

ABOUT CORROSION AND CONSERVATION PROBLEMS OF IRON ARTEFACTS COMING FROM ORADEA FORTRESS

Olimpia MUREȘAN*

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Abstract

A lot of metallic artifacts were discovered during diggings in the Fortress of Oradea (starting from 1991 and intensively restarted after 2007).

Iron and alloys of copper are the mainly metallic structures. The soil contains a lot of ruins coming from buildings of the XII-XVII centuries, that's why the artefacts are drastically corroded, especially the iron ones.

Having to conserve/restore a great quantity of metallic/iron artifacts with different degrees of mineralization may be a difficult task to do. To know the specific corrosion process and to divide the discovered artifacts on categories/degrees of urgency of interventions may be useful. May be burnt iron artefacts a privileged category? We must investigate such objects!

The importance of the examination of the artifact is out of question. Metallic artifacts affected by an advanced mineralization process allow to determine: the stratigraphy, the degree of mineralization and fragilisation, details hidden within corrosion products, the presence of different materials, the location of the original surfaces. The analysis of composition have their relevances too.

Some preliminary investigation on a cremated fragment of an iron armour are showed.

Key words: archaeological, iron oxidation, siderite on buried iron, soil ATR-IR analysis, examination by microphotography.

Introduction

The city of Oradea, residence of Bihor District was built around a fortress. During different historical times, the name of the fortress and of the growing town was the same: Nagyvárad, Großwardein and Oradea. At the beginnings, it was a fortification protecting a monastery (XI-XIII centuries) then, a new fortification surrounding a gothic cathedral and a gothic palace (XIV-XVI centuries). The today fortress was built during the XVI-XVII centuries. Ruins of these buildings, artefacts and fragments (discovered during archaeological diggings 1991-2001, 2005-2007, 2009) are a great challenge for the studies and conservation nowadays. (Rusu & co, 2002; Marta, 2002; Mureșan, 2004, 2009). A special attention will be paid to the corroded iron artefacts.

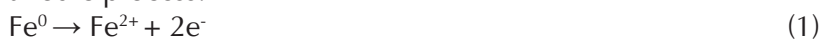
General considerations about archaeological iron corrosion

„Rust” is associated with iron corrosion which in the language of chemistry is called oxidation. During the burial period the iron undergoes ionization as a consequence of the

* Muzeul Țării Crișurilor Oradea, olimpia-muresan2010@yahoo.com.

electrochemical phenomena: the anodic process consisting of iron oxidation is balanced by the depolarization process at the cathodic areas. The general reactions are (Oniciu, 1973):

anodic process:



cathodic process:



the resulted corrosion compound: a salt of Fe(II)



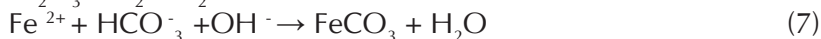
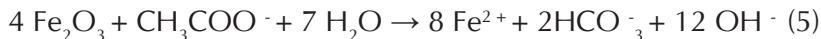
corrosion products: $\text{Fe}(\text{OH})_2$, FeO



corrosion compound: salt of Fe(II)

The depolarization depends on the parameters of the environment: reaction (2) take place at acid pH (when bio corrosion is possible too); reaction (3) take place at excess of air and humidity at a neutral or basic pH; reaction (4) take place in the presence of a redox system.

It is generally known (Selwyn, 2004) that the main phases of rust are oxides and oxyhydroxides such as: maghemite ($\gamma\text{-Fe}_2\text{O}_3$), magnetite (Fe_3O_4), and goethite, $\alpha\text{-FeOOH}$, lepidocrocite $\gamma\text{-FeO}(\text{OH})$. In addition to the above mentioned corrosion products, other specific ones may be identified due to the particular soil/environmental composition/parameters (pH, soluble salts, aeration, soil constituents, and synergic effects). The sulphate-reducing bacteria may be responsible for the presence of siderite, FeCO_3 on buried iron (Coleman & co, 1993) resulted by the oxidation of fermentation products as acetate and hydrogen:



But siderite (Blengino & co, 1995, Nef & co, 2006, Reffass & co, 2006) accompanied by green rust, $\text{CO}_3^{2-}[\text{Fe}_4^{\text{(II)}}\text{Fe}_2^{\text{(III)}}(\text{OH})_{12}][\text{CO}_3 \cdot 2\text{H}_2\text{O}]$, (Refait and Génin, 1993) (**Fig. 1**), and iron hydroxide carbonate, $\text{Fe}_2(\text{OH})_2\text{CO}_3$ (Bernard&co, 2002) is formed in anoxic soil too.

Iron artefacts from Oradea fortress

The soil of the fortress may be considered near-anoxic and carbonated, because of a stone pavement from the 18th century that was found at a deeper depth than 20 cm and the other ruins of ancient buildings present there, too. Therefore, carbonates (Saheb, 2007) were expected to be present. But things are not so simple: by means of ATR-IR [analysis realized at INCCR, (National Researching Institute for Conservation and Restoration, Bucharest) with Bruker Spectrometer (5000-400 cm^{-1} , 4 cm^{-1} resolution), organic components [aromatic structures (bands: 2931, 2918, 2851, 2655 cm^{-1}) probably oil (bands: 1638, 1639, 1647 cm^{-1})], kaolinite (bands around 1000 cm^{-1} for the groups Si-O, Si-O-Si, Si-O-Al, Al-O-OH, and again Al-O-OH, into 3600-3700 cm^{-1}) quartz, carbonates (1427, 1435, 1445, 874 cm^{-1}) and hydrated water (3378, 3331, 3298, 3200, 1647, 1630, 1639, 1441, 1435, 1427 cm^{-1}) were detected too. The heterogeneity of the soil caused a lot of problems in attributing the peaks and discriminating the components (for the iron corrosion components, too). It is difficult to distinguish (Neff & co, 2004) the various carbonates, by exemple: the calcite, CaCO_3 and siderite, FeCO_3 have the main peak at 1088 cm^{-1} respectively 1084 cm^{-1} . Conclusion: complementary analytical techniques are needed (coupling between μRaman and μXRD ensure the identification, Neff & co, 2004).

Now, speaking about the iron artefacts coming from Oradea fortress, each digging brought up hundreds of objects or fragments, with different degrees of mineralization and

deformation, even without possibility of being identified. The growth of the iron corrosion crust have disrupted the original surface (Fig. 2). Problems of on-going corrosion may occur on iron objects after excavation if they are contaminated with salts, especially Fe(II) chloride (Selwyn, 1999). The visual symptom of this active corrosion is the formation of reddish "bubbles" (Fig. 3). The "weeping" is attributed to the hygroscopic nature of the iron chlorides.

The conservation of the iron excavated objects requires solving a lot of problems. Great battle, few weapons! A strategy may be a useful tool. It is important to acknowledge: which are the problems to be solved; which are the ideal requirements to conserve the discovered artefacts and the realistic ways/possibilities to do that. The problems to be resolved are the following: a lot of metallic artefacts (hundreds) were discovered during each excavation; the iron ones were corroded and mineralized (most of the artefacts looked fragile); the artefacts must be stabilized and conserved; no supporting expenses for the research of the artefacts. To divide the iron artefacts, from the beginnings (by examination tools), in categories based on their emergency degree and degrees of mineralization seems time gaining.

Some of badly corroded iron artefacts from Oradea fortress didn't lost the original shape. It is the case of a fragment of medieval steel armour (Fig. 4 picture took by Szabo Alexandru) that was cremated.

Details of the morphology of the corrosion products were observed by optical microscope (different magnifications) (Fig. 5-7). By means of the examination of the microphotographs (Cornell, Schwertmann, 2002, Eastaugh & co, 2004) a mixture of goethite and lepidocrocite was recognized from the red-brown compounds (Fig. 8, 9) the goethite was recognized from the yellow-ochre compounds (Fig. 10), and calcite was recognized from the white crystallized compound (Fig. 6). Spectral analysis (Fig. 11) was performed by ATR-IR from the same samples and from the black iron compounds, too. Standard spectra (Derrick & co, 1999, IRUG spectra, 2003) and Kremer Pigments were used. Goethite, lepidocrocite, iron oxide, calcite, were detected by both methods. But the research must to be continued (complementary and non-destructive tools are necessary (Neff & Co, 2004).

Final considerations

The conservation of great quantities of excavated iron artefacts needs particular management strategy.

The examination methods are used on every artefact. Complex analysis is done to representative or particular artefacts.

Samples of soil, corrosion products, and fragments of artefacts may be collected for further analysis.

An interdisciplinary project on corrosion and conservation of iron artefacts coming from Oradea Fortress will be a desirable future stage of these considerations.

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Fig. 10. Plane polarized light micro-photograph of the red-brown iron compound containing goethite and lepidocrocite (x100)

Fig. 11. The over lap of the FTIR spectra of: the yellow-ochre compound (black spectra); the red-brown compound (grey spectra); the black compound (grey spectra)



Fig. 1

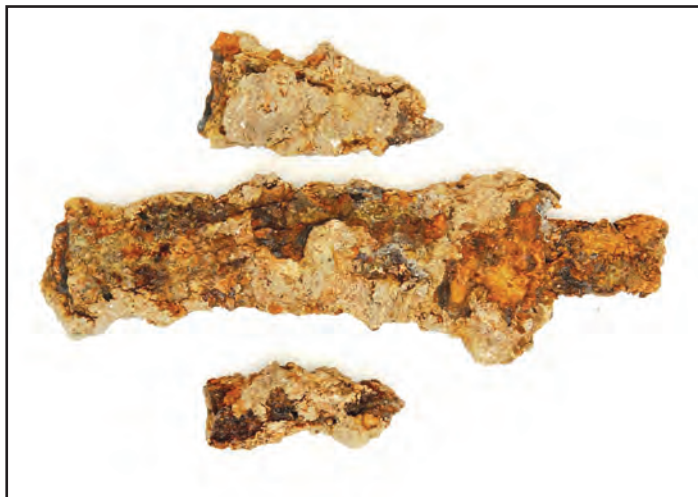


Fig. 2



Fig. 3



Fig. 4

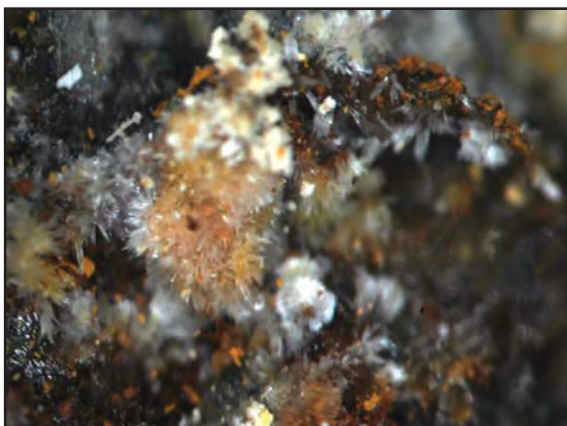


Fig. 5

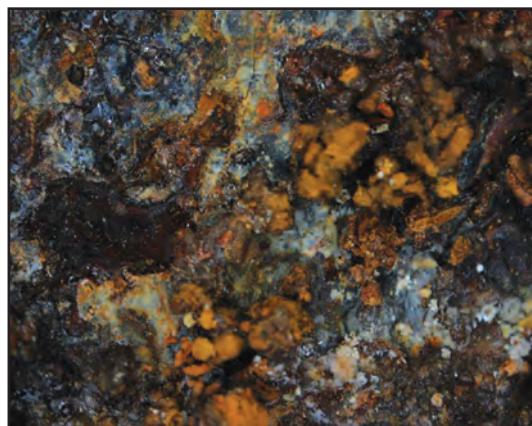


Fig. 6



Fig. 7



Fig. 8

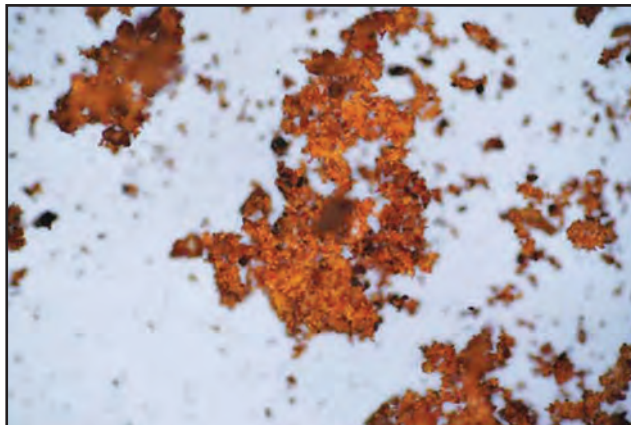


Fig. 9

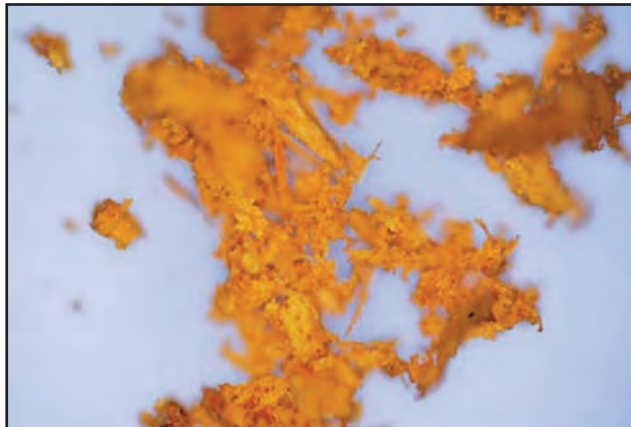


Fig. 10

