Influence of corrosion products nature on dechlorination treatment: case of wrought iron archaeological ingots stored 2 years in air before NaOH treatment

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Three wrought iron ingots immersed during 2000 years at 12 m deep in Mediterranean Sea were stored after excavation for 2 years without specific protection in air. After that period, two of them were treated by immersion in a NaOH solution, while the third was used to describe the corrosion system resulting from the storage conditions. This characterisation was achieved by a combination of microanalytical techniques. It could be concluded that though ferrous hydroxychloride β -Fe₂(OH)₃CI was the main CI containing phase at the time of excavation, akaganeite $[\beta$ -FeO_{1-x}(OH)_{1+x}Cl_x] was the only one present in the rust layers after storage. In order to determine the influence of corrosion products nature on dechlorination treatment, the evolution of a corrosion system composed of both CI containing phases β -FeOOH and β -Fe₂(OH)₃CI has been followed during *in situ* NaOH experimental treatment. Specific behaviours of each phase to the dechlorination treatment have been revealed.

Keywords: Storage, Dechlorination treatment, In situ treatment cell, Ferrous hydroxychloride, Akaganeite

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Introduction

After excavation of archaeological artefacts immersed in marine environment, the sudden supply of oxygen combined with the presence of chloride ions trapped within the corrosion product layers increases the decay due to corrosion, which can lead to a rapid destruction of the artefact.^{1,2} For that reason, dechlorination treatments have been developed to stabilise artefacts by extracting chloride ions. The different methods applied in conservation laboratories are the chemical immersion in neutral or alkaline solutions,³ subcritical water,^{4,5} immersion coupled with a cathodic polarisation⁶ and hydrogen plasma.^{7,8} The present study focuses on the immersion in alkaline solution (NaOH) method, most commonly used in restorer workshops. Although this treatment has been applied successfully for several decades for the chloride ions removal, the lack of knowledge about its physicochemical action limits its improvement.⁹ One way to reach a better understanding of dechlorination mechanisms occurring during immersion in NaOH solution is to fully characterise the corrosion products at microscopic scale (morphology, localisation of Cl containing phases in the rust layer, etc.). Until now, the corrosion pattern formed before excavation has remained controversial. It was first assumed that solid ferric oxychloride FeOCl was the main Cl containing compound present within the corrosion product layer of marine iron.3,10,11 Its presence was questioned¹²⁻¹⁴ and it was proposed that chloride ions were trapped within the lattice structure of akaganeite β -FeOOH and in pockets of ferrous chloride FeCl₂ at the corrosion products/metal interface.¹² In addition, phases such as goethite α-FeOOH, lepidocrocite γ -FeOOH, haematite α -Fe₂O₃ and magnetite Fe₃O₄ have been identified by X-ray diffraction but without any information on their location within the corrosion product layer.¹³ Recently, the use of complementary analytical techniques at the microscopic scale¹⁵ has underlined for the first time the presence of the ferrous hydroxychloride β -Fe₂(OH)₃Cl, phase already observed on terrestrial archaeological artefacts,16 as main Cl containing phase of wrought iron artefacts immersed in sea water. The synthesised phase β -Fe₂(OH)₃Cl is known to transform into akaganeite by oxidation mechanisms under specific conditions,^{17,18} which would explain the presence of akaganeite on marine iron after

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1 Ingot stored for 2 years under ambient atmosphere and detached corrosion products

exposure to oxygen. Although it is commonly assumed in the literature that akaganeite is formed after excavation, 9,12,14 the possibilities for its formation remain open. ^{16,19}

The aim of this study is first to characterise, by a set of complementary and microbeam analytical tools, the nature and the localisation of the corrosion products formed on marine artefacts kept in air storage. The second aim is to understand the effect of the NaOH dechlorination treatment on the two main Cl containing phases constituting the corrosion layers ferrous hydroxychloride β -Fe₂(OH)₃Cl and akaganeite β -FeO_{1-x}(OH)_{1+x}Cl_x respectively, for freshly and stored marine iron artefacts.

Materials and methods

Archaeological corpus

The studied objects were 2000-year-old iron ingots immersed at 12 m deep and 1.5 miles from the coasts near Les Saintes-Maries-de-la-Mer in Mediterranean Sea. Three ingots were excavated and stored during 2 years in ambient atmosphere without environmental control. During this storage period, a peeling and cracking of the corrosion products at the surface of the ingots was observed (Fig. 1). In order to monitor the evolution of the corrosion layer during a treatment, an ingot was dedicated to the study of the corrosion system before the treatment and the two others were treated by dechlorination. Densities of the ingots were calculated from the ratio of mass to the estimated volume. The obtained values are similar so that a comparison of the chloride ions quantity extracted during the treatment can be made directly from experimental measurements.

Treatment protocol

The two treated ingots were immersed either at room temperature or 50°C in a 0.25M NaOH solution during 39 days. After that period, the chloride ions concentration in the bath was less than 15 ppm, the threshold value for stopping the treatment. The ratio $V_{\text{solution}}/V_{\text{ingot}}$ was fixed at 15 to fully immerse the ingot and the chloride ion extraction was followed by argentimetry–potentiometry measurements. All of these dechlorination treatments were achieved at the Arc'Antique Laboratory.

Analytical protocol

Following the dechlorination treatment, the ingots were embedded in epoxy resin and transverse sections were cut for analysis. Each transverse section was ground using ethanol with SiC papers (grade 80-4000) and polished with diamond paste (3 and 1 µm).

First, the morphology of the rust layer was determined by optical microscopy and scanning electron microscope (SEM) observations. Then, elementary composition was obtained by energy dispersive spectrometry (EDS), coupled to SEM, with an acceleration voltage of 15 kV. EDS detection was carried out with a Si(Li) detector equipped with a beryllium window allowing quantifying oxygen with an error of 2% and other elements below 0.5% w content with 1% of error. Finally, structural identification of corrosion products was obtained by microRaman spectroscopy (μ RS) and Xray diffraction (XRD). μ RS analyses were carried out



2 a XRD set-up and b treatment cell (diameter: 1 in.)



3 Optical microphotographs of corrosion layers a before treatment and b after treatment



4 Structural investigations by *a*-d μRAMAN and *e* XRD on ingots before treatment: μRAMAN spectra of different phases analysed in corrosion layers were compared to reference spectra except in case of iron hydroxychloride (*a*), identified by comparison to literature;^{21,22} on XRD pattern: A: akaganeite β-FeO_{1-x}(OH)_{1+x}Cl_x (JCPDS 080-1770); L: lepidocrocite (JCPDF 044-1415); G: goethite (JCPDF 081-0464); I: iron (JCPDF 006-0696)

using a Renishaw spectrometer (InVia Reflex) with an excitation wavelength at 532 nm. The spot size and the spectral resolution using the $\times 50$ objective were

respectively 2 μ m and 2 cm⁻¹. Laser power was filtered down to 200 μ W to avoid heating and transformation of the corrosion products. The identification of the phases



5 EDS-SEM CI cartographies a before treatment, b after 0.25M NaOH/room temperature and c after 0.25M NaOH/50°C

was established by comparison to spectra reported in the literature. $^{20\mathchar`-22}$

The XRD patterns were collected on a rotating anode generator equipped with a Mo anticathode delivering a monochromatic beam of $30 \times 30 \ \mu\text{m}$ at $17.48 \ \text{keV}$. In reflection mode, the spot size at the sample surface was about $30 \times 600 \ \mu\text{m}$. Diffraction patterns were collected using a two-dimensional detector (image plate). Data processing was carried out with the EVA software and the ICDD-JCPDS database.

In situ treatment cell

The aim of this experiment was to monitor the transformation of the phases within the corrosion layer during the first stage of the dechlorination treatment. Therefore, a dedicated cell was designed in order to analyse *in situ* zones within the corrosion layer, while the NaOH solution was passing at the sample surface. For this experiment, a 0.5M NaOH solution was used at ambient temperature. In this case, the ratio $V_{\text{solution}}/V_{\text{sample}}$ was fixed at 100 in order to avoid a saturation of the treatment solution by chloride ions during the experiment. The treatment cell was made by sampling

 1 cm^3 of metal with adherent corrosion products from a transverse section of an ingot. The sample was embedded in resin in a 1 in. diameter mould. A canal was created in the cell to bring the solution near the surface of the corrosion products, using a peristaltic pump. A sheet of Kapton adhesive ensured the sealing of the transverse section to avoid any direct contact of this part of the sample with the solution. The structural evolution of the corrosion products within the layer was followed by XRD in reflection mode (Fig. 2).

Results and discussion

Corrosion products distribution within rust layers of stored artefacts

Before treatment

The corrosion layer has a thickness varying between 200 μ m and 2 mm. It displays a marble-like pattern under optical microscope (Fig. 3*a*). The matrix is composed of well crystallised goethite (α -FeOOH) and the marblings are made of poorly crystallised hydrated oxide ferrihydrite (5Fe₂O₃.9H₂O) (Fig. 4*c*). In addition, EDS analysis revealed the presence of Cl containing



6 Dechlorination curves

veins parallel to ferrihydrite. Their thickness varied from 10 to 100 μ m. They were detected indifferently either close to the metal surface or in the outer part of the rust layer (Fig. 5*a*). The veins were identified as akaganeite (Fig. 4*b*) with a Cl content between 6 and 7.5 wt-%. Localised zones of ~500 μ m² presented chloride contents as high as 8–10 wt-%. The average Cl content in the whole rust layer was ~4wt-%. Finally, lepidocrocite (γ -FeOOH) was sometimes detected by XRD and seemed to correlate with cracks (Fig. 4*e*). It is known that a high oxygen flow would favour the oxidation of Fe(II) containing compounds into lepidocrocite.²³ So it can be assumed that the cracks observed together with

lepidocrocite constituted a preferential access for O_2 to the reactive phases present within the rust layer.

After treatment

As expected and already observed in previous studies,^{3,24} extraction of chloride ions is favoured by a temperature increase. The amount of chloride ions extracted is increased by 15% at 50°C compared to at room temperature (Fig. 6). After this treatment, the corrosion product layers retained approximately the same thickness. The marblings were still observed under optical microscope. They corresponded to poorly crystallised ferrihydrite (Fig. 3b). Cl containing veins, with a thickness of 10-20 µm, were detected by EDS analyses only in the outer part of the rust layer (Fig. 5b and c). Akaganeite with chloride content between 4 and 6 wt-% was identified in these veins. The average Cl content in the whole rust layer for both ingots were close to 2 wt-% after the treatment. Despite the low Cl concentration in the dechlorination solution at the end of the treatment, the presence of akaganeite in the corrosion products showed that the dechlorination was not complete. Surprisingly, it seems that chloride ions were first extracted from the inner parts of the rust layer (Fig. 5), while an external chlorine depletion would be expected from diffusion processes. This unexpected chlorine distribution could be related to the different classes of chloride ions within the artefacts, adsorbed and bound Cl⁻. In fact, the first class of ions is not strongly linked to the structure and can be extracted easily. Nevertheless, this work will be pursued to better understand the location of chlorinated phases in the corrosion layer after treatment.



a freshly excavated and stored for a few months in tap water;¹³ b treated for 42 days; c stored for 2 years under O_2 atmosphere; d treated for 39 days; e treated for 39 days

⁷ Diagrams of corrosion product layers



8 *a* sample in treatment cell [H_{β}: ferrous hydroxychloride β -Fe₂(OH)₃Cl; A: akaganeite β -FeO_{1-x}(OH)_{1+x}Cl_x; white points correspond to diffracted areas], *b* Cl X-ray map before treatment and *c* Cl X-ray map after 3 h of treatment. Diffraction data *d* before treatment and *e* after 3 h of NaOH treatment [H_{β}: ferrous hydroxychloride β -Fe₂(OH)₃Cl (JCPDS 00-034-0199); A: akaganeite β -FeO_{1-x}(OH)_{1+x}Cl_x (JCPDS 01-080-1770); M: magnetite Fe₃O₄ (JCPDS 00-019-0629); F: ferrous hydroxide Fe(OH)₂ (JCPDS 00-013-0089)]

Schematic diagrams of the corrosion product layers can be proposed (Fig. 7c-e) and compared to those typical of freshly excavated ingots (Fig. 7a and b). The main effect of the storage in air is the oxidation of the rather homogeneous layer of β -Fe₂(OH)₃Cl²² into a heterogeneous layer containing veins of akaganeite and marbles of ferrihydrite parallel to the metal/corrosion products interface in a goethite matrix. Dechlorination treatments led to a complete transformation of β -Fe₂(OH)₃Cl into Fe(III) oxyhydroxides; however, they failed to transform all the akaganeite.

In conclusion, the characterisation of the ingots corrosion before and after treatment and with or without storage period, underlines different transformation paths for the corrosion products that have to be understood thoroughly. In particular, the behaviours of the two main Cl containing phases, β -Fe₂(OH)₃Cl and akaganeite, with exposure to the treatment solution, had to be specified.

Therefore, experiments were carried out in a cell specially designed for dechlorination treatments to monitor the transformations of the Cl containing phases *in situ* during the first steps of a treatment.

In situ treatment cell experiment

It was necessary to select a sample with a rust layer containing both Cl containing phases and observable in transverse section (Fig. 4*a* and *b*). An EDS chlorine mapping of the upper part of the corrosion products was collected before the start of the treatment (Fig. 8*b*). Micro-RS identified akaganeite on the left part and β -Fe₂(OH)₃Cl on the right part of the sample. Akaganeite had an average chlorine content between 6 and 9 wt-% and β -Fe₂(OH)₃Cl between 18 and 22 wt-%.

Diffraction data confirmed the presence of the two Cl containing phases in the sample before the start of the treatment (Fig. 8*d*).

Two areas, one for each Cl containing phase, were analysed at the same outer surface distance in order to ensure that the penetration front of the solution had reached both phases (Fig. 8a). After 3 h treatment in 0.5M NaOH, on the right part of the sample at a distance of 1–1.5 mm, the transformation of β -Fe₂(OH)₃Cl into magnetite (Fe_3O_4) and ferrous hydroxide ($Fe(OH)_2$) was noted. Where Fe(OH)₂ had been identified, the content of chlorine was less than 1 wt-%. In contrast, despite a decrease of nearly 25 wt-% in the average content of chloride in the analysed zone (8 wt-% before treatment and 6 wt-% after 6 h of treatment), the area consisting of akaganeite before treatment remained unchanged. It is likely that only the chloride ions adsorbed on the surface of the akaganeite grains were extracted. Such observations suggested that the removal of the chloride ions trapped within the crystal structure of akaganeite required a deeper and longer treatment, as already mentioned.²³

Conclusions

This study clearly confirms that the dechlorination treatment by NaOH solution is less efficient for corrosion layers consisting of akaganeite than layers consisting of ferrous hydroxychloride. Akaganeite is the main Cl containing phase present in corrosion layers of artefacts stored in air during several months, while ferrous hydroxychloride dominates within the corrosion layers of immersed artefacts. This could explain the difference in efficiency of dechlorination treatment observed by restorers between artefacts directly treated after excavation or storage in desaerated mediums and those exposed to air for a long period of time.

The next stage of this study is to extend this methodology to the alkaline sulphite and the electrochemical treatments to determine the efficiency of the dechlorination treatment currently used in restorers' workshops.

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