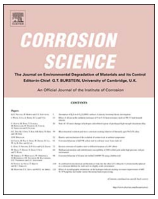
ARTICLE IN PRESS

Corrosion Science xxx (xxxx) xxx–xxx

Contents lists available at ScienceDirect

Corrosion Science

journal homepage: www.elsevier.com/locate/corsci



Stabilization treatment of cultural heritage artefacts: *In situ* monitoring of marine iron objects dechlorinated in alkali solution

F. Kergourlay[a,b], S. Réguer[b], D. Neff[a,*], E. Foy[a], F.-E. Picca[b], M. Saheb[c], S. Hustache[b], F. Mirambet[d], P. Dillmann[a]

[a] *LAPA-IRAMAT, NIMBE, CEA, CNRS, Université Paris-Saclay, CEA Saclay 91191 Gif-sur-Yvette CEDEX, France*

[b] *Synchrotron SOLEIL – L'Orme des Merisiers Saint-Aubin, BP 48, 91192 Gif-sur-Yvette CEDEX, France*

[c] *Laboratoire Interuniversitaire des Systèmes Atmosphériques (LISA), UMR CNRS 7583, CNRS UMR 7583, Université Paris-Est Créteil, Université Paris Diderot, Faculté des Sciences et Technologie, 61 avenue du Général de Gaulle, 94010 Créteil CEDEX, France*

[d] *Centre de recherche et de restauration des musées de France (C2RMF) Palais du Louvre, Porte des Lions, 14, quai François Mitterrand, 75001 Paris, France*

ARTICLE INFO

Keywords:
Iron marine corrosion
Stabilization treatment
in situ study
Synchrotron radiation
µXRD
Raman spectroscopy
SEM-EDS
Thermodynamic modelisation
dechlorination

ABSTRACT

The preservation of archaeological iron artefacts necessitates stabilization treatments. For this study, such treatments were applied, in aerated and deaerated NaOH solutions, to Roman iron bars excavated from a marine site in order to understand the evolution of corrosion layers composed of ferrous hydroxychloride β-$Fe_2(OH)_3Cl$. Their transformation was monitored *in situ* by micro-diffraction under synchrotron radiation and characterized *ex situ* using multi-scale complementary analytical tools. The formation of transient phases such as ferrous hydroxide $Fe(OH)_2$ was identified in both media and chlorinated green rust $GR(Cl^-)$ occurred in aerated solutions, showing the influence of dissolved oxygen on the transformation processes.

1. Introduction

Underwater archaeology began in the early 19th century with the introduction and development of specific equipment for underwater exploration. Excavation now employs scientific methodology to recover relatively well-preserved cultural heritage that often includes metallic artefacts. The exposure of ferrous alloys in more oxidizing media after excavation can cause damage that leads to the loss of this historic heritage [[1],2]. These phenomena arise from the extreme reactivity of the chlorinated corrosion product layer developed on the artefacts during their immersion period. The formation of new chlorine-containing phases of lower density within the corrosion system generates and amplifies the spectacular post-excavation degradations observed on ancient metallic objects [1].

Conservation scientists have thus carried out stabilization treatments based on chlorine extraction from the corrosion system such as electrolysis [3–5], hydrogen plasma [6–8], subcritical fluid [9–12], or the most common, alkaline solutions [4,13–19]. A large number of studies aiming to improve the efficiency of these stabilization treatments have been conducted using macroscopic [18] or microscopic scale approaches [20–22]. They were all conducted on samples analysed post-treatment, leading to a better understanding of the dechlorination effect on the artefacts in term of morphology, consistency and identification of the corrosion products.

Stabilization treatments have to be optimized in order to improve their duration and their efficiency, as some treated collections show further corrosion post-treatment. For this purpose, the identification and the influence of the transient phases on the dechlorination mechanisms, the species transport (dissolved oxygen, chlorine…) in the porous corrosion products network, the impact of the chemical residues left in the corrosion layers by the stabilization treatment, and treatment efficiency must all be investigated.

Focusing on marine corroded archaeological artefacts, the present study aims to identify the transformation of corrosion products during stabilization treatments through aerated or deaerated alkaline solutions at room temperature using complementary analytical tools. The study also highlights the formation of transient phases *in situ*, using X-ray micro-diffraction (µXRD) under synchrotron radiation.

---

[*] Corresponding author.
E-mail address: delphine.neff@cea.fr (D. Neff).

https://doi.org/10.1016/j.corsci.2017.12.028
Received 9 March 2017; Received in revised form 14 December 2017; Accepted 18 December 2017

Please cite this article as: Kergourlay, F., Corrosion Science (2017), https://doi.org/10.1016/j.corsci.2017.12.028

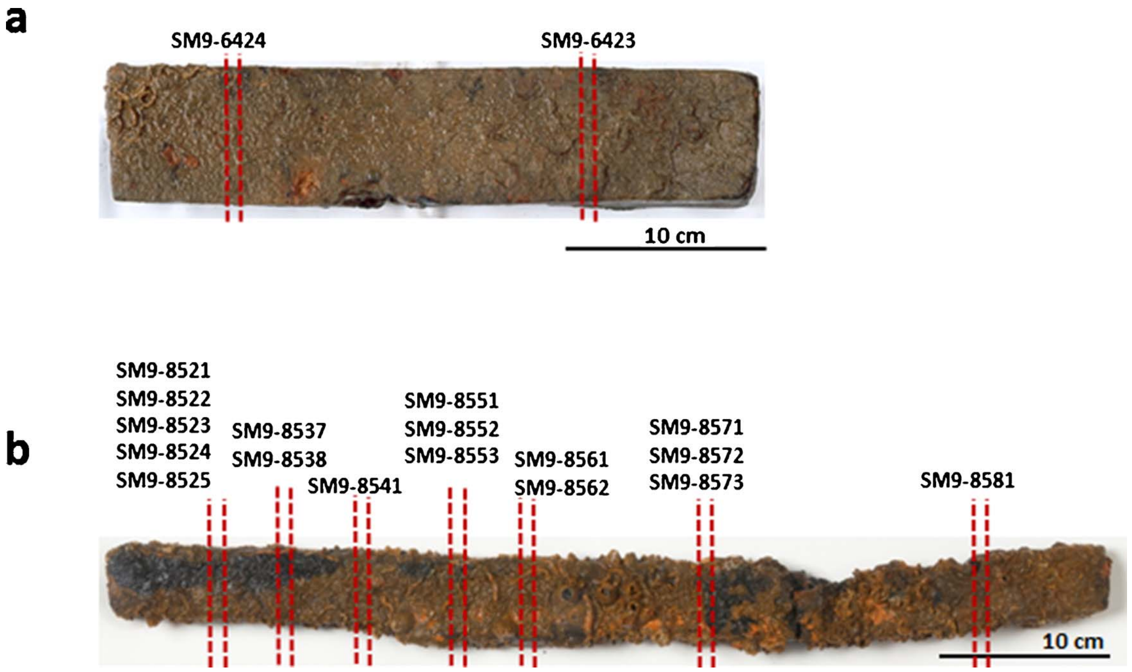


Fig. 1. Pictures and sampling design of the iron bars (a) SM9-64 and (b) SM9-85.

2. Materials and methods

2.1. Protocol

The stabilization treatment is divided into three steps:

- The **dechlorination step** aims to remove the chlorine present inside the initial corrosion system. It consists of immersing the artefacts in alkaline solutions for several hours [2]. Sodium hydroxide (NaOH) solution has been chosen for this study in both aerated and deaerated conditions. [2]
- The **washing step** aims to remove the chlorine and the residues belonging to the chemical solutions from the corrosion layers using a de-ionized non-deaerated H_2O solution.
- The **drying step** aims to remove the wash solution from the corrosion layer by letting the artefact dry under ambient conditions.

2.2. Preparation of the in situ cell

Twenty cubic samples of about 1 cm^3 were taken from two Roman iron bars to produce the in situ cells for this study. These bars shown in Fig. 1 were recovered from two shipwrecks dated from the Roman period (I BCE to II ACE). They are parallelepiped in shape with a square section of a few centimetres and about 40–60 centimetres in length. These bars were immersed until their excavation from a depth of 11 m, 1.5 miles offshore near Saintes-Maries-de-la-Mer in the Mediterranean Sea (France) [23]. The corrosion system of several similar bars was previously characterized by Rémazeilles et al. [24]. These authors showed that the corrosion layers mainly contain ferrous hydroxychloride β-$Fe_2(OH)_3Cl$, a phase characteristic of iron corroded in a deep marine environment. Due to the reactivity of β-$Fe_2(OH)_3Cl$ during exposure to air, the iron bars for the present study were stored immediately after excavation in a wet environment (tap water) before being transferred to the laboratory.

The treatment performed in this study mirrored normal laboratory scale treatments applied in conservation-restoration workshops [25]. A sodium hydroxide solution at room temperature (0.5 M $NaOH_{amb}$) was used. The effect of the presence of dissolved O_2 in the solution was studied by using either aerated or deaerated electrolytes. Deaerated conditions were obtained by bubbling a constant flow (200 mL min^{-1}) of N_2 for three hours before beginning the treatment to provide a level of dissolved O_2 lower than 100 ppb in the alkaline solution. The pH of the original solution for both aerated and deaerated solutions was 13.5. In order to decipher the effect of the washing step on the evolution of the corrosion system, half of the samples were washed after the dechlorination step. To simulate the drying step, samples were placed in an oven at 50 °C for 10 h. The full set of samples is presented in Table 1 but only part of it is addressed in the present paper. The whole set of samples showed the same tendencies and confirmed the observations of these archaeological artefacts delivered in this paper although they are not further commented upon.

In situ and *ex situ* dechlorination experiments were carried out using a dedicated cell (Fig. 2) described in a previous paper [20]. The cell is prepared by following the steps described below:

Table 1
Set of samples and treatment parameters (* states for the samples presented in this paper). Time of treatment corresponds to the duration of circulation of the solution.

Medium	Treatment duration	Samples
Untreated		SM9-8522
		SM9-8524
		SM9-8538
Aerated/unwashed	2 h	SM9-8562
	8 h	SM9-8551
	8 h	SM9-8552
	8 h	SM9-8563
	10 h	SM9-8521
	10 h	SM9-8571
	11 h	SM9-8573*
	18 h 30 min	SM9-6423
	22 h 30 min	SM9-8537
	35 h	SM9-8561
Aerated/washed	11 h 45 min	SM9-8522
	22 h 20 min	SM9-8523*
	24 h	SM9-6424*
	56 h	SM9-8553
Deaerated/unwashed	30 h 50 min	SM9-8525
Deaerated/washed	32 h	SM9-8541
	48 h	SM9-8581*