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Case study

Structural characterization of corrosion product layers on archaeological iron artifacts from Vigna Nuova, Crotone (Italy)

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ABSTRACT

A collection of archaeological iron artifacts, whose age could be assigned from the Iron Age up to the post-medieval period, and coming from the Archaeological National Museum of Crotone (Calabria, Italy) were investigated. They show evident forms of degradation although they were restored around twenty years ago. The aim of this work was to study the chemistry of the corrosion layers formed on the iron artifacts. Techniques such as optical and electronic microscopies (OM and SEM-EDS), X-Ray diffraction (XRD), Ion Chromatography, ATR/FTIR Spectroscopy and Micro-Raman Spectroscopy have been applied. It was found that corrosion products are mainly made up of goethite, maghemite, magnetite, hematite, lepidocrocite and ferrihyidrite. Akaganeite was often found at the interface between the corrosion products and the core of the metal. This could be considered as the main cause of the rapid post-restoration deterioration of iron objects investigated.

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1. Introduction and research aim

A collection of archaeological iron artifacts including agricultural implements, chains, arrowheads (Fig. 1A and B), from the archaeological site of "Vigna Nuova" in Crotone (Calabria, Italy), and kept at the Archaeological National Museum of Crotone (Calabria, Italy), were investigated.

Vigna Nuova site includes a sacred building (*oikos*) built by mud brick walls and roof tiles [1]. The investigated artifacts date back to the first quarter of the fifth century B.C. This period corresponds to the most important development phase of the Vigna Nuova's building. The objects are unusual ritual offerings which consist of chains, large metal blocks for hinges, hooks, shackles of iron and working tools such as shovels, hoes, axes, etc. They were found throughout the building. At the moment of their discovery, these

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http://dx.doi.org/10.1016/j.culher.2014.07.003 1296-2074/© 2014 Published by Elsevier Masson SAS. offerings were contained in ceramic "*pithoi*" (a large storage jar) or were buried in soil. Only in one case, they were contained in a bronze cauldron with a striking restoration consisting of an iron sheet attached to the bottom.

Although the archaeological artifacts were restored about twenty years ago, they show evident degradation patterns. They have been cleaned mechanically using scalpel and micro chisel cutters, treated with unspecified corrosion stabilizer, consolidated with properly pigmented epoxy resin "UHV plus" and finally protected with "Paraloid B72".

The aim of this work was to study corrosion product layers in the mentioned above archaeological iron artifacts in order to find the causes of the corrosion phenomena during their burial period and after excavation. Different techniques such as OM and SEM-EDS, XRD, Ion Chromatography, ATR/FTIR and Raman Micro Spectroscopy were used to study corrosion product layers formed on the iron artifacts.

2. Experimental

2.1. Materials

Archaeological artifacts show evident rust patina and they are characterized by metallic layer exfoliation (flaking). A total of

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Fig. 1. A. and B. Archaeological iron artifacts coming from Vigna Nuova (Calabria, Italy) with flaking phenomena.

17 flakes detached from artifacts was investigated. Their size vary from a few centimeters to a few millimeters.

Both the "inner corrosion layer" and "outer surface" of every flake were investigated. The first one is characterized by corrosion oxides that caused the detachment. This area appears to be very fragile and presents the typical red-orange color of the rust. The second one is the area of the artifact that has been in contact with the soil during the burial and that was restored. On this side the compactness increases and the color is that typical of iron. The artifacts have been stored at the museum in airtight polypropylene boxes with silica gel desiccant.

2.2. Methodologies

An optical stereomicroscope (Mehigi Techno UK, EMZ-5TRD Gemz with digital camera Canon "Power Shot A640") was used to observe the morphology of the corrosion products on the surface. Morphological analyses were also performed on the sample surface by scanning electron microscopy (SEM- Leo 420, Cambridge, England) coupled with energy-dispersive spectroscopy (EDS Inca Energy, Oxford).

In order to determine the crystalline structure of the corrosion products, X-ray diffractometer (Bruker D8 Advance) was used. To perform XRD analysis, samples were powered with an Agate mortar and pestle. To have a complete picture of the rust's nature and especially to determine the presence of amorphous matter, ATR Spectroscopy was used (FTIR PerkinElmer Spectrum 100) on the same powder. The chloride ion concentration of the rust was analyzed by ion chromatography using a DIONEX Model ics-1000 with columns Ion pac cs 5a and Ion pac as 1a. The soluble chloride ion of 3 samples was extracted into deionized water (20 cm³) at room temperature for 24h with an ultrasonic stirrer. The chloride ion obtained by water extraction is defined here as soluble chloride. With the aim of studying the corrosion layers and the distribution of chloride in artifacts, the samples were prepared as follows [2]: artifacts were put in a drying oven under a primary vacuum in order to withdraw the non-combined water from the sample; the objects were mounted in epoxy resin. Finally, these samples were cut to obtain cross-sections. After mechanical grinding using SiC papers (grade 80-4000), samples were polished with diamond paste (3 and 1 µm). Cross-sections were analyzed using a scanning microscope with Energy-dispersive X-ray analysis of elements (SEM Feg Quanta 200-Environmental Electron Microscope FEI/Philips with X-ray microanalysis system, Genesis-4000, EDAX). The analyses were performed under an accelerating voltage of 20 kV. To analyze minor elements in the metallic matrix a $2 \times 2 \,\mu m^2$ beam with an accelerating voltage of 15 kV was focused on the sample.

The optical microscope (Laborlux 12 pol. Leitz) was used to study the metallographic structure of the iron core. Cross-sections were studied also using a μ -Raman Spectrometer in order to analyze the structure locally inside the corrosion layer [3]. Measurement of μ -Raman Spectroscopy were performed by using Jobin Yvon Lab-Ram instrument, with He-Ne (632.8 nm) laser source using a 50X Olympus objective.

3. Results and Discussion

3.1. Surface corrosion product identification

The two sides of the analyzed flakes display completely different characteristics. From now on, the following definitions are used:

- inner corrosion layer: the side where the detachment occurred;
- outer surface: the restored side in contact with the soil during the burial.

Inner corrosion layer is the most corroded. It is characterized by two typical signs of active corrosion: "weeping" (the beads of liquid) and the presence of a compact reddish-brown or bright orange corrosion. The term "weeping" is used by archaeologists to describe the formation of 'tears' or 'sweat' on the surface of excavated iron due to the hygroscopic nature of iron chloride salts [4]. The phenomenon of "weeping" has been ascertained on the surface both by stereomicroscope through the hollow shells characteristic of weeping iron (Fig. 2A) [5] and by SEM morphological analysis. Fig. 2B shows typical weeping hallow shells [6]. The formation of these shells can be explained as a result of the oxidation and hydrolysis of Fe²⁺ ions or the hydrolysis of Fe³⁺ ions and the precipitation of FeOOH in the liquid drops. The compact yellow to dark brown layer of corrosion on the surface of most of the iron samples is composed mainly of lepidocrocite, γ -FeOOH; akaganeite, β -FeOOH and hematite, α -Fe₂O₃ as revealed μ -Raman Spectroscopy analysis (Fig. 3). Moreover, the presence of these corrosion products was confirmed by XRD (Supplementary material, Fig. S1). External rust powder was analyzed by ATR [7-9] and akaganeite was the main product. The spectrum shows strong maxima absorption at 644, 852, 1652, and 3328 cm⁻¹ indicating the presence of akaganeite (β -FeOOH), while the major features at 1652 and 3328 cm⁻¹ represents the H-O-H fundamental bending and stretching modes [10].

Outer surface is more preserved than the inner corrosion layer's surface. In fact, there are no signs of exfoliations, cracking or orange pitting. According to μ -Raman Spectroscopy (Fig. 4), this face is characterized by the presence of lepidocrocite, goethite and ferrihydrite (δ -FeOOH spectrum confirmed broad bands, due to its low crystallinity, around 664 cm⁻¹ and a weaker one at 397 cm⁻¹). The peak at 1087 cm⁻¹ is assigned to calcite (CaCO₃). The ATR spectrum (data not shown) shows the presence of γ -FeOOH, α -FeOOH and Fe₃O₄ which is confirmed by the appearance of peaks at 1051 cm⁻¹ (lepidocrocite), 894 cm⁻¹, (goethite) and 580 cm⁻¹ (magnetite) [11]. Moreover, the ATR analysis shows the presence of δ -FeOOH (ferrihydrite) as the major component of rust since the

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Fig. 2. A. Stereomicroscope picture showing hollow shells characteristic of weeping. B. SEM microphotographs made on iron surface showing typical weeping hallow shells.



Fig. 3. Inner corrosion layer's surface analyzed by μ -Raman Spectroscopy and some of Raman spectra of Lepidocrocite (L), Akaganeite (A) and Hematite.

related peak is relatively intense compared to the others. The presence of these corrosion products was confirmed by XRD except for ferrihydrite due to its amorphous nature.

3.2. Corrosion layer analysis

In order to study the entire corrosion system, cross-sections were investigated with μ -Raman and SEM/EDS. Usually archaeological iron artifacts are covered by a layered structure of corrosion products and all the analyzed artifacts present the same general layered corrosion system. Three corrosion layers were identified and according to the terminology as reported by Neff et al. [12] we indicate with acronym:

- DPL (dense product layer), the layer under burial surface;
- TM (transition zone), the layer under the surface where the corrosion led to detachment;
- M (metallic substrate), the core of the artifacts.

The DPL observed in this study shows numerous cracks easily identifiable by OM or SEM. In this layer maghemite, goethite, akaganeite and hematite were identified by μ -Raman Spectroscopy (Supplementary material, Fig. S2). A few other elements as Si, Cl

Table 1

EDS analysis of the layer described in Fig. S3.

Elements in p/p%	Si	Cl	Fe	Ca
1	5.74	8.18	86.1	0
2	2.14	5.68	92.2	0
3	4.78	9.20	86.0	0
4	2.21	4.96	92.8	0
5	2.46	1.05	96.5	0
6	2.83	1.18	94.9	1.04

and Fe were detected by EDS analysis at the amount of about 1 mass% calculated as average content (Supplementary material, Fig. S3, Table 1). The main element is Fe (86.1%), but also a large amount of Cl (9.2%) and Si (5.74%) was detected.

The iron substrate (M) shows iron (96.5%) as the main element; a small quantity of Si (2.46%) and Cl (1.05%) was identified. Ferrihyidrite (666, 400 cm⁻¹) was the main phase detected by μ -Raman Spectroscopy.

According to μ -Raman Spectroscopy, goethite, magnetite, hematite and lepidocrocite are the main phases identified in the TM. A cross section and several μ -Raman spectra obtained at different places in the TM are shown in Supplementary material Fig. S4. Carbon and calcite are also present in TM. EDS analysis shows a large

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Fig. 4. Outer surface analyzed by μ -Raman Spectroscopy and some of Raman spectra of Lepidocrocite (L), Calcite (C), Ferrihydrite (F) and Goethite.

Table 2			
lons contents of	powdered	corrosion	products.

Ions	loncontent (ppm) [*]	
Chlorides	5.9	
Nitrite	0.1	
Bromides	0.0	
Nitrates	0.6	
Sulfates	2.4	
Phosphates	0.0	

*Safety concentration (100-200 ppm).

amount of Fe (94,9%) as the main element; Si (2.83%), Cl (1.18%) and Ca (1.04%) was also detected. Exogenous elements such as calcium and silica are due to the presence of calcite, quartz (Supplementary material, Fig. S5), and slag inclusions derived from the soil. The stratified form of calcite indicates that the mineral crystallized during the period of burial, while the angular shape of quartz crystals suggests that it is an inclusion deriving from the soil, cemented by calcite and minerals of corrosion.

3.3. Ion distribution and content

Corrosion products were analyzed using ion chromatography to determine ion content. The results indicate that the ion content can vary between objects. The average content of chloride ion and other ions is reported in Table 2.

The amount of chloride is very low if compared to the "Safety concentration" (100–200 ppm) reported by Marabelli [13].

To locate distribution of chloride ions in corrosion layers, SEM/EDX linescans were performed (data not shown). The results indicated that the highest chloride ion content is on the metalcorrosion interfaces and than in the akaganeite corrosion area. There is a small amount of Si and Ca in the analyzed areas due to quartz and calcite crystal deriving from soil.

4. Discussion

The surface of the iron artifacts appears to be deteriorated with pitting and weeping. Flaking occurred on most of degraded objects.

Different techniques such as SEM-EDS, µ-Raman Spectroscopy, ATR. XRD were used to investigate the entire corrosion system. Corrosion products are mainly composed by goethite, maghemite, magnetite, hematite, lepidocrocite and ferrihydrite. These corrosion products are typical of the iron corrosion during the burial and our results are in agreement with data reported in literature [14,15]. Akaganeite is often found at the interface between the corrosion products and the core of the metal. Active corrosion is thought to occur as well. Though considered insoluble, Cl- ions are preferentially hosted in akaganeite crystal structure. This phenomenon is strongly correlated to the ongoing corrosion processes [16]. The presence of akaganeite is also known to affect the artifact. The expansive crystal formation causes severe stress within the artifact, specifically along the corrosion interface. These stresses are capable of pushing the exterior layers to a degree of complete delamination or spalling, and thus separation of the outer layers from the core of the artifact or even full disintegration can occur. These processes are due to the chloride corrosion cycle and, as reported in literature [2–5], occur after iron artifacts excavation.

The presence and quantities of Cl⁻ within the artifacts after excavation and consequently the formation of the chlorinated oxyhydroxide, akaganeite (β -FeOOH) is considered the main cause of the rapid deterioration of investigated iron objects. Elemental mapping indicates that chloride ions can be present at the interface between the metal and inner corrosion layer. In order to stabilize metallic artifacts the presence of chloride ion must be eliminated or made inactive. Desalination treatments are the main processes that can slow down the deterioration of iron artifacts.

5. Conclusions

Archaeological iron artifacts coming from the Archaeological National Museum of Crotone (Calabria, Italy) appear corroded. The main corrosion products are goethite, maghemite, magnetite, hematite, lepidocrocite and ferrihyidrite. In addition, the presence of akaganeite at the interface between the corrosion products and the core of the metal suggests a corrosion mechanism due to the presence of chloride within these artifacts.

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Appendix A. Supplementary data

Supplementary data (Figs. S1–S5) associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.culher.2014.07.003.

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