Anglophone Editor & Translator:
James Crawford
jamesbcrawford76@gmail.com
Francophone Coeditor:
Michel Bouchard
MBouchard@getty.edu
Francophone Translators:
Nathalie Richard
n.richard.elmesti@videotron.ca
Elodie Guilminot
elodie.guilminot@arcantique.org
Hispanophone Coeditor:
Emilio Cano
ecano@cenim.csic.es
Hispanophone Translator:
diana.lafuente@gmail.com

Bulletin of the Research On MEtal Conservation

Metals Working Group

August 2009

BROMEC 29

Editorial

This issue of BROMEC outlines two *new research projects* from France; the first being a PhD project optimising stabilisation treatments of excavated marine iron via investigation of its dechlorination mechanisms; while the second covers acoustic emission as a diagnostic tool for conservation of archaeological artefacts and historic monuments. Presented *ongoing research projects* include those from: Argentina, describing the metallurgical technologies and conservation conditions of the shipwreck HMS *Swift* (1770); Greece, where plasma has been used to restore hundreds of metal artefacts over the last 15 years; and France, with the description of a copper alloy coating on iron crossbow bolts of the late Middle Ages. *Finalised research projects* include: an international questionnaire distributed from Malta on current approaches to ferrous corrosion products on iron and steel munition armour; the efficacy testing of techniques in use around France for removal of chlorargyrite, or horn silver; and two separate Egyptian projects concerning the synthesis and removal of silver tarnish on contemporary silver alloys using electrochemical and chemical methods, and a developed approach for treating archaeological iron artefacts. Lastly, *research project implementation* into restoration laboratories is demonstrated by the transferral to a French laboratory of the subcritical fluid technologies developed in the USA for the stabilisation of archaeological marine iron.

The BROMEC Editorial Team has expanded with the welcome assistance of two further Hispanophone and Francophone translators, respectively Diana Lafuente, PhD student, and Elodie Guilminot, conservation scientist. Gratitude goes to both Diana and Elodie for their commitment to increasing multilingual dissemination of metal conservation research. The majority of abstracts in BROMEC 29 were originally submitted in languages other than English (5 in French & 1 in Spanish), while 3 from 4 of those submitted in English were by authors with English as a second language.

For your convenience, the BROMEC list of abstracts (issues 1-28) classified by subject has been updated by Elodie and can be downloaded (in English and French) from http://tech.groups.yahoo.com/group/Metals-WG-ICOM-CC/files/. Authors of any BROMEC abstracts who have had associated work published in peer reviewed journals are encouraged to contact Elodie with these bibliographic reference details for inclusion in future BROMEC lists of abstracts.

As usual, we hope you'll find this issue of interest and use.

Editor
James CRAWFORD

Coeditor
Michel BOUCHARD

Coeditor
Emilio CANO

Contents

Page

New research projects

Ongoing research projects

Finalised research projects

Research project implementations

General information

New research project

Understanding the dechlorination mechanisms of ferrous archaeological artifacts from underwater and application to the optimisation of dechlorination treatments. (***CEA, AA, SS, LEMMA***) [1]

To appease the deterioration of underwater ferrous archaeological artefacts after their excavation, conservation-restoration workshops have set up stabilisation treatments via extraction of chloride ions. The chlorides, present within the layers of corrosion products formed during immersion, are indeed participants in the degradation observed on archaeological artifacts. In spite of a clear effectiveness, these treatments remain under-optimized (treatment duration, impact on the object…).

Within the framework of these problems, the Laboratoire d'Archéomatériaux et Prévision de l'Altération à long terme[2], in collaboration with the SOLEIL synchrotron DiffAbs (X-ray diffraction and absorption) beamline, are interested in the comprehension of the dechlorination mechanisms involved in the stabilization treatments applied to archaeological artefacts coming from underwater excavations.

This work is structured around three approaches:

1. Characterization of the corrosion product layers, before, during and after treatment is made by morphological, elemental and structural analyses by coupled complementary characterization techniques at various scales (optical microscopy, SEM-EDS, Raman spectroscopy, XRD and XAS). Three stabilization treatments are studied:
   - aerated medium:
     - immersion in a sodium hydroxide (NaOH) solution
     - immersion in a solution of potassium hydroxide (KOH) under cathodic polarization (-1.45V/SSE)
   - deaerated medium:
     - immersion in an alkaline sulphite solution (0.5M equimolar mixture of NaOH and Na_2SO_3)
2. In order to more accurately understand the dechlorination mechanisms, the evolution of corrosion products is followed by in-situ analysis during the first stages of treatment. It is a matter of, on the one hand, working on corrosion systems coming from archaeological samples. While on the other hand, working on the pure chlorinated phases (iron hydroxychloride – β-$Fe_2(OH)_3Cl$, and akaganéite – β-FeOOH) identified during characterization in order to highlight the reactivity phenomena (chemical and electrochemical) of the phases and transport of the species (Cl^-, OH^-…) within the corrosion product layers.
3. Lastly, a more in-depth structural study of the chlorinated phase predominantly identified within the corrosion products, the iron hydroxychloride – β-$Fe_2(OH)_3Cl$, is planned.

The long term goal is to propose models of dechlorination allowing the optimization of the treatments.

This study is carried out within the framework of a BDI thesis co-financed by the CNRS and the SOLEIL Synchrotron. A close link is maintained between the cultural artefact restoration and research laboratory of Arc'Antique and the Laboratoire d'Etudes des Matériaux en Milieux Agressifs.

Contact: Florian Kergourlay (florian.kergourlay@cea.fr), Philippe Dillmann, Delphine Neff and Solenn Reguer (CEA)
Funding: CEA, CNRS and Synchrotron SOLEIL

[1] Translated into English by J. Crawford. Original language version submitted by author in French; refer to BROMEC 29 French version.
[2] CEA/IRAMIS/SIS2M/LAPA, ex-Laboratoire Pierre Süe

New research project

Listening to active corrosion using acoustic emission. (***A-C/EPA***) [3]

The aim of this research program is to explore the possibilities of acoustic emission (AE) technique as a diagnostic tool for cultural heritage. Acoustic emission is a technique permitting the detection of the elastic waves generated by the rapid release of energy from chemical reactions (and from the subsequent creation of corrosion products due to the reaction) or any physical transformation (cracking, delamination) within materials. It allows the detection of any evolving fault in the material. Acoustic emission analysis is currently typically used in industry for a wide range of applications to detect and localize defects: pitting corrosion of stainless steel, corrosion of reinforcing steel bar in concrete, crevice corrosion… The preliminary diagnosis step with this technique is the creation of a database documenting all the characteristic noises (of determined frequency and time period), also called "acoustic signatures", according to physical or chemical phenomena.

In the field of cultural heritage, we are working on the notion that any progressive defect in an archaeological artifact, such as cracking in stone and ceramics, crizzling of glass or active corrosion in metal could be recorded with the use of this technique. For this initial research program we have used AE technology on archaeological artifacts and an historic monument covering the 3 stages of conservation-restoration treatments:

- Before treatment: the technology was used for the post-excavation diagnosis of an iron artifact in the hope to detect active corrosion and plan whether a stabilization treatment was necessary or not. A stable 13th century nail was deliberately placed in a chlorinated solution (NaCl) for 24 hours and then left to dry at room temperature. At the end of the drying stage we were able to determine the acoustic signature characteristic of active corrosion produced by this artifact.
- During treatment: cathodic polarization has long been used to deconcrete and stabilize iron-based artifacts recovered from the sea. During the deconcreting step (made via a dihydrogen bubbling generated by the polarization) the recurrent difficulty for the conservator-restorer is controlling the polarisation parameters using only cell voltage and current intensity (and determination of the potential of the object) as adjustable variables. The eye of the conservator-restorer is then of paramount importance to control the size of dihydrogen bubbles in order to prevent formation of excessively large bubbles (between the metal-graphitized layer interface) that would destroy the original surface. With the aim of better following this critical step, we employed an AE system and recorded the signal, in real-time, during the bubbling of an 18th century cannon. This initial study made it possible to identify 2 sizes of bubbles and to show that the technique was adapted to the control of the cathodic polarization.
- After treatment: the acoustic emission technique can also be used as a post-treatment tool for checking if an archaeological artifact remains stable over time and, moreover, on industrial heritage and historic buildings as a diagnostic tool. During this study we used AE to detect *in-situ* and in real-time, the active corrosion of steel wire cables supporting the roof of an historic building created by the 20th century architect, Le Corbusier, in Firminy, in the department of the Loire (42). This more "traditional" use made it possible to draw up a condition report of the structures without having to entirely traverse them.

To conclude, acoustic emission is a promising technique because it allows a multi-material diagnosis, before, during and after conservation-restoration treatments. Additionally, it allows the diagnosis of hidden or inaccessible parts and thus facilitates decision making for the planned treatment. Nevertheless, it requires the preliminary creation of a database of acoustic signatures relative to studied phenomena or those that might occur on the object. For the year 2010, we envisage recording the acoustic signatures characteristic of archaeological artifacts of ferrous and copper alloys.

Contact: J.B. Memet (jbmemet@a-corros.fr), Ph. de Viviés, M. Boinet and D. Marlot
Funding: A-C, EPA and OSEO Innovation

[3] Translated into English by J. Crawford, N. Richard and E. Guilminot. Original language version submitted by author in French; refer to BROMEC 29 French version.

Ongoing research project

Investigation of the metallurgical technology of the sloop-of-war shipwreck HMS *Swift* (1770), Puerto Deseado (Santa Cruz, Argentina). (***PROAS, INAPL and GAM, Fi-UBA***)[4]

From its beginnings, one of the main aims of the GAM of the Facultad de Ingeniería of the UBA was the investigation of metallic finds from various shipwrecks that mostly occurred along Argentina's Atlantic coast between the 17th and 19th centuries.

Within this framework our work is focused on the metallic artefacts recovered from the shipwreck of the sloop-of-war HMS *Swift* (1770), which occurred in Puerto Deseado (Santa Cruz, Argentina). As with other cases, the investigation is within the framework of the PROAS of the INAPL. From its beginning in 1997, the main directorate of the archaeological project is in charge of Dr. Dolores Elkin. The particular history of the *Swift* shipwreck and the environmental conditions – low temperature, thin and compact sediment, low ambient oxygen – are responsible for the good preservation of the different examples of metallic artefacts coming from this site. Some of them were part of the ship's accessories and equipment, while others belonged to the wide variety of activities that were performed on board. We can mention: cannons, anchors, a water pump, deck drains, draught marks, a kitchen, a stove, cooking and table utensils (e.g. pots, strainers and spoons), buckles, buttons, and other artefacts that were also part of the furniture and the crewmember's personal belongings (e.g. a bell, a tap, counterweights, candlesticks, handles, coins, a dog collar and an ink bottle). The main metals that made up the collection are: iron, copper and alloys, lead, pewter and silver. Analysis made on some artefact samples mentioned above are based on the application of several analytical techniques from Materials Science: metallography, SEM-EDS, hardness test, radiography, XRD and EPMA.

Studies are included in one of the principal research lines of the archaeological project, for example, conditions for life on board (diet, clothes, health and social status) and technological development at that time (regarding naval architecture, armament, furniture and various utensils). Results obtained to date have allowed us to appreciate the different types and the quality of the materials used; to explore the knowledge about manufacture techniques and processes; to analyze uses and recycling of certain specimens; as well as to evaluate the conservation state of the artefacts and deterioration processes they suffered since the shipwreck. Some of the results were presented at conferences and were published in specialized media [5, 6, 7, 8]. We are about to widen and deepen the study within the mentioned thematic areas.

Contact: Nicolás C. Ciarlo (nciarlo@yahoo.com.ar) (PROAS / INAPL and GAM / Fi-UBA).
Funding: Agencia Nacional de Promoción Científica y Tecnológica, Ministerio de Ciencia, Tecnología e Innovación Productiva, Argentina (PICT 2006-02130).

---

[4] Translated into English by D. Lafuente, E. Cano & J. Crawford. Original language version submitted by author in Spanish; refer to BROMEC 29 Spanish version.

[5] Ciarlo, N. C. y H. De Rosa 2009. Caracterización de un conjunto de cucharas del naufragio de la corbeta británica HMS *Swift* (1770), Puerto Deseado. En M. O. Palacios, C. Vázquez, T. Palacios y E. Cabanillas (eds.), *Arqueometría Latinoamericana: II Congreso Argentino y I Latinoamericano*, vol .1, pp. 270-279. Buenos Aires, Argentina.

[6] Ciarlo, N. C., H. De Rosa, D. Elkin, H. Svoboda, D. Vainstub y L. Díaz Perdiguero 2009. Tecnología de anclas del siglo XVIII. Análisis de una pieza hallada en cercanías del sitio de naufragio *Swift* (1763-1770), Puerto Deseado (Santa cruz, Argentina). *III Congreso Argentino de Arqueometría y II Jornadas Nacionales para el Estudio de Bienes Culturales*, Córdoba, Argentina (Enviado a publicación).

[7] De Rosa, H., N. C. Ciarlo y H. Svoboda 2009. Características constructivas y microestructurales de un botón de un uniforme naval inglés del sitio *Swift* (1770). En M. O. Palacios, C. Vázquez, T. Palacios y E. Cabanillas (eds.), *Arqueometría Latinoamericana: II Congreso Argentino y I Latinoamericano*, vol .1, pp. 227-232. Buenos Aires, Argentina.

[8] De Rosa, H., D. Elkin, N. C. Ciarlo y F. Saporiti 2007. Characterization of a Coin from the Shipwreck of HMS *Swift* (1770). *Technical Briefs in Historical Archaeology* 2:32-36.

Ongoing research project

Plasma conservation of metal artifacts in the Plasma Physics Lab of NCSR "Demokritos". (***NCSR "Demokritos"***) [9]

During the last 15 years, hundreds of metal artifacts have been restored at the Plasma Physics Laboratory of NCSR "Demokritos" using plasma chemistry methods. The method is based on the reduction of corrosion products by a reactive reducing species such as hydrogen atoms in H_2 plasma. Two RF glow discharge plasma devices with different dimensions, similar to Veprek's prototype apparatus[10], are installed.

A lot of research has been carried out during the past years leading to standard conclusions that were published. The first experiments were occupied with the reduction of hydrogen plasma either on oxidized iron objects or on artificially corroded coupons[11-12]. An extensive search on a large number of historic objects with variable oxidation state has been carried out. A combination of gas and plasma parameters (pressure, plasma density and ion and electron temperatures) was used to take various values. This research was extended by using the influence of the external DC electric potential[13], while at the same time a full theoretical study of the plasma sheath's parameters was carried out under specific conditions adapted to our experiment. Furthermore, the research continues by studying the combination of the external DC, which comes through the processing objects, and the plasma. At the same time we confirmed the power of the Langmuir probe theory.

Recently, hydrogen plasma reduction has been used for the conservation of underwater iron objects in the framework of a PhD project. The technique is either used as the sole method of conservation, comparing treatments at different temperature, or as a combination with alkaline sulfite treatment using sodium hydroxide. Additional research is being carried out regarding artefacts made of different copper alloys[14] with chemical composition and metallurgical features similar to those of ancient copper alloys.

Contact: C. L. Xaplanteris & E. Filippaki (lfilip@ims.demokritos.gr) (NCSR "Demokritos")
Funding: Various funded programs

[9] Submitted by author in English – original version.
[10] Veprek,V., Eckmann, Ch., Elmer, J. (1988). Plasma Chemistry and Plasma Processing, 8 (4), pp. 445-465
[11] Kotzamanidi I., Sarris Em., Vassiliou P., Kollia C., Kanias G.D., Varoufakis G.J., Filippakis S.E., (1999). British Corrosion Journal, 34 (4), pp. 285-291.
[12] Kotzamanidi, I., Vassiliou, P., Sarris, Em., Anastasiadis, A., Filippaki, E., Filippakis, S. (2002). Anti-corrosion methods and materials, 49 (4).
[13] Xaplanteris, C., Filippaki, E. Topics on Chaotic Systems, Selected Papers from CHAOS 2008 International Conference, Chania, Crete, Greece, 3-6 June 2008, pp. 406-415.
[14] Novakovic, J., Papadopoulou, O., Vassiliou, P., Filippaki, E., Bassiakos, Y. (in press). Analytical Bioanalytical Chemistry, Special Issue Technart 2009.

Ongoing research project

Restoration and study of a collection of iron and copper alloy crossbow bolts. (***SADY***, ***UPIPS***, ***ENSCP***) [15]

The restoration and study of a collection of iron crossbow bolts typical of the late Middle Ages, coming from excavations of the Madeleine castle (Chevreuse, Yvelines), enabled highlighting the presence of a copper alloy coating, inside as well as outside their socket casings. On the majority of the strongly mineralized objects, remnants appeared in the form of areas of green copper corrosion products or, more rarely, of copper alloy in its metallic state, which was undetectable on radiographs. The presence of this coating was observed on approximately 80% of crossbow bolts from the site (numbering 68 specimens), and is found on objects belonging to different typologies. The bibliography on this phenomenon is nonexistent and we are aware of only one other site with comparable finds. In BROMEC 25 (February 2008) a call had been made to those who could have dealt with objects bearing this coating, but without success.

An analytical study, using an SEM and an analysis system of EDS, IMIX-PGT software, was carried out on a selection of crossbow bolts: two were sacrificed, which enabled making cuts in several directions and a metallographic study; five underwent surface analyses. The study made it possible to specify that the coatings were made from plating of different copper alloys, which annuls the hypothesis of a single manufacturing batch. Indeed, we can distinguish three alloys: the first is a binary bronze having an average mass tin concentration of 5.5%, the second is a ternary bronze (up to 5% tin, circa 2% zinc, lead being present in trace amounts); the last is a ternary bronze with a zinc (4.5%) concentration that is greater than that of tin (3.5%). One could also, using the analyses, make an hypothesis on the technical manufacture process, which would have been using a bath of molten metal, after shaping. Indeed, the arrangement of the copper components in relation to the ferrous remnants seems to indicate that objects of iron were put in contact with molten copper alloys for enough time to apply an adequate layer.

The practical purpose or symbolic value of this coating continues, on the other hand, to be inexplicable, as well as the prevalence of polymetallic crossbow bolts in the corpus excavated from the castle of Chevreuse. Is the coating a local particularity, or has the copper alloy that was originally present on the bolts not been preserved in other situations (and if so, for which reasons?) or perhaps it has been preserved, but never observed (some ferrous material publications study unrestored artefacts). The answer to these questions can only be ascertained from the discovery and study of other specimens, and consequently from the alertness of professionals towards the remnants of surviving plating, or from still unexplored documentary sources.

Contact: Silvia Païn (SADY) (spain@yvelines.fr), Nicolas Girault (UPIPS) & Aurore Doridot (UPIPS/ENSCP).
Funding: No external funding

[15] Translated into English by J. Crawford, N. Richard and M. Bouchard. Original language version submitted by author in French; refer to BROMEC 29 French version.

Finalised research project

Current approaches to ferrous corrosion products on munition armour: results from an international laboratory questionnaire. (***HM-UM***) [16]

Preservation approaches to arms and armour have changed considerably since their manufacture and use. Conservation-restoration literature of recent decades and our contemporary personal communications with armourers and conservator-restorers indicated a spectrum of methodologies: these are generally more scientifically aware and less interventive than before since intentional retention of some corrosion products (CPs) is now performed by some practitioners. However, deficits with the literature are that it's largely concerned with more prestigious decorated armour, and any specified approaches to CPs are limited in number and detail. Such inadequate information prompted a complementary and current source to establish the status quo on approaches to CPs on ferrous munition armour.

A questionnaire was distributed as an attachment to an introductory and individually addressed email to 109 persons working for armour collecting institutions/custodians. The questionnaire fitted within the context of research concerning the determination of original surface limits (*limitos*) of ferrous CPs on undecorated ferrous armour[17]. Techniques and motivations for practices were surveyed. Twenty-four armour conservator-restorers representing 21 organisations in Europe and North America responded. The main results were:

1. Corrosion product removal is unanimously (100%) the approach most commonly applied to ferrous CPs on the outer surfaces of undecorated ferrous munition armour.
2. The level of corrosion product removal is less decisive, but a clear majority (71.4%) take a moderated approach by "Removing red-brown corrosion products, leaving most/all dark grey/black corrosion products in/above the corrosion pits". Aiming to completely strip a surface of CPs appears to be a largely, but not entirely (9.5%), discontinued practice. The Palace Armoury's (PA) stated practice falls between these two extremes.
3. Corrosion prevention (76.2%), surface information (63.7%) and display aesthetics (54.5%) are the factors that largely determine which corrosion products are removed, since they were indicated as influencing practice to the highest degrees (i.e. high to very high).
4. The most often cited categories of equipment/materials in use to remove corrosion products are all physical, manual methods: handheld implements (91.7%); and steelwool handtools (66.7%). The strong preference for physically based processes is made clear when compared to chemically based processes in use (acid solutions (29.2%), chelating agents (16.7%)).
5. To homogenise the overall appearance, a majority (70.0%) of respondents polish adjacent metallic surfaces after corrosion product removal.

Attaining an international perspective provided a general consensus and benchmark for the PA and others to compare their current munition armour approaches, especially towards corrosion product removal. Polishing of adjacent metal after CP removal might indicate techniques are not localised to corroded areas and subsequent polishing is unnecessarily depleting the unaffected metal. From this research, it appears motivations for CP removal or retention are more concerned with revealing metal surfaces with markings, than concerned with ferrous CPs potentially preserving surface information deriving from the former metal surface.

Electronic copies of the questionnaire, results and analyses are available from the author on request. Subsequent laboratory research will be presented in BROMEC 30.

Contact: James Crawford (jamesbcrawford76@gmail.com) & Christian Degrigny (HM-UM)
Funding: No external funding

[16] Original version; submitted by author in English.
[17] Refer to BROMEC 22 (May 2007)

Finalised research project

Studies of the corrosion and the conservation-restoration treatments of artefacts with horn silver ($AgCl$). (***AA***) [18]

Silver deteriorates in the ground. The most common corrosion products are sulphides and chlorides. One of the main components of the corroded surface was identified as chlorargyrite, also called horn silver ($AgCl$). This compound is white, but in the presence of light and impurities, it becomes bulky and purplish. It has a waxy texture that makes its mechanical removal problematic; at least for removal from surfaces with complex geometry or fine details.

The study is made on a collection of jewels found in graves (dating to the 5th-7th centuries) coming from St Martin of Angers. Characterization (SEM-EDS, XRD…) of these objects showed the presence of various layers: the metal core and two layers of corrosion products (an internal and an external layer). The original surface is between these two layers. These two layers are differentiated by their porosities (greater porosity for the external layer). The internal layer is predominantly of silver and chlorides. The interface between the internal layer and the external layer, known to be the original surface, is sometimes characterized by the presence of gold or lead. Finally the external layer is characterized by a greater chloride concentration (20%).

A questionnaire distributed to numerous French restorers, together with a literature survey, enabled selection of various restoration techniques. All the solutions were individually tested. These tests were carried out on fragments of objects:

- Acid solutions: ineffective solutions
  The solutions tested ($pH<2$) are formic acid and orthophosphoric acid. They do not have any influence on the dissolution of horn silver.
- Basic solutions: promising solutions
  The solutions tested ($pH>13$) are sodium hydroxide and potassium hydroxide. The basic environment hardens and blackens the external layer. The external layer is thus weakened and thanks to ultrasound, separation occurs at the level of the original surface.
- Chelating solutions: effective solutions, but can be too much…
  The solutions tested are ammonia (pH 11.5), ammonium thiocyanate (pH 5.6), thiourea (pH 5.9) and ammonium thiosulfate (pH 6). They solubilize the silver chloride to form a complex with silver. The treatment time must be adapted to the thickness of the external layer.
- Another tested solution: glucose + sodium hydroxide: unsuitable solution
  A layer rich in silver forms on the surface of the external layer, but does not weaken it. Therefore this treatment is unsuitable for the removal of the external layer.

Contact: E. Guilminot (Elodie.guilminot@arcantique.org), S. Lemoine, L. Rossetti, M. Vieau (AA)
Funding: No external funding

[18] Translated into English by J. Crawford, E. Guilminot, N. Richard. Original language version submitted by author in French; refer to BROMEC 29 French version.

Finalised research project

Laboratory approaches to tarnishing and cleaning silver alloy. (***NRC***) [19]

Accelerated procedures for synthesizing silver tarnishing on contemporary silver alloy were developed based on electrochemical and chemical methods. High concentrations of sodium sulfide (0.1M Na_2S) quickly produced chemically-induced tarnishing. The electrochemical method accelerated tarnishing in low concentrations of Na_2S (6.4×10^{-6}M) by application of an anodic potential. The tarnish layer formed within a few minutes with different degrees of color (yellow to dark). Gloss level measurements indicated this variation of color by giving a lower gloss value (%) as tarnish darkened. Open circuit potential measurements indicated that the potential shifts in the anodic direction, being due to the formation of the tarnish layer on the silver surface.

Appropriate methods for silver cleaning (i.e. removing the synthesized tarnish) were tested. Electrochemical cleaning was based on cathodic reduction by application of a cathodic current in 10% (1:1) sodium carbonate and sodium bicarbonate solution for a certain period of time (10-30mins.) Also, galvanic cleaning by coupling with an aluminum anode was achieved in the same solution. The tarnish layer was instantly removed resulting in a clean surface. Tarnish removal was measured conversely by its increase in gloss value. The present results indicate that galvanic coupling with a piece of aluminum is one of the most effective methods for cleaning contemporary silver and has potential use on certain silver artifacts.

Contact: V. K. Gouda and A. A. El-Meligi (NRC) (ael_meligi10@hotmail.com)
Funding: European Commission-PROMET project

[19] Submitted by author in English – original version.

Finalised research project

Researching conservation treatments for archaeological iron artifacts and application to selected objects from Tell-El Farama, North Sinai, Egypt. (***FU***) [20]

Archaeological iron artifacts that are buried in soil are badly corroded; forming a red/brown rust of iron oxides and hydroxides, which are formed by very complicated series of processes and mixtures with soil. When salts are present they act as electrolytes, while the chemical reactions that cause corrosion are reinforced by electrochemical reactions and mineralization is greatly accelerated.

The aim of this work is therefore to understand the corrosion process related to the presence of chloride ions (Cl^-) in the soil, and to determine the best methods for their treatment. To achieve this aim a careful examination was made to determine the condition of the object before treatment. To determine the type of corrosion products XRD was used, while SEM & metallographic examinations were used to assess the internal condition of the object. Also, XRF was used for elemental determination of the object. An experimental study was made to select the best method to treat the object and an electrolytic reduction method was followed by a thermal treatment since it has a lot of advantages: it consolidates the object, extracts chlorides and reduces corrosion products. We recommend such a treatment for artifacts like these. Finally, in order to limit further deterioration, the artifact was coated with a wax.

Contact: E Mohamed Moatamed (mmoatamed_2@yahoo.com) (FU)
Funding: No external funding

[20] Submitted by author in English – original version.

Research project implementation

The stabilization of archaeological iron artifacts using subcritical fluids. (***A-C, CCC***) [21]

The stabilization of archaeological iron artifacts is an essential step in the conservation-restoration process of an artifact. Many techniques exist that make it possible to extract chlorides, a main agent of corrosion, from materials. However, it is not uncommon to have relatively long treatment times, from months to even years, in archaeological conservation, which lead to significant costs.

A new technology, based on the use of subcritical fluids, makes it possible to dramatically decrease the treatment duration. It also seems to noticeably improve the extraction of chlorides from the artifact, thus guaranteeing its long-term stability under normal conditions of temperature and humidity. This technology was developed and first tested in 2003, in the United States at the Clemson Conservation Center in Charleston, South Carolina, on archaeological iron artifacts[22, 23, 24].

In the specific case of stabilization of archaeological artifacts, one refers to subcritical fluids when a chemical solution (in this case NaOH) is pressurized so it can be heated to a working temperature around 180°C (best extraction temperature) and still remains in a liquid phase. At this temperature the chemical solution acquires properties nearing those of gases. Indeed, increasing the temperature increases the diffusion constant for chloride ions to a significant degree, while reducing the water viscosity and density improves transport of the fluids and their penetration into the corrosion layer interstices. Lastly, lowering of the chemical solution's surface tension improves its penetration within the material and facilitates the exchange of ions.

Since 2009, following the installation of a partnership between the Clemson Conservation Center and A-CORROS, engineering and conceptual studies are underway in order to set up this technology in France. In addition, the CCC is equipped with a new reactor system that allows it to raise its capacity to treat larger artifacts.

Contact: Philippe de Viviés (devivies@a-corros.fr), Typhaine Rosa-Brocard (CCC), Michael Drews (CCC), Nestor Gonzalez (CCC), Paul Mardikian (CCC) and Jean-Bernard Memet (A-C)
Funding: No external funding

[21] Translated into English by J. Crawford, E. Guilminot and M .Bouchard. Original language version submitted by author in French; refer to BROMEC 29 French version.

[22] M. J. Drews, P. de Viviés, N. G. González and P. Mardikian, "A study of the analysis and removal of chloride in iron samples from the *Hunley*," Metal 04, Proceedings of the International Conference on Metals Conservation, Canberra, Australia, October 2004, National Museum of Australia, Canberra, pp. 247-260 (2004).

[23] P. de Viviés, D. Cook, M. J. Drews, N. G. González, P. Mardikian and J.B. Memet, "Transformation of akaganeite in archaeological iron artefacts using subcritical treatment", Metal 07, Proceedings of the International Conference on Metals Conservation, Amsterdam, Netherlands, October 2007, Rijksmuseum Amsterdam, Vol 5, pp. 26-30 (2007).

[24] N. G. González, D. Cook, M. J. Drews, P. de Viviés, P. Mardikian, "The effect of cathodic polarization, soaking in alkaline solutions and subcritical water on cast iron corrosion products", Metal 07, Proceedings of the International Conference on Metals Conservation, Amsterdam, Netherlands, October 2007, Rijksmuseum Amsterdam, Vol 3, pp. 32-37 (2007).

Abbreviations and acronyms

AA: Arc'Antique
A-C: A-CORROS Expertises (France)
AE: acoustic emission
BDI: bourses de docteurs ingénieurs
CCC: Clemson Conservation Center (USA)
CEA: Commissariat à l'Energie Atomique (France)
CNRS: Centre National de la Recherche Scientifique (France)
CP: corrosion product
DC: direct current
EDS: energy dispersive spectroscopy/spectroscope
ENSCP: École Nationale Supérieure de Chimie de Paris (France)
EPA: Euro Physical Acoustics (France)
EPMA: electron probe microanalysis
FU: Fayoum University (Egypt)
GAM: Grupo de Arqueometalurgia (Argentina)
HM-UM: Heritage Malta (Institute of Conservation and Management of Cultural Heritage) – University of Malta (Malta)
IMIX-PGT: integrated microanalyzer for imaging and x-ray - Princeton Gamma-Tech
INALP: Instituto Nacional de Antropología y Pensamiento Latinoamericano (Argentina)
IRaMiS: Institut Rayonnement Matière de Saclay (France)
LAPA: Laboratoire d'Archéomatériaux et Prévision de l'Altération (France)
LEMMA: Laboratoire d'Etudes des Matériaux en Milieux Agressifs (France)
NCSR: National Centre of Scientific Research (Greece)
NRC: National Research Centre, Physical Chemistry Department, Egypt
PA: Palace Armoury (Malta)
PROAS: Programa de Arqueología Subacuática (Argentina)
RF: radio frequency
SADY: Service archéologique départemental des Yvelines (France)
SEM: scanning electron microscopy/microscope
SIS2M: Service Interdisciplinaire sur les Systèmes Moléculaires et les Matériaux d'IRaMiS (France)
SS: Synchrotron SOLEIL (France)
SSE: saturated mercurous sulphate ($Hg/HgSO_4/K_2SO_4$sat) electrode (SSE=0.658V/SHE (standard hydrogen electrode)
UBA: Universidad de Buenos Aires (Argentina)
UPIPS: Université Paris I - Panthéon-Sorbonne (France)
XAS: X-ray absorption spectroscopy
XRD: X-ray diffraction
XRF: X-ray fluorescence

General information

Future seminars and conferences

- **Archaeological Iron Conservation Colloquium** (24-26 June, 2010, Stuttgart, Germany). Held at the State Academy of Art and Design Stuttgart, in collaboration with AIAE "Archaeological Iron After Excavation", sub-WG of ICOM-CC Metals. For more information please contact Gerhard Eggert (gerhard.eggert@abk-stuttgart.de).

- **ENAMEL 2010** 3rd Experts meeting on Enamel on Metals Conservation (8-9 October, 2010, Frick Collection, New York, United States of America). Organised by ENAMEL, sub-WG of the WGs "Metals" and "Glass & Ceramics". For more information see http://www.icom-cc.org/52/event/?id=68.

- **Metal 2010: Triennial Metals Conservation Conference** (11-15 October, 2010, Charleston, South Carolina, United States of America). Metals Working Group of ICOM Committee for Conservation. Publication timeline: http://www.timetoast.com/timelines/4880 Further information: http://www.icom-cc.org/51/news/?id=22.

Announcements

New **New EFC Working Party – "Corrosion of Heritage Artefacts"**: The European Federation of Corrosion (EFC) has created a Working Party dedicated to "corrosion of heritage artefacts". In close collaboration with other already existing European institutions and working groups, this working party aims to fill the gap between scientific corrosion studies and different fields such as restoration, conservation or very long term corrosion prediction. The inaugural session of this working party was held at the 2009 EUROCORR (http://www.eurocorr.org/) congress in Nice (France). For further information: Philippe Dillmann (Philippe.dillmann@cea.fr), Head of "Archaeomaterials and Alteration Prediction Laboratory", SIS2M/LPS CEA/CNRS and IRAMAT LMC CNRS, CEA Saclay, 91191 Gif sur Yvette Cedex, France.

Websites

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

- **ARTECH network**: Network facilitating the access of conservation professionals to different investigation techniques for Cultural Heritage artefacts (http://www.eu-artech.org/).

- **BigStuff 2004**: Care of Large Technology Objects (http://www.awm.gov.au/events/conference/bigstuff/index.asp).

- **CAMEO**: 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://cameo.mfa.org/).

- **Cost Action G7: Artwork conservation by laser**: (http://alpha1.infim.ro/cost).

- **Cost Action G8: Non-destructive analysis and testing of museum objects**: Abstracts and booklets from previous workshops can be downloaded as well as announcements of past activities (Short Term Scientific Missions deadlines, training schools…) (http://srs.dl.ac.uk/arch/cost-g8/).

- **Cost Action D42: ENVIART**: Chemical Interactions between Cultural Artefacts and Indoor Environment. Register (free) to access all information (http://www.echn.net/enviart/).

- **e-Preservation Science**: Online publication of papers in conservation science (http://www.morana-rtd.com/e-preservationscience/).

- **European Cultural Heritage Network**: European network of professionals interested in the conservation of Cultural Heritage (http://www.echn.net/).

- **ICOMAM**: International Committee of Museums and Collections of Arms and Military History: (http://www.klm-mra.be/icomam/).

- **ICOM-CC Metals Working Group**: (http://www.icom-cc.org/31/working-groups/metals/). This site is for all official ICOM-CC Metals WG activities, forums, news, file downloads and information. The co-ordinator can email members from this site once members have registered on-line as a member of the Metals WG. Public access to this site is limited.

- **Industrial artifacts review**: Industrial design and the role of art and photography in promoting cultural heritage (http://industrialartifactsreview.com/).

- **Infrared and Raman for cultural heritage**: (http://www.irug.org/default.asp).

- **Laboratoire Pierre Sue**: LPS PhD thesis related to the alteration of archaeological artefacts can be downloaded in French. Follow the link to "Archéomateriaux et prévision de l'altération" (http://www-drecam.cea.fr/lps/).

- **LabS-TECH network**: (http://www.chm.unipg.it/chimgen/LabS-TECH.html).

- **METALCons-info**: Metals Conservation Information (http://metalsconservationinfomation.wetpaint.com/) is where the old METALCons-info site is being moved and redeveloped. This is a wiki based site, which means it can be grown by contributions from "writers" - i.e. you. Its power depends on how willing you are to use it. Each week it sends a summary of activity to members – so sign up! It is currently publicly visible, but this may change with any unwanted activity.

- **M2ADL**: Microchemistry and Microscopy Art Diagnostic Laboratory (http://www.tecore.unibo.it/html/Lab_Microscopia/M2ADL/).

- **New York Conservation Foundation**: (http://www.nycf.org/).

- **PROMET**: A 3.5 year European 6th Framework funded project (21 partners from 11 countries around the Mediterranean basin) that developed conservation strategies for outstanding metals collections throughout the Mediterranean (http://www.promet.org.gr).

- **Restauración Metal Sur America**: (http://www.restauraciondemetales.cl/).

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

- **Yahoo Groups Metals Conservation**: (http://tech.groups.yahoo.com/group/Metals-WG-ICOM-CC/). A discussion group for all who are interested in Metals Conservation. Join in and make this a "Metals Cons-Dist List".

National Contacts for the ICOM-CC Metals Working Group

Argentina: Blanca Rosales, researcher, CIDEPINT, La Plata.
Australia: David Hallam, senior conservator-restorer of objects, National Museum of Australia, Canberra.
Belgium: Annemie Adriaens, researcher and lecturer, head of the group "Electrochemistry and Surface Analysis", Ghent University (Universiteit Gent), Ghent and Gilberte Dewanckel, conservator-restorer, Royal Institute of Artistic Heritage (Institut Royal du Patrimoine Artistique), Brussels.
Bulgaria: Petia Penkova, conservator-restorer, National Academy of Arts, Department of conservation-restoration, Sofia.
Canada: Judy Logan, conservator-restorer (retired), Ottawa.
Chile: Johanna Theile, conservator-restorer and lecturer, Faculty of Art, University of Chile The Oaks (Facultad de Arte, Universidad de Chile Las Encinas), Santiago de Chile.
Croatia: Zoran Kirchhoffer, conservator-restorer, Zagreb Technical Museum (Tehnički muzej Zagreb).
Denmark: Karen Stemann Petersen, conservator-restorer, The National Museum of Denmark (National Museet), Copenhagen.
Egypt: Wafaa Anwar Mohamed, conservator-restorer, Giza.
Finland: Eero Ehanti, conservator-restorer, Maritime Museum of Finland (Suomen Merimuseo), Helsinki.
France: Marie-Anne Loeper-Attia, conservator-restorer and assistant-lecturer at the Conservation Department, National Heritage Institute (Institut National du Patrimoine), St Denis, Paris and Elodie Guilminot, conservation scientist, Arc'Antique, Nantes.
Germany: Britta Schmutzler, PhD "object conservation" student, State Academy of Art and Design (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-restorer, Conservation Department, Hungarian National Museum (Magyar Nemzeti Muzeum), Budapest.
Italy: Paola Letardi, scientist, Institute for Marine Corrosion of Metals (Istituto per la Corrosione Marina dei Metalli), Genova.
The Netherlands: Ineke Joosten, conservation scientist, The Netherlands Institute for Cultural Heritage (Instituut Collectie Nederlan), Amsterdam.
Norway: Douwtje Van der Meulen, conservator-restorer, Conservation Department, University of Oslo (Universitetet i Oslo), Oslo.
Morocco: Hind Hammouch, scientist, Laboratory of Electrochemistry, Corrosion and Environment, Faculty of Science, Ibn Tofail University, Kenitra.

Portugal: Isabel Tissot, conservator-restorer, Portuguese conservation-restoration Institute (Instituto Português de Conservação e Restauro), Lisbon.
Romania: Dorin Barbu, conservator-restorer, National Brukenthal Museum (Muzeul Național Brukenthal), Sibiu.
Russian Federation: Andrey Chulin, conservator-restorer, the State Hermitage Museum, St Petersburg.
South Africa: Jaco Boshoff, maritime archaeologist, Iziko Museums of Cape Town, South Africa.
Spain: Emilio Cano, scientist, National Centre for Metallurgical Research (Centro Nacional de Investigaciones Metalúrgicas), Spanish Council for Scientific Research (Consejo Superior de Investigaciones Científicas), Madrid.
Sweden: Helena Strandberg, conservator-restorer and conservation scientist, freelancer, Göteborg.
Switzerland: Valentin Boissonnas, conservator-restorer and lecturer, Technical University (Haute école de conservation-restauration Arc), La Chaux-de-Fonds.
United Kingdom: Catia Viegas Wesolowska, conservator-restorer, Victoria & Albert Museum, London & Mark Dowsett, physicist, University of Warwick, Coventry.
United States of America: John Scott, New York Conservation Foundation, New York.