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Conservation of the Archaeological Find from Roman Period

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Abstract: A degree of preservation of iron artefacts depends on the type of underground environment and the type of corrosion products formed on their surface. This paper analyses the conditions of an archaeological artefact made of iron, which was found to originate from the Roman period. The iron corrosion products, goethite, lepidocrocite and magnetite (determined by the X-ray diffraction method) have been noticed in the corrosion products of the artefact. The ion chromatography analysis has revealed chloride and sulphate anions, pointing to the necessity of having artefacts treated in adequate solutions immediately after their excavation. It has been found that the EDTA solution is very efficient in the process of desalination of the artefact. The aim of this study was to determine the influence of the corrosion product types and the effects of applying the EDTA solution, otherwise not commonly used for desalination of iron objects. This method was applied here due to the complex structures of the found archaeological artefacts and the presence of copper alloys besides iron. The aim of this paper is to determine the type of influence corrosion products have on an artefact and to determine the effect of desalination treatment.

Keywords: archaeological iron, corrosion, XRD, radiography, ionic chromatography.

1. Introduction

During the corrosion process on iron buried in aerated soil, a massive layer of corrosion products in a characteristic colour, cemented with soil and sand particles is gradually formed on its surface [1, 2, 3, 4]. Iron oxy-hydroxides, goethite and lepidocrocite, can be identified in the outer layer of corrosion products [1, 2, 3, 5, 6, 7]. Magnetite is the most common iron oxide, identified on archaeological iron and usually found directly next to the metal surface [1]. The corrosion product layer contains a significant quantity of amorphous substance, such as amorphous iron oxy-hydroxide, feroxyhit, δ-FeO(OH), discovered by Misawa [6, 7], and thus sometimes called misawite in his honour [5, 8].

Corrosion products formed during the period spent under the ground need not to be stable in the new environment. If such objects are left to dry after excavation then the remaining metal will continue to corrode in the process which can eventually affect the whole object. In such a process, the corrosion product appearing on iron and steel is akaganeite, β-FeO(OH).

In the conservation practice, the most frequently applied procedures for desalination of corrosion products on iron are the chemical procedures of immersion in the NaOH solution, in a concentration range from 0.1 to 0.5 mol dm^{-3} at the room temperature [3, 9], or in the alkaline solution Na_2SO_3 [3, 10] for a longer period. Electrochemical cathode treatments [3, 10] are also sometimes used as well as thermal treatments in an inert atmosphere at moderately high temperatures, followed by a subsequent treatment in alkaline solutions [11]. The aim of this paper is to determine the type of influence corrosion products have on an artifact and to determine the effect of desalination treatment.

2. Experimental

2.1. Radiographic Method

Radiographic tests were carried out applying the γ rays on the defectoscope γ volt SU50 with Iridium-192 isotope. The radiograms were analysed by placing them on a strong light source, which is a standard procedure. The original radiograms were scanned and presented in this paper in the form of images; therefore, many important details are not possible to be detected in them.

2.2. X-Ray Diffraction (XRD) Method

The analyzed samples were taken from mechanically powdered archaeological artifacts (fibula). The samples were analyzed on the PHILIPS PW 1710 powder diffractometer, under the following conditions: working voltage (U = 40 kV), current intensity (I = 30 mA), X-ray radiation from the copper (Cu) anti-cathode, wavelength (CuKα = 0.154178 nm), graphite monochromator, test range (4 – 70º 2θ), step (0.02º 2θ), time constant (0.5 s per step).

The data obtained on the positions of the diffraction maximum values 2 θ (º) and the values of the inter-planar distances dhkl (nm) for the most important (hkl) reflections are shown as graphs and tables as well as the corresponding

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relative intensities I/Imax. In addition to the graphic presentation, a large number of important XRD test results are presented in a tabular form (Miller indices of crystalline planes, inter-planar distances). On the basis of the obtained I/Imax and d values and the comparison with the JCPDS standards, the present crystalline phases were identified. Small differences in the results shown in the diagram and the table originate from different algorithms for finding diffraction maxima, installed in the used programs.

2.3. Ion Chromatography Method

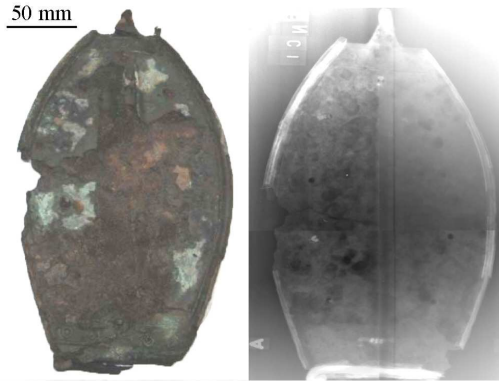
The corrosion product samples in the form of powder, weighing 0.9171 g, were prepared by the standard procedure. The anion concentration in the solutions was determined on a Metrohm ion chromatography instrument, 861 Advanced Compact IC MSM II. The instrument specifications are: PC-controlled compact ion chromatography instrument for anion analysis; conductivity detector with chemical suppression, controlled flow ranging from 0.2 to 2.5 cm3 min-1; maximum pressure of 35 MPa. The column specifications: Metrosep A Supp 5-150 (for anion analysis); anion eluent: 3.2 mmol Na2CO3 / 1.0 mmol NaHCO3; suppressor solution: 50 mmol H2S04. Before the analysis, all samples were filtered through 0.45 µm filters and degassed in the S100 ELMASONIC ultrasonic bath. Standard solutions were prepared from demineralized water and standard ion solutions. The signal to noise ratio was 3:1. The detection limit of the used IC column for fluorides, chlorides, nitrites, bromides, nitrates and sulphates was 10 ppb and for phosphates 30 ppb (µg cm-3).

3. Results and Discussion

In order to prevent accelerated corrosion of archaeological iron artefacts, it is advisable to treat them in a suitable solution after excavation. The artefact – fibula, originating from the B.C. period, was found on the Gomolava site in Srem, the territory of Hrtkovci village. To prevent active corrosion of the fibula following its excavation, regarding iron and copper alloy, the fibula was kept in the 5% solution of the EDTA (ethylene-diamine-tetra acetate) for a month. Being made of the combination of these two metals, the fibula was thus treated with the solution. During the fibula treatment in the solution, chloride ions from iron the corrosion products gradually pass into the surrounding solution.

Figure 1 shows a photo of the fibula after the treatment in the 5% EDTA solution. The photo shows nothing about the condition of the metal core below the layer of corrosion products or about the remaining quantity of non-corroded metal. It cannot be seen whether cracks or other defects are present, which is of great importance for a conservator before a final conservation of an artefact. A radiograph of the fibula (Fig. 1b) enables the identification of the iron core condition. It can be seen that the central left part of the fibula is completely damaged (material is missing). A big crack, starting from this point and ending in the central part of the fibula, is also visible. The rest of the fibula is in generally satisfactory condition, considering its age.

The XRD method was also used in analysing the presence of specific crystalline phases in the corrosion products taken from the archaeological find (the fibula), following the treatment in the EDTA solution. Table 1 specifies the values of Bragg's angle (2θ), the values of the corresponding crystalline planes for the identified phases (hkl), the distances between these planes (dhkl), as well as the X-ray radiation intensity ratios (I/Imax), determined by this method. It can be seen that the predominant crystalline phase in the corrosion products consist of goethite and magnetite. Wüstite, FeO, and lepidocrocite are present in a smaller quantity. Wüstite is a transient iron (II) oxide which usually transforms into more stable compounds with time [5].



a) b)

Figure 1. a) Photo; b) Radiograph of archaeological find, a fibula from Gomolava site in Srem, Serbia

TABLE 1. Bragg's angle values (2θ); Miller indices of crystallographic planes (hkl); inter-planar distance (d); and x-ray radiation intensity ratio (I/Imax) obtained in the course of analysing the corrosion products by XRD method.

	2θ (°)	Crystals plane (hkl)	d_{hkl}, (nm)	I/I_{max} (%)
α-FeO(OH)	21.360	110	0.4156	15.63
	33.320	130	0.2687	15.63
	36.505	111	0.2459	100.00
	53.325	221	0.1717	15.63
	68.435	302	0.1370	15.63
Fe_3O_4	30.125	220	0.2964	15.63
	35.555	311	0.2523	40.63
	36.505	222	0.2459	100.00
	43.320	400	0.2087	15.63
	53.325	422	0.1717	15.63
FeO	36.505	111	0.2459	100.00
	42.410	200	0.2130	15.63
γ-FeO(OH)	14.220	200	0.6223	18.75
	26.765	210	0.3328	46.88
	36.505	301	0.2459	100.00
	47.100	020	0.1928	15.63

Figure 2 shows the XRD diagram of the corrosion products taken from the archaeological artefact – the fibula. The predominant corrosion product in this sample is iron oxy-hydroxide, goethite, α-FeO(OH), (about 40%). In a smaller or equal quantity (approx. 20% each) there are two iron (II,III) oxides present, magnetite, Fe_3O_4 and wüstite,

FeO, as well as iron oxy-hydroxide, lepidocrocite, γ-FeO(OH) (JCPDS 44-1415). All these crystalline phases also have wide diffraction maxima of low intensity. No crystalline phases in the corrosion products containing chlorides were identified, which may be due to the fact that the artefact had previously been immersed in the 5% EDTA solution for a month.

After the completion of the EDTA solution treatment, a sample of the corrosion products was taken from the fibula and powdered to facilitate the extraction of chloride, sulphate and other ions that could have remained in the closed channels and pores of the corrosion product layer. The content of these ions, determined by the ion chromatography method, is presented in Fig. 3.

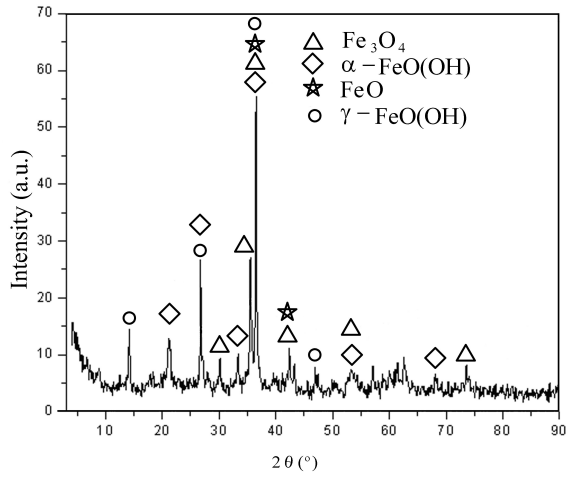


Figure 2. XRD diagram of archaeological find (fibula)

The chloride ion concentration was 0.583 mg dm^{-3} or, calculated to the mass of corrosion products, 0.016 mass %. The content of sulphate ions was 0.643 mg dm^{-3} or, calculated to the mass of corrosion products, 0.017 mass %. This is in accordance with the fact that akaganeite was not identified in the corrosion products by the XRD method.

The treatment by the immersion in the EDTA solution for the purpose of desalination was quite efficient as well.

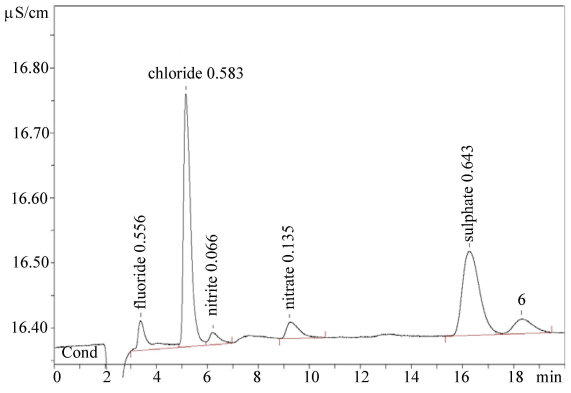


Figure 3. Test results of anion content in corrosion products taken from fibula analysed by ion chromatography.

Chloride ions located in the akaganeite tunnels can also be eliminated to a great extent by a treatment in pure water, up to approximately 1%. The applied solution was quite efficient in the process of desalination of the complex exhibit.

4. Conclusions

The conditions of an archaeological artefact made of iron originating from the Roman period were analysed. The radiographic method was used to determine the quantity of non-corroded material as well as the presence of cracks and other defects in the artefact. The composition of the corrosion products were analysed by the X-ray diffraction (XRD) method.

The presence of common iron and steel corrosion products, goethite α-FeO(OH), lepidocrocite γ-FeO(OH) and magnetite Fe_3O_4 was detected. A crystalline phase, quite unstable wüstite FeO, was identified on the artefact. The presence of akaganeite β-$Fe_8O_8(OH)_8Cl_{1.35}$ was not detected.

The corrosion products were tested for the presence of chloride, sulphate and other anions by ion chromatography (IC). After desalination, the fibula did not contain a significant quantity of chloride and sulphate anions.

Based on the carried out analyses, it can be confirmed that archaeological finds need to be treated in adequate solutions immediately after their excavation, in order to eliminate chloride, sulphate and other corrosion active anions. A treatment carried out immediately after the excavation of archaeological artefacts, even in almost neutral solutions, eliminates the mentioned anions quite efficiently.

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