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Archaeological Iron Conservation Colloquium 2010

Extended Abstracts

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DBU Deutsche Bundesstiftung Umwelt

Extended Abstracts

Session 3:

Alkaline Chloride Extraction

EFFICIENCY OF CHLORIDE EXTRACTION WITH ORGANIC AMMONIUM BASES: THE KUR-PROJECT "CONSERVATION AND PROFESSIONAL STORAGE OF IRON ARTIFACTS"

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Introduction

The Project "Conservation and Professional Storage of Iron Artifacts" has been launched by the Landesamt für Denkmalpflege Sachsen-Anhalt, Landesmuseum für Vorgeschichte Halle to ensure the long term conservation of our meaningful collection of archaeological iron artifacts. As part of the "KUR-Project" it is supported by the german Kulturstiftung des Bundes and Kulturstiftung der Länder.

The project work includes the practical conservation of our collection of iron artifacts, dating between the 10th century BC and the 16th century AD. Most of the about 3500 finds were excavated 50-150 years ago. The collection has been stored at uncontrolled conditions until now and many finds – restored or untreated - corroded after their excavation. A wide range of corrosion phenomena, typical for post excavation corrosion, can be observed. Our challenge now is the conservation of a large amount of iron objects, a well known problem to many archaeological collections throughout Europe.

The centre of the project´s research activities, which are conducted in cooperation with the State Academy of Art and Design Stuttgart and the University of Stuttgart, is the evaluation of a new desalination method, to enable an effective improvement of the corrosion stability of the iron finds by extracting chloride ions within the corrosion layers, which catalyse ongoing corrosion processes after excavation.

Desalination of iron artifacts with organic quaternary ammonium hydroxides

Although it is well known, that chloride extraction methods considerably improve the corrosion stability of treated archaeological iron artifacts (e. g. Keene and Orton 1985), particularly long treatment times require further ameliorations of established methods.

A desalination treatment in solutions based on organic solvents can be expected to be faster and more effective than aqueous methods, due to the lower surface tension of such solutions, resulting in better wetting abilities. Besides, no further corrosion of the artifacts has to be expected during treatment in waterless solutions (Watkinson 1982).

To shift the currently accepted desalination processes in alkaline, aqueous media to water free solutions, a hydroxide is needed, which shows a sufficient solubility in organic solvents, and also forms a sufficiently soluble chloride salt.

Research activities

Within the project solutions of tetra-methyl ammonium hydroxide (TMAH) in methanol and/or water are tested as an alternative to the common alkali hydroxide based desalination procedures (e. g. Watkinson 1982, Al Zahrani 1999).

Desalination experiments are conducted using roman nails as test objects. Different concentrations of TMAH in water, methanol, and mixtures of both are compared to the commonly used alkaline sulphite solution. Residual chloride in the test objects, as well as chloride washed into solution, is determined. The behaviour of objects in the tested solutions is monitored weekly by visual surveys, to observe possible ongoing corrosion processes or the partial dismantling of corrosion layers during the process.

Additionally, the insoluble, chloride containing corrosion product akaganéite, β-FeO(OH), has been synthesised and is treated in corresponding desalination solutions. Original and residual chloride content of the solid is also determined and possible phase transformations are surveyed using X-ray diffraction.

First results

First desalination experiments on synthetic akaganéite indeed show, that chloride extraction is basically possible in methanolic, as well as aqueous tetra-alkyl ammonium hydroxide solutions.

Perspective

Further experiments on akaganéite and archaeological artifacts will be carried out, to allow quantitative comparison of the efficiency of solutions of varying concentrations and solvent contents.

Acknowledgements

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THE USE OF SUBCRITICAL ALKALINE SOLUTIONS FOR THE STABILIZATION OF ARCHAEOLOGICAL IRON ARTIFACTS

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New technology for the stabilization of archaeological iron using subcritical fluids has been tested over the last six years at the Clemson Conservation Center. This technique originated from the extensive research carried out in the industrial world with sub and supercritical fluids for waste oxidation, radioactive waste reduction and other chemical reactions and synthesis.

Water heated under the appropriate pressure above its atmospheric boiling temperature of $100^{\circ}C$ and under its critical temperature (Tc) of $374^{\circ}C$ and pressure (Pc) of 221 bar is referred to as subcritical water. Above this temperature and pressure water becomes supercritical; that is, it exhibits properties between those of a liquid and a gas. For practical reasons, it was decided to remain within the subcritical region for the purposes of treating archaeological iron, and define a working temperature as low as possible to avoid alteration of the metallographic structure of the iron. In order to define the optimal operating temperature, experiments were conducted within the temperature range of 130 to $230^{\circ}C$ with a pH between 11.6 and 13.1. These temperatures and pH range were selected while taking into account the practical considerations of treating very large artifacts and the likely effectiveness of the treatment. Based on these results, it was decided to undertake treatment of the iron at $180^{\circ}C$ at a pH of 13.1, using 0.5% w/w sodium hydroxide (NaOH).

The reasoning behind using an alkaline liquid at subcritical conditions, for the treatment of chloride-ridden iron artifacts was that the treatment time would be significantly reduced due to the following reasons:

- The increase in temperature of the solution would result in a significant increase in the chloride diffusion constants.
- The decrease in the viscosity and density of the treatment solution would improve the diffusion of hydroxide ions into the corrosion layers and promote a more effective chloride exchange.

- The decrease in the surface tension of the solution would improve its wettability and capacity to penetrate the interstices of the corrosion layers.

A typical treatment using this technique involves the following steps: once the object is placed inside the pressure vessel, the chamber is filled with a solution of sodium hydroxide and air is purged from the system. Pressure is maintained at approximately 50 bar and the solution is gradually heated until it reaches 180°C. The flow of the solution during treatment is adjusted according to the size of the chamber. The eluent solution is regularly sampled in order to determine the chloride concentration at any given time of the treatment, as well as to calculate the total concentration of chlorides.

To date, over 150 experiments have been conducted at the Clemson Conservation Center using wrought and cast iron archaeologizal samples from marine and terrestrial sites as well as synthetic iron oxides. Most of the initial trials were conducted on a relatively small scale using 40 and 600 ml pressure vessels (Fig.1). The small size of these vessels has restricted the size of the samples and artifacts that can be treated using this technique. So far, hundreds of samples and relatively small artifacts have been successfully treated. These include rivets, nuts and bolts, tools and nails. Recently, a 40-liter reactor was designed and built to enable the treatment of larger artifacts such as ballast blocks from the *H.L. Hunley submarine* (1864), and other large and more complex artifacts and samples from both marine and terrestrial sites (Fig.2).
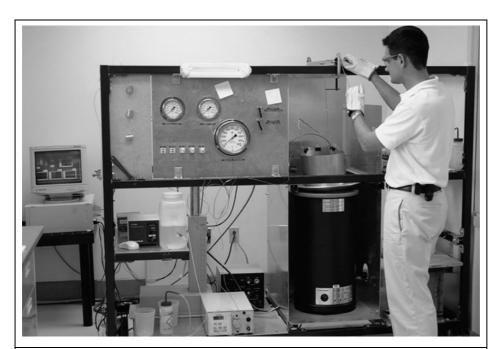

Figure 1. Research engineer Nestor Gonzalez operating the first generation subcritical reactor at the Warren Lasch Conservation Laboratory.

Figure 2. Research engineer Nestor Gonzalez and conservator Liisa Nasanen operating the second generation 40-L subcritical reactor.

The chloride release rates using the subcritical technique were found to be significantly higher and treatment times much shorter than those observed using electrolytic treatment. None of the treatments using this technique have exceeded 10 days, compared to over 6 months of treatment using traditional methods on some of the cast iron specimens.

During the first years of experimentation with this technique, chemical digestion of the specimen was used to determine the total amount of chloride remaining in the metal after treatment. The residual chloride levels in the treated samples were also found to be at least as low as chloride levels in those treated by electrolysis. In addition, no damage was observed to the graphitized layer on the cast iron samples, and the long-term stability for all of the subcritical treated specimens appears to be very good. Moreover, recent work has shown that the chlorinated oxyhydroxide phase akaganéite (β-FeOOH), thought to be responsible for the long-term instability of iron, was completely transformed into more stable corrosion products such as goethite, magnetite and hematite. These results are particularly encouraging for the stabilization of terrestrial artifacts where akaganéite is often found.

In these experiments undertaken at the Clemson Conservation Center, the subcritical technique effectively removed very high levels of entrapped chloride ions from terrestrial and marine iron objects in very short periods of time. While it is true that continuing research and development of the subcritical technique will require considerable investment, the potential is great for reducing the long-term costs associated with lengthy conservation treatments and expensive environmentally controlled post-excavation storage options. The capacity for this treatment to significantly assist the conservation community with the mass-treatment and long-term stabilization of archaeological iron may result in considerable savings both in terms of treatment time and cost of treatment.

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SOME NEW ADVANCES IN ALKALINE SULPHITE TREATMENT OF ARCHAEOLOGICAL IRON

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Introduction

We assume that condition of most archaeological iron finds can be correlated to one of the oxidation stages that we describe in our table "Degree of ironwork oxidation". This table is based on the analogous one that was proposed by J.M. Cronyn (Cronyn 1990: 183). For marine ironwork, we propose a similar one for archaeological iron. Our table includes some data of oxide films and corrosion crusts formation at each oxidation stage, and also a short description of permissible conservation treatments. According to our table from a conservation point of view the most problematic are iron objects of the IIIrd and IVth oxidation stages. At these stages the artifacts have already undergone a considerable mineralization and their original surface has been hidden by corrosion products. But these objects still have a sound metal core that continues to corrode and provoke flaking of the mineral crust. Finally the objects lose their shape and cannot be considered as historical artifact any more. We examined a number of mineral crusts of different archaeological iron objects with a scanning microscope. We found that the inner structure of mineral crusts of buried archaeological iron is uneven and non-regulated, cracked and capillary. Chloride-containing compounds are concentrated at goethite dominating iron oxyhydrates zones, and at metal – mineral crust interface. Presence of chloride has not been detected within magnetite zones. It is evidence of good protective properties of magnetite, but unfortunately it does not produce a smooth layer.

Problem formulation

The alkaline sulphite method for archaeological iron was proposed by N.A. North and C. Pearson (1975) for desalination of marine iron. They reported that the final product of the treatment is mixed iron oxide Fe_3O_4, magnetite. However N.A. North and C. Pearson did not describe thermodynamics of the process. Later M. Gilberg and N.J. Seeley (1981: 50-56) revealed that the magnetite formation is more complicated process than it was described by previous authors. In 1989 in the Institut de Recherches et de Restoration Archeologiques et Paleometallurgiques in France 107 Iron age axes were treated with the alkaline sulphite

method. After two years 27 of them showed new corrosion– pustules and craters have appeared (Beaudoin et al. 1997: 170-177). We decided to analyze once again the sequence of the chemical transformations that take place during the alkaline sulphite treatment of archaeological iron. We calculated chemical processes that take place during immersion of iron objects to alkaline sulphite solution (stage 1) and during washing out after immersion in distilled water (stage 2).

Experimental

Stage 1. When the alkaline sulphite solution reaches pores of the mineral crust it reacts with oxygen and takes it up. As a result the solution penetrates deeper into the pores:

$$2SO_3^{2-} + O_2 = 2SO_4^{2-} \tag{1}$$

At the same time Fe^{3+} cations get reduced to Fe^{2+} cations:

$$2Fe^{3+} + SO_3^{2-} + 6OH^- = SO_4^{2-} + 2Fe(OH)_2 + H_2O \tag{2}$$

According to thermodynamic calculations if in the solution both Fe^{3+} and Fe^{2+} are present, there is a high possibility for magnetite formation:

$$2Fe(OH)_2^+ + SO_3^{2-} + Fe(OH)^+ + 5OH^- = Fe_3O_4 + SO_4^{2+} + 5H_2O \tag{3}$$

This conclusion has been proved with experimental data. The pH of the solution falls from 10.4 to 8.8 but does not reach a critical value lower 7.

Stage 2. During the washing out procedure of the object after alkaline sulphite treatment concentration of iron (III) hydroxide ions increases, the reaction as follow can take place:

$$4Fe(OH)_2 + O_2 + (2n-4)H_2O \rightarrow 2(Fe_2O_3 \cdot nH_2O) \tag{4}$$

The presence of soluble Fe^{3+} and Fe^{2+} ions again is favorable for magnetite formation.

$$Fe(OH)_2 + Fe_2O_3 \cdot nH_2O \rightarrow Fe_3O_4 + (n+1) H_2O \tag{5}$$

According to experimental data:

- the total number of chlorides that were extracted during alkaline sulphite treatment is 10.52 times higher than those extracted during intensive washing in distilled water.

 - the mechanism of chloride ions extraction from the object happens due to diffusion and concentrations smoothening according to osmosis law. During washing out procedure the pH of the solution decreases. Washing out of the working solution (together with chloride anions) works only for not deep strata of the mineral crust, because the hydrolysis products $(Fe(OH)_3)$ block pores of the mineral crust when pH is lower than ~ 7. It means that some chloride anions are stuck within the object. This fact, together with long-term treatment itself, gives some disadvantages for this method.

To increase extraction of chloride ions and to shorten treatment time of objects we applied an ultrasonic field to the bath. During our experiment first we used samples to select a suitable regime, and then applied it to archaeological objects. Treatment time for objects in ultrasonic bath worked out 1-5 minutes every day during three days, depending object's size. Washing out the working solution till pH= 7 took only 5 minutes.

Conclusions

Ultrasonic waves intensify the reduction ability of the solution: the concentration of iron (II) cations increases, and consequently the output of magnetite from chemical reactions also increases. Moreover, in the ultrasonic field liquid degasification and colloids dispersion take place: altogether they favorably affect the penetration ability of the solution and washing water. The treated objects were tested with a scanning microscope. Chloride anions in the mineral crust and at the metal – mineral crust interface were not detected. However using ultrasonic bath in alkaline sulphite treatment has some disadvantages: wrong calculations of immersion time and cavitation energy can provoke the mineral crust to ruin. Objects that have fragile and badly adhered mineral crust also cannot be treated in the alkaline sulphite solution. To protect completeness of objects we propose to use gauze bandages that support fragile areas of mineral crusts. We fix these bandages with Paraloid B-72 glue. The testing shows that polymer films created with Paraloid B-72 do not affect seriously the penetration ability of the alkaline solution, and danger of mineral crust ruining is negligible. Thus we can conclude that nowadays the alkaline sulphite treatment completed with ultrasonic treatment is the most effective method for archaeological iron objects stabilization. For the first time this method has been successfully used in Russia for about ten years for archaeological iron finds from the Russian North and some regions of Siberia, both just after archeological dig and after long-term storage. A condition check of these objects did not detect corrosion renewal.

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DEGREE OF IRONWORK OXIDATION

Oxidation stage	Corrosion environment	Corrosion products appearance	Corrosion layer formation	Oxidation process	Oxidation products	Degree of conservation treatment
I	Atmospheric		Film formation	Formation of the primary oxide film that works as a protective layer. Very thin and transparent in the beginning, it gets thicker with the time and turns black or dark brown.	Black thin layer of FeO possibly through Fe_2O_3 (hematite) turns to Fe_3O_4 (magnetite).	The artifacts do not require any cleaning. Conservation coating is desirable. Artificial oxidation of the surface can be considered as conservation treatment.
II	Atmospheric		Film formation	Reaction of iron with oxygen and water produces rust on the surface upon oxide film. Film of rust is uneven and has different shades of yellow and light brown. At the same time pitting corrosion, which damages oxide film and irritates metal surface, occurs.	Iron hydroxide (II) $Fe(OH)_2$ oxidizes to iron hydroxide (III) $Fe(OH)_3$, which later turns to one of hydrated iron oxides (III) goethite (α-FeOOH) or lepidocrocite (γ-FeOOH)	All conservation cleaning methods are permissible: mechanical, chemical, electrochemical and electrolythic. Conservation coating after cleaning is required.
III	Underground		Crust formation	Original surface of an artifact is marked by the primary oxide film that was formed at the stage I of oxidation. Under this primary film the process of mineralization takes place towards the center of the artifact. This primary corrosion crust is dark brown; its thickness is about 1-2 mm (visible to the naked eye). On the primary crust another corrosion crust is formed – so-called secondary crust. This secondary crust is porous, fragile and mixed with organic remains and soil particles. Its color mainly depends on the type of soil in which the artifact was buried. But shades of brown and light brown are predominant. The primary oxide film marks the boundary between primary and secondary crusts.	<u>Primary crust</u> goethite (α-FeOOH) possibly through hematite Fe_2O_3 slowly turns to magnetite Fe_3O_4. <u>Secondary crust</u> goethite (α-FeOOH) + secondary corrosion products, soil particles, etc.	Chemical cleaning permissible but not desirable, especially in case of inlay or other surface decoration, mechanical cleaning is required. Stabilizing or desalinating treatment is necessary. Conservation coating after cleaning is required.
IV	Underground		Crust formation	Enlargement of the primary crust provokes the artifact to extend. The crust itself becomes porous and cracked. The secondary crust also enlarges and hides the original shape of the object. The loss of the primary corrosion crust at this stage means the loss of the artifact itself, because the remains of metal core do not indicate the original shape.	<u>Primary crust</u> hematite Fe_2O_3 slowly turns to magnetite Fe_3O_4. <u>Secondary crust</u> goethite (α-FeOOH) + secondary corrosion products, soil particles, etc.	Chemical cleaning can provoke the loss of the original surface of an artifact together with corrosion crust. Stabilizing treatment is necessary, but only special nondestructive methods can be applied. After stabilizing treatment deep polymer impregnation is required.
V	Underground		Crust formation	The artifact is totally mineralized and highly extended. The primary corrosion crust (i.e. the object itself) is porous and cracked; the cracks are filled with secondary corrosion products. The secondary corrosion crust totally hides the shape of object. Instead of metal core – a void filled with friable secondary products of iron corrosion. The object is stable from corrosion point of view. But the danger of its destruction during storage is very high.	<u>Artifact</u> magnetite Fe_3O_4. <u>Secondary crust</u> goethite (α-FeOOH) + secondary corrosion products, soil particles, etc.	The artifact needs only cleaning and recovering of its original shape. After cleaning deep polymer impregnation is necessary because the artifact destruction danger is very high.

INDEX

 Primary oxide film, original surface

 Sound metal

 Void instead sound metal

 Primary crust

 Secondary crust

THE EFFECTIVENESS OF CHLORIDE REMOVAL FROM ARCHAEOLOGICAL IRON USING ALKALINE DEOXYGENATED DESALINATION TREATMENTS

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Introduction

Desalination treatments for archaeological iron have not been in general use by British conservators for many years. The reasons for this include time and resource constraints, concerns about the effects of treatments on fragile mineral-preserved organic remains, and a lack of reliable quantitative data on desalination efficiency. Storage in reduced relative humidity (RH) has been adopted as the primary method of corrosion prevention for archaeological iron collections. A lack of adequate availability and maintenance of such storage often leads to RH levels that allow corrosion processes to occur, particularly those relating to chloride-containing β-FeOOH (akaganéite) which begins to induce iron corrosion above 12% RH (Watkinson and Lewis 2005). There is a growing worry among conservators that leaving chloride ions in objects poses significant risks if controlled RH storage fails.
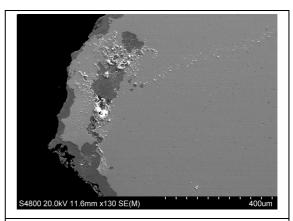
Research design

As part of a collaborative research project with Cardiff University and The British Museum, desalination treatments were re-examined by determining chloride extraction rate from a statistically significant number of archaeological samples. Two treatments were selected based on previous research (Watkinson and Al-Zahrani 2008), which suggested that chloride extraction of over 95% could be achieved using sodium hydroxide (0.5M NaOH) deoxygenated either with sulphite ions or nitrogen gas. In the study reported here, both treatments were modified to use 0.1M NaOH at room temperature; the sulphite ion concentration was also reduced to 0.05M, based on the method employed at the Swiss National Museum (Schmidt-Ott and Oswald 2006). Both treatments were tested using a large number of archaeological iron nails exhibiting varied corrosion morphologies and chloride ion content, originating from three British sites. The nails were desalinated for up to 96 days at room temperature, with up to six solution changes. Treatment was terminated when chloride levels in the treatment solution were less than 10 ppm for two consecutive solutions, although due to time constraints a small proportion of the objects did not complete the treatment. Chloride concentration was measured using a specific ion meter. After treatment, the nails were acid digested at room temperature in covered containers, and their residual chloride ion content determined.

Chloride extraction efficiency

Neither of the two treatments as tested achieved the >95% average extraction rate reported by Al-Zahrani. Both achieved similar results in terms of the average chloride extraction (c. 75%), and both treatments displayed significant variability in the extraction (11-99%). Alkaline sulphite treatment heated to 60°C resulted in shorter treatment times and slightly improved overall average extraction rate, although the extraction range remained large. Although this makes treatment appear to be an unpredictable process, in the majority of cases (c. 80% for all three treatments), over 60% of the total chloride present could be extracted. Although it is difficult to determine the precise reasons for poor extraction rates where these occur, several factors were identified: bulky corrosion products and/or adhering soil retarding the diffusion rate, bound chloride, most likely held within the structure of β-FeOOH, or chloride trapped deep within inaccessible pores and surrounded by metal (Figure 1).

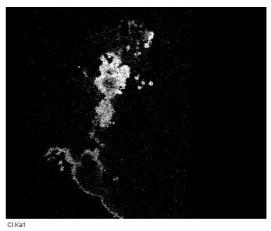

S4800 20.0kV 11.6mm x130 SE(M)   400um

Cl Ka1

Figure 1: Scanning electron microcope image (top) and energy-dispersive spectroscopy map of Cl, showing Cl-containing corrosion products surrounded almost completely by metal.

Statistical analysis of results

Due to the fact that large numbers of objects were treated and digested, statistical analyses of the results is possible. This shows that there is no significant correlation between the total chloride extracted during treatment and the residual chloride remaining in the object. A correlation was found between the final solution concentration and the residual chloride concentration, indicating that where objects did not reach the specified completion criteria (<10 ppm solution concentration), residual chloride levels tended to be high. This demonstrates that some objects require longer treatment times than others, and that monitoring of the chloride concentration in the desalination solution is important if treatments are to be completed.

The level of residual chloride which induces significant post-excavation corrosion is an unknown quantity. North and Pearson (1978) suggest that objects containing <200 ppm may be considered 'stable', while those containing >1000 ppm are at significant risk. Using these boundaries, approximately 80% of the objects had their chloride levels reduced to less than 1000 ppm by treatment, while 40% of the objects fell below the 'stable' 200 ppm boundary. It

must be stressed that these limits do not have any empirical basis; the level of chloride in objects which may be considered 'safe' is not known, and is the subject of further research.

Conclusion

The treatment of large numbers of archaeological samples in alkaline deoxygenated solutions has resulted in a significant body of data, providing statistically sound information about the extraction efficiency that can be expected when treating objects. Both nitrogen-deoxygenated 0.1M sodium hydroxide and 0.1M/0.05M alkaline sulphite were capable of extracting significant quantities of chloride ions from objects in the majority of cases. Although it is not known how much needs to be extracted from objects to prevent rapid and destructive post-excavation corrosion, it is considered that any reduction of chloride ion content is beneficial to an object in terms of reducing its susceptibility to corrosion, particularly where storage RH exceeds the recommended 12% limit. It is hoped that this new data will lead to the consideration of desalination treatments as part of iron conservation strategies in the UK.

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SIMPLIFYING SODIUM SULPHITE SOLUTIONS – THE DBU-PROJECT "RETTUNG VOR DEM ROST"

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Motivation

Especially in the field of archaeological heritage preservation, archaeologists and conservators are confronted with masses of iron finds and almost all of them suffer from the characteristic post excavation corrosion induced by chloride ions under uncontrolled storage conditions: the orange akaganéite needles growing vertically up from an iron object's metal core after the surface was flaking off.

To investigate the best possibility of conserving masses of iron finds under restricted personnel and budget facilities, the research project "Rettung vor dem Rost" was funded by the DBU (Deutsche Bundesstiftung Umwelt, Osnabrück/Germany). Closely connected to these questions is the aspect of saving our environment by reducing the needed amount of chemical agents or energy. Starting point of the project is the Alkaline Sulphite Desalination Method (North and Pearson 1975). The urgency of the research project was highlighted in 2006 by a German mail survey (Eggert and Schmutzler 2009). In this framework, the effort of time and budget were identified as main counter argument against the application of alkaline sulphite desalination. Only 20 % of all interviewed German conservators (nearly 40) applied the Alkaline Sulphite Method at this time. In this extended abstract, experimental results regarding the aspect of the simplification of the method and reducing the required budget are reported.

Aim of research in detail

From a theoretical point of view the Alkaline Sulphite Method should be successful (Cornell and Giovanoli 1990), and accordingly many comparing experiments show that caustic solutions are the most efficient desalination solutions (e.g. Rinuy 1979; Rinuy and Schweizer 1982; Watkinson 1996). Initially, sodium sulphite was thought to reduce iron(III)compounds mainly to magnetite. In fact, no reduction takes place at completely dried out iron finds from the soil, but the role of sulphite is as an oxygen scavenger in the bath solutions (Gilberg and Seeley 1987). Actually, the passivating power of the concentrated sodium hydroxide is enough to stabilize the soaked iron (Hjelm-Hansen et al. 1993). Nevertheless, the de-aeration function is welcome, since freshly precipitated iron(III)hydroxides are suspected to plug up the pores of the corrosion product layers which can inhibit in turn the diffusion of the desalination solution respectively chloride ions.

From this outline it can be deduced that de-aeration of desalination solutions is relevant and can be reached by chemical strategies - or alternatively by physical strategies. First, Al Zahrani tried in 1999 de-aeration by nitrogen atmosphere, but his experimental results based on 10 nails only (Al Zahrani 1999; Watkinson and Al Zahrani 2008). The role of sulphite for desalination success or more alternatives for chemical de-aeration in addition to nitrogen, e.g. vacuum and heat are to be considered. Furthermore, iron finds from the soil are not as much chloride contaminated as finds from the sea, that's why the diminishing of the sodium hydroxide and the sulphite component are also to be investigated (Stawinoga 1996; Schmidt-Ott and Oswald 2006). The subsequent aspect is to investigate the potential of omitting sulphite respectively any de-aeration method. These approaches offer the opportunity to reduce the costs of active conservation as well as the diminishment of environment pollution by chemical agents.

Methodology of research

The concept of the research project was to identify the most effective desalination method under consideration of the above mentioned criteria by comparing experiments, conducted using archaeological finds. The chloride content of the desalination solutions and the residual chloride content of the desalinated objects were measured.

Of course, working with archaeological iron finds at this large scale needs a courageous and generous contributor, which could be won in the Landesamt für Denkmalpflege Baden-Württemberg. Roman nails from the archaeological site "Köngen" were used as specimens. The desalination experiments were conducted using around 100 g nails in one litre desalination solution (alkaline sulphite (each 0.5 mol/l), diluted alkaline sulphite (NaOH 0.1 mol/l, Na_2SO_3 0.05 mol/l), sodium hydroxide NaOH 0.5 and 0.1 mol/l) at room temperature (20 °C ± 1 °C); all chemicals used were of high quality purchased for analytical purpose. One bath ran 60 days, and desalination was finished when little or no chloride could be detected in the bath solution (around 4 baths).

Results

In case of the Köngen finds, the contamination with chloride was quite low compared to finds from the sea. Nevertheless, this small amount of chloride is able to stimulate post excavation corrosion. Hence, as main criterion for an effective desalination, the residual chloride content is to be considered. The less chloride is inside the metal core and the more chloride was extracted, the more efficient was the desalination method, and the lower is the risk of post excavation corrosion.

A clear ranking of the varying desalination solutions can be worked out regarding their sodium hydroxide concentration: in 75 % of cases the 0.5 molar sodium hydroxide solutions extracted more chloride and left less inside the objects than desalination solutions with 0.1 mol/l NaOH. In contrast, in case of de-aeration the picture is less clear: the most effective desalination solutions are de-aerated by vacuum, nitrogen or sulphite (0.5 mol/l). But maybe

this impression is only caused by the cold desalination temperature, and is independent from de-aeration. Because one of the most efficient solutions is cold sodium hydroxide 0.5 mol/l without any de-aeration – it simply stood at room temperature in a box with an air-tight lid. This phenomenon was replicated in a second experiment. In contrast, reproducing this experiment at 55 °C, a result obtained which is quite contrary to expectations: cold desalination (with and without de-aeration) is more efficient than warm desalination (only de-aerated with sulphite, 0.5 mol/l and 0.05 mol/l). The initially planned enhancement of diffusion of the desalination solution as well as the chloride ions seems not to take place. Furthermore, the combination of physical de-aeration with sodium sulphite does not improve the desalination.

Discussion

The efficiency of extraction by treatment in our experiments varies between 79 % and 46 %, i.e. every object still contained chloride after desalination. However, how important are these differences in efficiency regarding long-term stability? This question has to be answered by systematic survey of desalinated objects.

Conclusions

As things are now, it is recommended to use 0.5 molar solutions – but all other approaches to save money work well: Cold desalination allows working with plastic containers, it saves energy, and it extracts chloride more efficiently. De-Aeration with sulphite is cheap, with nitrogen cheaper, but with vacuum it is "for free". A disadvantage to be mentioned is the equipment needed for mass treatment under vacuum or nitrogen, since air-tight vacuum drying ovens are recommended. However, smaller quantities can also be desalinated using exsiccators and pressure control. Finally, no other chemical agents are needed for disposal of sulphite, whereby the requirements for environment protection are matched.

Perspectives

The project will end in autumn 2010, so more results will be gained in the next months. It is planned to ensure the reported preliminary results by analysing finds from a second archaeological site. Furthermore, it is to be investigated, if the high efficiency of cold de-aerated desalination solutions is caused by de-aeration or temperature. Results from experiments with hot caustic solutions are still to be evaluated. At least, it has to be investigated the relevance of the desalination efficiency rank. Then it can be concluded, if diluted sodium hydroxide concentration is another way for low-cost mass conservation treatment. All these other aspects of the research project and the detailed experimental results will be published in near future.

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