electrolysis to prevent corrosion of the anodes. Dechlorination was considered complete when the concentration of chloride ions was less than $10\text{--}15\text{ mg l}^{-1}$ in the case of electrolysis and 5 mg l^{-1} in the case of immersion treatments. As the cathodic polarization protects the object, the rinsing can last longer than immersion treatments. Therefore, the criterion for completion in electrolysis was higher.

In the case of cathodic polarization, the rinsing steps were monitored by measuring conductivity. The baths were changed as soon as the conductivity value plateaued. Rinsing was stopped when the conductivity was less than $50\text{ }\mu\text{S cm}^{-1}$.

To determine the corrosion before, during, and after treatment, the following protocol was used. One bar (A) and one half-bar (O), from the excavations in 2006 and 2008, respectively, underwent no treatment at all, to characterize the corrosion products before treatment. Bars B, C, E, and F were only partially treated, to characterize the corrosion products during electrolysis (B: 25 days of treatment and C: 91 days of treatment) and immersion in sodium hydroxide (E: 29 days of treatment and F: 49 days of treatment). The other bars underwent a full treatment (Table 1). The corrosion products were analysed for several bars (Table 1), the results of which are detailed in previous articles (Réguer *et al.*, 2007a; Guilminot *et al.*, 2008; Rémazeilles *et al.*, 2009, 2010; Kergourlay *et al.*, 2010, 2011).

Results and discussion

The combination of the macroscopic observations of the objects before and after treatment, of the

measurements of the chloride contents in the baths, and of the physico-chemical analyses have led to some conclusions on various parameters influencing the evolution encountered by the objects during the treatments: among them are the storage protocol before treatment, the temperature, and the composition of the baths. These elements are examined in the following sections.

Influence of storage protocol of the objects before treatment

For bars stored in tap water (A, B, C, D, E, and F (Table 1)), the presence of akaganeite could be due to an oxidation of $\beta\text{-Fe}_2(\text{OH})_3\text{Cl}$ which corresponds to the beginning of chloride extraction (Rémazeilles *et al.*, 2009): 375 mg l⁻¹ of chlorides were measured in the storage water of bars E, F, and G, and 950 mg l⁻¹ of chlorides were detected in the storage water of bars A, B, C, and D (Table 1). For the bars stored in seawater (P and Q), the process could not be quantified because of the salinity of the medium, but it can be assumed that significant chloride extraction did not occur before the dechlorination treatment was initiated.

For bars stored in air (H, I, J, K, L, M, N, and O), the only chlorinated phase was akaganeite with a Cl content of about 5% w. Therefore, the quantity of chlorides to extract was lower than for bars stored in water.

The experiments on the bars in different storage conditions are presented in the following subsections.

Treatment by electrolysis

The accumulated Cl content extracted for the three tested bars are presented in Fig. 2. It provides some information on the influence of the storage protocol of the bars before the beginning of the treatment, on the kinetics, and on the efficiency of the Cl extraction. The fastest kinetics were obtained with the bars stored in air: 85% of the chlorides were extracted in 10% of the treatment time (1.7 g Cl extracted during the first 4 days of a total of 40 days of treatment). The bars

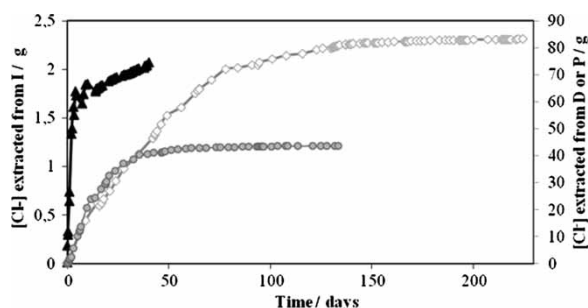


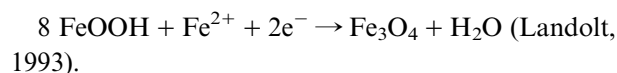
Figure 2 Dechlorination curves of bars treated by electrolysis at ambient temperature – influence of the storage: (▲) I stored for two years at atmosphere, (◁) D stored for six weeks in tap water, (●) P stored for seven months in seawater.

stored in water had slower kinetics. In the case of bar P stored for seven months in seawater, 92% of the chlorides were extracted in 25% of the treatment time (40 g Cl extracted during the first 35 days of a total of 134 days of treatment). In the case of bar D stored for six weeks in tap water, the kinetics were even slower: 87% of the chlorides were extracted in 35% of the treatment time (72 g Cl extracted during the first 78 days of a total of 225 days of treatment). Although the kinetics were slower for the bars stored in water, the chloride extraction rate was 20–40 times higher than for the bars stored in air. The main difference between the bars stored in water (P and D) and the bars stored in air (I) was their state of degradation. The bar stored for two years in air (I) had lost a large portion of the corrosion products and thus contained far less chloride.

Previous characterization studies help to explain these results (Kergourlay *et al.*, 2011). During the electrolysis treatment of the bars stored in water, the chlorides were localized in pockets consisting of a mixture of Fe^{II} hydroxychloride and akaganeite within the inner layer, mainly at the metal/oxide interface. These chloride-rich areas at the metal interface were often associated with the presence of inclusions initially present in the metal. As the treatment advanced, the residual chlorides were located only at the metal interface. After the electrolysis treatment of the bars stored in water, all the chlorinated compounds had transformed into poorly crystallized Fe^{III} phases: feroxyhyte ($\delta\text{-FeOOH}$), ferrihydrite ($\text{Fe}_2\text{O}_3\cdot n\text{H}_2\text{O}$), and goethite ($\alpha\text{-FeOOH}$). The thin layer of magnetite and the layer of concretion did not appear to be modified by the treatment.

In this case, chemical mechanisms were involved (Kergourlay *et al.*, 2011): the iron hydroxychloride ($\beta\text{-Fe}_2(\text{OH})_3\text{Cl}$) initially present in the layer was transformed into Fe(OH)₂ during immersion in the basic medium. Drying the bars after treatment induces the oxidation of Fe(OH)₂ into FeOOH compounds. Electrolysis therefore essentially plays a role in the kinetics of extraction of chlorides.

For the electrolysis treatment of the bars stored in air, all the corrosion products were transformed into magnetite (Fe₃O₄). In the case of these bars, it would appear that electrolysis caused the reduction of the Fe^{III} corrosion products:



Immersion treatments

As observed for the electrolysis treatment, the overall amount of chloride extracted from the bar stored in tap water is 25 times larger than for the bar stored two years in air (Fig. 2). This significant difference is due to the fact that the bars stored in air have lost

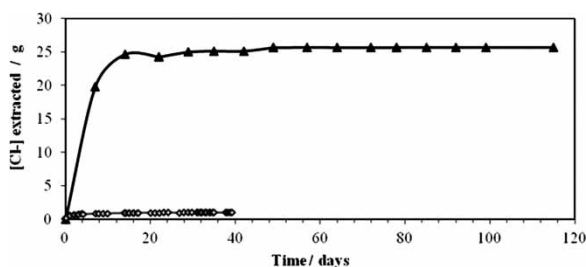


Figure 3 Dechlorination curves of bars treated by immersion in NaOH at 50°C – influence of the storage: (▲) G stored for six weeks in tap water, (◊) M stored for two years in air.

part of their corrosion layers. Storage choice also has a significant influence on the kinetics of extraction of chlorides during treatment by immersion in sodium hydroxide at 50°C (Fig. 3). Most of the chlorides were extracted during the first days of treatment regardless of the storage method, but the dechlorination was faster after storage in tap water:

- Storage in tap water: 92% of the chlorides were extracted in 10% of the treatment time (23.6 g Cl extracted during the first 11 days of a total of 115 days of treatment).
- Storage in air: 75% of the chlorides were extracted in 10% of the treatment time (755 mg Cl extracted during the first four days of a total of 40 days of treatment).

The physico-chemical results (Kergourlay *et al.*, 2010) obtained on the bars stored in air showed that dechlorination was incomplete even at the end of the treatment because akaganeite was detected in the outer layers of the corrosion products. Besides, the bars rapidly presented after drying a recurrence of corrosion (orange spots on the surface). In contrast, this was not the case for the bar stored in tap water, which indicates that all the chlorides were extracted. The initial outer layers (the concretions and the magnetite layer marking the original surface) were still present after treatment.

During treatment by immersion in sodium hydroxide (analysis of bar F after 49 days of immersion), a magnetite layer appeared at the metal surface. This layer was thicker after 115 days of treatment (bar G), reaching a thickness of 200–400 µm. As stated in the paragraph on the results obtained with electrolysis treatments, when immersed in a basic medium, the chlorinated compounds ($\beta\text{-Fe}_2(\text{OH})_3\text{Cl}$) transformed into $\text{Fe}(\text{OH})_2$ which oxidized into FeOOH during drying (Kergourlay *et al.*, 2011). In the case of immersion treatments in sodium hydroxide at 50°C, the presence of oxygen coupled with the high temperature (50°C) caused $\text{Fe}(\text{OH})_2$ to oxidize into magnetite (Fe_3O_4) during treatment (Kergourlay *et al.*, 2011). The formation of magnetite at the metal interface, detected on the bars treated in sodium hydroxide at 50°C (bars F and G), may also result from corrosion of the metallic core.

All the chlorinated compounds transformed into a highly porous layer consisting of iron oxides (feroxyhyte ($\delta\text{-FeOOH}$)/ferrihydrite ($\text{Fe}_2\text{O}_3\text{-}n\text{H}_2\text{O}$)/goethite ($\alpha\text{-FeOOH}$) and magnetite (Kergourlay *et al.*, 2011).

Influence of temperature

To study the influence of the temperature, bars stored two years in air have been selected.

Electrochemical treatment

The effect of temperature was tested (Fig. 4) on two half-bars stored in air. The curves are almost identical for ambient and 50°C temperatures. This indicates that the kinetics were similar. Most of the chlorides were extracted during the beginning of the treatment.

Hence it can be concluded that the influence of temperature in the experimental conditions tested here is negligible. The main factor favouring the extraction of chlorides during electrolysis is the electrokinetic effect of polarization slightly influenced by the temperature. Diffusion, a phenomenon activated by temperature, has a minor role here.

Immersion treatment

The influence of temperature on immersion treatments is illustrated for sodium hydroxide solutions in Fig. 5. At ambient temperature the kinetic was slower:

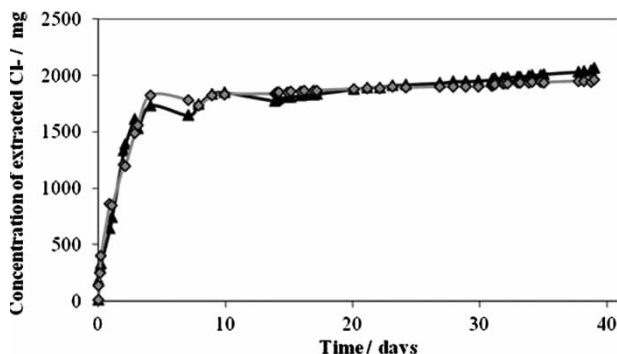


Figure 4 Dechlorination curves of bars treated by electrolysis – Influence of the temperature: (▲) I at ambient temperature, (◊) J at 50°C.

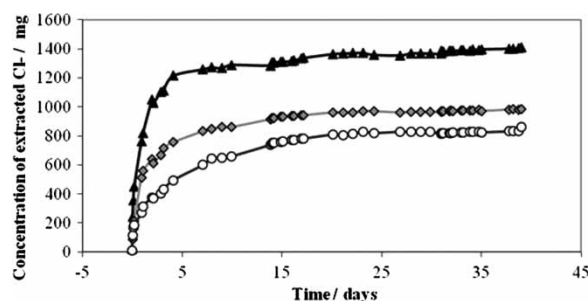


Figure 5 Dechlorination curves of bars treated by immersion: (▲) L treated by immersion in alkaline sulphite at 50°C, (◊) M treated by immersion in NaOH at 50°C, (○) N treated by immersion in NaOH at ambient temperature.

- At ambient temperature, 60% of the chlorides were extracted in 10% of the treatment time (495 mg Cl extracted during the first four days of a total of 40 days of treatment).
- At 50°C, 75% of the chlorides were extracted in 10% of the treatment time (755 mg Cl extracted during the first four days of a total of 40 days of treatment).

Increasing the temperature promoted, on the one hand, the reaction of transformation of chloride-containing phases and, on the other hand, the diffusion of chlorides, and thus their extraction. Analyses of the half-bar immersed in sodium hydroxide at ambient temperature (bar N) confirmed the results obtained on the half-bar M (Kergourlay *et al.*, 2010). The immersion treatments of the bars stored in air did not result in complete dechlorination. Akaganeite was also detected on the half-bar N, in larger amounts than the half-bar M. For the half-bar N, akaganeite had a chlorine content of about 4–6% and it was also localized in the outer zones of the corrosion layer.

Influence of the composition of the solution

Only immersion treatments at 50°C for bars stored in air are considered in this section. The dechlorination curves obtained on the half-bars stored in air and treated in sodium hydroxide or alkaline sulphite solutions (Fig. 5) are slightly different. The kinetics of immersion treatments can be compared. It appears that a slightly higher kinetic was obtained with the alkaline sulphite solution:

- Eighty-five per cent of the chlorides were extracted in 10% of the treatment time in the sulphite solution (1215 mg Cl extracted during the first four days of a total of 40 days of treatment).
- Seventy-five per cent of the chlorides were extracted in 10% of the treatment time in the hydroxide solution (755 mg Cl extracted during the first four days of a total of 40 days of treatment).

Influence of drying the object after treatment

Characterization studies conducted on the bars after treatment (Kergourlay *et al.*, 2010, 2011) suggest that drying causes Fe(OH)₂, resulting from the dechlorination of β-Fe₂(OH)₃Cl, to quickly oxidize into FeOOH. Note that the bars E, F, G, and H were dried by immersion in an ethanol solution, while the bars L, M, N, and Q were simply air dried after the rinsing step (Table 1). Drying in ethanol is faster than air drying. The bars dried in alcohol presented severe decohesion of their corrosion products, while the bars dried in air (except for bar Q) retained an adherent corrosion layer. It seems that rapid drying is not advisable, in order to preserve the mechanical integrity of the corrosion products.

Comparison between electrochemical and chemical treatments

Several observations can be drawn from this study. First, storage in water limits the transformation of the corrosion products formed during immersion in sea water. In this case, the layer of corrosion products is mainly composed of β-Fe₂(OH)₃Cl. The efficiency of the dechlorination treatments (immersion or electrolysis) proved to be the same with this kind of corrosion layer (Fig. 6). Chlorides are mainly extracted in the beginning of treatment. However, extracting the last of the chlorides required more time in the case of immersion in alkaline sulphite: it took 134 days to extract all the chlorides by electrolysis, but it took 238 days to completely dechlorinate the bar immersed in an alkaline sulphite solution.

In the case of artefacts stored in air, chlorides remain in the corrosion layer whatever the treatment is. But the electrolysis treatment should be preferred because the chloride extraction is higher and the total duration of the treatment is lower (Fig. 7). Characterizations of the bars stored in air and treated by electrolysis show that the corrosion products were reduced to magnetite (Fe₃O₄), giving them a black appearance, and all the chlorides were extracted. The bars stored in air and treated by immersion in sodium hydroxide still contained chlorides after the treatment.

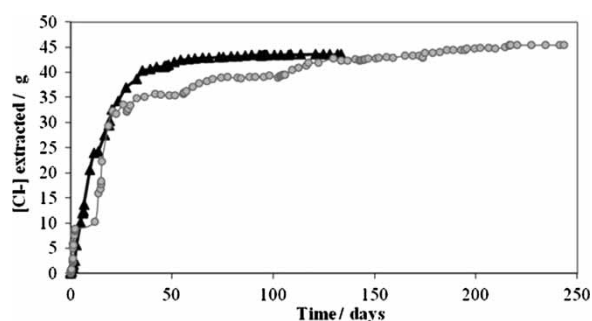


Figure 6 Dechlorination curves of bars stored in seawater: (▲) P treated by electrolysis at ambient temperature, (○) Q treated by immersion in alkaline sulphite at 50°C.

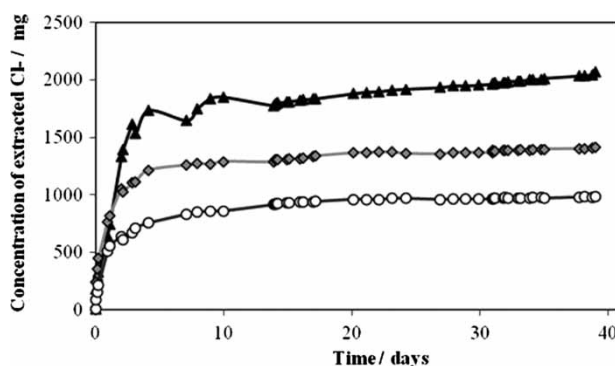


Figure 7 Dechlorination curves of bars stored in air: (▲) I treated by electrolysis at ambient temperature, (◇) L treated by immersion in alkaline sulphite at 50°C, (○) M treated by immersion in NaOH at 50°C.

The difficulty in extracting the chloride ions from ferrous objects exposed to air before treatment has already been observed by Gonzalez *et al.* (2003). They attribute this to a modification in the nature of the corrosion products during storage in air. Our results confirm this hypothesis: the extraction of chloride ions appears to be more difficult in the presence of akaganeite than in the presence of $\beta\text{-Fe}_2(\text{OH})_3\text{Cl}$. The storage step is crucial for the transformation of corrosion products.

Conclusions

Based on the productive research programme ODéFA comparing the different treatments applied on iron bars from a Gallo-Roman shipwreck off Saintes Maries de la Mer, some conclusions can be highlighted:

- Whatever the type of treatment, chemical or electrochemical, the chlorinated compounds ($\beta\text{-Fe}_2(\text{OH})_3\text{Cl}$) release chloride ions due to chemical transformation. After treatment, the corrosion layers are composed mainly of poorly crystallized goethite and ferrosiderite ($\delta\text{-FeOOH}$) or ferrihydrite ($\text{Fe}_2\text{O}_3 \cdot n\text{H}_2\text{O}$). For bars stored in water, treatment by cathodic polarization does not reduce the corrosion products. The transformation of Fe(III) compounds by cathodic polarization is found only on the bars stored in air, where Fe(III) oxyhydroxides are transformed into magnetite (Fe_3O_4). For the bars stored in water, the corrosion products are mainly composed of Fe(II). They are oxidized to Fe(III) oxyhydroxides after dechlorination treatment, i.e. after the cathodic polarization has been stopped.
- The influence of the temperature has been highlighted in the case of the immersion treatment but not for the electrolysis treatment. Chloride ions are extracted by diffusion during immersion treatments after being released into the solution by transformation of the chloride-containing phases. Increasing the bath temperature accelerates this process and therefore influences the chloride extraction rate. In the case of cathodic polarization, the chloride ions are extracted mainly due to the electric field effect. Based on the results of this study, electrolysis treatment at room temperature has similar kinetics as immersion treatment in alkaline sulphite at 50°C.
- In the case of the immersion treatment there is a risk of corrosion of the metallic core remaining in the artefact. The presence of magnetite (Fe_3O_4) at the metal interface is observed on the bars treated by immersion in sodium hydroxide at 50°C. The magnetite results mainly from the oxidation of $\text{Fe}(\text{OH})_2$, product of the dechlorination of $\beta\text{-Fe}_2(\text{OH})_3\text{Cl}$, but also perhaps from the corrosion of the metallic core. In the case of electrolysis, cathodic polarization protects the metallic core. In the case of immersion in alkaline sulphite solutions, the presence of the sulphite removes dissolved oxygen and prevents corrosion.
- For bars stored in water, drying causes rapid oxidation of $\text{Fe}(\text{OH})_2$ into ferrosiderite $\delta\text{-FeOOH}$. If the

object is dried too quickly (drying in alcohol), decohesion of the corrosion products occurs.

- The majority of the chloride ions are extracted at the beginning of the treatment in all cases. For the bars stored in water, residual chloride ions are located at the metal/corrosion products interface. It is important to eliminate even small amounts of residual chloride ions because they cause recurrence of active corrosion after treatment. It is therefore important to continue dechlorination treatment as long as chlorides are detected in the treatment solution. For the bars stored in air, the residual chlorides are located in the outer layer of the corrosion products, in the form of akaganeite. This shows that all the chlorides are not extracted when the objects are treated by immersion. These findings confirm the recommendations followed in restoration-conservation laboratories working on ferrous objects, namely that it is preferable to treat an object as soon as it is excavated. Storage in air endangers the ferrous objects, causing flaking of the layers which results in a loss of original surface and reduces the effectiveness of treatments by immersion in sodium hydroxide. In the case of objects exposed to air, it is preferable to recommend treatment by electrolysis, which eliminates all the chlorides.

Acknowledgements

This study was funded through the PNRG, and we thank the Ministry of Culture for its support. We also thank L. Long and the DRASSM (Département des Recherches Archéologiques Subaquatiques et Sous-Marines) for providing us with the samples needed for this study. We thank the interns, Ronan Talarmin, Medhi Meguelati, and Benjamin Guestre, for helping to obtain these results.

References

- Argo, J. 1981. On the Nature of 'Ferrous' Corrosion Products on Marine Iron. *Studies in Conservation*, 26: 42–4.
- Beaudoin, A., Clerice, M.C., Francoise, J., Labbe, J.P., Loeper-Attia, M.A. & Robbiola, L. 1997. Corrosion d'objets archéologiques en fer après déchloruration par la méthode au sulfite alcalin. Caractérisation physico-chimique et retraitement, électrochimique. In: I.D. MacLeod, S.L. Pennec & L. Robbiola, eds. *Metal 95, Proceedings of the ICOM-CC Metal Conference, Semur en Auxois*. London: James & James, pp. 170–77.
- Dalard, F., Gourbeyre, Y. & Degrigny, C. 2002. Chloride Removal from Archaeological Cast Iron by Pulsating Current. *Studies in Conservation*, 47: 117–21.
- Degrigny, C. 2004. Altération et conservation des objets métalliques issus de fouilles sous-marines. In: A. Siano, ed. *Studio e conservazione di manufatti archeologici*. Firenze: Nardini, pp. 243–74.
- Degrigny, C. & Spiteri, L. 2004. Electrochemical Monitoring of Marine Iron Artefacts During Their Storage/Stabilisation in Alkaline Solutions. In: J. Ashton & D. Hallam, eds. *Metal 04, Proceedings of the Interim Meeting of the ICOM-CC Metal WG*. Canberra: National Museum of Australia, pp. 315–31.
- Gilberg, M. & Seeley, N. 1981. The identification of Compounds Containing Chloride Ions in Marine Iron Corrosion Products: A Critical Review. *Studies in Conservation*, 26: 50–6.
- Gonzalez, N., De Vivies, P., Drews, M. & Mardikian, P. 2003. Characterizing the Chloride in the Wrought Iron Rivets from

- the Hunley. In: *NACE Northern Area Eastern Conference*, Ottawa, September 15–17, 2003, Proceedings on CD. Ottawa: NACE.
- Gonzalez, N., Cook, D., De Vivies, P., Drews, M. & Mardikian, P. 2007. The Effects of Cathodic Polarization, Soaking in Alkaline Solutions and Subcritical Water on Cast Iron Corrosion Products. In: C. Degryny, R. Van Langh, B. Ankersmit & I. Joosten, eds. *Metal 07, Proceedings of the Interim Meeting of the ICOM-CC Metal WG*. Amsterdam: Rijksmuseum, vol. 3, pp. 32–37.
- Gonzalez-Pereyra, N., Brocard, T., Cretté, S., De Vivies, P., Drews, M. & Mardikian, P. 2011. The Use of Subcritical Fluids for the Stabilization of Concreted Iron Artefacts. In: P. Mardikian, C. Chemello, C. Watters & P. Hull, eds. *Metal 2010, Proceedings of the Interim Meeting of the ICOM-CC Metal WG*. Charleston: Clemson University, pp. 22–30.
- Guilminot, E., Huet, N., Neff, D., Dillmann, P., Rémazeilles, C., Refait, P., et al. 2008. Dechlorination of Archaeological Iron Artefacts: Dechlorination Efficiency Assessment Assisted by Physico-chemical Analytical High-tech Methods. In: J. Bridgland, ed. *ICOM Committee for Conservation, 15th Triennial Conference in New Delhi*. New Delhi: Allied, vol. 1, pp. 435–43.
- Helm-Hansen, N., Van Lanchot, J., Szalkay, C.D. & Turgoose, S. 1993. Electrochemical Assessment and Monitoring of Stabilisation of Heavily Corroded Archaeological Iron Artefacts. *Corrosion Science*, 35: 767–74.
- Kergourlay, F., Guilminot, E., Neff, D., Remazeilles, C., Reguer, S., Refait, P., et al. 2010. Influence of Corrosion Products Nature on Dechlorination Treatment: Case of Wrought Iron Archaeological Bars Stored 2 Years in Air Before NaOH Treatment. *Corrosion Engineering Science and Technology*, 45: 407–13.
- Kergourlay, F., Remazeilles, C., Neff, D., Foy, E., Conforto, E., Guilminot, E., et al. 2011. Mechanisms of the Dechlorination of Iron Archaeological Artefacts Extracted from Seawater. *Corrosion Science*, 53: 2474–83.
- Lacoudre, N., Degryny, C. & De Lavergne, E. 1991. Traitements de conservation du patrimoine archéologique sous-marin: trois techniques. In: N. Lacoudre & C. Degryny, eds. *Electricité et Archéologie*. Paris: EDF, pp. 15–34.
- Landolt, D. 1993. *Corrosion et Chimie des surfaces des métaux*. Lausanne: Presses Polytechniques et Universitaires Romandes, p. 321.
- Liu, J., Li, Y. & Wu, M. 2008. Electrochemical Methods for Chloride Removal from Simulated Cast Iron Artefacts. *Studies in Conservation*, 53: 41–48.
- Long, L. 2003. Au Large des Saintes Maries de la Mer. In: Ministère de la Culture et de la Communication, ed. *Bilan scientifique du Département des Recherches Archéologiques Subaquatiques et Sous Marines (DRASSM) de 2002*. Paris: Ministère de la culture et de la communication, pp. 51–57.
- Mardikian, P., Gonzalez, N., Drews, M. & De Vivies, P. 2010. New Perspectives Regarding the Stabilization of Terrestrial and Marine Archaeological Iron. In: W. Williams & C. Peachey, eds. *The Conservation of Archaeological Materials: Current Trends and Future Directions. Proceedings of the Conference at Colonial Williamsburg*, Virginia, USA, November 13–17 2005. London: British Archaeological Reports.
- Neff, D., Dillmann, P., Bellot-Gurlet, L. & Beranger, G. 2005. Corrosion of Iron Archaeological Artefacts in Soil: Characterisation of the Corrosion System. *Corrosion Science*, 47: 515–35.
- North, N.A. & Pearson, C. 1978. Washing Methods for Chloride Removal from Marine Iron Artifacts. *Studies in Conservation*, 23: 174–86.
- North, N.A. 1987. Conservation of Metals. In: C. Pearson, ed. *Conservation of Marine Archaeological Objects*. London: Butterworths, pp. 207–32.
- Pagès, G., Long, L., Fluzin, P. & Dillman, P. 2008. Réseaux de production et standards de commercialisation du fer antique en Méditerranée: les demi-produits des épaves romaines des Saintes Maries de la Mer (Bouches du Rhône). *Revue Archéologique Narbonnaise*, 41: 261–83.
- Refait, P. & Genin, J.M. 1997. The Mechanisms of Oxidation of Ferrous Hydroxychloride $\beta\text{-Fe}_2(\text{OH})_3\text{Cl}$ in Aqueous Solution: The Formation of Akaganéite vs Goethite. *Corrosion Science*, 39: 539–53.
- Réguer, S., Neff, D., Rémazeilles, C., Guilminot, E., Nicot, F., Pelé, C., et al. 2007a. Desalination of Iron Archaeological Artefacts: Understanding of Chlorine Removal Mechanisms of the Corrosion Layers Supported by Characterisation Techniques. In: C. Degryny, R. Van Langh, B. Ankersmit & I. Joosten, eds. *Metal 07, Proceedings of the Interim Meeting of the ICOM-CC Metal WG*. Amsterdam: Rijksmuseum, vol. 2, pp. 60–8.
- Réguer, S., Dillmann, P. & Mirambet, F. 2007b. Buried Iron Archaeological Artefacts: Corrosion Mechanisms Related to the Presence of Cl-containing Phases. *Corrosion Science*, 49: 2726–44.
- Rémazeilles, C. & Refait, P. 2007. On the Formation of $\beta\text{-FeOOH}$ (Akaganéite) in Chloride-containing Environments. *Corrosion Science*, 49: 844–57.
- Rémazeilles, C., Neff, D., Kergourlay, F., Foy, E., Conforto, E., Guilminot, E., et al. 2009. Mechanisms of Long Term Anaerobic Corrosion of Iron Archaeological Artefacts in Seawater. *Corrosion Science*, 51: 2932–41.
- Rémazeilles, C., Saheb, M., Neff, D., Guilminot, E., Tran, K., Bourdoiseau, J.-A., et al. 2010. Microbiologically Influenced Corrosion of Archaeological Artefacts: Characterisation of Iron (II) by Raman Spectroscopy. *Journal of Raman Spectroscopy*, 41: 1135–43.
- Rimmer, M., Wang, Q. & Watkinson, D. 2010. The Effectiveness of Chloride Removal from Archaeological Iron Using Alkaline Deoxygenated Desalination Treatments. In: G. Eggert & B. Schmutzler, eds. *Archaeological Iron Conservation Colloquium 2010*. Stuttgart: State Academy of Art and Design, pp. 67–9.
- Schmidt-Ott, K. & Boissonnas, V. 2002. Low-pressure Hydrogen Plasma: An Assessment of Its Application on Archaeological Iron. *Studies in Conservation*, 47: 81–7.
- Selwyn, L., Sirois, P.J. & Argyropoulos, V. 1999. The Corrosion of Excavated Archaeological Iron with Details on Weeping and Akaganéite. *Studies in Conservation*, 44: 217–32.
- Selwyn, L., McKinnon, W.R. & Argyropoulos, V. 2001. Models for Chloride Ion Diffusion in Archaeological Iron. *Studies in Conservation*, 46: 109–20.
- Selwyn, L. 2004. Overview of Archaeological Iron: The Corrosion Problem, Key Factors Affecting Treatment, and Gaps in Current Knowledge. In: J. Ashton & D. Hallam, eds. *Metal 04, Proceedings of the Interim Meeting of the ICOM-CC Metal WG*. Canberra: National Museum of Australia, pp. 294–306.
- Selwyn, L. & Argyropoulos, V. 2005. Removal of Chloride and Iron Ions from Archaeological Wrought Iron with Sodium Hydroxide and Ethylenediamine Solutions. *Studies in Conservation*, 50: 81–100.
- Wang, Q. 2007. An Investigation of Deterioration of Archaeological Iron. *Studies in Conservation*, 52: 125–34.
- Wang, Q., Dove, S., Shearman, F. & Smirniou, M. 2008. Evaluation of Methods of Chloride Ion Concentration Determination Treatments and Effectiveness of Desalination Treatments Using Sodium Hydroxide and Alkaline Sulphite Solutions. *The Conservator*, 31: 67–74.