

BORE V. JEGDIĆ¹
SUZANA R. POLIĆ RADOVANOVIĆ²
SLAVICA S. RISTIĆ¹, ANA B. ALIL¹
VLADANA RAJAKOVIĆ-OGNJANOVIĆ³

Scientific paper
UDC:620.193.2:502.8(497.11)

Corrosion of an archaeological find from the roman period in Serbia

The degree of preservation of iron artifacts 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 find made of iron and originating from the Roman period and belonging to the collections of the Museum of Science and Technology in Belgrade. The radiographic method has been used to determine the quantity of non-corroded metal as well as to determine the presence of cracks and other defects in the artefact. The composition of the corrosion products has been analysed by the X-ray diffraction method (XRD). In addition to iron corrosion products (goethite $\alpha\text{-FeO(OH)}$ and magnetite Fe_3O_4), the presence of a significant quantity of akaganeite $\beta\text{-Fe}_8\text{O}_8(\text{OH})_8\text{Cl}_{1.35}$, has been noticed on the artifact. The content of chloride, sulphate and other ions in the corrosion products has been determined by ion chromatography (IC). The analyses have pointed to the necessity of having artifacts treated in adequate solutions immediately after their excavation in order to eliminate chloride and sulphate anions. The aim of this paper is to determine the type of corrosion products and their influence on the corrosion behaviour of an archaeological artefact.

Key words: archaeological iron, corrosion, XRD, radiography, ionic chromatography.

INTRODUCTION

The soil composition and corrosive activity change significantly due to human activities such as industrialization, modern agriculture and land-use change. Large quantities of industrial waste, road salts, weed-killing chemicals and atmospheric pollutants accumulate in surface soil layers [1]. In the environments where oxygen access is possible, the corrosion products on iron are red-brown iron (III) compounds, primarily goethite, $\alpha\text{-FeO(OH)}$, lepidocrocite, $\gamma\text{-FeO(OH)}$, and black magnetite, Fe_3O_4 , which can transform into magnetic maghemite $\gamma\text{-Fe}_2\text{O}_3$ [2] in time. The peaks of these two oxides in XRD diagrams overlap, so it is usually considered that the identified peak refers to magnetite, Fe_3O_4 [3, 4]. Hematite, $\alpha\text{-Fe}_2\text{O}_3$, red iron (III) oxide, is not commonly formed as a corrosion product in underground conditions; however, it can sometimes be identified on archaeological iron. Considering that hematite is formed when goethite is exposed to high temperatures, its presence is usually associated with a fact that the object was exposed to fire (heat treatment) before burial [1, 4, 5]. The corrosion product

layer contains a significant quantity of amorphous substance, such as amorphous iron oxy-hydroxide, ferroxihit, $\delta\text{-FeO(OH)}$, discovered by Misawa [6,7], and thus sometimes called misawite in his honour [3,4].

Following their excavation and exposure to the ambient atmosphere, cultural heritage artifacts can corrode rapidly. Corrosion products formed during the period spent under the ground need not to be stable in the new environment. Contamination, in particular with chloride ions, during the period spent under the ground often causes continuous corrosion of the remaining metal after excavation [1,5,8-14]. Reguer et al. [12,15] demonstrated that the phases formed in the corrosion products contain chloride ions even if the content of chloride ions in the surrounding environment is very low (~10 ppm). The corrosion products thus formed on the iron surface take up a larger volume and apply physical stress to the existing corrosion products and the metal core. In addition, the newly created corrosion products have a low pH value and act chemically on the remaining metal [8,9,16,17]. 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, $\beta\text{-FeO(OH)}$. These processes will be discussed in this paper. The aim of this paper is to determine the type of corrosion products and their influence on the corrosion behaviour of an archaeological artefact.

Author's address: ¹Institute GOSA, Milana Rakića 35, Belgrade, Serbia, ²Central institute for conservation, Terazije 26, Belgrade, Serbia, ³Faculty of Civil Engineering, Bulevar Kralja Aleksandra 73, University of Belgrade, Serbia

Paper received: 13. 05. 2012

TESTING METHODS

Radiographic Method

The majority of authors [10, 18, 19] consider that the most reliable method for estimating the quantity of non-corroded iron is the radiographic method. Since multiple radiographing gives the most reliable results [18], it has been used in this paper.

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.

X-Ray Diffraction (XRD) Method

A method often applied to examine the contents and the concentration of crystalline phases in corrosion products is the X-ray diffraction [3-7, 12, 15, 20-23]. This method cannot be used for analysing amorphous phases which are considerably present in corrosion products [3, 6, 7].

The analysed samples were taken from mechanically powdered archaeological artifacts a shovel-spade. The sample was 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 ($\text{CuK}\alpha = 0.154178$ nm), graphite monochromator, test range ($4 - 70^\circ 2\theta$), step ($0.02^\circ 2\theta$), time constant (0.5 s, per step).

The data obtained on the positions of the diffraction maximum values 2θ ($^\circ$) and the values of the inter-planar distances d_{hkl} (nm) for the most important (hkl) reflections are shown as graphs and tables as well as the corresponding relative intensities I/I_{\max} . 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/I_{\max} 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.

Ion Chromatography Method

A combination of the ion exchange column and conductivity detection (ion exchange chromatography (IEC)) represents the most important method of ion chromatography and it has been used in this paper.

Ion concentrations are obtained by the integration of the experimentally obtained chromatographic curve. The area below the curve is directly proportional to the concentration of the analysed ion types. Separated ions must be detected first. For detecting inorganic and organic ions, a commonly used procedure is measuring the conductivity of ions in a solution – conductometry. In order to measure ion conductivity in a solution in a reliable way, it is necessary to reduce the eluent conductivity to the minimum in a process called suppression [24].

The corrosion product samples in the form of powder, weighing 1.3133 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 $2.5 \text{ cm}^3 \text{ min}^{-1}$; maximum pressure of 35 MPa. The column specifications: Metrosep A Supp 5-150 (for anion analysis); anion eluent: $3.2 \text{ mmol Na}_2\text{CO}_3 / 1.0 \text{ mmol NaHCO}_3$; suppressor solution: 50 mmol H_2SO_4 . Before the analysis, all samples were filtered through $0.45 \mu\text{m}$ 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 ($\mu\text{g cm}^{-3}$).

RESULTS AND DISCUSSION

Fig. 1a shows a photograph of the shovel-spade with thick layers of corrosion products mixed with clay. Visual examination cannot detect either the presence of the core metal, iron, below the layer of corrosion products or the presence of cracks and other defects in it. The shovel (spade) X-ray is shown in Fig. 1b.

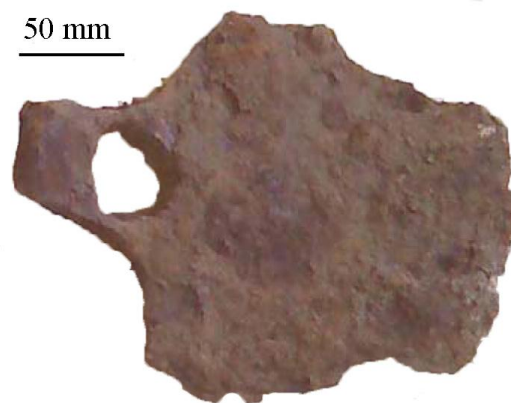


Fig. 1a

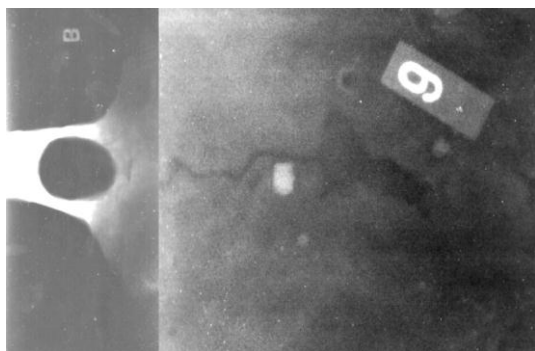


Fig. 1b)

Figure 1. a) Photo b) Radiograph of the archaeological find (shovel-spade)

The thicker part of the shovel metal is visible on the left side of the radiogram (Fig. 1b); it was not possible to radiate it sufficiently due to its considerable thickness. This part gradually becomes a thinner one, with visible corrosion-caused damage. On the right side of the same radiogram (Fig. 1b), considerable damage due to corrosion is visible, irregularly distributed on the surface. A large crack in the core iron is visible as well. One of the main advantages of radiography is detecting the presence, shape and size of cracks and other defects in the core metal.

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

	$2\theta, ^\circ$	Crystals plane, (hkl)	$d_{\text{hkl}},$ (nm)	$I/I_{\max},$ %
Fe_3O_4	18.300	111	0.4844	20
	35.500	311	0.2527	100
	43.140	400	0.2095	24
	56.965	511, 333	0.1615	28
	62.505	440	0.1485	32
$\alpha\text{-FeO(OH)}$	21.165	110	0.4194	20
	40.745	140	0.2213	20
	53.540	221	0.1710	20
	71.340	132	0.1321	20
$\text{Fe}_8\text{O}_8(\text{OH})_8\text{Cl}_{1.35}$	11.895	101	0.7434	20
	26.730	301	0.3337	20
	30.115	112	0.2965	28
	43.140	213	0.2095	24

The presence of specific crystalline phases in the corrosion products originating from the shovel-spade was analysed by the X-ray diffraction (XRD) method. Table 1 shows the values of Bragg's angle (2θ), the values of the corresponding crystalline planes for the identified phases (hkl), the distances between these planes (d_{hkl}) and the x-ray radiation intensity ratios (I/I_{\max}), determined by this method. It can be seen that the predominant crystalline phase in the corrosion products was magnetite. Goethite and akaganeite were present in a smaller or almost equal quantity.

Fig. 2 shows an XRD diagram of the corrosion products taken from one archaeological artifact (shovel-spade). On the basis of Table 1 and Fig. 2, it can be concluded that the predominant corrosion product in this sample is iron (II, III) oxide, magnetite, Fe_3O_4 , present in an amount of approximately 40%. Iron oxy-hydroxide, goethite, $\alpha\text{-FeO(OH)}$ and iron oxy-hydroxide, akaganeite, $\beta\text{-Fe}_8\text{O}_8(\text{OH})_8\text{Cl}_{1.35}$ are present in a smaller or equal quantity. In the literature, the formula $\beta\text{-FeO(OH)}$ denoting akaganeite can also be found, but it does not take into account the presence of chloride. All crystalline phases have wide diffraction maxima; they are of low intensity, which suggests a low level of crystallinity. A low level of crystallinity of the corrosion product samples could be a result of fine, inadequately crystallised particles of goethite, $\alpha\text{-FeO(OH)}$, as well as misawite (amorphous iron oxy-hydroxide, ferrosyhyte) $\delta\text{-FeO(OH)}$, which were impossible to identify by the XRD method.

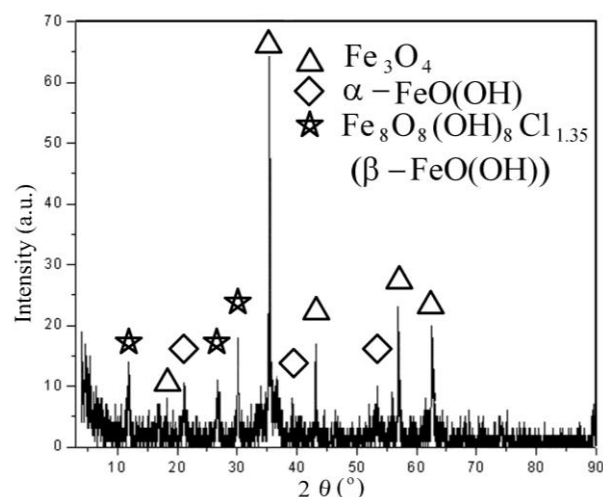


Figure 2. XRD diagram of corrosion products from archaeological find (shovel-spade).

Besides its high precision, the ion chromatography method, used here for the approximate determination of the content of chloride, sulphate and other anions in corrosion products, enables the determination of the presence of almost all anions in a solution in a single experiment (Fig. 3).

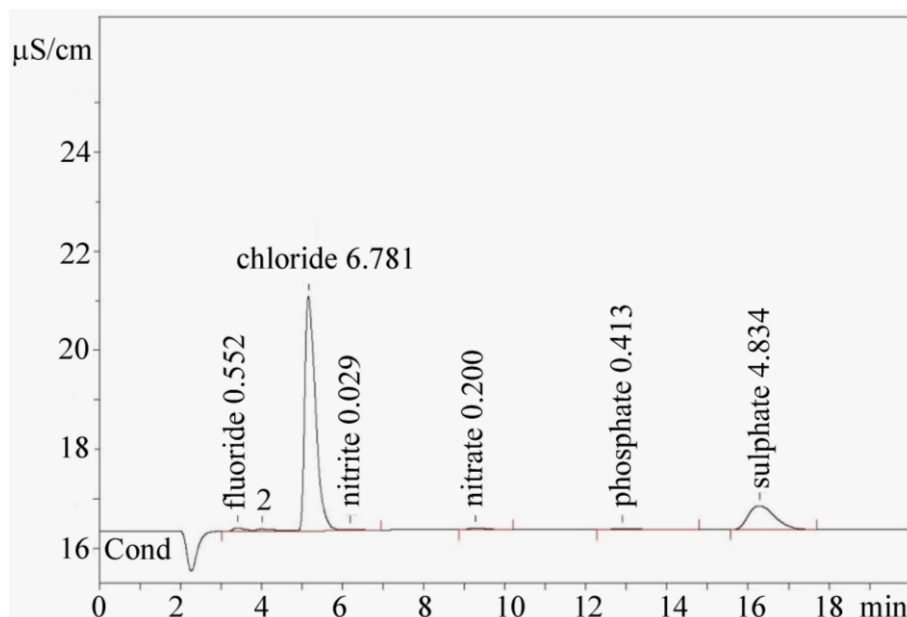


Figure 3. Test results of anion content in the corrosion products, taken from shovel-spade analysed by ion chromatography (IC) method.

The test results obtained by the ion chromatography method have shown that the chloride ions, taken from the shovel-spade archaeological artifact corrosion products, are present in a quantity of 6.781 mg dm⁻³, which represents 0.13 mass % of the mass of corrosion products. A significant amount of sulphate ions is found as well - 4.834 mg cm⁻³, which calculated to the mass of corrosion products is ~0.1 mass %. Chloride ions may increase the iron corrosion rate, since they participate in the regeneration cycle of HCl, as proposed by Asheby [25]. Similar cycles of corrosion, but with a regeneration of H₂SO₄ and an acceleration of corrosion processes, are proposed by Graedel [26].

The oxidation of Fe²⁺ ions in the presence of Cl⁻ ions results in the formation of β-FeO(OH). Other types of oxy-hydroxides (α-FeO(OH) and γ-FeO(OH)) can also be formed, but to a significantly lower extent, if the content of chloride ions is sufficiently low. The presence of akaganeite in the corrosion products is a sign of active corrosion of iron below the layer of corrosion products. During the precipitation of the given types of iron oxy-hydroxides under (or within) the corrosion product layer, the volume increase causes stresses, cracks and other defects in the layer, which then facilitates oxygen and humidity penetration and a more rapid progress of corrosion processes. The volumes of one mol oxy-hydroxides are approximately three times larger than the volume of one mol iron and are 20.9 cm³ for α-FeO(OH); 21.7

cm³ for γ-FeO(OH) and 26.7 cm³ for β-FeO(OH). The volume of one mol Fe₃O₄ is 14.9 cm³ [7].

The presented results suggest that it is necessary to perform desalination as soon as possible (for example, in the NaOH solution) in order to eliminate chloride and sulphate ions.

CONCLUSIONS

The conditions of an archaeological find 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 artifact. The composition of the corrosion product were analysed by the X-ray diffraction (XRD) method.

In addition to the presence of common iron and steel corrosion products, goethite α-FeO(OH) and magnetite Fe₃O₄, the presence of a significant quantity of akaganeite β-Fe₈O₈(OH)₈Cl_{1.35} was also detected on the artefact.

The corrosion products were tested for the presence of chloride, sulphate and other anions by ion chromatography (IC). The tested artifact (shovel) contains a significant quantity of chloride and sulphate anions. The presence of chloride in the corrosion products on iron and steel artifacts cause accelerated corrosion of the core metal and akaganeite formation after excavation. Similar processes occur in the tested

artefact because larger quantities of sulphate ions are present in the corrosion products.

Based on the carried out analyses, it can be concluded 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. 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, or in the alkaline solution Na₂SO₃.

Acknowledgements

The present paper has been financed by the Ministry of Education and Science of the Republic of Serbia, Project No. 34028, as well as by the Ministry of Culture of the Republic of Serbia.

REFERENCES

- [1] Selwyn, L.S., Corrosion of Metal Artifacts in Buried Environments, ASM Handbook, Volume 13C: Corrosion: Environments and Industries, Ohio, 2006, pp. 306-322.
- [2] Tamura, H., The role of rusts in corrosion and corrosion protection of iron and steel, Corrosion Science, 50 (2008) 1872-1883.
- [3] Balasubramaniam, R., On the corrosion resistance of the Delhi iron pillar, Corrosion Science, 42 (2000) 2103-2129.
- [4] Jegdić, B., Polić-Radovanović, S., Ristić, S., Alil, A., Corrosion Processes, Nature and Composition of Corrosion Products on Iron Artefacts of Weaponry, Scientific Technical Review, 61 (2011) 50-56.
- [5] Stahl, K., Nielsen, K., Jiang, J., Lebech, B., Hanson, J.C., Norby, P., Lanschot, J., On the akaganeite crystal structure, phase transformations and possible role in post-excavational corrosion of iron artifacts, Corrosion Science, 45 (2003) 2563-2575.
- [6] Misawa, T., Kyuno, T., Suetaka, W., and Shimodaira, S., The Mechanism of Atmospheric Rusting and the Effect of Cu and P on the Rust Formation of Low Alloy Steels, Corrosion Science, 2 (1971) 35-48
- [7] Jegdić, B., Polić-Radovanović, S., Ristić, S., Alil, A., Corrosion of archaeological artefact made of forged iron, *Metallurgical Materials & Engineering, Vol. 18, No3 (2012) (accepted)*.
- [8] Selwyn, L.S., Sirois, P.J., Argyropoulos, V., The Corrosion of Excavated Archaeological Iron with Details on Weeping and Akaganéite, Studies in Conservation, 44 (1999) 217-232.
- [9] Selwyn, L., Overview of archaeological iron: the corrosion problem, key factors affecting treatment, and gaps in current knowledge, Proceedings of Metal 2004, National Museum of Australia Canberra, ACT 4-8 October 2004.
- [10] Watkinson, D., Degree of Mineralization: Its Significance for the Stability and Treatment of Excavated Ironwork, Studies in Conservation, 28 (1983) 85-90.
- [11] Gilberg, M.R., and Seeley, N.J., The Identity of Compounds Containing Chloride Ions in Marine Iron Corrosion Products: A Critical Review, Studies in Conservation, 26 (1981) 50-56
- [12] Reguer, S., Mirambet, F., Dooryhee, E., Hodeau, J.L., Dillmann, P., Lagarde, P., Structural evidence for the desalination of akaganeite in the preservation of iron archaeological objects, using synchrotron X-ray powder diffraction and absorption spectroscopy, Corrosion Science, 51 (2009) 2795-2802
- [13] Turgoose, S., Post-Excavation Changes in Iron Antiquities, Studies in Conservation, Vol. 27, No. 3 (Aug., 1982), pp. 97-101.
- [14] North, N. A., and Pearson, C., Washing Methods for Chloride Removal from Marine Iron Artifacts, Studies in Conservation, 23 (1978) 174-186
- [15] Réguer, S., Dillmann, P., Mirambet, F., Buried iron archaeological artefacts: Corrosion mechanisms related to the presence of Cl-containing phases, Corrosion Science 49 (2007) 2726-2744.
- [16] Turgoose, S., The Corrosion of Archaeological Iron during Burial and Treatment, Studies in Conservation, 30 (1985) 13-18
- [17] Selwyn, L. S., and Argyropoulos, V., Removal of Chloride and Iron Ions from Archaeological Wrought Iron with Sodium Hydroxide and Ethylenediamine Solutions, Studies in Conservation, 50 (2005) 81-100.
- [18] Thickett, D., Lambarth, S., Wyeth, P., Determining the Stability and Durability of Archaeological Materials, 9th International Conference on NDT of Art, Jerusalem, Israel, 25-30 May 2008, pp.1-10
- [19] Watkinson, D., and Lewis, M.T., Desiccated Storage of Chloride-Contaminated Archaeological Iron Objects, Studies in Conservation, 50 (2005) 241-252
- [20] Labbe, J.P., Ledion, J., Hui, F., Infrared spectrometry for solid phase analysis: Corrosion rusts, Corrosion Science, 50 (2008) 1228-1234
- [21] Monnier, J., Neff, D., Réguer, S., Dillmann, P., Bellot-Gurlet, L., Leroy, E., Foy, E., Legrand, L., Guillot, I., A corrosion study of the ferrous medieval reinforcement of the Amiens cathedral. Phase characterisation and localisation by various microprobes techniques, Corrosion Science, 52 (2010) 695-710

- [22] Kamimura, T., Hara, S., Miyuki, H., Yamashita, M., Uchida, H., Composition and protective ability of rust layer formed on weathering steel exposed to various environments, *Corrosion Science*, 48 (2006) 2799-2812
- [23] Goehuer, R.P., X-Ray Powder Diffraction, ASM Handbook, Volume 10: Materials Characterization, Ohio, 1992, pp. 681-701
- [24] Weiss, J., Ion Chromatography, Sec. Ed., Weinheim, 1995.
- [25] Askey, A., Lyon, S.B., Thompson, G.E., Johnson, J.B., Wood, G.C., Cooke M., and Sate, P., The Corrosion of Iron and Zinc by Atmospheric Hydrogen Chloride, *Corrosion Science*, 34 (1993) 233-247.
- [26] Graedel T.E., and Frankenthal, R.P., Corrosion mechanisms for iron and low alloy steels exposed to the atmosphere, *Journal of the Electrochemical Society*, 137 (1990) 2385-2394.

IZVOD

KOROZIJA ARHEOLOŠKIH EKSPONATA IZ RIMSKOG PERIODA U SRBIJI

Koroziona postojanost eksponata od gvožđa zavisi od tipa podzemne sredine i vrste korozionih produkata koji se formiraju na njegovoj površini. Ovaj rad analizira stanje arheološkog predmeta koji potiče iz rimskog perioda i koji pripada kolekciji Muzeja za nauku i tehniku u Beogradu. Radiografska metoda je korišćena za određivanje količine nekorodiralog metala, kao i prisustva prslina i drugih defekata u eksponatu. Sasatv korozionih produkata je analiziran difrakcijom X-zraka (XRD). Pored korozionih produkata gvožđa (getita $\alpha\text{-FeO(OH)}$ i magnetita Fe_3O_4), uočena je značajna količina akagenita $\beta\text{-Fe}_8\text{O}_8(\text{OH})_8\text{Cl}_{1.35}$ u sloju korozionih produkata. Metodom jonske hromatografije (IC) je određen sadržaj hloridnih, sulfatnih i drugih jona u korozionim produktima. Pomenute analize su ukazale na neophodnost tretmana arheološkog predmeta u odgovarajućem rastvoru za desalinaciju, neposredno posle iskopavanja, u cilju uklanjanja hloridnih i sulfatnih anjona. Cilj ovog rada je određivanje tipa korozionih produkata i njihovog uticaja na koroziono ponašanje arheološkog predmeta.

Ključne reči: arheološko gvožđe, korozija, XRD, radiografija, jonska hromatografija.

Originalni naučni rad

Rad primljen: 13. 05. 2012.