JOSIPA LOVRIĆ

DESALINIZACIJA ARHEOLOŠKIH ŽELJEZNIH PREDMETA ALKALNO-SULFITNIM POSTUPKOM

DESALINATION OF ARCHAEOLOGICAL IRON OBJECTS BY ALKALINE-SULPHITE TREATMENT

U članku se opisuje postupak desalinizacije arheoloških željeznih predmeta alkalno-sulfitnim postupkom. Ovim se postupkom uklanjaju topljivi kloridi koji su se akumulirali u željeznim predmetima tijekom ukopa. Opisan je postupak određivanja koncentracije klorida poteciometrijskom titracijim.

Ključne riječi: desalinizacija, željezni predmeti, alkalno-sulfitni postupak, potenciometrijska titracija

The article describes the process of desalination of archaeological iron objects by an alkaline-sulphite treatment. This treatment removes the soluble chlorides that have accumulated in the iron objects during burial. The process of determining the concentration of chlorides by potentiometric titration is also described.

Key words: desalination, iron objects, alkaline-sulphite treatment, potentiometric titration

Korozija je termodinamički neizbježan proces. Dugoročno preživljavanje bilo kojeg arheološkog predmeta ne može se zajamčiti. Samo potpuno uklanjanje kisika i vode iz objektnog okoliša moglo bi spriječiti korozijske reakcije. Iako je to teoretski moguće, to bi spriječilo pristup, proučavanje ili upotrebu predmeta i nije dugoročno održiva opcija za konzervatore ili kustose. Arheološki željezni predmeti kontaminiraju se kloridima tijekom ukopa. Kloridi povećavaju elektrokemijsku koroziju. Da bi se mogla kontrolirati kloridno inducirana korozija, potrebno je takve predmete čuvati pri relativnoj vlažnosti (RH) manjoj od 15 %, što je u praksi teško postići.[1] Željezni predmeti moraju se podvrći postupku desalinizacije. Uklanjanje klorida iz željeznih predmeta i njihovo čuvanje u kontroliranim uvjetima jedini je ispravan put čuvanja željeznih predmeta. U ovom radu opisana je metoda desalinizacije koja se često provodi i daje zadovoljavajuće rezultate. Radi se o desalinizaciji alkalno-sulfitnim postupkom.

KOROZIJSKE PROMJENE NA ŽELJEZNIM PREDMETIMA

Željezni predmeti česti su nalazi arheoloških iskopavanja. Željezo je od prapovijesti bilo temeljni materijal za izradu predmeta koji su se koristili u svakodnevnom životu. Zbog svoje reaktivnosti lako korodira i na njemu se stvaraju korozijski produkti koji nastaju u slojevima tvoreći korozijske profile različitog sastava i gustoće.[2] Brzina korozije u tlu vrlo je promjenjiva. Ovisi o uvjetima ukopa kao što su sastav tla, vlažnost, salinitet, prisutnost kisika, pH-vrijednost i prisutnost mikroorganizama. Agresivnost tla najveća je ako je sadržaj vlage od 25 do 50 %.[3] Daljnjim povišenjem vlažnosti agresivnost se ne povećava zato što je otežan pristup kisiku iz zraka. Propusnost za vodu i zrak ovisi o vrsti tla. Pješčano tlo vrlo je propusno, a glina gotovo nepropusna. Važna značajka tla s obzirom na koroziju je i njegova pH-vrijednost. Prisutnost humusa nastalog raspadom organskih tvari snižava pH-vrijednost jer u njemu ima huminskih kiselina koje prilično agresivno djeluju na metale. Povećanu agresivnost ima i tlo koje sadrži sulfide ili topljive soli (sulfate i kloride). Agresivnost tla ovisi i o protoku i sastavu podzemnih voda koje su opasne ako sadrže CO_2, kloride ili soli bakra.[4] Željezni predmeti mogu ostati očuvani tisućama godina ako su bili u tlu u kojem je dotok kisika i vlage bio smanjen kao i aktivnost sulfat-reducirajućih bakterija.[5] U suprotnom slučaju, kad je korozija brza,

Corrosion is a thermodynamic and inevitable process. The long-term survival of any archaeological object cannot be guaranteed. Only the complete removal of oxygen and water from the environment of the object could prevent corrosive reactions. Although theoretically possible, it would impede access, study or use of the subject and it is not a viable option for conservators or curators in the long run. Archaeological iron objects are contaminated with chlorides during burial. Chlorides increase electrochemical corrosion. In order to control chloride-induced corrosion, such objects must be stored at a relative humidity (RH) of less than 15%, which is difficult to achieve in practice.[1] Iron objects must undergo desalination. The removal of chlorides from iron objects and their storage under controlled conditions is the only correct way to preserve iron objects. This paper describes a desalination method that is frequently performed and produces satisfactory results. It is a desalination by an alkaline-sulphite treatment.

CORROSIVE CHANGES ON IRON OBJECTS

Iron objects are common finds of archaeological excavations. Iron has been, since prehistoric times, the basic material for the production of objects used in everyday life. Due to its reactivity, it easily corrodes and produces corrosion products which are created in layers, forming corrosion profiles of different composition and density.[2] The rate of corrosion in soil is very variable. It depends on the burial conditions such as soil composition, humidity, salinity, presence of oxygen, Ph-value and the presence of microorganisms. Soil aggressivity is strongest if the moisture percentage is 25 to 50%.[3] Further increase in humidity does not increase soil aggressivity because the access of the oxygen from the air is impeded. Water and air permeability depend on the type of soil. Sandy soil is very permeable and clay soil is almost impermeable. An important feature of soil in regard to corrosion is its pH-value. The presence of humus created by the decomposition of organic matter lowers the pH-value because it contains humic acids that have a rather aggressive effect on metals. Soils containing sulphides or soluble salts (sulphates and chlorides) also exhibit increased aggressivity. Soil aggressivity also depends on the flow and composition of groundwater which is hazardous if it contains CO_2, chlorides or copper salts.[4] Iron objects can remain preserved for thousands of years if they are buried in soil in which oxygen and moisture inflow and the activity

1   D. Watkinson, M. B. Rimmer, F. Kergourlay 2013, 417.
2   Razlikujemo gusti korozijski sloj koji je pričvršćen za metalnu jezgru i vanjski voluminozni izmijenjeni sloj. Izmijenjeni sloj sastoji se od željeznih korozijskih produkata koji su nastali migracijom Fe^{2+} iona iz metalne jezgre i čestica tla. Izvorni oblik predmeta zadržan je u gustom korozijskom sloju. Gusti korozijski sloj sadrži a- FeO(OH) – getit, Fe_3O_4 – magnetit i Fe_2O_3 – hematit (D. Watkinson, M. B. Rimmer, F. Kergourlay 2013, 408).
3   I. Esih, Z. Dugi 1990, 131.
4   I. Esih, Z. Dugi 1990, 131.
5   Sulfat-reducirajuće bakterije su anaerobne bakterije koje reduciraju sulfate u sulfid. Biogena proizvodnja sulfida uzrokuje koroziju raznih tipova metala i

1   D. Watkinson, M. B. Rimmer, F. Kergourlay 2013, 417.
2   We distinguish between the thick corrosion layer that is attached to the metal core and the outer voluminous modified layer. The modified layer consists of iron corrosion products that are formed by the migration of Fe^{2+} ions from the metal core and soil particles. The original shape of the object is retained in a thick corrosion layer. The thick corrosion layer contains a-FeO(OH) – goethite, Fe_3O_4 – magnetite and Fe_2O_3 – hematite (D. Watkinson, M. B. Rimmer, F. Kergourlay 2013, 408).
3   I. Esih, Z. Dugi 1990, 131.
4   I. Esih, Z. Dugi 1990, 131.

predmeti mogu biti potpuno mineralizirani. Mineralizirani predmeti ne mogu se podvrći elektrolitičkoj koroziji što ih čini stabilnima od daljnje oksidacije osim ako ne dođe do transformacije korozijskih produkata. Predmeti koji zadržavaju metalnu jezgru podložni su stalnoj koroziji tijekom ukopa i brzoj elektrolitičkoj koroziji metalne jezgre nakon iskopa. Kloridi koji su se akumulirali u predmetu kako bi uravnotežili naboj Fe^{2+} iona predstavljaju najveći rizik za dugoročno očuvanje željeznih predmeta u muzejima.[6] Oni uzrokuju koroziju nakon iskopa. Nakon iskopa željezni predmeti izloženi su višoj koncentraciji kisika i nižoj razini vlažnosti zbog čega dolazi do sušenja kisele otopine željezovog klorida ($FeCl_2$) koja je nastala tijekom ukopa. Ta pojava stvara pukotine koje uzrokuju veće izlaganje metalne jezgre kisiku. Drugi problem uzrokovan kloridima jest nastajanje željezovog oksihidroksida β-FeO(OH) akaganeita. Akaganeit je mineral koji nastaje nakon iskapanja oksidacijom i hidrolizom otopine $FeCl_2$. Akaganeit je nestabilan korozijski spoj koji može osloboditi kloride u prisutnosti vlage i potaknuti daljnju koroziju. On je najproblematičniji željezni spoj u korozijskom sloju. Arheološki željezni predmeti zahtijevaju brzu obradu nakon iskapanja kako bi se akaganeit uklonio ili pretvorio u stabilniji spoj željeza. Raniji pokušaji da se spriječi korozija željeza nakon iskapanja, uključivali su primjenu visokih temperatura i kompletno uklanjanje korozijskih slojeva. Međutim, s vremenom se došlo do spoznaje da korozijski slojevi sadrže važne arheološke informacije. Kako visoke temperature mogu promijeniti metalografsku strukturu predmeta, razvili su se novi postupci kojima se uklanjaju kloridi na nižim temperaturama. Sredinom sedamdesetih godina prošlog stoljeća razvijena je alkalno-sulfitna metoda[7] koja se pokazala učinkovitom i danas ima široku primjenu u konzervaciji arheoloških željeznih predmeta.[8] Tijekom postupka dolazi do redukcije korozijskih komponenti što omogućuje pasivnu difuziju klorida iz predmeta.[9] Postupak je učinkovit u najvećem broju slučajeva. Ipak, teško je biti apsolutno siguran da se u predmetu i nakon uklanjanja klorida korozivni postupci neće nastaviti.

of sulphate-reducing bacteria is reduced.[5] Otherwise, when the corrosion is rapid, the objects can be completely mineralized. Mineralized objects cannot undergo electrolytic corrosion which makes them stable from further oxidation, unless the transformation of corrosion products occurs. The objects which retain the metal core are susceptible to constant corrosion during burial, and rapid electrolytic corrosion of the metal core after excavation. Chlorides accumulated in the object in order to balance the charge of Fe^{2+} ions pose the greatest risk for the long-term preservation of iron objects in museums.[6] They cause corrosion after excavation. After the excavation, iron objects are exposed to a higher oxygen concentration and lower humidity level, which causes the drying of an acidic solution of ferrous chloride ($FeCl_2$) which was formed during burial. This phenomenon creates cracks that cause greater oxygen exposure of the metal core. Another problem caused by chlorides is the formation of iron oxide-hydroxide β-FeO(OH) akaganeite. Akaganeite is a mineral formed after excavation by the oxidation and hydrolysis of $FeCl_2$ solution. Akaganeite is an unstable corrosion compound which can release chlorides in the presence of moisture and promote further corrosion. It is the most problematic iron compound in the corrosion layer. Archaeological iron objects require rapid processing after excavation to remove or convert akaganeite into a more stable iron compound. Previous attempts to prevent iron corrosion after excavation included the application of high temperatures and the complete removal of corrosion layers. However, over time, it became clear that corrosion layers contain important archaeological information. As high temperatures can change the metallographic structure of objects, new methods have been developed to remove chlorides at lower temperatures. In the mid-1970s, an alkaline-sulphite method[7] was developed which proved to be effective and is now widely used in the conservation of archaeological iron objects.[8] During the process, corrosion components are reduced, enabling passive diffusion of chloride from the object.[9] The procedure is effective in most cases. However, it is

---

njihovih legura u vodenim i kopnenim uvjetima. Iako su obligatni anaerobi, neke vrste toleriraju kisik i sposobne su rasti pri niskim koncentracijama kisika.

6   Kada je željezo izloženo vlazi tijekom ukopa, ono korodira elektrokemijskim procesom. Dolazi do anodne reakcije otapanja željeza na površini metala po jednadžbi $Fe_{(s)} \rightarrow Fe^{2+}_{(aq)} + 2e^-$. Istovremeno se događa katodna reakcija otapanja kisika $O_{2\,(g)} + 2H_2O + 4e^- \rightarrow 4\,OH^-$. Fe (II) ioni su otopljeni i akumulirani na površini metala i podvrgavaju se procesu hidrolize. Kako bi se održala električna neutralnost i uravnotežio naboj Fe^{2+} iona, dolazi do migracije Cl^- iona iz okoline. Konačna je posljedica korozije željeza tijekom ukopa da kisela otopina željezovog klorida ispunjava pukotine, pore i otvorene prostore unutar korozijskog sloja s Cl^- ionima koncentriranim na metalnoj površini (L. Selwyn 2004, 295).

7   Alkalno-sulfitnu metodu razvili su North i Pearson 1975. godine i prvo su je primijenili na željeznim predmetima iz mora. Kasnije se počela uspješno primjenjivati i na željeznim predmetima kopnene arheologije.

8   Iako ima široku upotrebu u konzervatorskoj struci, osim alkalno-sulfitnom metodom desalinizacija željeznih predmeta može se provesti i drugim metodama alkalnog ispiranja kao i elektrokemijskim postupcima.

9   L. Comensoli *et al.* 1917, 2.

---

5   Sulphate-reducing bacteria are anaerobic bacteria that reduce sulphate to sulphide. The biogenic production of sulphides causes corrosion in various types of metals and their alloys in water and land conditions. Although they are obligate anaerobes, some species tolerate oxygen and are able to grow at low oxygen concentrations.

6   When iron is exposed to moisture during burial, it corrodes by the electrochemical process. An anodic reaction of iron dissolving on the metal surface occurs according to the equation $Fe_{(s)} \rightarrow Fe^{2+}_{(aq)} + 2e^-$. At the same time, a cathodic oxygen dissolution reaction $O_{2\,(g)} + 2H_2O + 4e^- \rightarrow 4\,OH^-$ occurs. Fe (II) ions are dissolved and accumulated on the surface of the metal and they undergo hydrolysis. In order to maintain electrical neutrality and balance the charge of Fe^{2+} ions, the migration of Cl^- ions from the environment occurs. A final consequence of iron corrosion during burial is that the acid solution of ferric chloride fills cracks, pores, and open spaces within the corrosion layer and the Cl^- ions concentrated on the metal surface (L. Selwyn 2004, 295).

7   The alkaline-sulphite method was developed by North and Pearson in 1975 and was first applied to iron objects from the sea. Later it was successfully applied to the iron objects of terrestrial archeology.

8   Although widely used in the conservation profession, the desalination of iron objects can be carried out by alkaline-sulphite method, and by other alkaline rinsing methods as well as by electrochemical methods.

9   L. Comensoli *et al.* 1917, 2.

MEHANIZAM DJELOVANJA ALKALNO-SULFITNE OTOPINE

Alkalno-sulfitni postupak odvija se pri visokoj pH-vrijednosti. Koristi se natrijeva lužina (NaOH) i natrijev sulfit (Na_2SO_3). Kloridi će difundirati iz željeza u otopinu samo ako je korozija željeza zaustavljena ili usporena. Ako željezo i dalje korodira u otopini, kloridi neće difundirati jer će ih privlačiti Fe^{2+} nastali u korozivnom procesu. Korozija željeza zaustavlja se ili usporava pasivacijom željezne površine djelovanjem natrijeve lužine[10] i uklanjanjem otopljenog kisika djelovanjem natrijevog sulfita[11]. Time se stvaraju povoljni uvjeti za ekstrakciju klorida koji se oslobađaju svoje uloge kontraiona i olakšava se njihova difuzija u otopinu. Glavna pokretačka sila za uklanjanje klorida iz arheološkog željeza jest difuzija.[12] Sposobnost klorida da difundiraju u otopinu ovisi o poroznosti korozijskog sloja. Ako kloridi ostanu zarobljeni u područjima pod nepropusnim materijalom, neće moći difundirati. U tom slučaju postoji opasnost od korozivnih procesa koji bi se mogli dogoditi ako dođe do otvaranja tunela u tim nepropusnim područjima te ulaska vode i kisika. Poroznost korozivnog sloja može se povećati zagrijavanjem otopine za obradu, pa se otopina alkalnog sulfita zagrijava na 50 °C. U alkalnim otopinama topljivost oksihidroksida raste s porastom temperature. Tijekom alkalno-sulfatnog postupka dolazi do redukcije željezovog oksihidroksida FeO(OH) u magnetit Fe_3O_4 pri čemu se otvaraju pore u korozivnom sloju dozvoljavajući brzu difuziju klorida u otopinu. Alkalno-sulfitni postupak učinkovit je na željeznim predmetima koji su umjereno do jako korodirani i koji imaju očuvanu metalnu jezgru. U protivnom bi se mogli raspasti tijekom postupka.

PROVEDBA ALKALNO-SULFATNOG POSTUPKA

Za provedbu alkalno-sulfatnog postupka koristi se posebna kupelj izrađena od nehrđajućeg čelika. Kupelj je opremljena grijačima, protočnom pumpom, termostatom i pokazivačem temperature. Nakon fotografiranja i dokumentiranja predmeti se mehanički očiste da bi se uklonili tragovi pijeska i zemlje. Kako se predmeti i njihovi ulomci ne bi pomiješali, izoliraju se u polipropilenske mrežice koje se označavaju plastičnim trakicama s odgovarajućom signaturom (sl. 1). Ako željezni predmeti imaju dijelove izrađene od drugog materijala, npr.

difficult to be absolutely certain that corrosion processes will not continue even after the removal of chloride.

THE MECHANISM OF ACTION OF ALKALINE-SULPHITE SOLUTION

The alkaline-sulphite treatment is carried out at high pH-value. Sodium hydroxide (NaOH) and sodium sulphite (Na_2SO_3) are used. Chlorides will diffuse from the iron into solution only when the corrosion of the iron is stopped or slowed down. If the iron still corrodes in the solution, the chlorides will not diffuse because they will be attracted by the Fe^{2+} formed in the corrosive process. The corrosion of iron is stopped or slowed down by the passivation of the iron surface by the action of sodium hydroxide[10] and the removal of the dissolved oxygen by the action of sodium sulphite.[11] This creates favorable conditions for the extraction of chlorides, which are released from their role of counterions, and it facilitates their diffusion into the solution. The main driving force for the removal of chloride from the archaeological iron is diffusion.[12] The ability of chlorides to diffuse into solution depends on the porosity of the corrosion layer. If chlorides remain trapped in areas under impermeable material, they will not be able to diffuse. In this case, there is a risk of corrosive processes which could occur if tunnels open in these impermeable areas and if the water and oxygen enter. The porosity of the corrosive layer can be increased by heating the treatment solution, so the alkaline-sulphite solution is heated to 50°C. In alkaline solutions, the solubility of oxyhydroxide increases with the increase of temperature. During the alkaline-sulfate process, the iron oxide-hydroxide FeO(OH) is reduced to magnetite Fe_3O_4 whereby the pores in the corrosive layer are opened, allowing the rapid diffusion of chloride into the solution. The alkaline-sulphite treatment is effective on iron objects that are moderately to strongly corroded and which have a preserved metal core. Otherwise, they could fall apart during the procedure.

CARRYING OUT AN ALKALINE-SULPHATE TREATMENT

A special stainless-steel bath is used to perform the alkaline-sulphate treatment. The bath is equipped with heaters, a flow pump, a thermostat and a temperature gauge. After the photographing and documenting, the objects are mechanically cleaned to remove traces of sand and earth. In order to evade mixing the objects and their fragments, they are insulated with polypropylene meshes which are marked with plastic

---

10   Natrijeva lužina na anodnim mjestima neutralizira kiselinu koja se stvara hidrolizom Fe^{2+} iona, taloži Fe^{2+} kao $Fe(OH)_2$, osigurava veliku količinu OH^- iona da nadvladaju Cl^- ione na anodnim mjestima i oslobode ih uloge u balansiranju naboja. Isto tako imaju ulogu da zamijene kloridne ione na površini korozijskih produkata, posebno β-FeOOH (D. Watkinson, M. B. Rimmer, F. Kergourlay 2013, 413).

11   Sulfitni ioni SO_3^{2-} djeluju kao hvatači kisika. Kemijska reakcija kojom se uklanja kisik prikazana je kemijskom jednadžbom $2Na_2SO_3(aq) + O_2(g) \rightarrow 2Na_2SO_4(aq)$ (L. Selwyn 2004, 299).

12   Difuzija – proces spontanog kretanja čestica iz područja više koncentracije u područje niže koncentracije.

10   Sodium hydroxide on anode sites neutralizes the acid generated by hydrolysis of Fe^{2+} ions, deposits Fe^{2+} as $Fe(OH)_2$, provides a large amount of OH^- ions to overpower the Cl^- ions at anode sites and release them from the role of balancing the charge. They have a role in replacing the chloride ions on the surface of corrosion products, especially β-FeOOH (D. Watkinson, M. B. Rimmer, F. Kergourlay 2013, 413).

11   Sulphite ions SO_3^{2-} act as oxygen traps. The chemical reaction which removes oxygen is shown by the chemical equation $2Na_2SO_3(aq) + O_2(g) \rightarrow 2Na_2SO_4(aq)$ (L. Selwyn 2004, 299).

12   Diffusion – the process of spontaneous particle movement from a region of higher concentration to a region of lower concentration.

DESALINIZACIJA ARHEOLOŠKIH ŽELJEZNIH
PREDMETA ALKALNO-SULFITNIM POSTUPKOM

DESALINATION OF ARCHAEOLOGICAL IRON
OBJECTS BY ALKALINE-SULPHITE TREATMENT

567

JOSIPA LOVRIĆ

Slika 1. Pripremljeni željezni predmeti za alkalno-sulfitni postupak
Figure 1. Iron objects prepared for alkaline-sulphite treatment
foto / photo by: **J. Lovrić**

od kosti ili drva, na njih se nanosi zaštitni premaz koji ih štiti od djelovanja otopine alkalnog sulfita.[13] Treba pripremiti 50 litara 0,5 M otopine natrijevog hidroksida i 0,5 M[14] otopina natrijevog sulfita. Za pripremu otopine koristi se demineralizirana voda. Predmeti se poslože u kupelj koju se napuni pripremljenom otopinom do vrha (sl. 2). Uključi se protočna pumpa i prilagodi temperatura na 50 °C. Budući da je otopina jako alkalna (pH 13), treba izbjegavati kontakt s kožom. Kako je glavna pokretačka sila za uklanjanje klorida iz željeznih predmeta difuzija, potrebno je mijenjati otopinu u intervalima da bi se održao visoki gradijent difuzije između razine klorida u predmetu i razine klorida u otopini. U postupku će se izmijeniti devet kupki. Prva kupka mijenja se nakon 15 dana, a poslije jednom mjesečno. Duljina postupka određuje se praćenjem koncentracije klorida koji difundiraju u otopinu, pa se pri svakoj izmjeni uzima uzorak otopine u kojem se određuje koncentracija klorida. Postupak se obično smatra završenim kada je sadržaj klorida u otopini manji od 5 mg/l.[15] Nakon završetka alkalno-sulfitnog postupka predmeti se ispiru velikim količinama demineralizirane vode koja se također zagrijava na temperaturu od 50 °C i mijenja svakih sedam dana sve dok otopina ne postane neutralna (pH 7).

strips with appropriate signatures (Fig. 1). If parts of iron objects are made of other material, such as bone or wood, a protective coating is applied to protect them from the action of the alkaline-sulphite solution.[13] 50 liters of 0.5 M sodium hydroxide solution and 0.5 M[14] sodium sulphite solution should be prepared. Demineralized water is used to prepare the solution. The objects are placed in a bath filled to the top with the prepared solution (Fig. 2). The flow pump is turned on and the temperature is adjusted to 50°C. Because the solution is very alkaline (pH 13), skin contact should be avoided. Since diffusion is the main driving force for the removal of chloride from iron objects, it is necessary to change the solution in intervals in order to maintain a high diffusion gradient between the chloride level in the object and the chloride level in the solution. Nine baths will be interchanged in the process. The first bath is changed after 15 days and once a month afterwards. The length of the process is determined by monitoring the concentration of chlorides diffusing into the solution, so a sample of the solution is taken with each change to determine the concentration of chloride. The process is usually considered complete when the content of chloride in the solution is less than 5mg/l.[15] After the completion of the alkaline-sulphite process, the objects are rinsed with large quantities of demineralized water, which is also heated to a temperature of 50°C and changed every seven days until the solution becomes neutral (pH 7).

---

13   Kao zaštitni premaz koristi se *Cyclododecan*. On je na višim temperaturama tekući, a hlađenjem se stvara čvrsti zaštitni sloj koji štiti prekriveno mjesto od djelovanja kemikalija (M. Mustaček 2012, 172).

14   0,5 M otopine su otopine koje imaju množinsku koncentraciju 0,5 mol/dm³. U jednoj litri otapala treba biti otopljeno 0,5 mola natrijevog hidroksida i 0,5 mola natrijevog sulfita. Iz formule za molekulsku masu M = m/n dobiva se 20 g natrijevog hidroksida i 63 g natrijevog sulfita.

15   Predmeti s nepotpunim tretmanom (> 5 mg/l u konačnoj otopini) vjerojatno će biti nestabilni, dok je 93 % predmeta tretiranih s < 5 mg/l pokazalo stabilnost. Ovo naglašava važnost mjerenja ekstrakcije klorida tijekom postupka i nastavka ekstrakcije sve dok razina klorida u otopini ne bude niska (D. Watkinson, M. B. Rimmer, Q. Wang 2013, 333).

13   *Cyclododecan* is used as a protective coating. It turns into liquid at higher temperatures and, by cooling, creates a solid protective layer that protects the covered site from chemicals (M. Mustaček 2012, 172).

14   0.5 M solutions are solutions that have a molar concentration of 0.5 mol/dm³. 0.5 M of sodium hydroxide and 0.5 M of sodium sulfite should be dissolved in one liter of solvent. From the formula for molecular weight M = m/n, 20g of sodium hydroxide and 63g of sodium sulphite are obtained.

15   Objects with incomplete treatment (> 5 mg/l in the final solution) were likely to be unstable, while 93% of objects treated with <5 mg/l showed stability. This emphasizes the importance of measuring chloride extraction during the process and continuing the extraction until the chloride level in the solution is low (D. Watkinson, M. B. Rimmer, Q. Wang 2013, 333).

Slika 2. Kupelj za alkalno-sulfitni postupak
Figure 2. Alkaline-sulphite bath
foto / photo by: **J. Lovrić**

ODREĐIVANJE KONCENTRACIJE KLORIDA

Koncentracija klorida u uzorku mjerena je automatskim potenciometrijskim titratorom. Temeljni princip potenciometrijske titracije određivanje je nepoznate koncentracije ispitivane otopine titracijom nekom standardnom otopinom pri čemu nagla promjena potencijala indikatorske elektrode ukazuje i određuje završnu točku titracije. Određivanje klorida u uzorku na ovom instrumentu određuje se povratnom titracijom.[16] U uzorak se dodaje višak otopine srebrovog nitrata i titrira otopinom kalijevog klorida dok se ne postigne završna točka titracije (sl. 3). Najviša koncentracija klorida izmjerena je na početku i iznosila je 95,67 mg/l. Najniža koncentracija izmjerena je kod zadnje izmjene kupke i iznosila je 4,3 mg/l (sl. 4). Oslobađanje klorida tijekom alkalno-sulfitnog postupka može se pratiti na grafikonu (graf. 1).

DETERMINATION OF CHLORIDE CONCENTRATION

The concentration of chloride in the sample was measured by an automatic potentiometric titrator. The basic principle of potentiometric titration is to determine the unknown concentration of the tested solution by the titration with a standard solution, where a sudden change in the potential of the indicator electrode indicates and determines the end point of the titration. The determination of chloride in the sample by this instrument is determined by reverse titration.[16] An excess of silver nitrate solution is added to the sample and it is titrated with the potassium chloride solution until the end point of the titration is reached (Fig. 3). The highest chloride concentration of 95.67 mg/l was measured at beginning. The lowest concentration of 4.3 mg/l was measured at the final bath change (Fig. 4). The release of chloride during the alkaline-sulphite process can be monitored on the graph (Chart 1).

---

16 U povratnoj titraciji upotrebljavaju se dva reagensa. Prvi reagens (A) reagira s izvornim uzorkom, a drugi reagens (B) reagira s prvim reagensom. Prvo se precizno izmjeren višak reagensa A poznate koncentracije dodaje uzorku. Nakon što reakcija završi, preostali višak reagensa A povratno se titrira s drugim reagensom B. Razlika između dodanog iznosa prvog i drugog reagensa daje ekvivalentnu količinu analita (tvari koje se određuje). U ovom slučaju reagens A otopina je srebrovog nitrata koja se dodaje u uzorak kako bi se istaložili svi kloridi u uzorku, a njezin višak određuje se tako da se povratno titrira s reagensom B, a to je otopina kalijevog klorida. Kako je uzorak lužnat, potrebno ga je zakiseliti koncentriranom nitratnom kiselinom.

16 Two reagents are used in the reverse titration. The first reagent (A) reacts with the original sample and the second reagent (B) reacts with the first reagent. First, the accurately measured excess of the reagent A of a known concentration is added to the sample. After the reaction is complete, the remaining excess of reagent A is reverse titrated with the second reagent B. The difference between the added amount of the first and second reagents gives an equivalent amount of analyte (the substance which is being determined). In this case, the reagent A is a solution of silver nitrate which is added to the sample to precipitate all chlorides in the sample and its excess is determined by back titrating with reagent B, which is a solution of potassium chloride. Since the sample is alkaline, it must be acidified with concentrated nitric acid.

Slika 3. Mjerenje koncentracije klorida na potenciometrijskom titratoru
Figure 3. Chloride concentration determination by a potentiometric titrator   **foto** / photo by: **J. Lovrić**

```
877 Titrino plus          22324   5.877.0025
2019-08-28 08:32:51

RESULT REPORT
Method                MET U         Kloridi
Determination time   2019-08-28 08:29:05
Duration of determination          223.7 s
Sample number                            1
Sample size                          1.0 g

EP1        49.3 mV               24.8790 mL
           198.0 s                  ERC 99.8
Manual stop
Kloridi                          4.30 mg/L
```
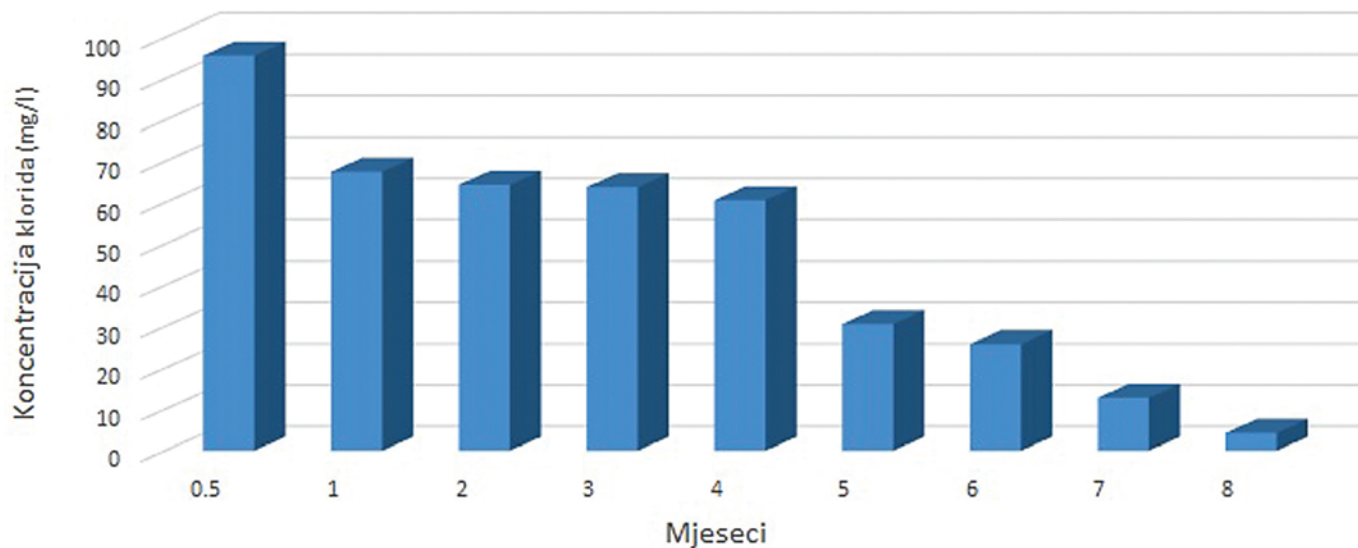
Slika 4. Najniža izmjerena koncentracija klorida u uzorku
Figure 4. The lowest determined concentration of chloride in the sample

foto / photo by: **J. Lovrić**

Grafikon 1. Oslobađanje klorida u alkalno-sulfitnom postupku
Chart 1. Chloride release in alkaline-sulphite treatment   **izradila** / made by: **J. Lovrić**

ZAKLJUČAK

Teško je spriječiti korozijske procese na željeznim predmetima koji nisu desalinizirani. Da bi se potpuno izbjegla aktivna korozija željeznih predmeta, relativna vlažnost mora biti ispod 11 %.[17] Pri toj vrijednosti smanjuje se kondenzacija vodene pare u porama korozijskih produkata i sprječava da higroskopne soli povuku vlagu i potaknu koroziju. Samo oni željezni predmeti kojima su uklonjeni kloridi oduprijet će se korozijskim procesima prilikom pohranjivanja i izlaganja u muzejskim prostorima. Alkalno-sulfitni postupak jedan je od često korištenih postupaka kojim se uklanja velika količina topljivih klorida. Iako se njime ne mogu u potpunosti ukloniti svi kloridi jer dio zaostaje unutar akaganeitne strukture, ovaj postupak značajno produljuje vijek trajanja željeznih predmeta.

CONCLUSION

It is difficult to prevent corrosion processes on iron objects that are not desalinated. In order to completely avoid the active corrosion of iron objects, the relative humidity must be below 11%.[17] This value reduces the condensation of water vapor in the pores of the corrosion products and prevents the hygroscopic salts from drawing in moisture and promoting corrosion. Only those iron objects in which chlorides have been removed will resist corrosion processes when stored and exhibited in museum spaces. The alkaline-sulphite treatment is one of the frequently used methods which removes a large amount of soluble chlorides. Although all chlorides cannot be completely removed because a portion of them remains within the akaganeite structure, this process significantly extends the life of the iron objects.

Literatura / Bibliography

Comensoli, L., Maillard, J., Albini, M., Sandoz, F., Junier, P., Joseph, E. 2017 – Use of Bacteria To Stabilize Archaeological Iron, *Applied and Environmental Microbiology* 83 (9), 1–14, https://www.ncbi.nlm.nih.gov/pmc/articles/PMC5394308/ (17. 9. 2019).

Esih, I., Dugi, Z. 1990 – *Tehnologija zaštite od korozije*, Zagreb.

Hamilton, D. L. 1999 – *Methods of Conserving Archaeological Material from Underwater Sites*, Texas.

Jegdić, B., Polić-Radovanović, S., Ristić, S., Alil, A. 2011 – Corrosion Processes, Nature and Composition of Corrosion Products on Iron Artefacts of Weaponry, *Scientific Technical Review* 61 (2), Beograd, 50–56.

Jegdić, B., Polić-Radovanović, S., Ristić, S., Alil, A. 2012 – Corrosion stability of corrosion products on an archaeological iron artefact, *International journal conservation science* 3 (4), Beograd, 241–248.

Jegdić, B., Polić-Radovanović, S., Ristić, S., Alil, A., Rajković-Ognjanović, V. 2012 – Corrosion of an archaeological find from the roman period in Serbia, *Zaštita materijala* 53, Beograd, 247–252.

Mustaček, M. 2012 – Konzerviranje i restauriranje željeznih arheoloških nalaza s nalazišta utvrde Čanjevo, *Portal: godišnjak Hrvatskog restauratorskog zavoda* 3, Zagreb, 171–180.

Rimmer, M., Thickett, D., Watkinson, D., Ganiaris, H. 2013 – *Guidelines for the Storage and Display of Archaeological Metalwork*, London.

Rimmer, M., Watkinson, D., Wang, Q. 2012 – The efficiency of chloride extraction from archaeological iron objects using deoxygenated alkaline solutions, *Studies in Conservation* 57, London, 29–41.

Rimmer, M. B. 2010 – *Investigating the treatment of chloride-infested, arcaelogical iron objects*, disertacija (neobjavljeno), Cardiff University, Cardiff, https://pdfs.semanticscholar.org/4e96/b6d25adb4974792816af74b7111c2da48e90.pdf (17. 9. 2019).

Selwyn, L. 2004 – Overview of archaeological iron: the corrosion problem, key factors affecting treatment, and gaps in current knowledge, in: Ashton, J., Hallam, D. (eds.), *Metal 04, Proceedings of the International Conference on Metals Conservation*, 4-8 October 2004, Canberra, 294–306,

https://www.nma.gov.au/__data/assets/pdf_file/0008/346058/NMA_metals_s3_p06_overview_archaeological_iron.pdf (17. 9. 2019.).

Wang, Q. 2007 – Effescts of relative humidity on the corrosion of iron: an experimental view, *The British Museum Tehnical Research Bulletin* 1, London, 65–73.

Wang, Q. 2007 – An investigation of deterioration of archaeological Iron, *Studies in Conservation* 52 (2), London, 125–134.

Watkinson, D., Rimmer, M. B., Kergourlay, F. 2013 – Alkaline desalination techniques for archaeological iron, *Corrosion and Conservation of Cultural Heritage Metallic Artefacts* 65, Oxford – Cambrige – Philadelphia – New Delhi, 407–433.

Watkinson, D., Rimmer M. B., Wang, Q. 2013 — The impact of chloride desalination on the corrosion rate of archaeological iron, *Studies in Conservation* 58 (4), London, 326–337.

17   M. Rimmer *et al.* 2013, 10.

17   M. Rimmer *et al.* 2013, 10.