

Editor:

Christian Degriigny
christian.degriigny@gmail.com

Assistant editor:

James Crawford
jamesbcrawford76@gmail.com
& james.crawford@gov.mt

METALConsn-info



Bulletin of the Research On MEtal Conservation

February 2007

BROMECC21

Editorial

Most of the abstracts in this BROMECC issue refer to the presentations given at the AIAE sub-working group meeting held in Mannheim (D) at the Reiss-Engelhorn Museum on the 11th of October 2006. It was the first day of the 2006 conference of the Verband der Restauratoren (VDR) (Fachgruppe Archäologische Objekte) entitled 'Archaeological metal finds – from excavation to exhibition'. Associating a sub-working group meeting with an annual conference of a national conservation association proved to be highly beneficial for both parties. AIAE members were able to present their research to a wide international audience who gave a widespread feedback. For the VDR, the association with the AIAE sub-working group gave the conference an additional day where international research and projects were presented. Most of the AIAE abstracts presented in Mannheim will be published in the VDR publication 'Beiträge zur Erhaltung von Kunst- und Kulturgut' or in other conservation publications. Most presentations can also be viewed on the ICOM-CC Metal homepage (<http://icom-cc.icom.museum/WG/Metals/>) and the Metal group homepage (<http://rsc.anu.edu.au/~hallam/METALConsn-info.html>).

In this issue you will also find the outcomes of the SmartPlasma project that was already presented in BROMECC 12. The treatment presented seems to be effective on tarnished silver and will continue in the next years on other materials. Most of you are aware that the EU PROMET project aims at developing innovative protection systems on metal artefacts from Mediterranean countries. National research projects are setup aside to further study some promising protection systems like the one presented by E. Cano (Spain) based on the use of plant extracts. Another abstract treats the delicate problem of lead inlays in composite Japanese artefacts. The last abstract refers to the well-known effect of tin on the corrosion of tin bronze artefacts. This new PhD research project has the objective to fully understand the complicated corrosion processes involved in the formation of a patina in a specific environment.

As usual we hope that you will find this issue as useful and interesting as ever.

Editor

Christian DEGRIGNY

Assistant editor

James CRAWFORD

Contents

Page

Ongoing research projects

	Experimental iron at Fiskerton: results after burial for 30 months	3
	Blue Iron Rust – A review on the formation and stability of vivianite	4
	Deterioration of iron archaeological artefacts: local and structural investigations on Cl-containing corrosion products	5
	The study, stabilization, and conservation of large iron elements recovered from the American Civil War ironclad USS <i>Monitor</i> (1862)	6
	The effect of relative humidity (RH) on archaeological iron deterioration	7
	Effects of relative humidity (RH) on the corrosion of iron—an experimental view	8
	Investigation into the potential of low-oxygen and dry/cold storage for freshly excavated iron artefacts	9
	Can dried out iron alloy artefacts be stabilized after 20 years of excavation?	10
	(Re)treatment of archaeological ironwork: necessary or just a waste of time?	11
	Alkaline sulfite desalination- tips and tricks	12
	Smartplasma project	13

New research projects

	Natural corrosion inhibitors for the protection of metallic cultural heritage	14
	Investigation of corroding lead inlays on Japanese lacquer objects	15
	Electrochemical study of the influence of the Sn content on the formation of patina on Cu-Sn bronzes	16

Ongoing research projects



Experimental iron at Fiskerton: results after burial for 30 months (EH)

Samples of modern iron were installed in the peat at Fiskerton, Lincolnshire (England) in December 2003. The coupons serve as analogue materials for the artefacts buried in the vicinity of an Iron Age causeway. Together with other modern materials buried there, analysis of the samples allows investigation of the possible condition and deterioration of the archaeological materials, and the effects of the deliberate rewatering of the site during 2004. Soil and groundwater characteristics are also monitored.

The iron coupons were recovered at burial intervals of 6, 12 and 18 months, and the final recovery was at 30 months in June 2006. Coupons were analysed by X-ray diffraction to characterise the corrosion products, and corrosion rate was calculated from weight loss measurements. The results show that in the anaerobic peat below the water table, the corrosion products are principally iron sulphides and the iron carbonate, siderite. Those above the water table yield mostly goethite and magnetite. These results are similar to those from the archaeological metalwork recovered in excavations during 1981 and 2001. The corrosion rates, however, increased throughout the duration of the burial experiments, in particular on those coupons that were near or just below the water table. The reasons for this may be that the clean modern iron had not acquired well-formed and protective corrosion layers, facilitating rapid corrosion. The results from the groundwater monitoring are presently being interrogated and these may yield other clues.

Further information about this project can be found in BROMECC 10.

Contact: Vanessa Fell (EH)

Funding: no external funding

Ongoing research projects



Blue Iron Rust – A review on the formation and stability of vivianite (SABKS/UCLA)

Vivianite, $\text{Fe}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$, is a pale blue iron phosphate mineral which occurs naturally in association with decaying bones, wood, and other buried organic matter and on excavated iron objects, particularly those recovered from wet clay soils and waterlogged deposits. Farrer, Biek, and Wormwell (1953) concluded that there were inhibitive effects on the corrosion of buried iron objects afforded by tannates and phosphates in waterlogged, slightly acidic deposits, where bacterial decay of the iron objects would normally result in severe deterioration of the buried iron. They found a mixture of ferric phosphate hydrate, $\text{FePO}_4 \cdot 2\text{H}_2\text{O}$ (most likely strengite), and vivianite, together with some iron tannates.

When freshly made or mined vivianite is almost colourless, but soon begins to darken upon exposure to light and air. First the compound turns green, then blue, then a very dark bluish-black, although on excavated iron objects it is usually a light blue, occasionally purple. In the pristine state, all of the iron is present as ferrous iron, and as oxidation proceeds some ferric iron is present too. The transformation of vivianite can stop at this state, but with further oxidation the colour sequence can be continued to the final yellow-coloured ferric phosphate. This could happen also after excavation.

Stability diagrams show that the environmental conditions required for the formation of strengite are highly oxidizing, at a low pH with high levels of phosphate anions. Small amounts of sulphide ions stabilize the formation of pyrite over a wide range of Eh and HPO_4^{2-} activities at the expense of both vivianite and strengite, which are stable only at very high phosphate concentrations.

Contacts: Gerhard Eggert (SABKS) and David Scott (UCLA)

Funding: no external funding

Ongoing research projects

Deterioration of iron archaeological artefacts: local and structural investigations on Cl-containing corrosion products (DED-SS)

The deterioration after excavation of archaeological artefacts buried in soil is often associated with the presence of chlorine ions (i.e. chlorides - Cl⁻) in corrosion products. Indeed, with environmental change, there is an abrupt break in the equilibrium that was established during the artefact's burial, resulting in accelerated and destroying corrosion processes. The Cl⁻s, play an important role in such corrosion mechanisms, making post-excavation desalination necessary. These desalination treatments allow slowing down the corrosion processes. However, they are not optimised in many cases. The limits of these treatments are mainly due to the poor knowledge of the Cl-containing corrosion products formed on the archaeological objects. Thus, the understanding of the corrosion mechanisms in soil and related to the presence of chlorine is required. Our work aims to determine the composition, the structure and the local distribution of Cl-containing phases formed on archaeological samples through analytical techniques.

The samples available are cross sections from iron objects recovered from terrestrial archaeological excavation sites dating from 12th to 16th century AD. The artefacts were analysed using classical techniques (optic and electronic microscope) but also specialised ones: μ Raman spectroscopy and synchrotron based micro X-Ray Absorption Spectroscopy and micro X-Ray Diffraction. These examinations allow obtaining fundamental results as regards the localisation and characterisation of the chlorinated phases.

These investigations have highlighted the presence at the metal/oxide interface of two different Cl-containing crystalline phases. The oxyhydroxide β -FeOOH akaganéite (5-10%mass) is a compound usually present in the corrosion products of objects exposed to a chlorinated environment. Another phase with a more strongly chlorine content (15-20 %mass), the β -Fe₂(OH)₃Cl hydroxychloride was found as well. This result is significant because, to our knowledge, this phase was rarely previously observed on archaeological samples, whereas it is present in considerable proportions on the artefacts observed in this study.

Associated to the specific study of Cl content influence on the structure of synthesised akaganéite, these findings help to gain new insights concerning the influence of such phases on the complex mechanisms of long-term iron corrosion in soil containing chloride species. This provides fundamental results for the improvement of the desalination methods used in the context of the preservation of iron archaeological artefacts.

Contact: Solenn Reguer (DED-SS)

Funding: no external funding

Ongoing research projects



The study, stabilization, and conservation of large iron elements recovered from the American Civil War ironclad USS *Monitor* (1862) (TMM)

The USS *Monitor* (1862) was the first United States warship to be completely clad in iron armour plating. Built for the Union Navy during the American Civil War to a revolutionary design by the Swedish-American inventor John Ericsson, the *Monitor* had a brief but successful career against the Confederate Navy before sinking in a sudden storm. The wreck of the *Monitor* was discovered in 1973 off the coast of Cape Hatteras, North Carolina, at a depth of 240ft (73m), and is managed and studied by the US National Oceanic and Atmospheric Administration (NOAA) through the National Marine Sanctuary Program.

Since its discovery, many large iron and composite metal elements have been excavated and recovered from the wreck including the engine, condenser, propeller, revolving gun turret and Dahlgren guns. NOAA managed all of the recovery efforts for these artefacts along with the United States Navy. The Mariners' Museum in Newport News, Virginia, USA, has been designated the repository of this material since 1987 and, in cooperation with NOAA, is responsible for its conservation, curation, and interpretation. The very large size, weight, and great complexity of the *Monitor* objects present a formidable task to conservators at The Mariners' Museum working to stabilize them after 140 years of submersion in seawater.

Minimizing post-excavation iron corrosion and removal of chlorides are particular concerns for *Monitor* conservators who have collaborated with other conservators, conservation scientists, chemists, physicists, and corrosion engineers to better understand the current condition of the *Monitor* artefacts and to develop strategies for their stabilization and conservation.

Further information about this project can be found in BROMECE 16.

Contact: Eric Nordgren (TMM)

Funding: Primary funding by The Mariners' Museum and NOAA

Ongoing research projects



The effect of relative humidity (RH) on archaeological iron deterioration (EH)

Archaeological iron still presents a great challenge to the conservation community. The 15% RH threshold discovered in Turgoose's early work and recently confirmed by Watkinson forms the basis of most preventive conservation strategies. Whilst this RH is achievable with significant effort in storage, technological and resource limitations mean it can rarely be maintained in a display situation. This poses the question of how great is the risk when 15% RH is exceeded. The formation of akaganéite is now widely recognised as the major (but certainly not only) cause of post excavation deterioration of archaeological iron. The risk to an artefact is probably determined at least to some degree by the amount of akaganéite formed. Tests with model powders have been undertaken at a series of RH intervals (with and without varying concentrations of acetic acid) over a period of 30 months. The amount of akaganéite formed in the tests has been quantified with FTIR spectroscopy.

Considering the amount of akaganéite and not just the weight gain, a second threshold around 30%, has been identified where the akaganéite formation rate increased significantly. It is suggested that this should form an achievable limit to aim display conditions towards.

Showcases have been procured that can readily achieve this with silica gel in the most aggressive, high RH environments. Indeed the cases have performed so well that 15% can be achieved for a six month period, although these results are unlikely to be maintained with a suite of different showcase designs.

Contact: David Thickett (EH)

Funding: no external funding

Ongoing research projects



Effects of relative humidity (RH) on the corrosion of iron—an experimental view (TBM)

A project “The investigation of deterioration and stabilisation of archaeological iron in the British Museum” has been carried out in the Department of Conservation, Documentation and Science. The aim of the project was to identify the main causes of deterioration of archaeological iron in the Museum collection and to identify a suitable storage environment. Two approaches, including the investigation of deterioration of archaeological iron and experimental tests on the effects of RH on the corrosion of iron, have been conducted. The results of the investigation are to be published in *Studies in Conservation* (2007). The brief results of the experiments are reported here and the full paper is to be published in *British Museum Technical Research Bulletin* (2007 or 2008).

Industrial powder $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ and mixtures of iron coupons with $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ have been exposed to variable RH levels at room temperature for over a year. Changes in these tested materials were documented and analysed using microscopy, Raman spectroscopy, X-ray diffraction, and ion chromatography.

The chloride powder liquefied and the formation of akaganéite occurred in hours at 75%RH and within a month at 54%RH. Akaganéite was also detected in the powder exposed to RH levels below 44% in less than a year, although deliquescence has not occurred at these levels. Pitting was observed on the tested iron coupons after one week of exposure at 75%RH. At 54%RH, pitting was observed under the microscope within a month and was visible after six months. Pitting was hardly observed on the coupons exposed to RH of 33% or below within a year. The mass loss of the coupons after six months of exposure was approximately 14% at 75%RH, 1.6% at 54%RH, and less than 0.4% at lower RH levels.

The formation of akaganéite on the control coupons indicated that akaganéite found on archaeological iron could be formed even though little chloride is present in the objects. The morphology and composition of the corrosion depends on the RH levels, although the surface condition of the objects also has an impact. The elongated crystalline akaganéite often found on archaeological iron was probably formed at RH levels of 50-60%, while the akaganéite bubbles probably formed at higher RH levels. Keeping iron at RH levels below 35% can slow deterioration significantly.

Further information about this project can be found in BROMECC 16.

Contact: Quanyu Wang (TBM)

Funding: no external funding

Ongoing research projects



Investigation into the potential of low-oxygen and dry/cold storage for freshly excavated iron artefacts (RCS)

Akaganéite (β -FeOOH) remains one of the most problematic corrosion products on freshly excavated iron artefacts and causes major losses in objects that are allowed to dry in an uncontrolled climate. Exposure of archaeological iron artefacts to high relative humidity and oxygen triggers this corrosion in the presence of chlorides. Adapted packaging of excavated iron finds on site is fundamental for their long term preservation and can shorten stabilisation treatments. This work aimed to look into possible short-term storage environments for freshly excavated iron artefacts until their treatment in the laboratory and for methods applicable for long-term storage.

To observe akaganéite formation in various storage environments, synthetic corrosion samples were prepared with a mixture of equal amounts of (Fe) and iron chloride tetrahydrate ($\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$). Storage systems using resealable polyethylene bags and polypropylene boxes (Stewart® boxes) were tested. The influence of added silica gel and low temperature was also examined. A closer look was taken into low-oxygen environments using the Revolutionary Preservation System® (RP-System®) manufactured by Mitsubishi Gas Chemical Company. Two different oxygen absorbers (RP-A and RP-K) were evaluated.

Analysis of corrosion products was carried out using optical microscopy, Fourier Transform Infrared Spectroscopy (FTIR) and X-ray Diffraction (XRD) and Raman spectroscopy.

Contact: Salomé Guggenheimer (RCS)

Funding : no external funding

Ongoing research projects



Can dried out iron alloy artefacts be stabilized after 20 years of excavation? (TEI)

Most archaeological museums in Greece house vast collections of excavated iron artefacts, which have not been properly dechlorinated prior to their storage in a museum. However, the problems encountered for iron artefacts in Greek museums vary – since many of the finds even for the same period (e.g. Hellenistic period) at different sites can range from artefacts that are completely mineralized to those that retain a substantial metal core. As a result, during the condition survey of the collection, one must carry out X-ray radiography of the entire collection prior to any conservation assessment, in order to determine the amount of remaining metal and the initial shape of the artefacts. Also, it is necessary for archaeologists (and conservators) to be educated on the proper handling of iron objects during and after excavation. However, the vast majority of iron artefact collections in Greece have not undergone proper dechlorination treatments. Furthermore, it is difficult to find in the literature discussion on the effectiveness of stabilization treatments for iron artefacts, dried out after excavation where akaganéite formation has occurred.

Under the auspices of the 6th FP EC funded project, PROMET, the T.E.I. of Athens has developed an approach for surveying quickly the condition of large metals collections prior to treatment and after some years of excavation, so as to help the curators confront the relevant problems and understand the real needs of their collection, in order to make the necessary value-judgments for the treatment and the protection of the artefacts.

Such an approach was developed for the metals collection housed in the Museum of Ancient Messene in Greece. Most of the iron alloy artefacts of collection exhibit clear signs of active corrosion (e.g., formation of akagenéite, spalling), since they were not treated properly after excavation. Thus, it is unknown if dechlorination methods commonly used in conservation will be effective in removing the chlorides. For this reason, 16 iron artefacts of different shapes and dimensions and substantial metal core were selected and immersed in 2% NaOH solution, and the amount of chlorides removed was monitored using potentiometric measurements. After successful dechlorination, the objects have been stored in uncontrolled museum environment – typical conditions for most museums in Greece, and we will observe the success of the treatment after 6 months. The paper discusses the approach for a condition survey of the collection as well as the effectiveness of treating dried out excavated iron artefacts with 2% NaOH solutions.

Further information this project can be found in BROMEC 12, 15 & 16.

Contacts : Vassilike Argyropoulos, Maria Giannoulaki and M. Scaramanga (TEI)

Funding : EU PROMET project

Ongoing research projects

(Re)treatment of archaeological ironwork: necessary or just a waste of time? (ArcheoSpecialists)

For a long time, ironwork was a finds category that did not received much attention from Dutch archaeologists. Not counting exceptions, these finds were generally stored in non-climatically controlled storage facilities. This inevitably led to continuing corrosion and eventually, loss of the objects, which of course, is a very unwanted development for future research of archaeological metal collections. However, the attitude towards these unwanted developments is gradually changing, as is visible in the Dutch Standard for Archaeological Research. Confronted with the deterioration of metal artefacts, climatically controlled metal storage cabins are built and increasing numbers of ironwork are (re)treated to stabilize their condition. Most objects undergo desalination when necessary. Archaeospecialists in Amersfoort (re)treat archaeological ironwork using the alkaline sulphite treatment, as developed by North & Pearson in the mid '70s.

For recently carried out and future excavations this new *ex situ* policy obviously has huge consequences, as all find categories, including metal artefacts, have to be stabilized before final storage. This applies particularly to ironwork, which is by definition unstable. Since stabilization of metal is rarely included in the project's budget, a thorough selection policy has to be used. This conflict of interest between the archaeologist and the specialist leads to the following point of discussion: (re)treatment of metal finds: necessary or just a waste of time?

Contact : Karin A.N. Abelskamp-Boos (ArcheoSpecialists)

Funding : no external funding

Ongoing research projects



Alkaline sulfite desalination- tips and tricks (SNM)

Archaeological iron objects tend to corrode. This process is influenced by the presence of salts that have migrated into the artefacts during burial. Here chlorides play an important role. After excavation the corrosion process is intensified in the presence of oxygen. In order to conserve iron artefacts and to prevent their further decay, it is necessary to remove the chlorides contained within. At the Swiss National Museum we have adopted the alkaline sulphite desalination method proposed by Rinuy & Schweizer for this purpose.

The experiences gained within the past twelve years have lead to a number of changes in the conservation process that make the application easier, more time efficient and economical. Suggestions for the necessary infrastructure to perform the treatments and chloride measurement of the solutions are studied. Also varying solutions, protection of associated organic material during treatment and the rinsing and drying procedures are considered. Further experience in the use of pre-treatments, post-treatments and the long-term stability of the desalinated iron artefacts are examined.

Reference:

Rinuy, A. et Schweizer, F., *Méthodes de conservation d'objets de fouilles en fer. Etude quantitative comparée de l'élimination des chlorures*, Studies in Conservation, 26 (1981) 29-41

Schmidt-Ott, K. and Oswald, N., Neues zur Eisenentsalzung mit alkalischem Sulfit, VDR Beiträge, Heft 2, (2006) 126-134

Contacts: Katharina Schmidt-Ott and Dr. Niklaus Oswald (SNM)

Funding: Swiss National Museum

Ongoing research projects



Smartplasma project (HA-RAFA)

The conservator has a large variation of techniques to his disposal to clean the metal parts in objects of art and artefacts, but up to now they haven't always been satisfactory. Especially in case of combined or delicate materials such as metal threads in textiles or daguerreotypes, cleaning the metal with minimal risk to the other parts of the object is still very difficult. The purpose of the two years (2005-2006) SMARTPLASMA project setup by the Hogeschool Antwerpen, Conservation / Restoration Department of Metals, in cooperation with the Vito and the University of Antwerp, department of Chemistry was to develop a prototype capable of cleaning such pieces by using atmospheric plasma.

At the end of the project, we can state that a prototype has been developed successfully, both for use in open air (without limitations caused by shape or dimensions of the object), as well as in a closed glovebox with a computer controlled system to circulate the H-He gas and thus saving enormously on operating costs. The treatments in the closed box also offered several other advantages, such as the possibility of creating a secondary plasma and an active treatment area up to 8 cm between the plasma-torch and the object. The temperature of the plasma afterglow stays below 50°C and the temperature in the box does not exceed 30°C.

Although the project concentrated on the development of this system and its components, a series of tests on metal coupons were carried out. From these observations the best results were obtained on pure silver covered with a tarnish layer of silver sulphide. Here the cleaning took about 15 seconds per spot of approx. 10 mm. Also gilded silver, silver alloys and copper alloys were tested, but showed some difficulties that have to be examined further.

The fact that pure silver shows the best results is related to the initial research topic, i.e. the development of a dry, low temperature and non-contact cleaning method for combined materials and/or delicate surfaces. It is exactly for these kinds of objects that the application of plasma reduction can be of interest. Leaf silver on polychromed wood, silver coins, daguerreotypes, silvered surfaces, silver threads in textiles, silver with enamel and even silver objects with an originally burnished surface consist of a pure silver top layer.

In the next years, we plan to carry out further tests on a variation of surfaces, including research into the possible alteration of other materials such as wood, textile, etc. and develop an automated operation system such as a motorized table and a robot arm (for which a new research project has already commenced, called 'Flexpo'). For the installation and further tests with the plasma unit at our conservation department, a BOF-project has been approved for 2007.

Contact: Patrick Storme (HA-RAFA)

Funding: Private 7,5 % - IWT (Flemish research support) 92,5 % through TETRA-funds (Technology Transfer)

New research projects



Natural corrosion inhibitors for the protection of metallic cultural heritage (CENIM-CSIC)

Corrosion inhibitors (CIs) are substances that, when added to a given environment, slow down or reduce corrosion of a metal in that environment. These substances are widely used in industrial applications. In conservation and restoration of cultural heritage, some CIs are used during the cleaning treatments or for protection of metallic artefacts. The main disadvantage of most of these compounds is that they are toxic and/or carcinogenic, like the widespread benzotriazole (BTA) used for copper alloys.

The majority of the recent research on CIs has been focused in the search of inhibitors without health or environmental problems. Some authors have tested the efficiency of other azoles, like imidazole, indole, 5-mercapto-1-phenyl-tetrazole, 2-mercapto benzoxazole or 2-mercapto benzimidazole. While its efficiency is good, sometimes even better than BTA, these compounds cannot be considered completely safe. Other authors, on the other hand, have focused primarily on safety and health concerns. One research line has been the study of the inhibitor effect of aminoacids, like alanine, cysteine, tryptofan (or its derivative, tryptamine). But the most important research line in this topic has been the study of the inhibiting effects of plant extracts. The main advantages of these products are their ease of use, low obtaining cost and safety for both people and the environment.

Most of the time, these CIs have been studied in aqueous media at different pH (mainly acid) and/or with chlorides. However, the main use for CIs in conservation is in the form of conversion coatings or “dry-films”, that is, forming an inhibitor layer chemically bonded to the surface of the metal. There are very few studies on this CI method of use and none of them have been carried out using natural inhibitors.

The main objectives of this project are:

- to study the applicability and efficiency of plant extract-based CIs used as “dry-films” for the restoration and conservation of metallic cultural heritage. Extracts from *Pimpinella anisum*, *Nigella sativa*, *Rosmarinus officinalis* and *Thymus vulgaris* will be studied, applied on iron and copper based alloys, using different extraction systems
- to study the use of these natural inhibitors combined with the traditional coatings used in conservation and restoration: acrylic resins (like Paraloid B72) and microcrystalline wax.

The efficiency of the inhibitors will be studied using electrochemical techniques (Rp and EIS) and the surface of the metals and the films will be characterized using SEM and XPS. Samples will be exposed to low concentrations of pollutants using a mixed flowing gas chamber, and the corrosion rate will be measured using a quartz crystal microbalance (QCM) with a sensitivity of few nanograms.

Contact: Emilio Cano (CENIM-CSIC)

Funding: Spanish National Research Council (CSIC)

New research projects



Investigation of corroding lead inlays on Japanese lacquer objects (TBM)

The lead inlays on a number of Japanese lacquer objects from the Asia department in the British Museum are severely corroded. Corrosion on lead caused by carboxylic acids and carbonyl compounds being emitted from storage or display case materials is generally acknowledged. Strategies suggested in literature comprise: remove or avoid using materials that can off-gas organic acids, put scavengers in place, treat to consolidate or remove the corrosion. Objectives for the project are: to identify the storage history of the objects and the cause of the corrosion; to identify original materials and construction of the objects; to establish a strategy of preventive conservation to halt further deterioration; to establish a strategy of interventive conservation to address the detrimental effects of the corrosion to the aesthetics of the objects and to liaise with expert conservators in the field of lacquer conservation.

There is uncertainty about when the corrosion started and what the source of the organic acids was. Opinions vary on the possibility of materials used in manufacture of the objects being a source. So far there is no conclusive scientific evidence. The number of available treatments normally used on corroding lead is limited due to the combination of materials used in the manufacture of these objects. The risks to the lacquer posed by materials used in common treatments for corroding lead are not entirely known. Nor is the effectiveness of localized methods for the treatment of the lead. There is some specific literature available dating to the late nineteen eighties, but this does not suggest a current acceptable conservation treatment for these objects.

To investigate the problem and to monitor the effects of suggested measures the following tests or analyses will be initiated:

- Analyze materials of three selected objects by XRF, Raman, FTIR spectroscopies and possibly XRD (where samples are available)
- Measure organic acid levels in storage with diffusion tubes and IC.

The authors acknowledge the complex nature of both the type of objects and the problems occurring and would greatly welcome any suggestions or collaboration.

Contacts: Maickel van Bellegem, L. Harrison, Q. Wang, P. Fletcher, T. Clark (TBM)

Funding: No external funding.

New research projects

Electrochemical study of the influence of the Sn content on the formation of patina on Cu-Sn bronzes (CECM, LECSO, ENSCP-LMS)

Understanding of the corrosion processes on cultural metal artefacts and more particularly bronzes (Cu-Sn alloys) presents a great interest for their conservation. Indeed, it gives us information on their alteration, the nature of the burial medium, the presence and nature of original surface treatments, the reasons for the artefact's abandonment. ... as well as the precautions to take to assure their long-term conservation.

The combined analysis of superficial layers, naturally or intentionally made, of archaeological objects and artificial patina synthesized in laboratory presenting similar characteristics to those of ancient bronzes gives information on the composition and structure of these patina. At the moment a model of formation is proposed in the literature [1]. It consists in a two steps process: the first one is the oxidation of copper and tin and the formation of a corrosion layer composed of complexes of Cu (II) and Sn (II), and the second step can take two forms. Either the layer does not allow any exchange and thereby conserves the original surface. Corrosion is then of type I. Or the layer is porous such as in aggressive environments. In that case we refer to corrosion type II. In both cases the selective dissolution of copper is observed and contributes to the presence of a tin-enriched layer at the surface of the alloy.

According to literature [2], the understanding of this decuprification phenomenon is essential to the determination of the corrosion processes of bronzes. But until today no method could be used to precisely characterise corrosion products. Results obtained in previous diffraction (TEM and XRD) studies [3,4] have shown the presence of Cu_2O and SnO_2 on one hand, and CuCl in NaCl medium. But in both cases peaks do not all correspond to theoretical peaks of reference materials and their intensity is sometimes superior. These observations seem to indicate that the bronze corrosion products are more complex than described in the literature.

The objective of this study is to exactly determine the constituents of bronze corrosion products in order to specify the mechanisms of patina formation in a specific environment. The manufacturing of highly pure bronze alloys (3.5 to 13 wt %Sn) has been carried out and will allow obtaining the laboratory analogues covered with artificial patina. The formation of patina will be studied electrochemically and characterised through the clustering of the following analytical techniques: surface analysis (XPS and Auger), micro-Raman spectroscopy, electronic microscopies (microprobe, analytical TEM...), micro-X-ray diffraction on generator with rotating anode or the use of large instruments (μXANES ...).

Références :

- 1.L. Robbiola, J.-M. Blengino, and C. Fiaud, *Morphology and mechanisms of formation of natural patinas on archaeological Cu-Sn alloys*. Corrosion Science, 1998. **40**(12): p. 2083-2111.
- 2.I. Mabilie, et al., *Mechanism of dissolution of a Cu-13Sn alloy in low aggressive conditions*. Corrosion Science, 2003. **45**: p. 855-866
- 3.C. Debiemme-Chouvy, F. Ammeloot, and E.M.M. Sutter, *X-ray photoemission investigation of the corrosion film formed on a polished Cu-13Sn alloy in aerated NaCl solution*. Applied Surface Science, 2001. **174**: p. 55-61.
- 4.M.L. Young, et al., *Synchrotron X-ray diffraction and imaging of ancient Chinese bronzes*. Applied Physics A, 2006. **83**: p. 163-168.

Contacts : Johanna Muller and Ivan Guillot (CECM), Barbara Laik (LECSO), and Luc Robbiola (ENSCP - LMS).

Funding : Ministère de la Recherche et de la Technologie, Chim'Art.

General information

Websites

- **ARTECH network:** http://server.icvbc.cnr.it/progetti_futuri/progetto_artech.htm. Network facilitating the access of conservation professionals to different investigation techniques of Cultural Heritage artefacts
 - **BIGSTUFF (Care of Large Technology Objects) 2004:** <http://www.awm.gov.au/events/conference/bigstuff/index.asp>
 - **CAMEO:** website containing chemical, physical, visual, and analytical information on over 10,000 historic and contemporary materials used in the conservation, preservation, and production of artistic, architectural, and archaeological materials
http://www.mfa.org/_cameo/frontend/
 - **Cost Action G8: Non-destructive analysis and testing of museum objects.** <http://srs.dl.ac.uk/arch/cost-g8>. Abstracts and booklets from previous workshops can be downloaded as well as announcements of future activities (Short Term Scientific Missions deadlines, training schools...).
 - **Cost Action G7: Artwork conservation by laser** <http://alpha1.infim.ro/cost>
 - **ENVIART** (Chemical Interactions between Cultural Artefacts and Indoor Environment): www.enviart.org. You have to register (free access) to get access to all information.
 - **e-Preservation Science:** <http://www.e-preservation-science.org>. Online publication of papers in conservation science.
 - **European Cultural Heritage Network:** <http://www.echn.net/>. European network of professionals interested in the conservation of Cultural Heritage.
 - **IR and Raman for cultural heritage:** <http://www.irug.org/default.asp>
 - **LabS-TECH network** <http://www.chm.unipg.it/chimgen/LabS-TECH.html>
 - **Laboratoire Pierre Sue:** LPS PhD thesis related to the alteration of archaeological artefacts can be downloaded from <http://www-drecam.cea.fr/lps/> (in French) and go to “Archéomatériaux et prévision de l’altération.”
 - homepage: <http://rsc.anu.edu.au/~hallam/METALConsn-info.html>
 - **M2ADL - Microchemistry and Microscopy Art Diagnostic Laboratory** is now available at the following website: http://www.tecore.unibo.it/html/Lab_Microscopia/M2ADL/
 - **New York Conservation Foundation** website: <http://www.nycf.org/>
 - **PROMET** website: <http://www.promet.org.gr>
 - **RESTAURACION METAL SUR AMERICA:** www.restauraciondemetales.cl
-

- **TEL (PhDs on line):** <http://tel.ccsd.cnrs.fr/>

- **Working Group Metals ICOM Committee for Conservation**

<http://icom-cc.icom.museum/WG/Metals/>

- **Online publications of Surface Engineering Journal.** Issue addressing specifically to Metal issues: **Surface Modification Issues in Art**, Volume 17, Issue 3, June 2001. Can be downloaded

from: (<http://www.ingentaconnect.com/content/maney/se/2001/00000017/00000003;jsessionid=1xpmlw91522a3.victoria>)

- **ANDRA** (Agence Nationale pour la Gestion des Déchets RadioActifs)

http://www.andra.fr/interne.php3?publi=publication&id_rubrique=82&p=produit&id=5. The following documents can be ordered for free from this website : *Analogues archéologiques et corrosion* (in French only) and *Prediction of Long Term Corrosion Behaviour in Nuclear Waste Systems* (in English).

Future seminars and conference

- **Conservation Strategies for Saving Indoor Metallic Collections (CSSIM)** (25 February – 1st March 2007, Cairo, Egypt). Organised by the Applied Laser Spectroscopy Group (NILES, Egypt) and EU PROMET project. Both the ICOM-CC Legal Issues in Conservation and Metal WGs will contribute. For more information visit the following website: <http://www.nileslaser.edu.eg/>

- **Workshop “The protection of cultural heritage from air pollution”** (15-16 March 2007, Paris, France) coorganised by the EU Project CULT-STRAT and ICP Materials Task Force of the Convention on Long-Range Transboundary Air Pollution. For more information please contact Ron Hamilton (r.hamilton@mdx.ac.uk)

- **Conservation Science 2007** (10-11 May 2007) organised by Università degli studi di Milano, ICON and the Institute of Conservation Science. For more information please contact Joyce Townsend (joyce.townsend@tate.org.uk)

- **2nd conference Archaeometallurgy in Europe** (17-21 June 2007, Grado and Aquileia, Italy) organized by the Associazione Italiana di Metallurgia. For more information visit the following website: www.aimnet.it/archaeometallurgy2.htm

- **METAL07**, triennial meeting of the ICOM-CC Metal WG (17-21 September 2007, Amsterdam, NL). For more information visit the following website: www.metal07.org

- **Conference on Surface Modification Technologies (SMT 21), Session on “Arts and Surfaces”** (24-26 September 2007, Paris). The session on “Arts and Surfaces” will be scientifically coordinated by Dr Alessandra Giumlia-Mair. For more information please contact Alessandra Giumlia-Mair (giumlia@yahoo.it)

- **Symposium 2007 – Preserving Aboriginal Heritage: Technical and traditional approaches** (24-28 September 2007, Ottawa, Canada) organised by the Canadian Conservation Institute. For more information visit the following website: http://www.cci-icc.gc.ca/symposium/index_e.aspx

- **Art2008**, 9th International Conference (25-30 May 2008, Jerusalem, Israel) on the non-destructive testing, microanalysis and preservation in the conservation of cultural and environmental heritage, organised by the Israel National Society for NFT. For more information visit the following website: www.isas.co.il/art2008

Abbreviations and acronyms

BOF: Bijzonder Onderzoeks Fonds – Special Research Funding, a funding system within the Association of the University of Antwerp and the Hogeschool Antwerpen, Royal Academy of Fine Arts

CEM: Centre d'Etudes de Chimie Métallurgique (UPR 2801)

CENIM – CSIC: National Centre for Metallurgical Research-Spanish National Research Council

DED-SS: Division Expérience DIFFABS – Synchrotron SOLEIL

EH: English Heritage

ENSCP-LMS : Ecole Nationale Supérieure de Chimie de Paris – Laboratoire de Métallurgie Structurale

FTIR : Fourier Transform InfraRed

HA – RAFA: Hogeschool Antwerpen, Royal Academy of Fine Art

IC: Ion Chromatography

IWT: Instituut voor de aanmoediging van Innovatie door Wetenschap en Technologie in Vlaanderen (Institute for the encouragement of Innovation through Science and Technology in Flanders) www.iwt.be

LECSO: Laboratoire d'Electrochimie, Catalyse et Synthèse Organique (UMR 7582)

LRMH: Laboratoire de Recherche des Monuments Historiques

RCS : Reto CH Sarl

SABKS: Staatliche Akademie der Bildenden Kuenste Stuttgart

SEM: Scanning Electron Miscroscopy

SNM: Swiss National Museum

TBM : The British Museum

TEI: Technological Education Institute

TEM: Transmission electron microscope

TMM: The Mariners' Museum

UCLA: University of California at Los Angeles

VITO: Vlaamse Instelling voor Technologisch Onderzoek (Flemish Institute for Technological Research) www.vito.be

XANES: Absorption of X-ray spectroscopy

XPS: X-Ray Photoelectron Spectroscopy

XRD: X-Ray Diffractometry

XRF: X-Ray Fluorescence

Contacts

Karin A.N. Abelskamp-Boos / ArcheoSpecialists (K.Abelskamp@archeologie.nl)

Vasilike Argyropoulos/ TEI (bessie@teiath.gr)

Emilio Cano / CENIM-CSIC (ecano@cenim.csic.es)

Gerhard Eggert / SABKS (gerhard.eggert@abk-stuttgart.de)

Vanessa Fell / EH (vanessa.fell@english-heritage.org.uk)

Salomé Guggenheimer / RCS (sg@reto.ch)

Johanna Muller / CECM (muller@glvt-cnrs.fr)

Eric Nordgren / TMM (enordgren@marinersmuseum.org)

Solenn Reguer / DED-SS (solenn.reguer@synchrotron-soleil.fr)

Katharina Schmidt-Ott / SNM (katharina.schmidt-ott@slm.admin.ch)

David Scott / CIA (Dascott@ucla.edu)

Patrick Storme / HA-RAFA (patrick.storme@skynet.be)

David Thickett / EH (David.Thickett@english-heritage.org.uk)

Maickel van Bellegem / BM (mbellegem@thebritishmuseum.ac.uk)

Quanyu Wang / TBM (qwang@thebritishmuseum.ac.uk)

National contact persons for the homepage **METALConsn**-info

Argentina: Blanca Rosales, researcher, CIDEPIINT, La Plata

Australia: David Hallam, senior conservator of objects at the National Museum of Australia, Canberra

Belgium: Annemie Adriaens, researcher and lecturer, head of the group “Electrochemistry and Surface Science”, Ghent University, Ghent and Gilberte Dewanckel, conservator at IRPA (Institut Royal du patrimoine artistique), Bruxelles

Bulgaria: Petia Penkova, conservator, National Academy of Arts, Department of conservation-restoration, Sofia

Canada: Judy Logan, conservator (retired), Ottawa

Chile: Johanna Theile, conservator and lecturer, Facultad de Arte - Universidad de Chile Las Encinas, Santiago de Chile

Croatia: Goran Budija, conservator, Museum of Arts and Crafts, Zagreb

Czech Republic: Dusan Perlik, conservator, Museum of Central Bohemia, Roztoky

Denmark: Karen Stemann Petersen, conservator, The National Museum of Denmark, Copenhagen

Egypt : Wafaa Anwar Mohamed, conservator, Giza

Finland : Eero Ehanti, conservator, Maritime Museum of Finland, Helsinki

France: Marie-Anne Loeper-Attia, conservator and assistant-lecturer at the Conservation Department, Institut National du Patrimoine, St Denis, Paris and Christian Degriigny, conservation scientist, Château de Germolles, Germolles

Germany: Gerhard Eggert, head, study program “Object Conservation”, Staatliche Akademie der Bildenden Künste, Stuttgart

Greece: Vasilike Argyropoulos, assistant professor, Department of Conservation of Works of Art, Technological Educational Institution, Athens

Hungary: Balazs Lencz, senior conservator, Conservation Department, Hungarian National Museum, Budapest

Italy: Paola Letardi, scientist, Istituto per la corrosione marina dei metalli (ICMM), Genova

Malta: Christian Degriigny, conservation scientist, Diagnostic Science Laboratories, Heritage Malta, Kalkara

The Netherlands: Ineke Joosten, conservation scientist, The Netherlands Institute of Cultural Heritage, Amsterdam

Morocco: Hind Hammouch, scientist, Laboratory of Electrochemistry, Corrosion and Environment, Faculty of Science, Université Ibn Tofail, Kenitra

Norway: Douwtje Van der Meulen, conservator, Conservation Department, University of Oslo, Oslo

Portugal: Isabel Tissot, conservator, Portuguese conservation-restoration Institute, Lisbon

Romania: Dorin Barbu, conservator, Brukenthal Museum, Sibiu

Russian Federation: Andrey Chulin, conservator, the State Hermitage Museum, St Petersburg

South Africa: Jaco Boshoff, maritime archaeologist, Iziko Museums of Cape Town, South Africa

Spain: Emilio Cano, conservator, National Centre for Metallurgical Research (CENIM), Spanish Council for Scientific Research (CSIC), Madrid

Sweden: Helena Strandberg, conservator and conservation scientist, freelancer, Göteborg

Switzerland: Valentin Boissonnas, conservator and lecturer, Haute école d'arts appliqués Arc, La Chaux-de-Fonds

United Kingdom: Catia Viegas Wesolowska, conservator, Victoria & Albert Museum, Londres & Mark Dowsett, physicist, Warwick University, Coventry

USA: Paul Mardikian, senior conservator, Warren Lasch Conservation Centre, North Charleston & John Scott, New York Conservation Foundation, New York
