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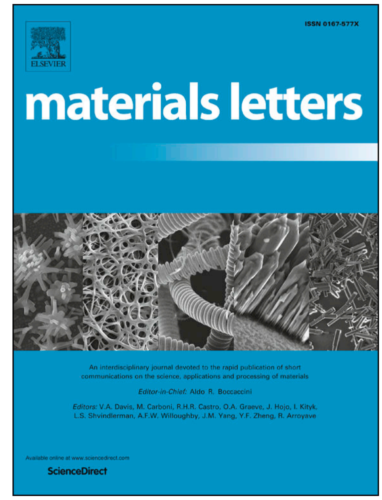

Dechlorination of iron artefacts: a novel approach

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Dechlorination of iron artefacts: a novel approach

Raffaele Emanuele Russo[a], Silvia Zamponi[a], Paolo Conti[a], Roberto Piloni[a], Maria Isabella Pierigè[b], Amalia Faustoferri[b], Martina Fattobene[a], Mario Berrettoni[a]

[a] University of Camerino, School of Science and Technology, ChIP, via Madonna delle Carceri 62032 Camerino (MC) Italy

[b] Soprintendenza Archeologia, Belle Arti e Paesaggio per le province di Chieti e Pescara

HIGHLIGHTS

- A novel approach of a dechlorination process with ultrasounds;
- Comparison of performance of dechlorination procedure;
- Iron artefacts conservation.

ABSTRACT

The dechlorination process on iron artefacts of archaeological interest has been performed by using alkaline medium. We demonstrated that the use of mild ultrasonic bath fastens the dechlorination process. An analytical procedure based on Atomic Absorption Spectroscopy was developed to detect the amount of residual chlorine. The results highlight the potentiality of the proposed method.

Keywords: Dechlorination, iron conservation, analytical methods, ultrasound assisted

1. INTRODUCTION

The stabilization, preservation and restoration of metallic artefact is a challenging topic in the contest of archaeometric management of iron remaining.

The main problem found during the recovery and conservation of archaeological iron findings is their contamination by the surroundings (moist soils or marine environment) and the brutal break of the equilibrium established during artefacts burial and storage conditions. The interaction of iron objects with highly oxidizing media after excavation can cause severe damages that can lead to the complete loss of the shape of the remaining[1,2].

The presence of chloride ions stabilizes akaganeite (β-FeOOH), an iron oxyhydroxide, that can incorporate Cl^- anions in the tunnels of its hollandite tetragonal lattice and adsorb it onto its surface[3]. The formation of oxyhydroxydes is associated to a volume expansion that cause cracks and exfoliation of the corrosion layer. A detailed study of evolution of corrosion products formed in different conditions is reported by Kergourlay[4].

Several Chloride removing procedures from the corroded metal have been implemented and studied. Most alkaline dechlorination procedures need several months to be completed[5,6]. Recently Veneranda reports detailed studies based on experimental design of dechlorination of synthetic akaganeite to find the best operating conditions.[7 and references therein]

The present study proposes the use of ultrasound bath to shorten the dechlorination process. The results in comparison with the traditional immersion treatment are very promising.[8]

The aim was to:

- compare chloride extraction efficiency for each treatment;
- investigate the possibility to shorten the time of the treatment by using an ultrasonic bath. This treatment can help also in removing concretions or corroded layers.

2. EXPERIMENTAL DETAILS

2.1. Materials

Sodium Hydroxide (NaOH), Silver Nitrate ($AgNO_3$) 0,1 MOL/L RPE-NORMEX analysis, ultrapure Nitric acid (HNO_3), Sulfuric acid (H_2SO_4) and Sodium Sulfite (Na_2SO_3) were purchased from Sigma-Aldrich and used as received. Ultrapure 0.1M Ammonia (NH_3) 25% was purchased from Fluka Honeywell, Standard AAS Silver solution 1000 ppm was purchased from Merck and used as received.

2.2 Experimental procedure

Several iron finds belong to an archaeological site from the VIII to II century B.C., discovered in Carsoli (AQ-Italy) in 1906 and excavated from the former Archaeological Superintendence of Abruzzo in 1950 and 1951. The materials used for this research refer to a votive "stipe" dated to the IV-II century B.C.[9,10]

We test four pieces (A, B, C, D figure 1) belonging to a toroidal ring of 5 cm diameter, one spearhead (E) and part of a flat ring (F) (figure 1). None of the objects had been previously treated. Before desalination procedure the objects have been weighed to know the amount of material lost during the treatment (Table S1).

Figure 1. Archaeological finds photo (see text for details).

The iron samples (A, B, C, D) have been kept in 25 ml screw-top HDPE bottles filled with 15 ml of alkaline solution and thermostated in a sand bath at 50 °C. All the solutions were deoxygenated by bubbling a constant flow of argon during the whole experiment. During desalination treatment the alkaline solutions were kept under stirring to warrant a constant renewal on the surface of the sample. The solutions were replaced every 10 days and analyzed for Cl^- concentration. The other two samples (E and F) were inserted separately in a test tube filled with 25 ml of alkaline solution under Argon flow and immersed in ultrasonic bath (120W, 35 KHz) kept at 50°C. The solutions were replaced every 2 hours and analyzed for Cl^- concentration.

The synoptic Table S.1 summarizes all the experimental conditions.

Ion Chromatography has been used to determine Cl^- concentration on the desalination solutions.

2.3 Characterization methods

With the aim to identify the initial morphology of highly corroded archaeological artefacts, macro and micro structural observations were performed using Optical Microscopy (OM; Leica WILD M8) and Scanning Electron Microscope (SEM; ZEISS SIGMA 300) equipped with Energy Dispersive X ray analysis

(EDX) to investigate elemental composition. X-ray Diffraction (XRD; Philips PW 1830) with Cu-Kα radiation was used to identify the crystalline phases of solid residual produced by ultrasonic baths.

3. Results and discussion

The samples, retrieved from the same votive archaeological site, show a very similar morphological and elemental composition inferred by OM and SEM-EDX.

In figure 2 we report the optical image of sample A showing yellow/orange, red and brown spots and presence of weeping demonstrating active corrosion and formation of Goethite, Lepidocrocite and iron sulfate/ferric chloride.[11] Similar images are obtained for the other samples.

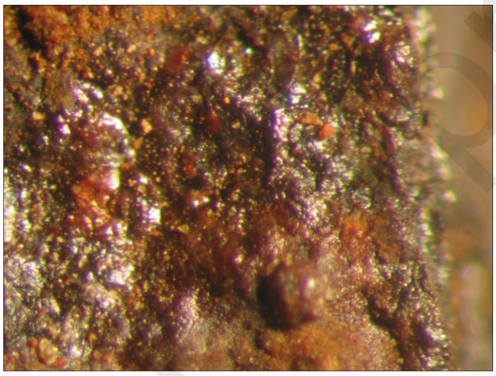

Figure 2: Hollow shells characteristic of weeping iron of sample A (Magnification x40).

The corrosion at micro scale is highlighted on the SEM micrograph (figure 3(a)) showing the metallic core, the first layer of corrosion (dense product layer) and the external part of the layer containing both corrosion products and markers from the soil.[12] The SEM-EDX map (figure3 (b)) shows the corrosion layer in which is highlighted the presence of chlorinated species (red dots).

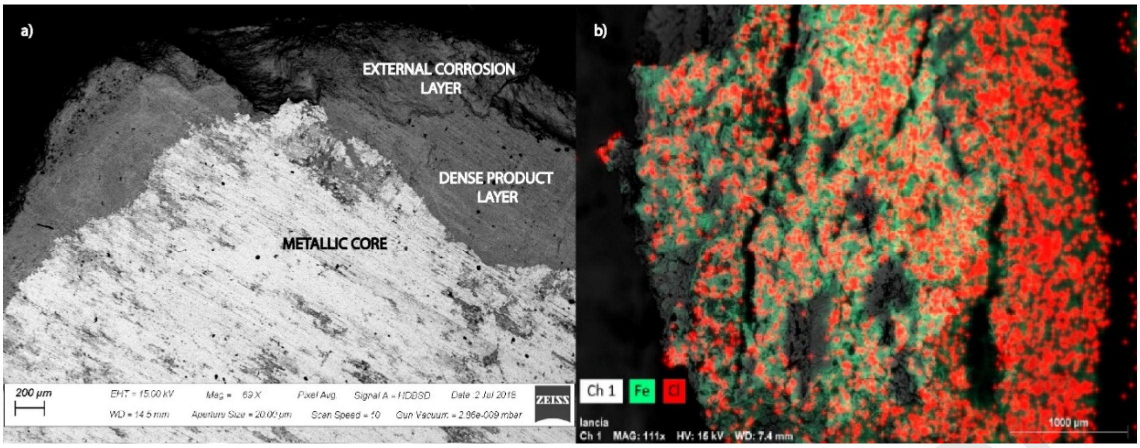

Figure 3. a) Cross section of the sample D; b) SEM-EDX map of sample E highlighting the presence of chlorides in red and the metallic core in green. (Magnification x111).

The efficiency of chloride extraction in the ultrasonic free alkaline baths were investigated at different experimental conditions (see Table S1). The efficiency of dechlorination increased linearly with NaOH concentrations and no effect was observed for sulphite addiction. These results are presented in figures S1, S2 and S3 discussed therein.

The ultrasonic bath experiments were performed only in NaOH 0.5 M solution since there isn't influence by sulphite. The performance of ultrasound dechlorination is shown in figure S4. The two samples tested present the same behavior.

Figure 4 reports the comparison of the percentage of exctracted chloride, defined by equation (1), between conventional (sample A) and ultrasound bath (sample F).

$$\% Cl^- = \frac{Cl^- extracted}{Cl_T^-} \quad (1)$$

Where:

- $Cl^-_{extracted}$ is the sum of the extracted chloride determined on each bath; one every 2 hours if ultrasound assisted or one every ten days when conventional extraction is used;
- Cl_T^- is the sum of Cl^- extracted plus the chloride retained in the artefact.

The amount of retained chloride (Cl_r^-) was determined by a procedure based on AAS and it was used to confirm the results of the Ion Chromatography (IC) method. The procedure is detailed in the supplementary material.

The determination of retained chloride is mandatory in order to asses the performance of a dechlorination method.

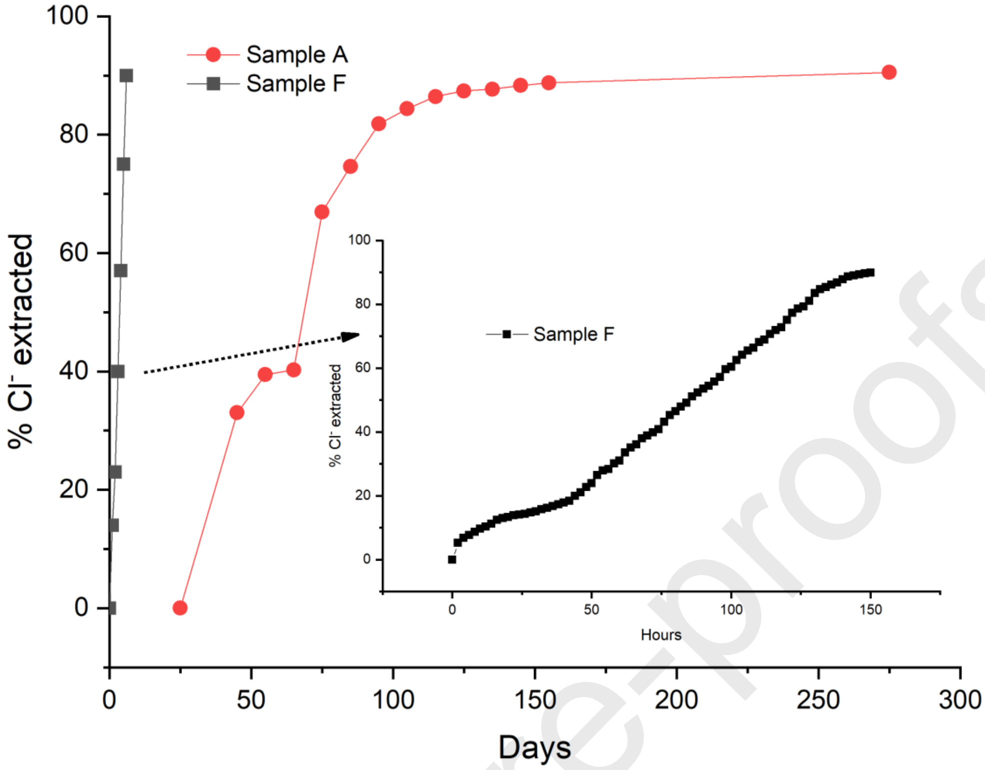

Figure 4. Comparison of dechlorination ultrasounds (sample F) and conventional (sample A) methods. We plotted only the representative points. Inset shows the magnification of ultrasonic bath behaviour.

The data in figure 4 clearly demonstrated the greater efficiency of ultrasonic bath compared with the conventional one. In particular, the ultrasonic bath reaches 90% of extracted chloride in one week versus 150 days needed for the conventional one.

To check the absence of damages caused by the ultrasounds, we analysed both the solution and the solid residues, finding the absence of iron in the solution and only small amount of Lepidocrocite and Goethite in the solid residues. (See figure S5)

Conclusions

Two main differences can be observed in both bath treatments:

i. In the case of conventional dechlorination method (Figure S3), the chloride extraction rate is not constant, but shows repeated increments over time. This behaviour can indicate that the solution reached sites containing the chlorurated phases (such as akaganeite) with different rate. On the contrary, in the case of ultrasound bath, the extraction rate shows a rapid decrease in the first hours of the treatment, becoming constant up to 90% of removed chloride. The ultrasounds act as a driving force to allow the penetration of the alkaline solution in the inner layers located at the interface between the corrosion products and the metal core.

ii. The ultrasonic bath drastically reduces the time necessary to extract a given percentage of chlorides with respect to conventional method

Although the samples used in this analysis are differently shaped, nevertheless all come from the same archaeological site and have the same shelf live. In addition, Sample E and F present a ratio surface/volume higher than the others and hence can more easily undergo exfoliation during the treatment. These considerations make reasonable the comparison between the artefacts used.

Furthermore, the ultrasonic treatment does not seem to be destructive for the archaeological find because of absence of metal iron in the extraction solution. Only small amounts of Lepidocrocite and Goethite, that are part of the corrosion products mechanically removed by ultrasound bath, are observed in the solid residues. The proposed method based on ultrasonic bath can be applied to large artefacts by adapting the ultrasound sources. It is important to underline that, although the samples used in this study have been excavated for over 50 years and have been preserved without special attention, the dechlorination process both conventional and with the ultrasonic bath has proved effective.

REFERENCES

1. D. Neff, P. Dillmann, L. Bellot-Gurlet, G. Beranger. Corrosion of iron archaeological artefacts in soil: characterisation of the corrosion system. Corros. Sci. 47 (2005) 515–535, doi:10.1016/j.corsci.2004.05.029
2. L. S. Selwyn, P. J. Sirois, V. Argyropoulos. The corrosion of excavated archaeological iron with details on weeping and akaganeite. Stud. Conserv. 44 (1999) 217-232.
3. D.E. Watkinson, M. B. Rimmer, N. J. Emmerson. The Influence of relative humidity and intrinsic chloride on post-excavation corrosion rates of archaeological wrought iron. Stud. Conserv. 64(8) (2019) 456-471, DOI:10.1080/00393630.2018.1565006
4. F. Kergourlay, S. Réguer, D. Neff, E. Foy, F.-E. Picca, M. Saheb, S. Hustache, F. Mirambet, P. Dillmann. Stabilization treatment of cultural heritage artefacts: In situ monitoring of marine iron

objects dechlorinated in alkali solution. Corros. Sci. 132 (2018) 21-34, DOI:10.1016/j.corsci.2017.12.028

5. L. M. E. Näsänen, N. G. González-Pereyra, S. A. Cretté, P. De Vivieś. The applicability of subcritical fluids to the conservation of actively corroding iron artifacts of cultural significance. J. Supercrit. Fluids 79, 289–298 (2013), DOI:10.1016/j.supflu.2012.12.033
6. M. Bayle, P. De Vivieś, J.-B. Memet, E. Foy, P. Dillmann, D. Neff. Corrosion product transformations in alkaline baths under pressure and high temperature: The sub-critical stabilisation of marine iron artefacts stored under atmospheric conditions. Mater. Corros. 67(2) (2016) 190-199, DOI:10.1002/maco.201508257
7. M. Veneranda, N. Prieto-Taboada, J. A. Carrero, I. Costantini, A. Larrañaga, K. Castro, G. Arana, J. M. Madariaga. Development of a novel method for the in - situ dechlorination of immovable iron elements: optimization of Cl^- extraction yield through experimental design. Sci. Rep. (2021) 11:10789, DOI:10.1038/s41598-021-90006-y
8. M. Rimmer, D. Watkinson, Q. Wang. The efficiency of chloride extraction from archaeological iron objects using deoxygenated alkaline solutions. Stud. Conserv. 57(1) (2012) 29-41, DOI:10.1179/2047058411Y.0000000005
9. A. Cederna, Carsoli. Scoperta di un deposito votivo del III secolo a.C., in Notizie degli Scavi (1951), 169-224
10. A. Faustoferri, La "stipe" di Carsoli. Qualche osservazione, in S. Lapenna (a cura di), Gli Equi tra Abruzzo e Lazio, Catalogo della mostra, Sulmona (2004), 197-213
11. L. S. Selwyn, P. J. Sirois,V. Argyropoulos. The Corrosion of Excavated Archaeological Iron with Details on Weeping and Akaganéite. Stud. Conserv. 44 (1999) 217-232.
12. D. Neff, S. Reguer, L. Bellot-Gurlet, P. Dillmann, R. Bertholon. Structural characterisation of corrosion products on archaeological iron. An integrated analytical approach to establish corrosion forms. J. Raman Spectrosc. 35(8-9) (2004) 739-745, DOI: 10.1002/jrs.1130

CRediT authorship contribution statement

Raffaele Emaluel Russo: Investigation, Visualization

Silvia Zamponi: Conceptualization, Writing - Original Draft

Paolo Conti: Data Curation

Roberto Piloni: Resources

Isabella Pierigè: Conceptualization Writing - Review & Editing

Amalia Faustoferri: Conceptualization

Martina Fattobene: Investigation

Mario Berrettoni: Supervision, Methodology, Writing - Review & Editing