

Corrosion Processes, Nature and Composition of Corrosion Products on Iron Artefacts of Weaponry

Bore Jegdić¹⁾
Suzana Polić-Radovanović²⁾
Slavica Ristić¹⁾
Ana Alil¹⁾

The paper outlines the corrosion processes occurring in different types of iron artefacts of weaponry and military equipment while buried and after excavation. Special attention was given to the description of the nature and the composition of corrosion products on the surface of iron artefacts, which provided their protection over thousands of years. The corrosion processes occurring after the excavation can cause a rapid deterioration of these objects in relatively mild conditions. Being particularly dangerous for archaeological iron weapons and military equipment, these processes are dealt with here in detail.

Key words: armament, weaponry and military equipment, iron, corrosion, corrosion products.

Introduction

IN the literature there is a lack of review articles devoted to the matters of corrosion of the archaeological iron. It is necessary to mention the works by Gilberg et al. from 1981. [1] and by Selwyn et al. from 1999. [2] describing the processes occurring on archaeological artefacts made of iron, the characteristics of corrosion products, etc. New works have emerged during the last ten years and consequently the results that additionally describe the processes and supply the results listed in these review articles.

Many archaeological iron weapons have remained in undamaged conditions for many centuries, because of the relatively small local aggressive corrosive environment (soil) where they had been buried, and due to the protective properties of formed layers of corrosion products. Advent of industrialization (acid rain), the application of fertilizers based on various chemical substances, and the salt use on streets and roads led to a change of character of soil and their increased corrosion aggressiveness [3]. This paper reviews the processes that occur on the surface of archaeological iron weapons during the period of their burial in soil, as well as the processes that take place after their excavation.

Briefly about corrosion

Corrosion is the destruction of metals and alloys caused by chemical or electrochemical reactions with the surrounding environment. Electrochemical corrosion is the result of electrochemical reactions and is under the rules of electrochemical kinetics. An essential condition of its

occurrence is the contact of metal with the second phase that has the properties of the electrolyte, when a thin layer with the characteristics of an electrochemical double-layer forms on the metal surface [4,5]. This includes all cases of corrosion in the soil. Different forms of corrosion of metals and alloys are discussed in the literature [4-16].

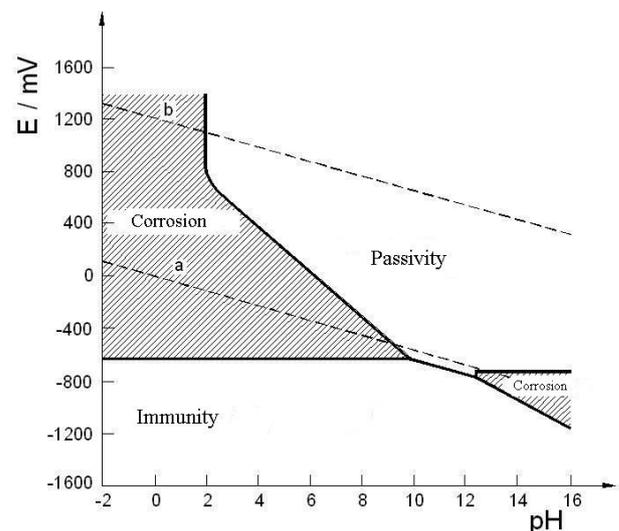


Figure 1. Pourbaix diagram of iron [5].

A potential-pH diagram for iron (Pourbaix diagram) shown in Fig. 1 indicates the areas of immunity, passivity and corrosion of iron in the function of potential and pH. Four separate areas-regions can be seen on the diagram. The region at the bottom of the diagram indicates the condition where iron is immune and thermodynamically

¹⁾ Institute GOŠA do.do., Milana Rakića 35, 11000 Belgrade, SERBIA

²⁾ CIK, Central Institute for Conservation, Terazije 26, 11000 Belgrade, SERBIA

stable. This region includes the reduction conditions (low value of potential) across the entire range of pH from acidic to basic environment. For any combination of potential and pH values in this area, iron is thermodynamically stable and it will not corrode. The two hatched areas indicate the regions where iron corrodes. In both areas (the large one on the left side of the diagram (oxidizing and acidic environment) and the small one at the far right (reduction and alkaline), iron reacts and forms the soluble corrosion products and corrosion takes place. The central area in this Pourbaix diagram shows the region of the passive state of iron. In oxidizing conditions, in neutral and alkaline solutions, iron reacts and forms insoluble products, and further evaluating of corrosion reaction is difficult, due to the presence of a protective film [4,17].

The assumption used in these diagrams is that any insoluble corrosion products can protect metal against corrosion. In practice, it is not always the case and the application of these diagrams should be careful. For example, insoluble corrosion products on steel are often porous and they are not protective in many types of environment. The described potential-pH diagram is the result of thermodynamic calculations and it does not give any information about the kinetics or the rate of corrosion reactions [4,17]. Potential-pH diagrams give a lot of important information about the corrosion system, in a simple manner and in a compact form, which can also be studied and completed.

Besides the thermodynamic conditions, described by Pourbaix diagrams, kinetic factors are very important as well. During the corrosion on a metal surface, two or more electrochemical reactions occur simultaneously. The anodic reaction is the dissolution of metal and the cathodic reaction is a reduction of some oxidation species, mostly the oxygen. In the acidic environment, the reaction reduction of hydrogen ions takes place at the same time. During the electrochemical corrosion on the metal surface, corrosion potential (mixed potential) is established when the rates of the anodic and cathodic processes are equal. The value of corrosion potential depends on the nature of the metal, its surface state, composition and concentration of electrolytes, temperature, etc. [4,18]. The anodic current, or the current dissolution of metals, is called the corrosion current I_{corr} , and it could be taken as a measure of the corrosion rate. Faraday's law connects the mass of dissolved metal to a value of the corrosion current [4,19].

In general (uniform) corrosion, anodic and cathodic reactions take place on the same surface, so that the corrosion rate is expressed as the ratio the corrosion current and the surface, $j_{\text{corr}} = I_{\text{corr}}/A$, so-called by corrosion current density. In case of the localized forms of corrosion, anodic and cathodic currents must be equal as well, but the anodic and cathodic surface area can be very different, so that metal dissolution in some places is much more intense.

Corrosion of iron artefacts under soil

The corrosion rate of iron is significantly higher than the corrosion rate of other ancient metals in a numerous burial environments [3]. The degree of preservation of weapon artefacts and military equipment made of iron depends on the underground environment. In aggressive environments, artefacts can be mineralized to a hard lump of the corrosion products, with little or no residual metals. On the other hand, the artefacts buried under anaerobic conditions can survive, well preserved, thousands of years if the activity of

bacteria that reduce sulphate is aggravated [2,3,20-23]. Soils are complex mixtures of moisture, organic matter and rocks particles formed over the centuries. The composition and corrosion activity of soil are greatly changed by human activities such as industrialization, modern agriculture and changed use of soil. The surface layers of soil accumulate large quantities of industrial wastes, anti-icing salt for streets, chemicals used to destroy weeds as well as atmospheric pollution products. [3].

In soil environments with a possible access of oxygen, the iron corrosion products are iron (III) compounds, red-brown colour, mainly goethite, $\alpha\text{-FeOOH}$, lepidocrocite, $\gamma\text{-FeOOH}$ and magnetite, Fe_3O_4 , which temporally may also transform into a magnetic maghemite, $\gamma\text{-Fe}_2\text{O}_3$ [22]. The peaks of those two oxides in XRD diagrams match, and it is usually considered that it is related to the magnetite, Fe_3O_4 [4,25,26]. Hematite, $\alpha\text{-Fe}_2\text{O}_3$, the red iron (III) oxide, is not usually formed as a corrosion product of underground conditions, but it can be sometimes identified on the parts of military equipment made of iron. Since hematite is formed when goethite is exposed to elevated temperatures; its presence is usually associated with the fact that the artefact was subjected to thermal treatment before being buried [3,4,22,23].

During corrosion of iron artefacts buried in moist, aerated soil, layers of massive corrosion products gradually form on their surface, with a characteristic colour, cemented with soil and sand particles [2,3,27,28]. Corrosion products are usually layered with the iron compounds of a lower oxidation state, next to the metal surface, and the layers of iron compounds with a higher oxidation state in the outer layer. In the outer layer of corrosion products, iron oxy-hydroxides, goethite and lepidocrocite can be identified [2,3,23,25,29,30]. The formed layers of the corrosion products can significantly reduce the corrosion rate of iron in relation to the initial corrosion rate, immediately after the burial of the artefact. Magnetite is the most common iron oxide identified on the archaeological iron and is usually located next to the metal surface [3]. Reguer et al. [28] showed that the layer of corrosion products consists of two parts. The compact part is on the metal surface and consists of various iron oxy-hydroxides and magnetite particles. Magnetite particles are usually not in the continuous layer and are not in contact with the metal surface. The outer layer is less compact and it is mixed with fine particles of soil and sand from the surrounding environment. Corrosion products contain a significant amount of amorphous materials, such as amorphous oxy-hydroxide feroxyhite [1,31-35], $\delta\text{-FeOOH}$ discovered by Misawa [29,30], and in his honour it is sometimes called misavit [25,26].

The relative ratio of compounds in the layer of corrosion products is very important, because their protective ability depends on this relationship. Lepidocrocite is a semiconductor compound, active electrochemically and considered not to have protective properties. Goethite is a thermodynamically stable compound and it shows good protective properties, especially if it is in the form of fine particles. Magnetite is a good electrical conductor; it is noticed that it has protective properties due to its thermodynamic stability [36]. Some authors have the opposite opinion [37]; since magnetite is conductive; it allows the flow of cathodic reaction oxygen reduction and therefore accelerates the corrosion processes. Several formulas were proposed for determining the protective ability index of layers corrosion products. Hoerle et al. [36]

have proposed the mass ratio α -FeOOH/ γ -FeOOH, Kamimura et al. [37] α -FeOOH/(γ -FeOOH + β -FeOOH + Fe_3O_4), while Dillmann et al. [31] have proposed the relationship $(\alpha\text{-FeOOH} + \text{Fe}_3\text{O}_4)/(\gamma\text{-FeOOH} + \beta\text{-FeOOH})$. The most general formula, according to the authors of this review paper, is proposed by Kamimura et al. [37]. If the index is more than 1, in case of special steels resistant to atmospheric corrosion (weathering steels), the formed corrosion products have good protective properties [37].

Table 1 shows the characteristics of some corrosion products identified on weapons and military equipment parts made of iron.

Table 1. Some corrosion products identified on weapons and military equipment parts made of iron [3,4].

Chemical name	Mineral name	Chemical formula	Color
Iron(II,III) oxide	Magnetite	Fe_3O_4	Black
Iron(III) oxide	Hematite	$\alpha\text{-Fe}_2\text{O}_3$	Red or black
Iron oxy-hydroxide	Goethite	$\alpha\text{-FeOOH}$	Yellow-brown
Iron oxy-hydroxide	Akaganeite	$\beta\text{-FeOOH}$	Red-brown
Iron oxy-hydroxide	Lepidocrocite	$\gamma\text{-FeOOH}$	Orange
Iron carbonate	Siderite	FeCO_3	Yellow-brown
Iron(II) chloride	-	FeCl_2	White
Iron(III) chloride	-	FeCl_3	Green
Iron phosphate octahydrate	Vivianite	$\text{Fe}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$	Dark blue (or white)
Iron phosphate dihydrate	Strengite	$\text{FePO}_4 \cdot 2\text{H}_2\text{O}$	Pink
Iron sulphide	Pyrrhotite	Fe_{1-x}S ($x=0-0.2$)	Yellow-brown
Iron sulphide	Mackinawite	Fe_{1-x}S ($x=0.01-0.08$)	Yellow-brown
Iron sulphide	Pyrite	FeS_2	Yellow
Iron sulphide	Greigite	Fe_3S_4	Blue-black
Iron sulphate tetrahydrate	Rozenite	$\text{FeSO}_4 \cdot 4\text{H}_2\text{O}$	Green
Iron sulphate heptahydrate	Melanterite	$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$	Blue-green
Iron hydroxide sulphate dihydrate	Butlerite	$\text{Fe}(\text{OH})\text{SO}_4 \cdot 2\text{H}_2\text{O}$	Orange
Iron potassium hydroxide sulphate	Jarosite	$\text{Fe}_3\text{K}(\text{OH})_6(\text{SO}_4)_2$	Yellow-brown
Iron sodium hydroxide sulphate	Natrojarosite	$\text{Fe}_3\text{Na}(\text{OH})_6(\text{SO}_4)_2$	Yellow-brown

When the carbonates or phosphates are present in the soil as well as more reductive conditions than necessary for the formation of magnetite, protective layers of yellow-brown siderite (FeCO_3) or vivianite ($\text{Fe}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$) can be formed. Although the pure vivianite is white, the colour of artefacts is usually dark-blue, because a certain amount of Fe^{2+} ions oxidized to Fe^{3+} , so that the blue colour comes from the charge transfer between Fe^{2+} and Fe^{3+} [3]. The source of phosphate ions may come from the burial of bones, skeletons of fish, garbage dumps or in recent time of phosphate fertilizers.

Traditional wrought iron, opposite to modern low strength steel is a fairly pure iron containing inclusions of glassy slag from iron silicates and has a characteristic fibrous structure resulting from stretching of the slag during the process of forging. As a certain amount of iron, dissolved from the surrounding wrought iron, slag inclusions become uncovered surface, which takes the characteristic of a fibrous structure. Finally, the whole iron in the artefact of wrought iron is dissolved, leaving cavities in the limestone-mould that could often be used to determine the original shape of the object [3]. Fig. 2 shows several underground artefacts taken out from different places in Serbia that were used, as weapons, in different

historical periods. The artefacts made of cast iron (iron alloy with about 2-4% C in the form of cementite or graphite) come to dissolution of the iron and cementite, in the end, leaving a matrix of graphite. This corrosion process is known as graphite corrosion and is sometimes called graphitization in the older literature. The original form of the object (i.e. cast iron cannon balls and cannon) is preserved by the graphite matrix, which is usually filled with corrosive products of iron [3].

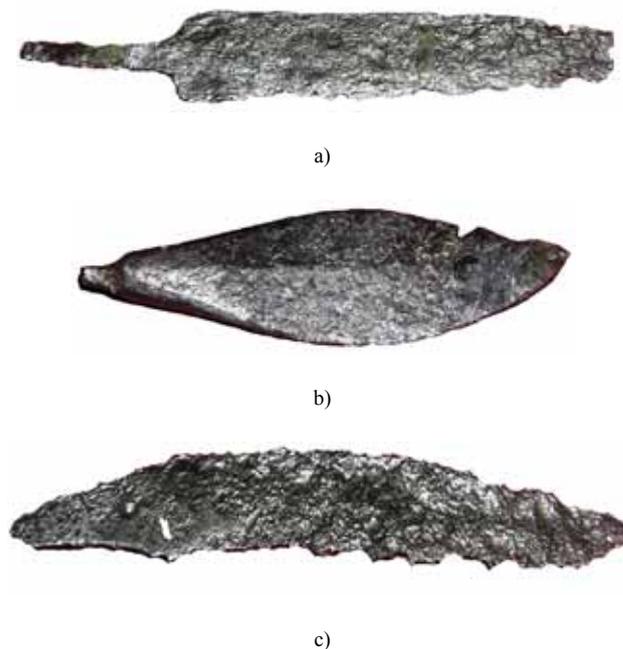
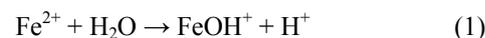


Figure 2. Artefacts excavated from different places in Serbia (Miroč, Mihail abyss) and once used as weapons: a) a knife, b) an arrow head c) a blade of cast iron [4].

Iron (II) sulphides, of black or gold colour, are formed on buried artefacts under anaerobic conditions where sulphate-reducing bacteria are active. Yellow-brown mackinawite (Fe_{1-x}S), blue-black greigite (Fe_3S_4) and yellow pyrite (FeS_2) were identified in the artefacts excavated from five different places in England [3]. Mackinawite, initially formed on the buried iron artefacts in the presence of sulphate-reducing bacteria, can be transformed into greigite, pyrrhotite or pyrite by increasing the oxidative capacity of the local environment. Some iron sulphides (pyrite, pyrrhotite) have a metallic glow and a yellow brown colour that looks like gold (pyrite is known as fool's gold), and objects made of iron (or other materials) covered with iron sulphide, which looks like gold, are called pseudo-gilding [3].

Archaeological iron, exposed to moisture and oxygen in burial conditions, is subject to corrosion processes that are electrochemical by their nature. On the surface, there is the accumulation of iron Fe^{2+} ions, which leads to hydrolysis in accordance with the following equation:



In solutions containing only the Fe^{2+} oxidation state, the dominant ionic species are hydrated Fe^{2+} under pH9; FeOH^+ at pH9-10 and $\text{Fe}(\text{OH})^{3-}$ at pH higher than 10. In the presence of oxygen, Fe^{2+} ions could oxidize to Fe^{3+} ions, which lead to hydrolysis as well. In environments that contain only Fe^{3+} ions, the dominant ionic species are hydrated Fe^{3+} at pH less than 2; FeOH^{2+} at pH2 to 3.5, $\text{Fe}(\text{OH})^{2+}$ at pH3.5 to 8.5 and $\text{Fe}(\text{OH})^{4-}$ at pH higher than

8.5 [22].

Fe(OH)₂ is deposited as a protective film at pH higher than 6 and has minimum solubility at pH 11. The Fe(OH)₂ film is easily oxidized under the effect of dissolved oxygen and forms intermediate Fe (II,III) compounds (magnetite and green rust). Magnetite is an electrically conductive compound and it is a common corrosion product identified on archaeological iron artefacts. Green rust may be formed in the presence of chloride, carbonate or sulphate ions. It has a clearly defined layered structure of positively charged iron hydroxide and negatively charged anions. Green rust easily oxidizes to iron oxy-hydroxide (FeOOH) when it is exposed to air so that it is rarely identified in the corrosive products [29,30].

Iron (II) hydroxide can oxidize to iron (III) hydroxide or iron oxy-hydroxide (FeOOH). Freshly formed iron (III) hydroxide is amorphous but over time it is transformed into a crystalline form of iron oxy-hydroxide. However, the first formed lepidocrocite γ -FeOOH, can be transformed into goethite α -FeOOH, which is thermodynamically more stable. FeOOH compounds are an order of magnitude less soluble than Fe(OH)₂. Akagaenite β -FeOOH is formed in the presence of chloride ions, but it is not observed as a corrosion product of archaeological iron artefacts during a period in soil [22]. For some time Fe (III) oxy-chloride, FeOCl, was considered as the main corrosion product containing chloride ions on archaeological iron [1].

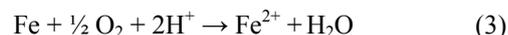
As noted, during the corrosion of archaeological iron, the formed Fe²⁺ ions on the border of the remaining metal and the layers of the existing corrosion products are subject to hydrolysis. Electrical neutrality is achieved by the diffusion of negative ions from the surrounding environment in a layer of corrosion products, all in order to balance the charge with the formed Fe²⁺ and H⁺ ions. Chloride ions tend to concentrate on that border in particular. The extent, to which chloride ions are adsorbed, depends on the pH value. The maximum adsorption of chloride ions is achieved at low pH values, because of the excess positive charge formed on the surface of iron, due to the presence of H⁺ ions. The final result of the corrosion of iron artefacts during the time in soil is that cracks, pores and open spaces in the layer of corrosion products, or below the corrosion product layer, fill with acid solution of iron (II) chloride with chloride ions concentrated on the metal surface [38,39].

Corrosion iron artefacts after excavation

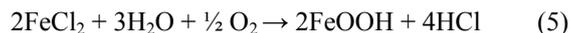
According to the model of the Turgoose et al. [38,39] the pores of corrosive products of the freshly excavated military artefacts are filled with acidic FeCl₂ solution, i.e. solution containing ions Fe²⁺, FeOH⁺, H⁺ and due to electrical balance also of chloride anions. If an archaeological artefact after excavation is left to dry, the acidic FeCl₂ solution will become more concentrated, leading to a rupture of corrosion products and facilitating access of oxygen to the base metal. The facilitated access of oxygen causes rapid iron oxidation and Fe²⁺ ions are formed in the solution:



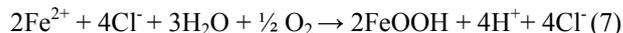
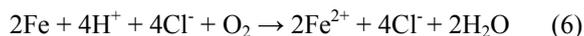
As it can be seen from reaction (2), the deposition of iron oxy-hydroxide (FeOOH) occurs with hydrogen ions formation. It is important to notice that the presence of an acid solution allows further corrosion of the remaining iron in accordance with reaction (3):



In addition to these reactions, the presence of chloride and sulphate anions in corrosion products has an important effect as well. As it was mentioned before, due to charge balance to the present positive ions close to the surface of iron, chloride ions accumulate in the corrosion product layer due to their high mobility and their dominance in the surrounding environment. Sometimes the accumulation of sulphate ions occurs as well if they are present in the surrounding environment. Askey et al. [40] have proposed a corrosion cycle that shows how chloride ions promote the corrosion of iron:



Askey called this cycle "acid regeneration cycle" because the hydrochloric acid consumed in the first reaction regenerates in the second one. This cycle shows that chloride ions play a direct role in the process of corrosion. Turgoose et al. [38,39] on the other hand, believe that chloride ions play an indirect role in the process of corrosion, increasing the solution conductivity. In addition, due to its high hygroscopic ability, the presence of FeCl₂ provides moisture necessary for the evaluation of electrochemical reactions. Their point of view can be easily seen, as Selwyn et al. [2] demonstrated, when the previous two reactions are displayed as a complete dissociate:



Chloride ions are not involved in the mechanism of electrochemical reactions; they are present only to equalize the charge in reactions. It is known that these ions accelerate the corrosion of iron, because of their difficulty to establish and maintain a passive film on the iron surface and because of their ability to form soluble compounds to be incorporated into a passive film due to their high charge density [2]. Whether chloride ions directly or indirectly participate in the process of corrosion of weapons and military equipment made of iron after their excavation is less significant than the fact that these ions form a soluble iron salt that allows the progress of a corrosion cycle in accordance with the above reactions. If FeCl₂ were an insoluble salt, it would be a precipitate and the corrosive cycle would break.

In addition to chloride ions, it is well known that sulphate ions accelerate iron corrosion too if present in the corrosion products. Graedel et al. [41] proposed a similar corrosion cycle, but the regeneration of the sulphuric acid and accelerate the corrosion process. Instead of forming FeCl₂ in the reaction with sulphuric acid, iron initially forms FeSO₄, a soluble salt (analogous to reaction 4). The oxidation of Fe²⁺ ions to the FeOOH, releasing H₂SO₄ (similar to the release of HCl), then leads to further corrosion. In contrast to chloride ions, sulphate ions are gradually separated from the corrosion cycle since they form insoluble iron (III) hydroxyl sulphates [2,41].

The oxidation of the Fe²⁺ ions in the solution (equations 5 and 7) leads to the deposition of several types of oxy-hydroxides, such as goethite, α -FeOOH, lepidocrocite, γ -FeOOH and akagaenite, β -FeOOH. The third form of oxy-hydroxide, akagaenite, is often detected on untreated archaeological artefacts exposed to air. Although it is not

evident from its chemical formula, its structure is stabilized by Cl⁻ ions. The formula of akagaenite, stabilized by chloride ions, often found in the literature, is FeO_{0.833}(OH)_{1.167}Cl_{0.167} [3,22,27,42]. The structure of akagaenite is shown in Fig. 3.

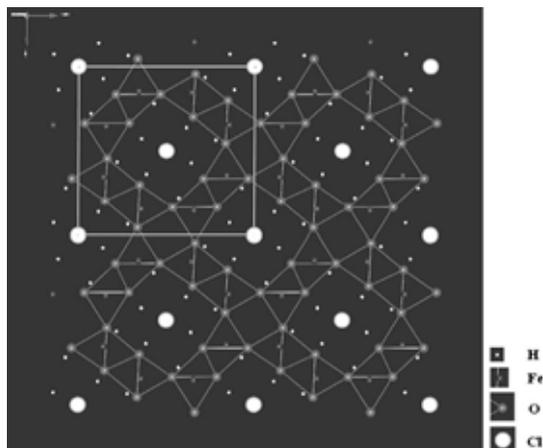


Figure 3. Structure of akagaenite, FeO_{0.833}(OH)_{1.167}Cl_{0.167} [42].

As indicated above, except akagaenite, β -FeOOH, other types of oxy-hydroxides (α -FeOOH and γ -FeOOH) can be formed, but in a lesser degree, according to equations 5 and 7, if the content of chloride ions is low enough. The presence of akagaenite in corrosion products is a sign of active corrosion of iron, under a layer of corrosion products. A higher molar volume of the precipitated types of iron oxy-hydroxides under (or inside) a layer of corrosion products causes stress, occurrence of cracks and other defects in the layer, which facilitates the access to oxygen and moisture and faster progress of corrosion processes. The volume of 1 mole oxy-hydroxide is approximately three times higher than the volume of one mole of iron, and is 20.9 cm³ for α -FeOOH, 21.7 cm³ for γ -FeOOH and 26.7 cm³ for β -FeOOH. The volume of one mole of Fe₃O₄ is 14.9 cm³ [22]. These data impose the conclusion that it is necessary to perform, as soon as possible, desalination of the historical iron artefacts (e.g. in a solution of NaOH) in order to remove chloride (and sulphate) ions.

Another symptom of corrosion problems on excavated artefacts is the formation of either wet droplets of acidic liquid (known as the formation of tears), or dry, hollow and red spherical membranes on the object surface, visible under the microscope at low magnifications. The formation of tears is associated with the hygroscopic nature of iron chloride salts. When humidity is relatively high and salt absorbs water, wet orange paints dissolve and form liquid droplets. Iron oxy-hydroxides (FeOOH) are deposited along the edges of drops (because iron (II) ions in the solution are subject to oxidation and hydrolysis) and form a frame for a spherical shell [2,3,22,23].

Visually, by the appearance of an artefact covered with a layer of corrosion products, it is not possible to estimate how much of iron core is left and whether there is a presence of cracks and other defects in the material. Watkinson et al. [21] suggested one of such determination procedures, based on measuring the ratio of the artefact mass (determined on the analytical balance) and its volume (based on the amount of fluid displaced after immersion in an appropriate solution). The ratios lower than 2.9 indicate that the artefact is fully mineralized. Another method, proposed by Thickett et al. [43] is based on the measuring

of the amount of oxygen consumed along time. The consumption of oxygen is related to the development of the corrosion process under a layer of corrosion products. The majority of authors [20,43,44] consider the most reliable method to be the radiographic method for estimating the amount of iron core and the types and forms of damage. Multiple radiographic gives the most reliable results [43].

Conclusions

This paper deals with the corrosion of archaeological iron weapons and military equipment as well as the thermodynamic and kinetic conditions in evaluating corrosion processes on buried and excavated artefacts. The mechanisms of the corrosion processes, the hydrolysis of the corrosion products occurred on iron, acidification and the accumulation of positive ions on the metal surface under a layer of corrosion products and the diffusion of anions, mainly chloride and sulphate ones from the surrounding environment, were also considered.

A large number of different corrosion products formed on the surface of iron weapons and military equipment have been described, with their chemical compositions, formulas, structures, colors and other characteristics. Corrosion products formed on the iron surface have been considered in the oxidation conditions as well as in the reduction conditions in the presence of sulphate-reducing bacteria. The characteristics of akagaenite (β -FeOOH) are described in detail, the formation of which is a sign of active corrosion of archaeological iron objects after excavation.

The conditions that often cause accelerated corrosion of archaeological iron artefacts after excavations were also described. A particular attention was given to the conditions when corrosion takes place in the cycle which leads to the regeneration of the hydrochloric acid, in the case of the presence of chloride ions in the layer of corrosion products (Askey cycle). A similar cycle of regeneration of the sulphuric acid (Graedel cycle) is described with fewer details, since it occurs less frequently in practice.

A special attention was paid to the description of the symptoms of active corrosion of archaeological iron weapons and military equipment after excavation, such as the formation of akagaenite and the formation of tears on the surface of artefacts.

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] GILBERG,M., SEELEY,N.J.: *The Identity of Compounds Containing Chloride Ions in Marine Iron Corrosion Products: A Critical Review*, Studies in Conservation, 26 (1981) pp. 50-56.
- [2] SELWYN,L., SIROIS,P., ARGYROPOULOS,V.: *The Corrosion of Excavated Archaeological Iron with Details on Weeping and Akaganéite*, Studies in Conservation, 44 (1999) pp. 217-232.
- [3] SELWYN,L.: *Corrosion of Metal Artefacts in Buried Environments*, ASM Handbook, Volume 13C: Corrosion: Environments and Industries, Ohio, 2006, pp. 306-322. ISBN-13:978-0-87170-709-3
- [4] POLIĆ-RADOVANOVIĆ,S., RISTIĆ,S., JEGDIĆ,B., NIKOLIĆ,Z.: *Metodološki i tehnički aspekti primene novih tehnika u zaštiti kulturne baštine*, Centralni institute za konzervaciju u Beogradu, Institut Goša, Beograd, str. 141-230., ISBN 978-86-86917-12-6
- [5] DRAŽIĆ,D., JEGDIĆ,B.: *Corrosion and Stress Corrosion*

- Cracking*, IFMASS 8, From Fracture Mechanics to Structural Integrity Assessment, Ed. S. Sedmak and Z. Radakovic, Belgrade, 2004., pp. 255-276.
- [6] DRAŽIĆ,D., JEGDIĆ,B.: *Naponska korozija, Integritet i vek konstrukcija*, 2007, Vol. 7, No. 2, str. 89-95.
- [7] JEGDIĆ,B., RADENKOVIĆ,G.: *Fracture Mechanics Approach to Stress Corrosion Cracking (SCC)*, 3rd International Conference RaDMI 2003, Herceg Novi, 19-23 September 2003, str. 743-749.
- [8] MARKOVIĆ,R., FRIEDRICH,B., STEVANOVIĆ,J., JEGDIĆ,B.: *Electrochemical Behaviour of Copper with non-standard Impurities Content*, Journal of Engineering annals of Faculty of Engineering Hunedoara, VII, (2009) pp. 47-50.
- [9] JEGDIĆ,B., DRAŽIĆ,D., POPIĆ,J.: *Open circuit potentials of metallic chromium and 304 stainless steel in aqueous sulphuric acid solution and the influence of chloride ions on them*, Corrosion Science, 50 (2008) pp. 1235-1244.
- [10] JEGDIĆ,B., ALIL,A., MILUTINOVIĆ,Z., ODANOVIĆ,Z., GLIGORIJEVIĆ,B., KATAVIĆ,B.: *Primena elektrohemijskih metoda za ispitivanje interkristalne korozije zavarenog spoja austenitnog nerđajućeg čelika 19Cr-9Ni*, Hemijska Industrija, 2011, Vol. 65, No. 2, str. 179-186.
- [11] JEGDIĆ,B., DRAŽIĆ,D., POPIĆ,J., RADMILOVIĆ,V.: *Structural effect of metallic chromium on the its electrochemical behavior*, Journal of the Serbian Chemical Society, 72 (2007) pp. 563-578.
- [12] BOBIĆ,B., JEGDIĆ,B.: *Korozija zavarenih spojeva*, Deo I: Vidovi korozije zavarenih spojeva, Zavarivanje i zavarene konstrukcije, 2005, Vol. 50, No. 1, str. 33-39.
- [13] BOBIĆ,B., JEGDIĆ,B.: *Korozija zavarenih spojeva*, Deo II: Ugljenični i niskolegirani čelici, Zavarivanje i zavarene konstrukcije, 2005, Vol. 50, No. 2, str. 111-115.
- [14] BOBIĆ,B., JEGDIĆ,B.: *Pitting Corrosion of stainless Steels in Chloride Solutions*, Scientific Technical Review, ISSN 1820-0206, 2005, Vol. LV, No. 3-4, pp. 3-8.
- [15] JEGDIĆ,B.: *Behavior of Stress Corrosion Crack in a High-Strength Aluminum Alloys Structure*, Scientific Technical Review, ISSN 1820-0206, 2003, Vol. LIII, No. 4, pp. 19-24.
- [16] STOJANOVIĆ,M., BOBIĆ,B., JEGDIĆ,B.: *Opšta i kontaktna korozija Zn-Al legura u uslovima neutralne slane magle*, Zaštitna materijala, 2001, No. 2, str. 1-5.
- [17] DAVIS,J.: *Corrosion, understanding the basic*, ASM, Ohio, 2000. pp. 49-99. ISBN: 0-87170-641-5
- [18] ŽUK,N.: *Kurs teorije korozije i zaštite metalov*, Moskva, Metallurgija, 1976. pp. 149-180. UDK 620.193.197 (075.8)
- [19] LANDOLT,D.: *Corrosion and Surface Chemistry of Metals*, Lausanne, Switzerland, 2007, pp.119-179, ISBN 978-2-940222-11-7
- [20] WALKER,R.: *Instability of Iron Sulfides on Recently Excavated Artefacts*, Studies in Conservation, 46 (2001) pp. 141-152.
- [21] WATKINSON,D.: *Degree of Mineralization: Its Significance for the Stability and Treatment of Excavated Ironwork*, Studies in Conservation, 28 (1983) pp. 85-90.
- [22] 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.
- [23] SELWYN,L.: *Metals and Corrosion: A Handbook for the Conservation Professional*, Canadian Conservation Institute, 2004. pp. 89-115. ISBN 0-662-37984-5
- [24] TAMURA,H.: *The role of rusts in corrosion and corrosion protection of iron and steel*, Corrosion Science, 50 (2008) pp.1872-1883.
- [25] BALASUBRAMANIAM,R.: *On the corrosion resistance of the Delhi iron pillar*, Corrosion Science, 42 (2000) pp. 2103-2129.
- [26] BALASUBRAMANIAM,R., RAMESH,K.,A.: *Characterization of Delhi iron pillar rust by X-ray diffraction*, Fourier transform infrared spectroscopy and Mossbauer spectroscopy, Corrosion Science, 42 (2000) pp. 2085-2101.
- [27] STAHL,K., NIELSEN,K., JIANG,J., LEBECH,B., HANSON,J., NORBY,P., LANSCHOT,J.: *On the akaganeite crystal structure, phase transformations and possible role in post-excavational corrosion of iron artefacts*, Corrosion Science, 45 (2003) pp. 2563-2575.
- [28] RÉGUER,S., DILLMANN,P., MIRAMBET,F.: *Buried iron archaeological artefacts: Corrosion mechanisms related to the presence of Cl-containing phases*, Corrosion Science, 49 (2007) pp. 2726-2744.
- [29] 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) pp. 35-48.
- [30] MISAWA,T., KYUNO,T., SUETAKA,W. AND SHIMODAIRA,S.: *The Mechanism of Atmospheric Rusting and the Protective Amorphous Rust on Low Alloy Steel*, Corrosion Science, 14 (1974) pp. 279-289.
- [31] DILLMANN,PH., MAZAUDIER,F., HOERLE,S.: *Advances in understanding atmospheric corrosion of iron. I. Rust characterisation of ancient ferrous artefacts exposed to indoor atmospheric corrosion*, Corrosion Science, 46 (2004) pp. 1401-1429.
- [32] KERGOURLAY,F., NEFF,D., GUILMINOT,E., REMAZEILLES,C., REGUER,S., REFAIT,P., MIRAMBET,F., FOY,E., DILLMANN,P.: *Effect of Dechlorination in NaOH of Iron Archaeological Artefacts Immersed in Sea Water*, Archaeological Iron Conservation Colloquium 2010, G. Eggert and B. Schmutzler (Eds.), Session 4, Stuttgart, 24-26 June 2010.
- [33] LABBE,J., LEDION,J., HUI,F.: *Infrared spectrometry for solid phase analysis: Corrosion rusts*, Corrosion Science, 50 (2008) pp. 1228-1234.
- [34] 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) pp. 695-710.
- [35] ANTONY,H., LEGRAND,L., MARECHAL,L., PERRIN,S., DILLMANN,PH., CHAUSSE,A.: *Study of lepidocrocite γ -FeOOH electrochemical reduction in neutral and slightly alkaline solutions at 25°C*, Electrochimica Acta, 51 (2005) pp. 745-753.
- [36] HOERLE,S., MAZAUDIER,F., DILLMANN,PH., SANTARINI,G.: *Advances in understanding atmospheric corrosion of iron. II. Mechanistic modelling of wet-dry cycles*, Corrosion Science, 46 (2004) pp. 1431-1465.
- [37] 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) pp. 2799-2812.
- [38] TURGOOSE,S.: *Post-Excavation Changes in Iron Antiquities*, Studies in Conservation, 27 (1982) pp. 97-101.
- [39] TURGOOSE,S.: *The Corrosion of Archaeological Iron during Burial and Treatment*, Studies in Conservation, 30 (1985) pp. 13-18.
- [40] ASKEY,A., LYON,S., THOMPSON,G., JOHNSON,J., WOOD,G., COOKE,M., SATE,P.: *The Corrosion of Iron and Zinc by Atmospheric Hydrogen Chloride*, Corrosion Science, 34 (1993) pp. 233-247.
- [41] GRAEDEL,T., FRANKENTHAL,R.: *Corrosion mechanisms for iron and low alloy steels exposed to the atmosphere*, Journal of the Electrochemical Society, 137 (1990) pp. 2385-2394.
- [42] REGUER,S., MIRAMBET,F., DOORYHEE,E., HODEAU,J., 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) pp. 2795-2802.
- [43] 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.
- [44] WATKINSON,D., LEWIS,M.: *Desiccated Storage of Chloride-Contaminated Archaeological Iron Objects*, Studies in Conservation, 50 (2005) pp. 241-252.

Korozioni procesi, priroda i sastav produkata korozije na naoružanje od legura gvožđa

U ovom radu razmotreni su korozioni procesi koji se odvijaju na različitim vrstama naoružanja i vojne opreme izrađenim od gvožđa, tokom perioda provedenog pod zemljom i nakon iskopavanja. Posebna pažnja je posvećena opisu prirode i sastava korozionih produkata prisutnih na površini eksponata od gvožđa, koji su obezbedili njihovo očuvanje hiljadama godina. Korozioni procesi, koji se odvijaju nakon iskopavanja mogu da izazovu ubrzano propadanje predmeta u relativno blagim uslovima. Ti procesi predstavljaju posebnu opasnost za naoružanje i vojnu opremu izradenu od gvožđa i njima je posvećena velika pažnja u ovom radu.

Кljučне речи: naoružanje, NVO (naoružanje i vojna oprema), gvožđe, korozija, korozioni produkti.

Коррозионные процессы, характер и состав продуктов коррозии и влияние на вооружение из сплав железа

В настоящей работе рассматриваны коррозионные процессы, которые происходят на различных видах вооружения и военного оборудования из железа, в течение периода проведенного в подполье и после погребения раскопки. Особое внимание было уделено описанию характера и состава продуктов коррозии на поверхности артефактов из железа, которые обеспечили их защиту и сохранность на протяжении тысяч лет. Коррозионные процессы, которые происходят после раскопок могут привести к быстрому ухудшению объектов в сравнительно мягких условиях. Эти процессы представляют собой особую опасность для вооружения и военного оборудования из железа и они получили существенное внимание в данной работе.

Ключевые слова: Вооружение, НПО, (вооружение и военное оборудование), железо, коррозия, продукты коррозии.

Les processus de corrosion, la nature et la composition des produits de corrosion chez l'armement en alliage de fer

Dans ce papier on a considéré les processus de corrosion qui ont lieu sur les différentes sortes des armes et de l'équipement militaire fabriqués en fer, pendant qu'ils sont enterrés ou après leur excavation. L'attention particulière est prêtée à la description de la nature et de la composition des produits de corrosion présents à la surface des objets en fer qui ont assuré leur conservation pendant des milliers d'années. Les processus de corrosion produits après l'excavation peuvent causer une détérioration rapide dans les conditions relativement éléments. Ces processus présentent un particulier danger pour l'armement et l'équipement militaires fabriqués en fer et c'est pourquoi on leur a prêtée une grande attention dans ce travail.

Mots clés: armement, AEM (armement et équipement militaire), fer, corrosion, produits de corrosion.