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THE EFFICIENCY OF CHEMICAL CLEANING OF DIFFERENT METAL ARTEFACTS FROM FELIX ROMULIANA AND GRADINA ARCHAEOLOGICAL SITES (SERBIA)

ABSTRACT

The research considers the effects of chemical cleaning of metal archaeological artefacts, made of silver, copper, bronze, lead and iron, from the archaeological sites in modern Serbia of Felix Romuliana (Gamzigrad) in the vicinity of Zaječar and Gradina (Jelica) near Čačak. Due to various corrosive products, artefacts were treated with different chemical solutions: citric acid, ethylenediaminetetraacetic acid sodium salts: EDTA-Na₂ and EDTA-Na₃. Corrosion products and surfaces before chemical treatments as well as products on various metal artefacts after chemical treatments were observed by SEM-EDS microanalysis. As expected, the EDTA-Na₂ solution removed all lead corrosion products (carbonates) within a very short period of time, whereas citric acid was most efficient in removing copper corrosion products (malachite, cuprite). As for the EDTA-Na₃ solution, impurities and corrosion products of silver (oxides) and copper (malachite and cuprite) were gradually removed, whereas the solution was partially selective in the silver sample. In iron deposits, corrosion layers such as goethite and magnetite were unevenly removed using the EDTA-Na₂ solution and citric acid. This research provides insights into the efficiency and risk estimation of the chosen chemical treatments, including the transformation of corrosion products, formation of chemical residual substances and the physical effects of the treatments.

KEYWORDS: SEM-EDS ANALYSIS, METAL ARTEFACTS, CORROSION, CONSERVATION.

INTRODUCTION

Archaeological metal artefacts can be exposed to complex physical and chemical decaying processes from the moment of production until the time of excavation or restoration. These physical-chemical processes induce various decaying processes, from the formation of layers of corrosion to a complete transformation (mineralization) into corrosion products (Schweizer 1994; Bertholon 2007). Deposits of both organic and inorganic composition are present on metal artefacts, and the latter, such as carbonates, oxides, hydroxides, phosphates, sulphides, sulphates, silicates, etc., are more difficult to remove (Gerwin and Baumhauer 2000; Kibblewhite et al. 2015). The choice of cleaning method is crucial for the effective preservation of the artefacts, since the cleaning is an irreversible reaction and it is, therefore, the most sensitive part of the conservation treatment (Casaletto et al. 2008). Cleaning methods are selected according to the physical, chemical and structural nature of both the original material of the artefact and the material that should be removed. By applying an appropriate cleaning technique and respecting the relevant ethical codes, i.e., the preservation of the cultural, historical and aesthetic value of the artefact (Brandi 2000), the stability and aesthetically acceptable form of the artefacts should be achieved.

Chemical cleaning is frequently applied in the corrosion treatments of metal artefacts with the purpose of removing deposits that occur in the form of massive corrosion products and impurities. It is especially used when the metal matrix of the artefact is highly preserved. Chemical cleaning is based on the use of chemical agents partially dissolving impurities and corrosion deposits, then rinsed and removed. The choice of solvents or solutions needs to be highly selective because only excess layers should be removed, whereas the original material and the structure of the artefact should be preserved. The excess layers are gradually removed, even in the case of inaccessible parts of the artefact, without any risk of causing sudden mechanical damage that may occur during mechanical cleaning (Pearson 1988; Bertholon and Relier 1990; Meyer-Roudet 1999; Cronyn 2004; Rodgers 2004; Selwyn 2004a). During the application of chemical methods, chelation agents have

proved to be highly efficient in removing corrosion products and other impurities. During surface adsorption of chelate, the chelate binds specific metal ions, thereby releasing chelating complexes into the solution and weakening the structural integrity of the corrosion products (Meyer-Roudet 1999; Cronyn 2004; Casaletto et al. 2008; Abd-Allah 2013).

The disadvantage of chemical cleaning is reflected in the higher effort required in the control of chemical processes. It could significantly reduce the possibility to preserve any patina and protective layers. Also, the extent of the safe impact of chemical cleaning on certain parts of the artefacts, such as their original surface (metal substrate), is still uncertain. This is especially significant in the case of heterogeneous corrosion. Additionally, residual compounds that can cause dissolution or oxidation of metals may also occur, and thereby endanger the stability of the artefact. As chemical solutions act in microcracks, the integrity of artefacts can be endangered after the removal of corrosion products. Moreover, the residual substances can affect the stability of artefacts due to inadequate rinsing after chemical cleaning (Pearson 1988; Bertholon and Relier 1990; Meyer-Roudet 1999; Cronyn 2004; Rodgers 2004; Selwyn 2004a).

This research was performed on several selected archaeological metal finds from two archaeological sites in Serbia: Felix Romuliana (Gamzigrad) in vicinity of Zaječar and Gradina (Jelica) nearby Čačak, different in function and form, and made from various types of metals (silver, bronze as a copper alloy, lead and iron). The research aims to present all steps in the application of chemical treatments in the conservation process of metal artefacts, such as the analyses used for the determination of the condition of the artefact before treatment, the characterisation of the corrosion products, and the determination of the chemical cleaning surface effects before, during and after chemical cleaning. It includes non-destructive macroscopic examination, X-ray (radiography) image analysis, optical microscopy, and SEM-EDS analysis. The samples were treated with different chemical solutions, depending on the type of metal and corrosion products (citric acid, ethylenedi-

aminetetraacetic acid sodium salts, EDTA-Na₂ and EDTA-Na₃).

This research shows the importance of choosing the appropriate chemical treatments, which is crucial for the both the efficiency of the cleaning process and the preservation of the artefacts. Furthermore, the research highlights the importance of traditional cleaning methods as part of the conservation process of the metal artefacts, which are easily available and applicable in the laboratories of local museums and institutions for the preservation of archaeological heritage.

FELIX ROMULIANA AND GRADINA SITES

Felix Romuliana (Gamzigrad) is an archaeological site with a continuity of life from the Neolithic to the Middle Ages, yet best known for the remains of a monumental fortified imperial residence from the beginning of the 4th century AD (Fig. 1a). In 2007, it became the first archaeological site in Serbia to be listed as a UNESCO cultural monument (Срејовић 1983; Поповић 2010). After excavations conducted in the second half of the 20th century, which were concentrated on the palace itself, research based on geophysical methods, started in 2004 in cooperation with the German Archaeological Institute, revealed the presence of a number of architectural units around the palace, which have yet to be examined in detail (Bülow et al. 2009; Pop-Lazić et al. 2014).

Thirty years of exploration of Gradina on Mt Jelica have shed light on the life of an early Byzantine city (6th century AD) that was an important regional centre of the Central Balkans (Milinković

2017) (Fig. 1b). Five churches and dozens of residential and economic buildings, as well as kilometres of ramparts have been unearthed so far. The daily life of the inhabitants of this urban settlement is documented by numerous finds of ceramic and glassware, some of which represent imports of Eastern origin (North African or Eastern Mediterranean). In addition, a large number of iron and bone tools were found, some of which were certainly produced in Gradina itself. Lead objects and lead as a raw material (ingots, lead strips) are relatively common finds in Gradina (Milinković 2017).

SAMPLES AND METHODS

Samples

From a total of 35 available metal archaeological finds excavated at the sites of Felix Romuliana and Gradina, seven were selected and stored in the depots of the National Museum Zaječar and the National Museum in Čačak under stable conditions after archaeological excavation and field cleaning (partial removal of soil). This includes the following samples: No. 1 – silver part of a bronze necklace - catch, No. 2 – part of a bronze brooch - pin, No. 3 – bronze coin, No. 4 – part of an iron key, No. 5 – iron fitting from a bag, No. 6 – fragment of a fitting - lead and No. 7 – lead plate. Samples Nos. 1, 2, 3, 4 and 5 belong to the Felix Romuliana site, whereas samples Nos. 6 and 7 are from the Gradina site, from the excavation of the Upper Town (Table 1). During the selection of the investigated collection of samples, the main adopted criteria were the diversity of the artefacts'

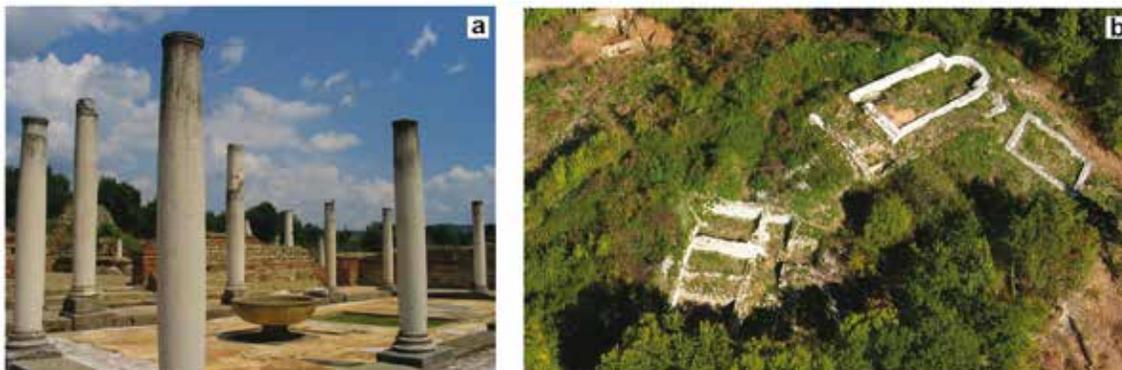


Fig. 1. Appearances of the archaeological sites: (a) Gamzigrad – Felix Romuliana (photo: K. Šarić), (b) Gradina – Jelica, (Narodni muzej Čačak, Gradina na Jelici, https://www.cacakmuzej.org.rs/gradina_na_jelici.html, accessed October 13th, 2022).

Sample label	Material	Sample	Archaeological site	Item, field number (C), dimension (cm)	Manufacturing technique, age*
1	Ag		Gamzigrad-Romuliana; Necropolis III	silver part of a bronze necklace, catch; C 1036/12; (3.27 x 0.58 x 0.64)	hammering, bending; second half of 4 th -5 th century
2	Cu-Sn		Gamzigrad-Romuliana; Northern rampart	part of a bronze brooch pin; C 1233/12; (length 6.88; spring 0.96)	casting, bending; 6 th century, Early Byzantine Period
3	Cu-Sn		Gamzigrad-Romuliana; Tower 15	bronze coin; C 8/14; (R – 2.07)	hammering; M. Aurelius Probus (276-282)
4	Fe		Gamzigrad-Romuliana; Northern settlement	part of an iron key; C 1093/11; (length 7.59; ring end: 1.36)	hammering; Late Antiquity
5	Fe		Gamzigrad-Romuliana; Tower 15	bag fitting out of iron and bags; C 13/13; (10.68 x 1.98 x 0.34)	hammering; 6 th century, Early Byzantine Period
6	Pb		Gradina - Jelica; Building II	fragment of a fitting – lead; C 8/96; (3.62 x 2.99 x 0.29)	casting; 6 th century, Early Byzantine Period
7	Pb		Gradina - Jelica	lead plate; C 94/15; (4.06 x 2.22 x 0.46)	casting; 6 th century, Early Byzantine Period

* Data on the technique of making the object and age are taken from the unpublished fund material of the National Museum Čačak

Table 1. Description and origin of samples, applied techniques and dating

composition, the degree of preservation of the metal matrix and the heterogeneity of the corrosion products.

Optical examination

Optical examinations were conducted in the Laboratory for Conservation and Restoration of the National Museum in Čačak. The method ap-

plied in the research included macroscopic and microscopic analysis, involving the use of lenses of different magnification and an optical microscope of the Carl Zeiss type (Jena).

Radiography

Radiographic methods such as X-rays and mammography were used to determine the degree of metal matrix preservation, which is one of the prerequi-

sites for the application of chemical cleaning (Jones 2006). The X-ray results provide more accurate information about the original shape and surface details of the studied artefacts, that are hidden below the corrosion products. Comparative X-ray analyses were performed only for the iron samples, being the most damaged items in the collection (Nos. 2, 4, 5), using a SIEMENS Multix Fusion analogue X-ray system, digital Shimadzu FLEXAVISION X-ray system, and Siemens MAMMOMAT 1000 digital mammography system. The recording conditions were as follows: for the analogue X-ray system 81 kW and 0.93 mAs; for the digital mammography system 81 kW and 0.91 mAs, whereas for the digital X-ray system samples were recorded under various conditions: 9 kW and 1 mAs (sample 2), 54 kW and 4.3 mAs (sample 4) and 54 kW and 4.9 mAs (sample 5). The radiographic investigations were conducted in the Radiology Department of the Čačak Health Centre.

SEM-EDS analysis

The surface morphology and chemical composition of the samples were analysed before and after chemical cleaning. The analyses were carried out in the SEM-EDS Laboratory at the University of Belgrade – Faculty of Mining and Geology, using a JEOL JSM-6610LV scanning electron microscope that was connected to an X-Max energy dispersive spectrometer (SEM-EDS system). The images presented in the paper were obtained using secondary electrons (SE) and backscattered electrons (BSE) detectors. A tungsten filament was used as the electron source. The samples were not coated with carbon or gold, as metal objects are electrical conductors. Semi-quantitative chemical analyses of the samples before and after the chemical treatment were conducted, both on a selected area and in a specific spot of interest of the sample surface. Quantification of the elements was conducted using internal standards, and all analyses were normalized at 100%. The detection limit for all the analysed elements was approximately 0.1 wt.%. The content of light elements (atomic number from 1 to 5) was not determined.

Preliminary cleaning tests

Preliminary (spot) cleaning was conducted on bronze and lead finds using small wooden tools

combined with distilled water and ethanol. The cleaning process was carried out on the selected minimal surfaces of finds (spot tests) in order to determine the preservation degree of the metal substrate, or the possible presence of metal coating on bronze finds.

Chemical cleaning method

Three substances were selected for chemical cleaning of the artefacts – citric acid ($C_6H_8O_7 \cdot H_2O$, *Fisher Chemical*) and disodium and trisodium salts of ethylenediaminetetraacetic acid (EDTA- Na_2 : EDTA- $Na_2 \cdot 2H_2O$, *Fisher Chemical*; EDTA- Na_3 : EDTA- $Na_3 \cdot xH_2O$, *Acros Organics*). The aqueous solutions were prepared with distilled water HPLC (Fisher Chemical) for all samples. Table 2 shows the concentrations and pH values of the selected solutions in detail. An AQUALYTIC - AL15 Set pH/Con instrument was used for determining the pH values of the solutions.

Chemical treatments were carried out in four daily cycles/chemical baths (4 days, 5 hours/one bath cycle). In the bronze sample (No. 3) and in the lead finds, the application period of two cleaning baths was affected by the nature of the corrosion products and the efficiency of the solutions, whereas the treatment of sample No. 6 was interrupted on the second day after two and a half hours. Without running the risk of damaging the metal matrix, a solution of higher concentration was initially applied on the iron sample No. 4 in order to accelerate the removal of hard surface corrosion products incorporated with additional substances from soil particles. The volumes of the solutions were from 100 to 200 cm³ and were determined according to the size of the artefact (the artefacts were completely immersed in the solution). The treatment employed slight heating (the temperature of the magnetic stirrer – *Heidolph Instruments*, *Hei-Standard* ranged between 30 and 50 °C) with occasional solution stirring. Moreover, after daily chemical treatments, the soil deposits and encrustations, as well as surface corrosion products, were removed with cotton gauze in order to eliminate partially separated and dissolved corrosion products. Metal tools were not used in this phase, in order to avoid contamination and interference of the results.

Sample / Composition	Chemical solution (T = 30 - 50 °C)	Concentration (%)	pH value (T = 25 °C)
1 / Ag	EDTA – Na ₃	9.09	6.85
2 / Cu-Sn	EDTA – Na ₃	9.09	6.85
3 / Cu-Sn	citric acid	4.74	1.40
4 / Fe	citric acid	9.01	1.83
	citric acid	4.74	2.24
5 / Fe	EDTA – Na ₂	6.50	3.93
6 / Pb	EDTA – Na ₂	6.50	3.90
7 / Pb	EDTA – Na ₂	6.50	3.90

Table 2. Concentrations and pH values of selected solutions for cleaning metal artifacts

At the end of each cycle and after the final cleaning, a brief rinsing of the artefacts was carried out in slightly heated distilled water until a neutral reaction was achieved. The next step was drying in ethanol and acetone baths. A brief rinsing was carried out to avoid the possibility of interference of the chemical cleaning results. Interference of the results, or the formation of new compounds in the form of films or coatings, occurs if the artefacts are immersed in distillate water for a longer period. This particularly refers to the previously mentioned lead artefacts, on which a thin corrosion film is quickly formed in distilled water in the presence of dissolved gasses. Therefore, rinsing must be carried out in the shortest possible time (Selwyn 2004a). The artefacts were dried and stored in polyethylene zip bags, where they remained until the beginning of a new cycle of the SEM-EDS analysis.

RESULTS

Optical observations before treatments

An optical examination, both macroscopical and microscopical, indicated complete surface corrosion over all of the selected samples; additionally, layered corrosion had developed on the iron, bronze and lead findings. Although the items were stored for many years after excavation without any conservation, their stable condition was noted (the effect of active corrosion is not noticeable). The presence of impurities, like soil remains, was detected on the surface of all the ar-

tefacts. These particles are incorporated within the structure of the corrosion products (transformed medium) in the iron and lead findings.

On the surface of the silver sample No. 1, a thin, dark, transparent film, typical for silver, together with partially evident soil remains, was observed. Considering that the finds were not photo-documented immediately after the excavation, it is not possible to determine whether the dark film was formed in the soil (e.g., anaerobic conditions with the effect of sulphate-reducing bacteria activities) or whether it was partially formed after excavation, as a result of the atmospheric conditions (Bertholon and Relier 1990; Marchand et al. 2014).

On the basis of several parameters, the bronze coin (sample No. 3) was identified as silver during the archaeological excavations, even though the existing corrosion products indicated bronze (heterogeneous, uneven, corrosion layer with dark green parts). Soil remnants were also noticeable on the sample. Nevertheless, the cleaning test proved that sample No. 3 was made from bronze, and that it was possible that the coin was coated in silver, but the majority of the silver layer was lost over time. The relief structure of the coin is barely visible. On the bronze brooch-pin (sample No. 2), an incoherent layer of corrosion products occurred accompanied with visible soil remains. This artefact is dominantly featured by various layers of green shades with the partial appearance of dark layers.

On both samples made of iron (Nos. 4 and 5), layered deposits of the corrosion products typical for iron (shades of dark reddish-brown and orange) were present in both of the examined iron

finds. The surface of the finds comprises a transformed medium, i.e., a mixture of corrosion products and components from soil.

The optical examination of the lead artefacts (samples No. 6 and 7) indicated the presence of an uneven and soft greyish–white layer.

X-radiographic screening

Radiographic images showed that sample Nos. 2, 4 and 5 had a highly preserved metal core (Fig. 2). Lighter parts on radiographic images indicate the presence of the metal matrix, whereas dark spots represent corroded or mechanically damaged parts of the artefact. The line shapes of the artefacts are irregular, due to mechanical deformations, damage and corrosion. The alternation of light and dark parts indicates the impacts of mechanical damage and corrosion (possibly pitting or some other form of local corrosion).

Chemical cleaning effects – macroscopic observations and SEM-EDS analyses before and after the treatment

The SEM-EDS analysis covered all seven selected finds analysed before and after the chemical treatment. The targeted parts of the surfaces were related to both the existing corrosion products and external material (soil) before the treatment, and the analysis of the artefact surfaces after the chemical cleaning.

Silver artefact. Soil particles and other impurities were removed from the silver find (sample No. 1) in the EDTA-Na₃ solution immediately after the first treatment, which was followed by the appearance

of a smooth surface of the artefact. The intensity of patina significantly decreased after the first few treatments with the solution, but it gradually decreased later. The surface of the artefact contained an uneven, transparent film, which could be removed with polishing process.

The concentrations of Si, Al and other elements (Fig. 3a) before chemical treatment indicate the presence of aluminosilicate and silicate phases on the surface of the silver artefact, i.e., soil and sand remains, whereas the silver basis of the artefact was most likely covered with a dark film of silver sulphide – Ag₂S. Separate chemical analyses of particles within the aluminosilicate layer indicated the presence of quartz (SiO₂), alkali feldspar (KAlSi₃O₈), albite (NaAlSi₃O₈), and some clay minerals.

Almost all the aluminosilicates were removed after the chemical treatment (Fig. 3b). Nevertheless, a thin film of silver sulphide remained unaltered on a large surface area. Individual spot chemical analyses, performed on the cleaned surfaces, indicated the presence of copper and gold in low concentrations (below 1%).

Bronze artefacts. Over a long treatment period of sample No. 2, the EDTA-Na₃ solution (pH ≈ 7) gradually dissolved corrosion products until the metal matrix was revealed. However, in sample No. 3, the citric acid solution dissolved almost all corrosion products in a short period of time. The surfaces of both artefacts obtained the expected appearance after chemical cleaning (the reddish-coloured bronze was covered with a thin uneven dark film). The cleaning process was completed with the necessary additional polishing in order to attain an aesthetically acceptable artefact

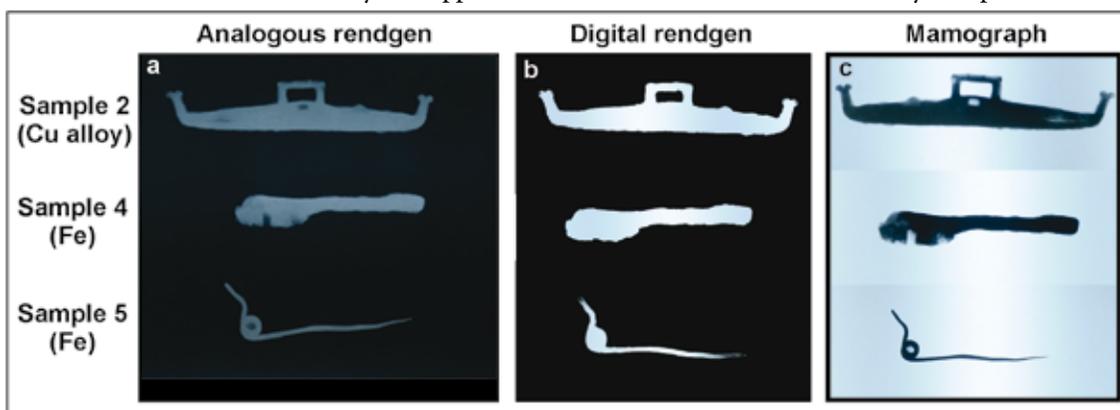


Fig. 2. Radiographic images of the examined samples 2, 4 and 5: a -analogue X-ray system, b - digital Xray system, c - digital mammography system.

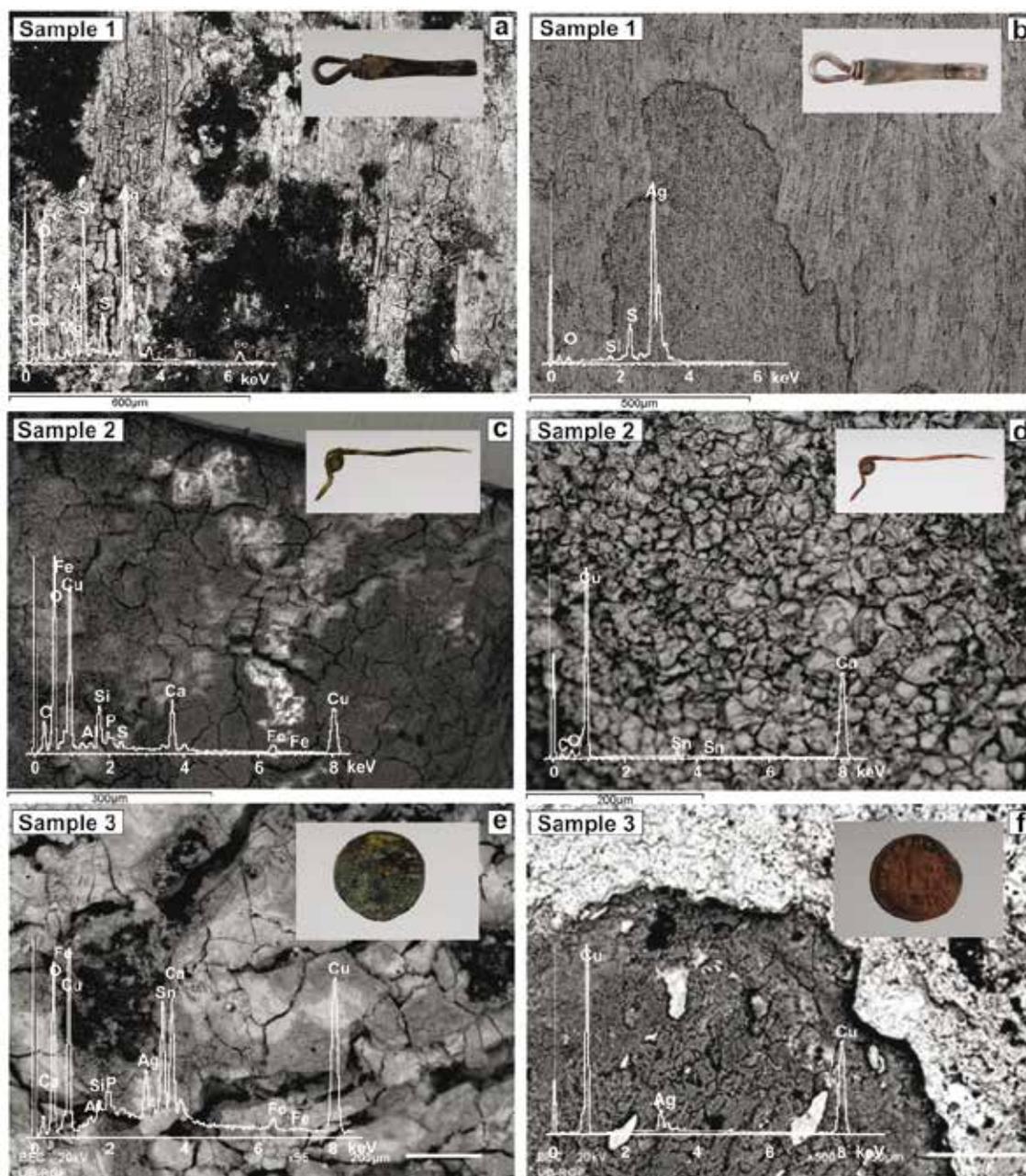


Fig. 3. BSE images and spectrums of the surface chemical analyses: Sample 1 (silver part of a bronze necklace): a - before treatment, b - after treatment; Sample 2 (part of a bronze brooch pin): c - before treatment, d - after treatment; Sample 3 (bronze coin): e - before treatment, f - after treatment.

appearance. In the bronze brooch-pin thread (the access of the solution to the metal surface was difficult due to thick corrosion layers), it was necessary to remove the additional corrosion products, which is usually performed in a mechanical way.

Before chemical cleaning, secondary copper phases were dominant in the samples of bronze brooch-pin and coin, and they mainly included copper carbonates and/or hydrated copper carbonates, such as malachite

($\text{Cu}_2\text{CO}_3(\text{OH})_2$) and azurite ($\text{Cu}_3(\text{CO}_3)_2(\text{OH})_2$). Besides carbonates, small amounts of copper oxide – cuprite (Cu_2O) could be traced, whereas the presence of sulphur (Fig. 3c) could indicate some of the copper sulphate phases. The presence of impurities (aluminosilicate and calcite) was negligible. After the chemical treatment, all impurities were removed, whereas the presence of copper carbonate was insignificant. The presence of tin (Fig. 3d) in some spot analyses on the

cleansed needle confirms the hypothesis that the finds are made of bronze. Besides the previously mentioned copper carbonates, an increased amount of calcite (CaCO_3) could be traced on the bronze coin before the chemical treatment (Fig. 3e). Random silver accumulations on the surface of the coin were also detected (Fig. 3f). Illustration of the appearance of samples 1 to 3 before and after the treatment is given in Fig. 4.

Iron artefacts. For the iron items, a solution of citric acid solution (which had a significantly lower pH value than EDTA- Na_2 solution) proved to be more efficient. It should be noted that the first bath of sample No. 4 (a key) was carried out in a

more concentrated citric acid solution, so that the initial remnants of soil and other materials could be easily removed. On a large surface area of the same sample, corrosion products were completely removed to the metal substrate. Additionally, a cleaning with a cotton cloth was performed on the key blade, due to the thin and corroded metal matrix, which carried a risk of losing the original shape of the artefact. On smaller surface areas of sample No. 5, an EDTA- Na_2 solution removed corrosion products to the metal matrix. The partially revealed metal surface possesses a characteristic stable silver-grey colour. Secondary iron phases are most dominant in the iron key sample,



Fig. 4. Illustration of cleaning effects: Sample 1 (silver part of a bronze necklace – catch), before (a) and after treatment (b); Sample 2 (part of a bronze brooch – pin), before (c) and after treatment (d); Sample 3 (bronze coin), before (e) and after treatment (f) (photos by M. Bojović).

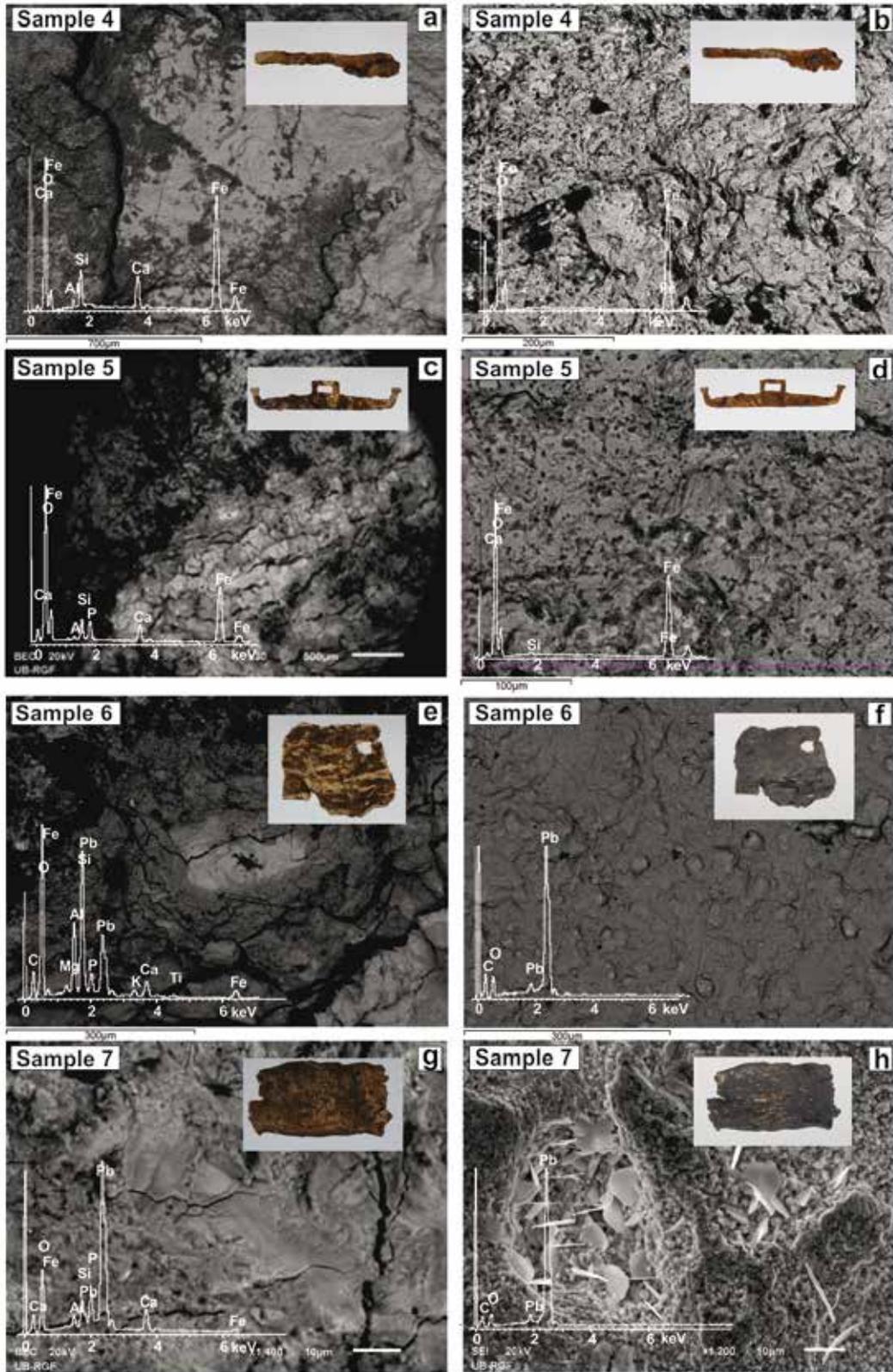


Fig. 5. BSE images and spectrums of the surface chemical analyses: Sample 4 (part of an iron key): a - before treatment, b - after treatment; Sample 5 (bag fitting out of iron and bags): c - before treatment, d - after treatment; Sample 6 (fragment of a fitting - lead): e - before treatment, f - after treatment; Sample 7 (lead plate): g - before treatment, h - after treatment.

whereas the presence of aluminosilicate is negligible (Fig. 5a). These phases are most likely present in the form of a mixture of various oxides and/or iron hydroxides. Chemical analysis of the surface after chemical cleaning shows that the aluminosilicates have been removed, whereas the mixture of oxides and/or iron hydroxides is still significantly present (Fig. 5b). Almost identical phases occurred in the case of the iron bag fitting sample (sample No. 5), both before and after chemical cleaning (Figs. 5c, 5d).

Lead artefacts. As expected, the EDTA-Na₂ solutions were highly efficient in removing corrosion products formed on sample Nos. 6 and 7. In sample No. 6, cleaning was mostly performed very quickly after the first bath. In the case of the second lead sample (No. 7), the solution reacted a bit slower owing to large recesses as well as to the deformed and curved structure of the lead plate. In both artefacts, corrosion products remained in the cracks. The cleaned surfaces of both finds were covered with a dark, thin film formed after the cleaning, i.e., during and after rinsing, or possibly as an effect of a short atmospheric corrosion. In the case of sample No. 6, cleaning was completed with the necessary additional polishing, which added the appropriate aesthetic look, whereas sample No. 7 required additional mechanical cleaning in hard-to-reach areas, such as recesses and the inner parts of the curved structure.

On both lead finds, very similar impurities were found, mostly in the form of various silicate and aluminosilicate phases (Fig. 5e). After chemical treatment, the surface of the lead finds mostly contained lead carbonates – cerussite (PbCO₃) and/or hydrocerussite /Pb₃(CO₃)₂(OH)₂/ – (Fig. 5f). The high concentration of phosphorus may be related to clayey fractions of the soil (Fig. 5g). After chemical treatment, lead carbonate crystals occurred in the cavities of the lead finds. These crystals displayed orthorhombic symmetry and this phase is most probably cerussite (Fig. 5h). Illustration of the appearance of samples 4 to 7 before and after the treatment is given in Fig. 6.

The results of the chemical analyses, after the chemical cleaning of all the treated artefacts, did not show any trace of characteristic elements that could refer to any possible residual compounds (reaction with the examined aqueous solutions).

Table 3 shows the summarised review of the identified phases, before and after the chemical treatment for all the studied artefacts.

DISCUSSION

A chemical cleaning treatment with the selected chelating agents was applied on various metal finds (silver, bronze, lead and iron) from two archaeological sites in Serbia. As expected, after the chemical treatment, silicates, aluminosilicates, and calcite (CaCO₃) – as usual constituents of

Sample/composition	Composition of untreated metal surfaces	Corrosion products after chemical treatment
Sample 1: Ag	- silicates and aluminosilicates from sand and soil - Cu sulphide	- Ag sulphide
Samples 2, 3: Cu-alloy (bronze)	- silicates and aluminosilicates from sand and soil - calcite - Cu carbonates and sulphates	- Minor quantity of Cu carbonate
Samples 4, 5: Fe	- calcite - silicates, aluminosilicates and phosphates from sand and soil - Fe oxides and hydroxides - Fe carbonates	- Fe oxides and hydroxides
Samples 6, 7: Pb	- silicates, aluminosilicates and phosphates from sand and soil - Pb carbonates	- Pb carbonates

Table 3. Effects of applied chemical cleaning

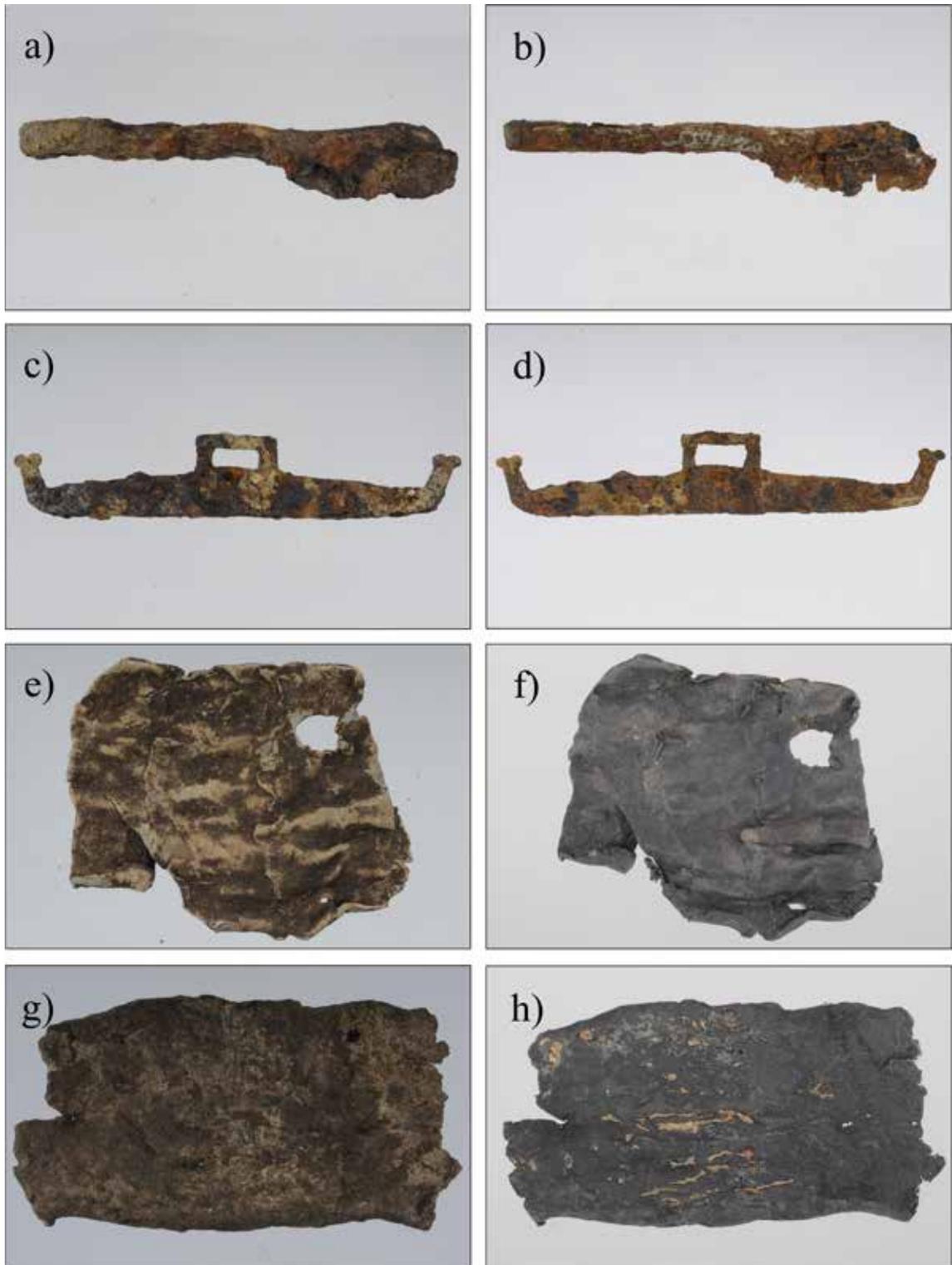


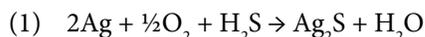
Fig. 6. Illustration of cleaning effects: Sample 4 (part of an iron key), before (a) and after treatment (b); Sample 5 (iron fitting from a bag), before (c) and after treatment (d); Sample 6 (fragment of a fitting – lead), before (e) and after treatment (f); Sample 7 (lead plate), before (g) and after treatment (h) (photos by M. Bojović).

sand and soil, were almost completely removed from all metal finds. Moreover, a significant part of the secondary phases formed from dominant

metals were also removed from the artefacts.

Silver artefact. The main dark-greyish secondary phase of the silver find, which was, in addition

to mechanical impurities, observed before chemical cleaning, was identified as silver sulphide (Ag_2S – possible phases are acanthite and/or argentite). The presence of silver sulphide on silver artefacts is a common corrosion product that usually occurs in the form of a thin, dark film formed in a reaction with hydrogen sulphide (H_2S) or carbonyl sulphide (OCS) in the environment, with moisture as an accelerator of reactions (reactions 1 and 2 – Selwyn et al. 1999; Graedel 1992; Polomar et al. 2016).



Gases, such as hydrogen sulphide and/or carbonyl sulphide, which were necessary for the formation of silver sulphide on the examined artefact, most likely originated from the soil. Namely, the soil is highly significant both as a source and as a consumer of carbonyl sulphide. This type of gas plays a key role in the process of photosynthesis, since it is an analogue substrate of carbon dioxide (Masaki et al. 2016 and references therein), while bacteria and fungi release hydrogen sulphide during the decomposition of proteins that contain sulphur, as well as through the direct reduction of sulphates. Moreover, the final metabolic product of prokaryotes that oxidise organic compounds using sulphate as a terminal acceptor of electrons is hydrogen sulphide (Lamers et al. 2013).

The analysis of the silver finds after the treatment shows that the silver sulphide was still present. However, this result, indicating partial remains of silver sulphide, was also found in a significant number of other silver cleaning treatments (Archi Olsoufieff et al. 2004; Ioanid et al. 2011; Marchand et al. 2014; Moreno-Suárez et al. 2016; Palomar et al. 2016). One of the main reasons this sulphide is not completely removed is its inability to dissolve in the slightly acidic environment of the heated EDTA – Na_3 solution (Table 2). Low oxygen concentrations without the presence of Si and Al (Fig. 3b), in the analyses after the treatment, may indicate the possible presence of silver oxide (Ag_2O). However, it is likely that, during the treatment, silver sulphide transformed into silver sulphate (Ag_2SO_4).

Some chemical analyses of the silver find show low concentrations of copper and silver (before

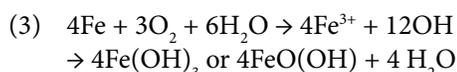
and after cleaning). Bearing in mind that silver has often been alloyed with this element, the results of the analyses are not unusual (Goffer 2007; Artioli 2010).

Bronze artefacts. The applied chemical treatment with citric acid and EDTA- Na_3 solutions removed calcite and aluminosilicate in bronze finds (Fig. 3c), whereas the corrosion products such as copper carbonates were still present, but to a lesser extent, after the chemical treatment (Fig. 3d). Given that there are many hydrated copper carbonates – malachite / $\text{Cu}_2(\text{CO}_3)(\text{OH})_2$ /, azurite / $\text{Cu}_3(\text{CO}_3)_2(\text{OH})_2$ /, marklite / $\text{Cu}_3(\text{CO}_3)_2(\text{OH})_6 \cdot 6\text{H}_2\text{O}$ /, georgeite / $\text{Cu}_2(\text{CO}_3)(\text{OH})_2 \cdot 6\text{H}_2\text{O}$ / etc., it is difficult to distinguish the exact phase or phases without the application of some destructive methods of identification (e.g. X-ray diffraction analysis). The presence of sulphur before chemical cleaning may indicate certain green hydrated copper sulphates, such as antlerite – $\text{Cu}_3(\text{SO}_4)(\text{OH})_4$, brochantite – $\text{Cu}_4(\text{SO}_4)(\text{OH})_6$ etc. These phases (carbonates and copper sulphates) may be formed in a reaction with oxygen, CO_2 and SO_2 from the air, in the presence of water at the place from which the artefacts originate.

The citric acid solution removed almost all corrosion products from sample No. 3 in a short period of time, whereas the EDTA- Na_3 solution ($\text{pH} \approx 7$) gradually removed corrosion products to the metal matrix from sample No. 2 over a longer time period. The above-mentioned hydrated copper carbonates and hydrated copper sulphates are mainly dissolved in highly acidic conditions. Since the slightly acidic EDTA- Na_3 solution proved to be more efficient in removing corrosion products, it is possible that easily soluble secondary phases, e.g., chalcantite – $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, were also formed in these artefacts. In the natural environment it can be found as a secondary phase of copper and other metals (Moncur et al. 2015).

The content of tin (Fig. 3), as well as the minor lead content, identified in some analyses after the applied chemical treatment, originate from metal substrate, i.e., from the composition of the bronze alloy Cu–Sn–Pb (Goffer 2007; Artioli 2010), whereas the confirmed presence of silver (Figs. 3e, 3f) on the bronze coin shows that the coin was silver plated.

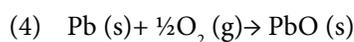
Iron artefacts. Small amounts of silicates, aluminosilicates and calcite occurring in the iron finds before the applied chemical treatment were removed to the greatest extent. Nevertheless, iron phases which show considerable concentrations in the form of the mixtures of oxides, hydroxides and iron carbonates, were still present in significant amounts in these iron finds (Figs. 5b, 5d). This layer is commonly called 'a thick corrosion layer' and it is characterised by the following phases: yellow-brownish goethite / $\alpha\text{FeO}(\text{OH})$ / and black-greyish magnetite ($\text{FeO}\cdot\text{Fe}_2\text{O}_3 - \text{Fe}_3\text{O}_4$) (Neff et al. 2005; Neff et al. 2007; Wang 2007; Jegdić et al. 2012). Although some chemical analyses of cubic crystals confirm the presence of magnetite, the complete identification of all secondary phases could not be conducted without destructive X-ray diffraction analysis. The origin of phosphorus found in traces both in the corrosion layer and the metal substrate can be related not only to the soil in which the artefacts were found, but also to the slag inclusion (Neff et al. 2005). It is less likely that the presence of phosphorus indicates ferrous phosphate (vivianite) / $\text{Fe}_3(\text{PO}_4)_2\cdot 8\text{H}_2\text{O}$ /, either blue or white compound, frequently found in the excavated iron finds located near sources of phosphorus ions, such as bones or fish remains, or in the vicinity of landfills that are full of organic material (Selwyn 2004b). Although a series of chemical reactions is responsible for the formation of the corrosion layer, i.e., a mixture of various phases of iron, a simple mechanism for the formation of iron hydroxide can be described through the reaction between oxygen and water on the metal substrate, i.e., reaction 3.



The main reason for the partial removal of the iron secondary phases is primarily the thickness and inhomogeneity of the formed layer, whereas the long-term and more aggressive treatments could damage the metal matrix.

Lead artefacts. Uneven greyish-white and dark grey layers could be clearly seen on the lead findings before chemical cleaning, possibly due to contamination with the surrounding soil, or owing to the effect of atmospheric corrosion after the excavation (Mattias et al. 1984; Selwyn 2004a; Schotte and Adriaens 2006). The absence of chlo-

rine and phosphorus shows that the corrosion phases cannot be constituted by chlorides and sulphates, but only by carbonates in the form of orthorhombic cerussite (PbCO_3) or by rarely found trigonal hydrocerussite $\text{Pb}_3(\text{CO}_3)_2(\text{OH})_2$. It is well-known that a thin layer of lead carbonates can be quickly formed under atmospheric conditions in which the lead is rapidly coated with a thin corrosion layer of monoxide (reaction 4) that reacts with absorbed carbon dioxide, thereby forming lead carbonate (reaction 5), or lead carbonate hydroxide – hydrocerussite in an additional reaction with moisture (Selwyn, 2004b; Polić Radovanović et al., 2010).



After the conducted chemical cleaning, silicates and aluminosilicates were mostly removed, while the dark greyish layer of lead carbonate occurred on the entire surface area of the lead finds (Fig. 5f). Plated orthorhombic crystals (Fig. 5h), formed in the cavities, indicate that lead carbonate occurred in the form of cerussite.

CONCLUSIONS

The paper presents an analysis of the reactivity and efficiency of the chosen chelating agents (EDTA-Na_2 and EDTA-Na_3) and citric acid in the process of conservation treatments of metal archaeological artefacts made of silver, bronze, iron and lead. The chemical composition and the distribution of chemical elements on the surface of the artefacts before cleaning indicate the presence of characteristic corrosion products as well as some other foreign matter (soil).

As expected, the EDTA-Na_2 solution removed the lead corrosion products within a very short period of time, whereas citric acid was most efficient in removing copper corrosion products. Both solutions show a low level of selectivity and control, which further supports the fact that they can be mostly used for removing hardly soluble surface layers or entire corrosion layers. The reactivity of the EDTA-Na_3 solution on silver artefacts indicates a higher selectivity and control. Therefore, partial conservation of patina can be carried

out simultaneously with the removal of impurities. In iron artefacts, corrosion layers were unevenly removed using the EDTA-Na₂ solution and citric acid. This was expected, taking into account the presence of hardly soluble iron compounds.

When the visual appearance is considered, it is necessary to carry out an additional mechanical cleaning, such as polishing, so that the artefacts can obtain an aesthetically acceptable appearance. In the case of iron artefacts (corrosion products are weakened and partially dissolved), it is necessary to carry out both chemical and mechanical cleaning.

SEM-EDS analyses of metal surfaces after cleaning did not indicate the presence of the characteristic chemical elements that could be related to possible residual compounds, as a result of reactions with the analysed aqueous solutions. Besides the necessity for further research, the overall conclusion is that the proposed chemical methods (chemical solutions) are highly efficient, easy to apply and easily available. Accompanied with the previous diagnostic examination of the artefacts' conditions, as prerequisites for the application of chemical cleaning, the proposed EDTA salts enable a wide range of possibilities regarding the selectivity and control of the chemical cleaning of archaeological findings.

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BIBLIOGRAPHY

Abd-Allah, R. 2013

Chemical Cleaning of Soiled Deposits and Encrustations on Archaeological Glass: A Diagnostic and Practical Study, *Journal of Cultural Heritage* 14: 97-108.

Archi Olsoufieff, A., Colacicchi Alessandri, O. and Ferretti, M. 2004

An Approach to the Conservation of Deeply Corroded Archaeological Silver: the Polos from Crucinia, in *Metal 04: Proceedings of the International Conference on Metals Conservation, Canberra, Australia, 4-8 October 2004*, eds. J. Ashton and D. Hallam, Canberra: National Museum of Australia, 261-272.

Artioli, G. 2010

Scientific Methods and Cultural Heritage: An Introduction to the Application of Materials Science to Archaeometry and Conservation Science, Oxford, UK: Oxford University Press.

Bertholon, R. 2007

Archaeological Metal Artefacts and Conservation Issues: Long-term Corrosion Studies, in *Corrosion of Metallic Heritage Artefacts: Investigation, Conservation and Prediction of Long Term Behaviour*, eds. P. Dillmann, G. Beranger, P. Piccardo, H. Matthiessen, Sawston, UK: Woodhead Publishing Limited, 31-40.

Bertholon, R. and Relier, C. 1990

Les métaux archéologiques in *La conservation en archéologie: méthodes et pratique de la conservation-restauration des vestiges archéologiques*; eds. M. Berducou, Paris: Masson, 163-221.

Brandi, C. 2000

Teoria del restauro, Torino: Piccola Biblioteca Einaudi.

Bülow, G. V. et al. 2009

Das deutsch-serbische Gemeinschaftsprojekt "Romuliana-Gamzigrad". Bericht über die Arbeitskampagnen 2004 bis 2007, *Germania* 87/1: 105-171.

- Casaletto, M. P. et al. 2008**
Chemical Cleaning of Encrustations on Archaeological Ceramic Artefacts Found in Different Italian Sites, *Appl. Phys. A* 92: 35-42.
- Cronyn, J. M. 2004**
The Elements of Archaeological Conservation, Routledge, London: Taylor and Francis.
- Graedel, T. E. 1992**
Corrosion Mechanism for Silver Exposed to the Atmosphere, *J. Electrochem. Soc.* 139(7): 1963-1970.
- Gerwin, W. and Baumhauer, R. 2000**
Effect of Soil Parameters on the Corrosion of Archaeological Metal Finds, *Geoderma* 96: 63-80.
- Goffier, Z. 2007**
Archaeological Chemistry, New Jersey: John Wiley & Sons, Inc.
- Ioanid, E. G. et al. 2011**
Surface Investigation of Some Medieval Silver Coins Cleaned in High-Frequency Cold Plasma, *Journal of Cultural Heritage* 12: 220-226.
- Jegdić, B. et al. 2012**
Corrosion of Archaeological Artefact Made of Forged Iron, *Metall. Mater. Eng.* 18(3): 233-240.
- Jones, D. M. 2006**
Guidelines on the X-radiography of Archaeological Metalwork, Swindon, UK: English
- Heritage.Kibblewhite, M., Tóth, G. and Hermann, T. 2015**
Predicting the Preservation of Cultural Artefacts and Buried Materials in Soil, *Science of the Total Environment* 529: 249-263.
- Lamers, L. P. M. et al. 2013**
Sulfide As a Soil Phytotoxin – a Review, *Front. Plant Sci.* 4: 268.
- Marchand, G. et al. 2014**
Degradation of Archaeological Horn Silver Artefacts in Burials, *Heritage Science* 2: 5
- Masaki, Y et al. 2016**
Degradation and Emission of Carbonyl Sulphide An Atmospheric Trace Gas, by Fungi Isolated from Forest Soil, *FEMS Microbiol Lett* 363/18: fnw197.
- Mattias, P., Maura, G. and Rinaldi, G. 1984**
The Degradation of Lead Antiquities from Italy, *Studies in Conservation* 29(2): 87-92.
- Meyer-Roudet, H. 1999**
A la recherche du métal perdu: Nouvelles technologies dans la restauration des métaux archéologiques, Paris: Éditions Errance.
- Milinković, M., ed. 2017**
Gradina on Mt Jelica, A fortified Centre in 6th century Illyricum and a multi-layered archaeological site, Belgrade: Serbian academy of Sciences and Arts and Čačak: National Museum in Čačak
- Moncur, M. C. et al. 2015**
Long-term Mineralogical and Geochemical Evolution of Sulphide Mine Tailings Under a Shallow Water Cover, *J. Appl. Geochem.* 57: 178-193.
- Moreno-Suárez A.I., Chaves, F. and Pliego, R. 2016**
Feasibility of Different Cleaning Methods for Silver-Copper Alloys by X-ray Fluorescence: Application to Ancient Greek Silver Coins, *Spectrochimica Acta Part B* 116: 85-91.
- Neff, D. et al. 2007**
Contribution of Iron Archaeological Artefacts to the Estimation of Average Corrosion Rates and the Long-Term Corrosion Mechanisms of Low-Carbon Steel Buried in Soil, in *Corrosion of Metallic Heritage Artefacts: Investigation, Conservation and Prediction of Long Term Behaviour*, eds. P. Dillmann, G. Beranger, P. Piccardo, H. Matthiessen, Sawston, UK: Woodhead Publishing Limited, 41-74.
- Neff, D. et al. 2005**
Corrosion of Iron Archaeological Artefacts in Soil: Characterisation of the Corrosion System, *Corrosion Science* 47: 515-535.
- Palomar, T. et al. 2016**
A Comparative Study of Cleaning Methods for Tarnished Silver, *Journal of Cultural Heritage* 17: 20-26.

Pearson, C. 1988

Conservation of Marine Archaeological Objects, Oxford: Butterworth-Heinemann.

Polić Radovanović, S. et al. 2010

Metodološki i tehnički aspekti primene novih tehnika u zaštiti kulturne baštine, Beograd: Institut Goša and Centralni institut za konzervaciju.

Pop-Lazić, S., Popović, B. i Vujadinović, V. 2014

Gamzigrad – Felix Romuliana: iskopavanja 2012. godine – Severno naselje, in *Arheologija u Srbiji, projekti Arheološkog instituta u 2012. godini*, eds. D. Antonović, S. Golubović, and V. Bikić, Beograd: Arheološki institut, 78-81.

Поповић, И. 2010

Предговор, Трансформације једног вишеслојног локалитета: анонимна насеља у Гамзиграду–Felix Romuliana–Romulianum–Romuliana – анонимна насеља у Гамзиграду, in *Felix Romuliana – Гамзиград*, ed. И. Поповић, Београд: Археолошки институт, 7-9.

(Popović, I. 2010)

Predgovor, Transformacije jednog višeslojnog lokaliteta: anonimna naselja u Gamzigradu–Felix Romuliana–Romulianum–Romuliana – anonimna naselja u Gamzigradu, in: *Felix Romuliana – Gamzigrad*, ed. I. Popović, Beograd: Arheološki institut, 7-9).

Rodgers, B. A. 2004

The Archaeologist's Manual for Conservation, A Guide to Non-Toxic, Minimal Intervention Artefact Stabilization, New York: Springer New York.

Schotte B. and Adriaens A. 2006

Treatments of Corroded Lead Artefacts, *Studies in conservation* 51/4: 297-304.

Selwyn, L. 2004a

Metals and Corrosion: A Handbook for the Conservation Professional, Ottawa: Canadian Conservation Institute.

Selwyn, L. 2004b

Overview of Archaeological Iron: the Corrosion Problem, Key Factors Affecting Treatment, And Gaps in Current Knowledge, in *Metal 04: Proceedings of the International Conference on Metals Con-*

servation, Canberra, Australia, 4-8 October 2004, eds. J. Ashton and D. Hallam, Canberra: National Museum of Australia, 294-306.

Selwyn, L. S., Sirois, P. J. and Argyropoulos, V. 1999

The Corrosion of Excavated Archaeological Iron with Details on Weeping and Akaganéite, *Studies in Conservation* 44(4): 217-232.

Schweizer, F. 1994

Chemistry and the Conservation of Archaeological Metals, The Science of the Total Environment 143, 127-129.

Срејовић, Д. 1983

Царски дворцац, in *Гамзиград, Касноантички царски дворцац*, ed. С. Ђелић, Београд: Галерија САНУ, 24-93.

(Srejović, D. 1983)

Carski dvorac, in *Gamzigrad, Kasnoantički carski dvorac*, ed. S. Ćelić, Beograd: galerija SANU, 24-93).

Wang Q. 2007

An Investigation of Deterioration of Archaeological Iron, *Studies in Conservation* 52(2): 125-134.

REZIME

EFIKASNOST HEMIJSKOG ČIŠĆENJA RAZLIČITIH METALNIH PREDMETA SA ARHEOLOŠKIH LOKALITETA FELIKS ROMULIJANA I GRADINA

KLJUČNE REČI: SEM-EDS ANALIZA, METALNI ARHEOLOŠKI PREDMETI, KOROZIJA, KONZERVACIJA.

U radu su razmatrani efekti hemijskog čišćenja metalnih arheoloških predmeta sa lokaliteta Feliks Romulijana - Gamzigrad i Gradina - Jelica. Studija je obuhvatila odabrane metalne arheološke nalaze, različite po funkciji i formi, izrađene od srebra, bakra - bronzе, olova i gvožđa. Određivan je stepen efikasnosti različitih vodenih rastvora u kontrolisanim uslovima (pH vrednost, temperatura i vreme). Uzorci su u zavisnosti od vrste metala i korozionih produkata, kao i očuvanosti metalnog jezgra, tretirani različitim hemijskim rastvorima (limunska kiselina, natrijumove soli etilen diamin

tetra sirćetne kiseline, EDTA-Na₂ i EDTA-Na₃). Makroskopska opservacija, rendgensko snimanje uzoraka (radiografija), optička mikroskopija i SEM-EDS analiza su korišćeni kako bi se utvrdilo zatečeno stanje predmeta pre tretmana, izvršila karakterizacija produkata korozije, ali i utvrdili površinski efekti hemijskog čišćenja na metalnim nalazima pre, u toku i nakon hemijskog tretmana. Rastvor EDTA-Na₂ je očekivano u vrlo kratkom roku uklonio olovne korozione produkte (karbonate), dok je limunska kiselina najveću efikasnost pokazala u uklanjanju bakarnih korozionih produkata (malahit, kuprit). Oba rastvora pokazuju nizak stepen selektivnosti i kontrole što potvrđuje činjenicu da se oni uglavnom mogu koristiti za uklanjanje kompletnih korozionih slojeva. Kada je reč o rastvoru EDTA-Na₃ nečistoće i korozioni produkti srebra (oksidi) i bakra (malahit, kuprit) su postepeno uklanjani. Ovim rastvorom u najvećoj meri je uklonjen srebro oksid u odnosu na sulfid što ukazuje na veći stepen selektivnosti i kontrole otvarajući mogućnost za očuvanje patine uz istovremeno uklanjanje nečistoća. Kod gvozdenih nalaza korozioni slojevi su neravnomerno uklonjeni pomoću rastvora EDTA-Na₂ i limunske kiseline, što je i očekivano s obzirom na prisutna teško rastvorna jedinjenja gvožđa (getit, magnetit). Kada je reč o površinskom vizuelnom izgledu neophodno je poliranje kako bi predmeti dobili estetski prihvatljiv izgled, dok je kod gvozdenih nalaza neophodno dodatno mehaničko čišćenje. Ovo istraživanje pruža odgovore vezane za efikasnost i procenu rizika izabranih hemijskih tretmana uključujući transformaciju korozionih proizvoda, formiranje hemijskih rezidualnih supstanci i uticaja fizičkih efekata tretmana na informacije sadržane u korozionim slojevima predmeta.

* * *

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