PHYSICS AND CHEMISTRY
OF SOLID STATE
V. 23, No. 2 (2022) pp. 195-203

Section: Chemistry

DOI: 10.15330/pcss.23.2.195-203

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**ФІЗИКА І ХІМІЯ ТВЕРДОГО ТІЛА
Т. 23, № 2 (2022) С. 195-203**

Хімічні науки

PACS: 75.50.Bb ISSN 1729-4428

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An overview of Modern Ways of Cleaning from Rust and Preservation of Iron Historical Artefacts

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This overview focused on the recent advances in rust cleaning and conservation of iron-based historical artefacts. Archaeological iron artefacts undergo various forms of corrosion, including soil and atmospheric. In general the main corrosion products are goethite α-FeO(OH), acaganeite β-FeO (OH), lepidocrocite γ-FeO (OH), magnetite Fe_3O_4, siderite $FeCO_3$, vivanite $Fe_3(PO_4)_2 \cdot 8H_2O$, etc. A number factors contribute to the process corrosion, but Cl^- anion embedded in the crystal lattice of acagenite is crucial. It has been considered corrosion product removers from the artefact surface, and found out that all of them should contain inhibitors slowing down the interaction of the artefact iron core with acids. Organic acids, in particular citric, maleic and acetic acids are considered to be non-aggressive and environmental-friendly. After removing corrosion product layer, iron historical heritages are affected by atmospheric corrosion thus stabilizing substances and protective coatings must be applied. The most common protectors are tannin-iron complex compounds, which provide an anti-corrosion coatings and prevent further destruction of artefacts. Preservation of iron-based historical artefacts with synthetic polymer waxes, resins and synthetic polymers is thought to be promising.

Key words: corrosion, artefact, protective coating, inhibitor.

Received 5 September 2021; Accepted 14 March 2022.

Introduction

Metal-based historical artefacts, except gold and platinum products, corrode. As a rule corrosion starts on the metal surface and gradually spreads deeper. The appearance of metal changes: it loses shine, the smooth surface becomes rough and covered with corrosion products. The nature and rate of corrosion depend on the elemental composition of the metal product and its storage conditions. In the soil, where of chlorine ions, water, carboxylic and humic acids are presented, iron artefacts undergo the destruction [1]. In the soil this process is quite fast and then can continue even in a museum. The complexity of this process is due to the variety of compounds that are formed during corrosion. Iron objects are covered with a layer of metal oxides, various salts and other complex compounds. Running of soil corrosion and the variety of corrosion products on the surface of archaeological iron artefacts are affected by the following factors: the dissolved oxygen content in the soil, soil humidity, pH and electrical conductivity, which depends on the composition and concentration of salts presented in the soil [2].

Ukraine is rich in archaeological finds dating back to the Iron Age. After excavation from the soil a large number of artefacts require resuscitation and special treatment for further storage in museum collections. However, experts face the problem of storing artefacts even in special museum conditions. Therefore, the creation of new, more advanced technologies for cleaning and conservation of corroded iron historical artefacts is one of the urgent concerns.

I. Experimental

1.1. Types of corrosion

Corrosion is an oxidation destruction of metals and alloys caused by interaction with the environment.

According to the mechanism of destruction, there are chemical and electrochemical corrosion. Chemical corrosion of metals occurs in the dry gas environment or in solutions of non-electrolytes. This type of corrosion causes the formation of oxide films on the metal surface, which leads to passivation of metal. Electrochemical corrosion related to physical and chemical heterogeneity of a metal or medium and an electrically conductive liquid phase - electrolyte. Since metal surface is always covered with a thin, electrically conductive film of moisture, which contains dissolved salts comming from the environment, and the metal surface is not homogeneous, so metal objects are seriously threatened due to electrochemical corrosion [3]

Depending on environment, there are atmospheric and soil corrosion. Iron artefacts are prone to atmospheric corrosion when exposed to air during storage in the museum. There are dry, dewy and wet atmospheric corrosion. Dry corrosion usually occurs in the complete absence of moisture and leads to the formation of oxide films. Dewy atmospheric corrosion occurs when there is a thin invisible film of moistre on the metal surface. This film is always formed by the condensation of vapour as liquid on metal surface even at low relative humidity. The average relative humidity in museum is up to 60-65%, which also contributes to the metal surface moistering. Huminity, which accelerates corrosion rate is called critical (≈ 70 %). Wet atmospheric corrosion caused by visible water film on metal surface at the humidity of 100%. The most chemically active impurities of atmospheric air are sulfur dioxide, hydrogen sulfide, sodium chloride, ammonia and hydrogen chloride. For instance, chlorine ion content in rainwater, melt-water ang fog can reach 440 mg/l reducing critical humidity to 58% [2].

Soil corrosion causes active destruction of metal. Moisture containing dissolved salts turns a soil into an electrolyte and makes an electrochemical corrosion possible. Basing on salt content in groundwater there are fresh (> 0.1 %), slightly saline (0.1 - 1 %), saline (1 -5 %) solutions and brines (5-40%). Soil pH values vary depending on total mineralization of groundwater and presence of acids, acidic and basic salts [3].

Typically, soil microorganisms are the main reason of biocorrosion. They are present in the soil in large quantities and accelerate corrosion of black metals. The most active are anaerobic sulfur-reducing bacteria, which are common in silty, clay and swamp soils. These microorganisms during their life cycle can oxidize hydrogen sulfide to sulfur and to sulfuric acid, which causes severe corrosion [4].

Marine corrosion is caused by the specific composition of the corrosive environment. The water of the seas and oceans is a well-aerated electrolyte with a pH within 7.2 - 8.6 and a highly conductive because of dissolved salts, mainly chlorides and sulfates of sodium, magnesium, calcium and potassium. In marine environment, metal objects are covered with a layer of plant and animal remains. Silicon-containing compounds, calcium carbonate and organic layers can form a protective coating, but in open areas, in places of wetting, corrosion runs much more faster due to easier access of oxygen to the metal surface [5].

Depending on the duration of corrosion and condition of metal, iron archaeological objects can be classified as follows:

- items, which have a massive iron core; the metal is strong and covered with a thin layer of corrosion products, the shape of the object is not changed;
- the metal core is partially preserved; the object is covered with a thick layer of loose, cracked corrosion products, the shape of the object is distorted;
- items in which the metal core is absent. The whole pure metal is replaced by loose formless iron oxides;
- pieces of completely oxidized object, the shape and size of which cannot be established [6].

The corrosive environment causes the composition of the corrosive products. The mechanisms of destruction of iron artefacts in the soil and in the air differ significantly.

1.1.1. Composition of soil corrosion products

Archaeological iron objects made by ancient technologies have a heterogeneous structure and contain defects in metallurgical production and granular inclusions (Fig. 1).

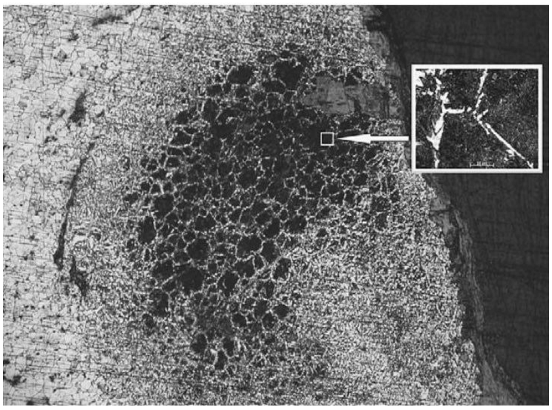

Fig. 1. Heterogeneity of an ancient iron product microstructure [7].

The authors [7] studying the microstructure of ancient iron-based artefacts by a metallographic microscope found that the main phase is ferrite (Fig. 2). The ferrite structure of iron archeological finds is due to low carbon content (0.02 %). The phase distribution in the alloy shows its heterogeneity - the crystallites are randomly distributed.

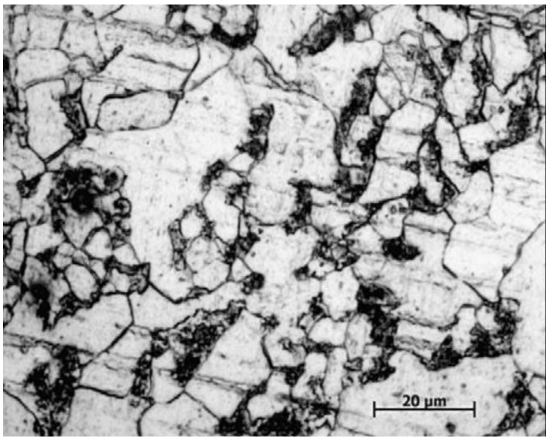

Fig. 2. The structure of the ancient alloy (ferrite phase - light areas) [7].

Definitely, the microstructure of the alloy and the conditions of the soil environment play a crucial role in the composition of corrosion products. Soil corrosion is an electrochemical process. Anodic dissolution of iron takes place on the metal surface (Fig. 1). In aqueous solutions with pH > 4 cathodic processes occur according to scheme 2. At low oxygen concentrations, iron atoms acquire mainly have an oxidation state of +2, and Fe^{+2} cations accumulate on the metal surface in hydrates coordinating six water molecules $[Fe(H_2O)_6]^{2+}$ [8].

$$Fe^0\ (s.) \rightarrow Fe^{2+}\ (p.) + 2e^- \qquad (1)$$

$$O_2\ (g) + 2H_2O + 4e^- \rightarrow 4OH^-. \qquad (2)$$

Water molecules associated around iron ions cause hydrolysis (1.3) and a local decrease in pH affecting the composition of ions formed with Fe^{2+}.

$$Fe^{2+}\ (p.) + H_2O \rightarrow Fe(OH) + (p.) + H + (p.). \qquad (3)$$

In the presence of small amounts of oxygen, some of the Fe^{2+} cations are oxidized to Fe^{3+}. Fe^{3+} cations are hydrated forming $[Fe\ (H_2O)_6]^{3+}$ aqua complex, which in turn can also be hydrolyzed. Table 1 shows the products of hydrolysis of hydrated iron cations.

Table 1

Composition of products of hydrolysis of aquacomplex iron cations at different pH [9].

$[Fe(H_2O)_6]^{2+}$ hydrolysis products		$[Fe(H_2O)_6]^{3+}$ hydrolysis products	
Fe^{2+}	pH	Fe^{3+}	pH
$[Fe(H_2O)_6]^{2+}$	< 9	$[Fe(H_2O)_6]^{3+}$	< 2
$Fe(OH)^+$	9 - 10	$Fe(OH)^{2+}$	2 – 3,5
$Fe(OH)_3^-$ $Fe(OH)_4^{2-}$	> 10	$Fe(OH)_2^+$	3,5 – 8,5
		$Fe(OH)_4^-$	> 8,5

Insoluble iron (II) hydroxide is formed at pH > 6 and is the least soluble at pH = 11. In the presence of carbonate and phosphate ions in the soil, corrosion products contain siderite $FeCO_3$, or vivanite $Fe_3(PO_4)_2 \cdot 8H_2O$. In soils that are rich on organic substances siderite is preferable in corrosion products. As a result of an oxidation of the ion (II) oxide intermediate compounds such as magnetite Fe_3O_4 and iron (III) compounds: hydroxide and oxyhydroxides are formed. Freshly formed $Fe(OH)_3$ has an amorphous structure, but over time it is transformed into crystalline oxyhydroxides, in particular, lepidocrocite γ-FeO (OH), which turns into a more thermodynamically stable goethite α-FeO(OH). In the presence of Cl^- ions. acadenite β-FeO(OH) and chlorine derivatives $Fe_2(OH)_3Cl$ are formed. Iron (III) oxyhydroxide have worse solubility compared to iron (II) hydroxide [10].

To study the structure of the corrosion system, the authors [11] used a special technique. After removal from the soil, the iron artefacts were dried in a vacuum oven to remove residual water and covered with epoxy resin. The sample was cut to obtain a cross section from which a thin film (50 μm) was taken and the structure of the layers was analysed by micro – X-ray diffraction, spectrometry, and electron microscopy. It was found that the corrosion system of iron artefacts has a similar structure and consists of the following layers (Fig. 3):

- metal surface (M), which may contains slag inclusions (SI);
- dense product layer (DPL), which consists of oxides, oxyhydroxides, chlorides and/or carbonates. This phase has a crystalline structure and is denser than the next layer and may also contain slag inclusions;
- transit zone between (DPL) and soil, which contains corrosion products and soil markers, such as quartz grains. This layer is called transformed medium (TM). The surface between the (DPL) and the TM indicates the initial size and shape of the artefact that changed during corrosion;
- soil layer (S), where no corrosion products.

DPL composition varies according to soil composition (Fig. 4).

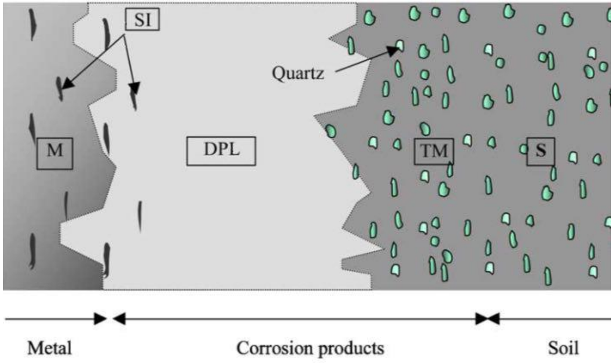

Fig. 3. Schematic description of the corrosion system on an iron artifact buried in soil: M – metal, SI – slag inclusions; DPL – dense product layer; TM – transformed medium; S –soil [11].

1.1.2. Atmospheric corrosion product composition

Pores of corrosion products of just removed wet archaeological artefacts are filled with soil solution, which contains Fe^{2+}, $Fe(OH)^+$, H^+ cations and Cl^- anions. When the archaeological find dries, the chlorides contained in the pores and channels of the corrosion layers crystallize and put pressure on the pore walls in the material, which leads to their cracking and destruction. As a result, access of oxygen to the internal corrosion layers and to the surface of metal is provided. Oxygen oxidizes Fe^{2+} ions and forms an iron oxyhydroxides [13]:

$$4Fe^{2+}(l.) + O_2(g.) + 6H_2O \rightarrow 4FeO(OH)(s) + 8H+(l.) \ (4)$$

Such processes causes the acidity and activates the corrosion of the undamage metal core:

$$Fe^0\ (s) + 1/2O_2\ (g) + 2H^+ \rightarrow Fe(OH)^+\ (l.) + H^+\ (l) \qquad (5)$$

$$2Fe^0(s.) + 4Cl^-(l.) + O_2\ (g.) + 4H^+ \rightarrow \\ \rightarrow 2Fe^{2+}(l.) + 4Cl^-(l.) + H_2O \qquad (6)$$

$$2Fe^{2+}\ (l.) + 1/2O_2\ (l.) + 4Cl^-\ (l.) + 3H_2O \rightarrow \\ \rightarrow 2FeO\ (OH)(s) + 4H^+\ (l.) \qquad (7)$$

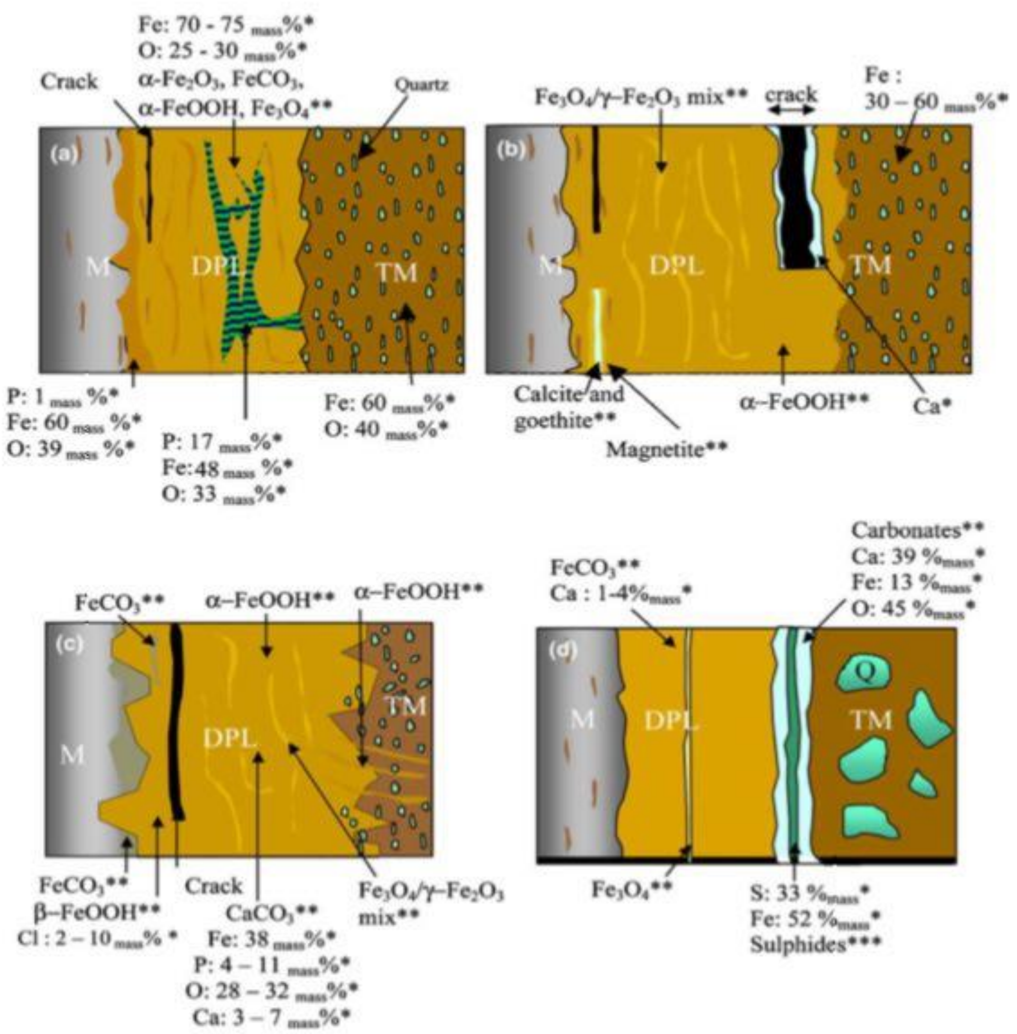

Fig. 4. Schematic representation of SHPK was obtained using X-ray diffraction and Raman spectroscopy [11, 12].

The decisive factor in this corrosion process is that Cl^- ions form soluble salts with Fe^{2+} iron ions. The solubility of these salts leads to the processes according to equations 6 and 7. The formation of iron oxyhydroxides significantly complicates corrosion processes. The increase in their number causes stress in the corrosion layers of the metal, which leads to cracks and other damage, which contribute to further access of oxygen and increase the corrosion process [13, 14].

Laboratory studies of $FeCl_2$ oxidation and hydrolysis have shown that at low concentrations of Cl^- ions a precipitate of goethite α-FeO (OH) and/or lepidocrocite γ-FeO (OH) is formed, but at high concentrations of Cl- ions - acagenite β-FeO(OH). Since acagenite contains Cl^- ions in structure, the authors [15] proposed a representative chemical formula $FeO_{0.833}(OH)_{1.167}Cl_{0.167}$, which reflects the presence of chlorine ions in the crystal structure. Chukanovite $Fe_2(OH)_2CO_3$ can also be formed in the atmosphere of carbon dioxide.

One of the visual symptoms of active corrosion of iron extracted from the soil in the air medium is the formation of wet bubbles of acidic liquid (so-called "sweating" of iron) on the surface of the artefact, or dry, hollow red spherical scales on the surface of the artefact. "Sweating" is due to the hygroscopic nature of iron chlorides, which, depending on the relative humidity, form a number of crystal hydrates with different numbers of water molecules in their structure. For example, at relative humidity below 20 % iron (II) chloride exists as yellow crystals ($FeCl_2{\cdot}2H_2O$), and at humidity between 20 - 55 % - as green crystals ($FeCl_2{\cdot}4H_2O$). At high relative humidity, these salts absorb water, dissolve and form drops of orange liquid around which iron oxyhydroxides are deposited, creating a framework of spherical scales [16].

Since the presence of Cl^- is one of the most important factors causing an atmospheric corrosion of iron artefacts, we should focus on the processes that occur during the transformation of acagenite, which is formed only at the presence of Cl^- ions and contains them in its crystal lattice. Basically, acagenite is formed on archaeological iron after entering the oxygen-containing environment and at high humidity can release Cl^- ions, thus boostering corrosion processes [17].

Although chlorine cannot be washed out of the acagenite structure, some reactions promote the conversion of β-FeO(OH) acagenite to α-FeO(OH) goethite or to Fe_3O_4 magnetite releasing Cl^- ions. At room temperature, water participates in these reactions. In addition, all of the iron oxyhydroxides can react with Fe^{2+}

ions or Fe $(OH)_2$, forming magnetite:

$$Fe(OH)_2 (s.) + 2FeO (OH)_2 (s.) \rightarrow Fe_3O_4 (s.) + H_2O \quad (8)$$

$$Fe^{2+} (l.) + 2FeO(OH)_2 (l.) \rightarrow Fe3O4 (l.) + H + (l.) \quad (9)$$

Laboratory studies have shown that α-FeO(OH), β-FeO(OH) and γ-FeO(OH) react with $Fe(OH)_2$ to form Fe_3O_4 in the following order:

β-FeO(OH)> γ-FeO(OH) >> α-FeO(OH).

Therefore, chlorine trapped in the newly formed acagenite is releasing during convertion to goethite or magnetite [18].

1.2. Ways to clean artifacts

There are four approaches to clean corroded iron artefacts:

- mechanical cleaning to remove the layers of external corrosion;
- dry cleaning to remove corrosion products;
- electrochemical cleaning to reduce the intensity of corrosion and to remove the corrosion products;
- thermal cleaning.

Today, traditional cleaning methods include laser cleaning of metals. Pulses of high-energy laser light are directed to the surface of the metal, causing it to heat up quickly. The decomposition of corrosion products and their release is due to the effect of laser ablation. A combination of several cleaning methods is often used for best results [19].

1.2.1. Mechanical cleaning

It is difficult to remove solid, external corrosion products from an archaeological iron object without the risk of damaging the artefact, which can be quite fragile. One of the common methods is the use of rotary grinders, which are similar in principle to dental drills. Vibrating needle probes (vibrating tools) is also used to clean small objects from corrosion. A more delicate approach is to use air-abrasive machines, where a small stream of compressed air containing abrasive powder directed to the corroded surface [20].

1.2.2. Electrolytic and electrolytic cleaning

Archaeological and museum iron objects, which have a massive metal core, can be cleaned by electrolytic method (electrolysis). The presence of the core is determined by a magnet, X-ray method, mechanical scraping of oxides from a small area of the surface, as well as the specific weight. Depending on the method of application of direct current, there are anodic and cathodic removal of rye. Anode purification of iron is widely used in industry however, during storage in the museum and archaeological objects cathodic purification, which is less aggressive to the iron core should be used. As the electrolyte it is used 5 - 10 % NaOH solution, 0.5 M NaCl solution, dilute Garrison solution ($0.35\ \%\ (NH_4)_2SO_3 + 0.005\ \%\ NaCl$), a mixture of 0.5 M NaCl and 0.05 M $NaCO_3$. As auxiliary electrode, in addition to stainless steel, can be used and sheet iron. Electrolysis is carried out at a voltage of 4 – 6 V and a current of 0.5 - 2 A. The cleaning process lasts from several minutes to several days, depending on the thickness of the corrosion layer. The current flowing through the cathode (iron artefact) facilitates the process of reducing iron from a higher oxidation state to a lower oxidation state. Large items can be cleaned without immersion in an electrolytic bath. A layer of lignin is applied to the objects and moistened with a 10 % alkali solution. Thin sheets of lead are placed on the lignin, which are connected to the anode of a direct current source, and the object is connected to the cathode [21].

The cathode method of removing corrosion products is carried out without the use of an external source of electric current. To do this, you need to make an electrochemical system of cleaned metal artefact, a metal with a more electronegative potential compared to the artifact and the electrolyte. The processes on the metal surface in this method do not differ from the cleaning processes when the current is supplied from an external current source. Electrochemical treatment is a gentler method of purification used to purify archaeological metal in the absence of a metal core. Zinc or aluminum granules, shavings, powder or foil are used as the anode metal. As the electrolyte it is used 5% alkali solution or 10% sulfuric acid solution. Items are placed in iron or heat-resistant glassware, covered with granular metal and filled with electrolyte [22].

After complete removal of rust by electrolytic or electrochemical methods, the surface of the metal object is in an active state, which leads to a rapid formation of fresh red rust. Therefore, the interoperable storage time should be minimized. Reduces the rate of formation of fresh rust by wetting the object with a 5 % solution of sodium nitrite [23].

1.2.3. Dry cleaning

Chemical cleaning method allows to remove all iron corrosion products, so it is used for items with a solid metal core and surface corrosion layers. Before chemical cleaning, the object should be cleaned mechanically, and after cleaning and washing - moistened with a solution of sodium nitrate [24].

One of the safest chemical methods of cleaning is cleaning with compositions containing phosphoric acid, which forms insoluble secondary and tertiary iron phosphates, which are able to protect the surface from further destruction. The authors [25] give the following cleaning composition (% vol.): orthophosphate acid – 46 %, butyl alcohol – 3.7 %, distilled water – 50.3 vol,%, corrosion inhibitor of iron in orthophosphate acid, for example, methyl ethyl ketone – 0.1 %. Alcohol facilitates the penetration of the solution into the rust, its pores and cracks them. For chemical purification also use inhibited sulfuric acid – 10 % solution of sulfuric acid with the addition of 10 g/l of thiourea or benzotriazole. After removing the rust, the object should be thoroughly washed in running water, and acid residues neutralized with 1 % sodium carbonate solution.

Many compositions for chemical cleaning of metal objects from corrosion products are developed on the basis of organic acids. Oxalic, citric trichloroacetic acids slowly dissolve the corrosion products of iron. When treated with a 5 % solution of citric acid as an inhibitor 0.08 % catamine (alkyldimethylbenzylammonium chloride) or 0.04 % captax (2-mercaptobenzotriazole) is used [26]. Citric acid is neutralized with ammonia to pH = 3 - 4 and 0.01 % captax is added as an inhibitor. The authors [27] propose to remove corrosion products with a solution of the following composition: 5 % oxalic acid solution mixed with 20% ammonium citrate solution in a ratio of 1: 1.

Ferrous metal products can be cleaned with 10% solution of ethylenediaminetetraacetic acid, which dissolves not only iron compounds, but also insoluble carbonates, which are often accompany of corrosion products of iron artefacts [28].

To clean large items or to remove local corrosion, pastes, in which any chemically stable material is soaked with a prepared solution for removing rust, are often applied. Cotton wool, filter paper, lignin, sawdust, etc. are used as fillers. Sometimes these pastes need to be applied several times, having previously removed the used one. The authors [29] recommend the following composition of anti-corrosion paste: 100 g of zinc orthophosphate or equivalent amount of zinc oxide and orthophosphoric acid, 2 g of sodium nitrate; 6 g of sodium fluoride and talc or polyvinyl alcohol pre-filled to swell with water.

III. Results and Discussion

3.1. Stabilization of the artefact surface chemical state

After cleaning, by any means, the surface of the object is in an active, reactive state, which can promote the re-formation of corrosion products. The main goal of the stabilization step is to remove chlorine ions and salts, which are usually formed after electrolytic and chemical purification.

The most common, but not the most effective way to remove Cl^- ions is washing object in distilled water with periodic heating - the Organ’s method. The process of washing in water is quite long, for example, massive objects with a thick layer of corrosion products can be washed for several months. To control the process, it is important to periodically perform qualitative determination of chlorides with argentum nitrate [30].

Cathodic reduction in water is a more efficient desalination process compared to soaking in water. Under the action of an electric field, a negatively charged chlorine ions move to a positively charged electrode. Thus, when the object is connected to the negative pole of the current source, and to the auxiliary electrode - to the positive, the desalination process begins. Iron artefacts wrapped in metal mesh and filter paper, which serves as a semipermeable barrier for chlorides, are placed in a container with tap water. A lead plate is used as the anode. Current density is 0.1 A/ dm^2. Distilled water is added to the bath if it evaporates [31].

Alkaline washing with 2 % sodium hydroxide solution reduces the desalination time due to the higher activity of the OH- ion, which allows it to better penetrate into the corrosion products [32].

To stabilize the archaeological iron object, you can use a solution of tannin, the pH of which is lowered to 2 with orthophosphate acid (100 ml of 80% acid solution per 1 liter of solution). This pH value provides a better interaction of iron oxides with tannic acid. First, a wet object is moistened several times with an acidic solution of tannin, and then several times with an acidified solution of tannin [33].

3.2. Protective coatings for the preservation of artefacts

Protective coatings used to preserve historical artefacts must meet certain requirements. In general, they should not lose their protective properties over a long period of time without the need for further processing. At the same time, they should be easy to remove for artefact processing and research. Protective coatings must not alter the original appearance of the sample, its color and also be safe for humans and the environment. In addition, preservatives should act as barriers to oxygen, moisture and air pollutants, including Cl^- ions. They must also have high adhesive properties, even to completely stacked surfaces [34].

Varnishes, resins, waxes, or mixtures thereof are used to preserve archaeological objects. As preservatives, a solution of polyvinyl butyral in a mixture of butyl and ethyl alcohol or toluene and isopropyl alcohol in a ratio of 1: 1, polyethylene wax in xylene, epoxy varnish, etc. [35].

The authors [36] use electrically conductive polymers as protective coatings, which contain various heteroatoms and double bonds. The most studied systems are polyacetylene, polythiophene, polypyrrole, polyaniline, polyparaphenylene and polyphenylvinylene

Self-assembled monolayers are ordered and densely packed layers formed by spontaneous adsorption of organic molecules on metal surfaces, as schematically shown in Fig. 5. The high stability and structure of the layers is due to the chemical bond between the main group (eg, thiol, disulfide, phosphonate, carboxylate) and the solid substrate and Van der Waals interaction between the alkyl chains of the tail group [37].

Since weak carboxylic acids and their derivatives have corrosion inhibitor properties, the authors [38] proposed the possibility of using these acids for the technology of self-assembled monolayers. The ability of monocarboxylic acid anions to bind to oxide-coated metal surfaces is increasingly being used to replace environmentally harmful traditional methods. It is generally accepted that a negatively charged carboxyl group reacts with a positively charged metal surface to form carboxylate bonds [39]. The corrosion resistance of such coatings increases with the length of the alkyl chain and shows good efficiency over very long periods of time. Polarization studies of artefacts coated with a monolayer of carboxylic acids clearly show that the layer is resistant to the presence of Cl^- ions, and the protective effect is quite long. The length of the hydrocarbon chain also has a significant effect on corrosion inhibition. Some authors explain the protective effect of carboxylates with a long carbon chain, the hydrophobic nature of the organic film, which significantly reduces wettability and prevents the ingress of aggressive substances on the metal surface [40].

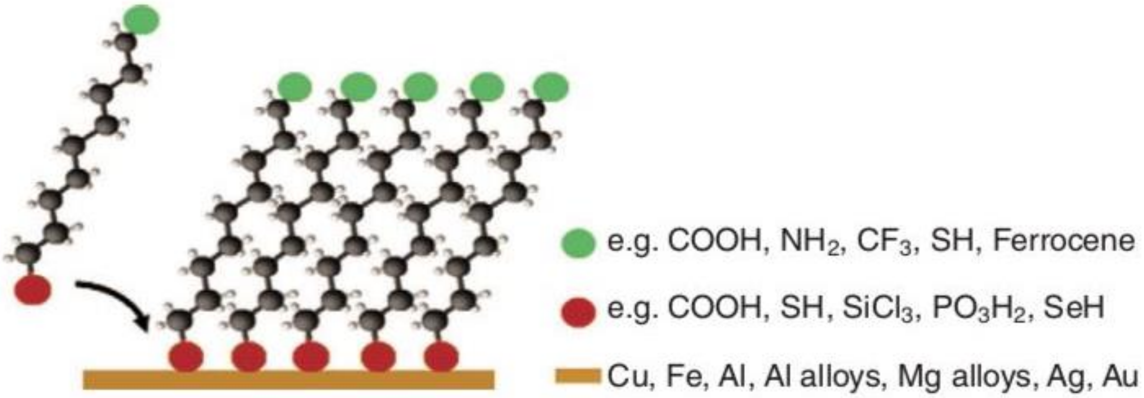

Fig. 5. Schematic description of a self-assembled monolayer on a metal surface [37].

Recently, the latest used technologies combine the technology of coating with conductive polymers and the technology of self-assembled monolayers (Fig. 6).

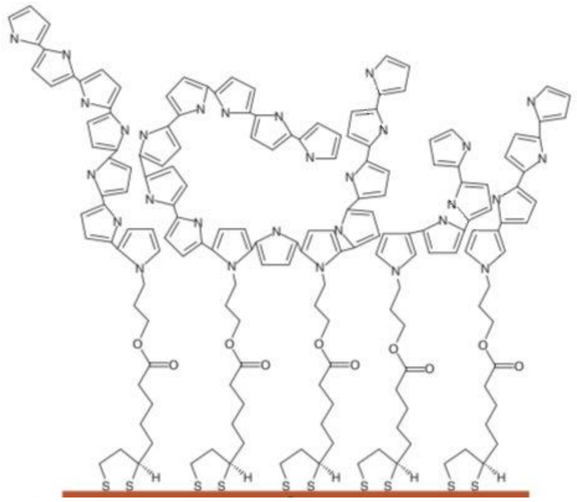

Fig. 6. Schematic description of a polypyrrole film modified with a self-assembled monolayer of pyrrolipoic acid [40].

Conclusions

As a result of the analysis of literature sources it has been established that iron historical artefacts are subject to both soil and atmospheric corrosion. The main products of their corrosion are iron oxyhydroxides. Cl^- anions are embedded in the crystal lattice of acagenite and accelerate corrosion processes. The use of corrosion inhibitors and the creation of protective anti-corrosion coatings based on environmentally friendly materials is an important step in the restoration and preservation of iron historical artefacts.

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Огляд сучасних способів очищення від іржі та консервації залізних історичних пам'яток

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В даній роботі приведений огляд сучасних способів очищення від іржі та консервації залізних історичних пам'яток. З’ясовано, що залізні артефакти піддаються різним видам корозії, зокрема грунтовій та атмосферній. Основними продуктами корозії є гетит α-FeO(OH), акагеніт β-FeO(OH), лепідокрокіт γ-FeO(OH), магнетит Fe_3O_4, сидерит $FeCO_3$, віваніт $Fe_3(PO_4)_2 \cdot 8H_2O$ тощо. Важливу роль в корозійному процесі відіграють аніони Cl^-, які вбудовуються в кристалічну гратку акагеніту та сприяють прискоренню корозії. Розглянуто ряд композицій, які вилучають з поверхні артефактів продукти корозії, проте кожен з них повинен містити інгібітори, що сповільнюють взаємодію залізного ядра артефакту з кислотами. Менш агресивними та екологічно чистими вважають органічні кислоти, зокрема лимонну, малеїнову та оцтову кислоти. Після видалення продуктів корозії залізні пам’ятки стають дуже вразливими до атмосферної корозії, тому потребують негайного нанесення стабілізуючих речовин та захисних покриттів. Найпоширенішим захистом вважають комплексні сполуки таніну із залізом, так звані танати, які створюють антикорозійне покриття та перешкоджають подальшому руйнуванню артефактів. Перспективними для консервації залізних пам'яток є синтетичні полімерні воски, смоли та синтетичні полімери.

Ключові слова: корозія, артефакт, антикорозійне покриття, інгібітор.