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METALConsn-info



Bulletin of the Research On METal Conservation

May 2006

BROMECC18

Editorial

In the past months our Metal WG has been quite active. In fact we had two meetings of the BAC / NDTMA and ETIC sub Working Groups. The first one took place at Gif-sur-Yvette and was held at Synchrotron SOLEIL; the second one in Ghent at the Department of Analytical Chemistry of the University. The outcomes of the meetings (minutes and PowerPoint presentations of speakers) will be available soon on both the ICOM-CC Metal WG and **METALConsn**-info websites.

Several meetings related to metal artefacts and their conservation will be held in the next months. We wanted to highlight a few of them. More information can be found at the end of this document under General information. The first will be held in France: it is the annual meeting of the French section of the ICOM-CC Metal WG (28-29 September 2006, INP, Paris). The two days meeting will include a workshop to update the participants on research in iron conservation. It will be followed by the meeting of the Archaeological Objects WG of the Verband der Restauratoren (VDR) (12-13 October 2006, Mannheim, Germany) on *Archaeological metal finds – from excavation to exhibition*. The AIAE sub WG will have a special session during that conference. Another important meeting for the ETIC subWG will be the 2006 Conservation Science Annual (11-16 November 2006, Sommerset, USA) organised by EAS / NYCF. The mini-symposium will be entirely dedicated to the *use of electrochemical techniques in metal conservation*. It is the first time that specialists from Europe and America have the chance to meet and discuss about this important topic. Next year, 2007 will be the year of METAL 07 in Amsterdam (September). Those specifically interested in the conservation of indoor metallic collections should not miss the forthcoming *Conservation Strategies for Saving Indoor Metallic Collections* (CSSIM) (25 February – 1st March 2007, Cairo, Egypt). It is organised by the Applied Laser Spectroscopy Group (NILES, Egypt) and EU PROMET project and both the ICOM-CC Legal Issues in Conservation and Metal WGs will contribute.

In parallel to these special sessions contributors of both the **METALConsn**-info homepage and members of the Metal WG continue to support the dissemination of information on research projects through BROMECC. This issue of BROMECC is once again showing that most of the research in the field is carried out on copper and iron based materials. Two projects relate to conservation and examination of buried archaeological objects, one reviews the effectiveness of a stabilisation treatment (immersion in hydroxylamine) for iron archaeological artefacts and the second is a notable first contribution to BROMECC from China that discusses the effect of burial environment parameters. Two others relate to the protection of outdoor monuments and large structures.

For your information the ICOM-CC website is once again freely available until October 2006.

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

Editor

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Ongoing research projects

 Development of a method of interpretation of radiographies for the study of iron archaeological artefacts: a contribution to the study of their corrosion structure and diagnosis (UPS – Paris I)

Treatment of iron archaeological objects within conservation laboratories poses a certain number of issues due to their number and their extensive alteration. In most cases, visual examination alone is not enough to identify them and recognize their shape. Moreover, iron archaeological objects are very unstable and there is a high risk that they deteriorate in the short term.

French conservation laboratories had to equip themselves with X-ray devices. Today this non-invasive and commonly used technique has become for archaeologists and conservators a true management tool for metallic artefacts and a major diagnostic instrument. It can provide invaluable information on the structure of the metallic objects, the manufacturing techniques used and on their conservation state. Radiographic examination is also essential to localize the limit of the original surface and understand the stratigraphy of the corrosion products although in practice the reading and interpretation of the radiographs has proven to be delicate.

The principal objectives of this PhD research supervised by both C. Volfovsky and R. Bertholon are; to elaborate a method and vocabulary of description that intend to refine the reading of the radiographs and the localization of the limit of the original surface or "limitos"; to refine the observation and to develop the criteria of interpretation of the stratigraphy of corrosion; to allow the recognition of the specific characteristics of active corrosion and to carry out an atlas representative of the data collected by the observation, the comparison or even the digitization of the radiographs in order to assist and optimize the diagnosis.

The material and the methods used are scientific, industrial and medical bibliographical sources such as; methodology of sensory analysis; descriptive method of the corrosion of the metallic archaeological objects (cf. R. Bertholon's PhD [1]), a representative corpus (i) of medieval iron objects from the site of Saint Denis, France (Unit of Archaeology), (ii) of geometry (square or rectangular section) and (iii) of state of conservation, radiographs from the Institut de Restauration et de Recherches Archéologiques et Paléometallurgiques (I.R.R.A.P). The following are also considered; radiographs of the corpus; metallographic and radiographic material from the Conservation, Restoration and Research Laboratory of the Var Archaeological Centre and finally the knowledge compiled by the conservation laboratory of the Master of Conservation of Cultural Properties of the Pantheon-Sorbonne University of Paris I and the Municipal Unit of Archaeology of St Denis.

The results already obtained are the following: a determination of a specific vocabulary of "descriptors" based on the bibliographical sources, observation of radiographs and metallographic cross-sections; determination of the full range of parameter intensity of the sensory analysis (scaling techniques) and realization of cross-sections of objects embedded in paraffin.

Further work will concentrate on the atlas of radiographs, the establishment of a panel of experts in order to make the method accessible and usable by the conservation laboratories, the improvement of the choice of treatments to be applied to the objects according to their

state of conservation and the provision of elements for archaeologists to give them the possibility to carry out a proper selection of objects that require conservation treatment.

Reference:

1. Bertholon, R. La limite de la surface d'origine des objets métalliques archéologiques. (2000). Université Paris Sorbonne – Paris I. PhD thesis.

Contact: Françoise Mielcarek (UPS – Paris I)

Funding: No external funding

Ongoing research projects



Study of the corrosion protection of copper and its alloys applied to cultural heritage conservation (CITEFA/EF-UBA)

This PhD research supervised by Dr Blanca Rosales aims at electrochemically studying copper's and copper alloys' corrosion behaviour and protectiveness of the surface films formed. The composition and morphology of these surface films have been characterised through surface analysis techniques SEM/EDX, XPS, XRD and FTIR.

This study consists of 2 approaches: the effect of organic compounds on copper corrosion inhibition, analysing the mechanism by means of electrochemical impedance spectroscopy (EIS) and the protectiveness evaluation of patinas formed on outdoor bronze sculptures compared to accelerated laboratory tests. These evaluations were carried out in situ by means of an electrochemical technique, which allows measuring the open circuit potential of metallic surfaces covered with their corrosion products (Pourbaix technique). This technique was applied to quantify the potential evolution with time.

The use of electrochemical techniques for non-destructive in situ analysis on metallic monuments is a new internationally significant contribution to the conservation of metallic cultural heritage. Work will continue in an interdisciplinary project with the Restoration Area of the Culture Secretariat of Buenos Aires city. The Pourbaix technique and a current density measurement technique are both applied for diagnosis and to establish selection criteria to follow up restoration processes.

Contact: Gabriela Cicileo (CITEFA)

Funding: No external funding

Ongoing research projects



Relationship between the conservation state of unearthened bronze artefacts and the burial environment (DC – XJTU / SAM – PKU)

Corrosion is the damage and deterioration process of metallic materials when exposed to the environment. The corrosion degree or the conservation state of unearthened bronze artefacts depends on the bronze itself (its composition) and the environment. So to evaluate the corrosion degree and to find out the relationship between the bronze and the burial environment is fundamental to assess corrosion-resistance of the artefact's material, the corrosiveness of the soil, as well as to investigate the corrosion mechanism and determine an appropriate conservation method.

Although some previous research mentioned the relationship between the parameters of soil and the excavated metals, the cluster analysis method was seldom used to draw the decisive parameters that influence the decay of buried metals. In this research, the spearman coefficients* between the state of bronze and the parameters of soils, from where bronzes were excavated, were calculated separately. It showed that soils with higher value of pH, resistivity and HCO_3^- have a positive effect (positive correlation) on the condition of the bronzes. Meanwhile, the higher the value of the total amount of salt content, Cl^- , SO_4^{2-} , NO_3^- (taken separately), the worse the condition (negative correlation). But in most cases where the absolute value of the spearman coefficients is below the critical value at a significance level of 0.05, the strength of the relationship is not significant.

So, one single parameter of the soil cannot reflect its corrosion property well. In order to access the corrosion property, the integrated parameters of the soil must be considered. Through cluster analysis of the characters of the soil, it is shown that there is an obvious relationship between the conservation state of archaeological bronzes and the characters of soil. Discriminant analysis method is used to determine the functions that can be considered to assess the corrosion property of the soil or the state of buried metals.

The functions have been used on objects from different archaeological sites and it has been found that the state of bronzes excavated from these sites is very consistent with that of the theoretical one drawn from the functions.

*: The spearman coefficient is a concept from statistics that is used to summarize the strength and direction (negative or positive) of a relationship between two variables

Contact: Sun Feipeng (DC- XJTU) and Zhang Xiaomei (SAM – PKU)

Funding: No external funding

New research projects



CONSIST: Coating Materials and Strategies for the Preservation of Iron / Steel Industrial Cultural Heritage (ISC)

An EC-funded 3-year research project titled “Comparison of Conservation Materials and Strategies for Sustainable Exploitation of Immovable Industrial Cultural Heritage made of Iron and Steel” (Acronym: CONSIST) has been set up in summer 2005. The background and the objectives of the project are as follows.

Suitable conservation materials and preservation / management concepts are required to treat indoor and outdoor immovable industrial heritage with weathered / corroded / coated iron and steel surfaces. For this purpose and especially for comparison, various established protective resins ranging from traditionally used oil paints to modern microcrystalline waxes and organic lacquers like acrylics, polyurethanes, or silanes will be tested. For evaluation, accelerated weathering, subsequent stress tests, and instrumental analyses are performed. Moreover, new coatings and consolidants with improved properties are to be developed. This new class of lacquers should be transparent, long-term resistant against weathering and sunlight, applicable on site e.g. by spraying, and reversible. The synthesis will be based on sol-gel reactions resulting in water-based, solvent-free hybrid ORMOCER[®] (ORganically MODified CERamics) systems.

Research activities and related test applications are closely connected to restoration demands of selected pilot objects and areas. Moreover, integral action plans for future exploitation will be developed and will influence the restoration and conservation attempts, based on initial preservation documentation of the pilot sites and on the project’s scientific results. As pilot objects, locomotives from the inventory of an open air Railway Museum in Jaworzyna Slaska (Lower Silesia, Poland), typical underground machines of the Mining Museum Bochum in Germany, and architectural ironworks of Palladian Houses in Ireland have been selected.

The partners of the project are the Technical University, Institute of History of Art and Technology (Wroclaw, Poland), the German Mining Museum (Bochum, Germany), Naylor Conservation (Telford, England) and Haber & Brandner Metal Restoration GmbH, (Regensburg, Germany).

Contacts: Peter Mottner (Fraunhofer Institute for Silicate Research (ISC), Bronnbach Branch, Competence Team “Environmental Monitoring and Conservation Research”)

Funding: The work is supported by the EC, DG RTD I (STREP Contract 513706-SSPI-CONSIST)

New research projects



The desalination of archaeological iron objects with hydroxylamine (*SABKS*)

In 1998, Wunderlich and Neubacher presented the desalination of archaeological iron objects with hydroxylamine as reducing agent at the ADR Conference “Archaeological Iron” in Mainz, Germany [1]. They saw a lot of advantages compared with other methods, which made the desalination treatment really promising: Apart from a short treatment time (about 2-4 weeks), a hydroxylamine solution has inhibitive properties during the desalination and drying process. Moreover a post-treatment is not necessary, because hydroxylamine decays after several weeks into the volatile compounds ammonia, nitrogen and nitrous oxide. So far, the suitability of this method has been proven only with few objects, experience was mixed. To understand how the desalination with hydroxylamine is working and to determine the efficiency of the treatment, an advanced student’s project was started in the Object Conservation Course at the State Academy of Art & Design Stuttgart (*SABKS*).

Akaganeite (β -FeO(OH,Cl)) samples were synthesized and immersed in aqueous hydroxylamine and in common washing solutions (alkaline sulphite, sodium hydroxide solution, lithium hydroxide solution and water). The chloride extraction rates were compared and the remaining samples analysed by XRD. The result was, that akaganeite could not be destroyed by a hydroxylamine solution during four weeks of treatment. The desalination efficiency in the first wash solution was best. In subsequent wash solutions hardly any chloride could be quantified. Then the sample desalinated with hydroxylamine and the untreated akaganeite sample were put on an iron sheet. The desalinated akaganeite did not cause corrosion, but the untreated sample did corrode under high RH.

The desalination treatment with hydroxylamine was also tested on original archaeological iron objects, which were corroding during desalination. After the treatment, residual chlorides in some of the objects could be determined by EDX. Moreover the iron objects were not stable at high RH and the samples were corroding in not ideal conditions. A completely desalinated object, having a chloride concentration lower than 2 ppm in the last solution, was corroding during storage in a high RH for some weeks.

The chemical behaviour of hydroxylamine in contact with iron is dependent on pH, so that in alkaline solutions Fe(II) is oxidised to Fe(III) in an opposite behaviour to alkaline sulphite treatments where this is prevented. Fresh FeOOH is visibly precipitated in solution (and most likely in the micropores of the object preventing effective desalination).

Further research will determine the chloride content of akaganeite treated with hydroxylamine and alkaline sulphite and test more objects, but at the moment the method does not look promising.

1. Wunderlich, C.H., “Archäosideroprophylakt” – Entsalzung von Eisenfunden mit Hydroxylamin, Jahresschrift für mitteld. Vorgeschichte **83** (2000) 305-316.

Contact: Ingrid Wiesner (idl2000@yahoo.de)

Funding: no external funding

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>
 - **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-drecom.cea.fr/lps/> (in French) and go to “Archéomatériaux et prévision de l’altération.”
 - **METALConsn**-info 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/
 - **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**
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<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>)

Future seminars and conference

- **Journée " Techniques métallurgiques pré-industriels. Etude et Conservation"** (17 May 2006, Brussels, Belgium) organised at the Musées Royaux d'Art et d'Histoire on the following topics : *La métallurgie des alliages à base de cuivre au XIV^e s. dans le Bassin Parisien : apports de l'archéologie, de l'analyse physico-chimique et de l'expérimentation* (David Bourgarit and Nicolas Thomas) and *Le contenu retrouvé d'un prestigieux contenant : les reliques du chef-reliquaire de Saint Alexandre (Albert Lemeunier)*. For more information contact Monique de Ruelle (m.de.ruelle@kmkg-mrah.be)

- **Final workshop of COST Action G8 "Non-destructive analysis and testing of museum objects"** (18-20 May 2006, Nicosia, Cyprus). For more information contact Annemie Adriaens (annemie.adriaens@ugent.be)

- **X^e journées-débats de conservation préventive - Constats, diagnostics, évaluations : la conservation préventive en action** (14-15 June 2006, Institut National d'Histoire de l'Art, Paris). Call for papers will be closed on the 15th of March. For more information contact Silvia Païn (spain@cg78.fr)

- **IRON, STEEL AND STEAM; a progressive seminar on developments "down-under"** (26 June – 1st July 2006, Fremantle, Melbourne and Sydney, Australia). Australia's second on-site iron and steam ship archaeology seminar. For more information please contact the convenor m.mccarthy@museum.wa.gov.au

- **The Beginnings of the Early Use of Metals and Alloys: metallurgy and civilisation** (15-20 September 2006, Beijing, China). Deadlines for abstracts: 15 March 2006. For more information contact Alessandra Giumlia-Mair (giumlia@yahoo.it)

- **French Section of the ICOM-CC Metal WG** (28-29 September 2006, INP, Paris). For more information contact Christian Degriigny (christian.degrigny@gmail.com) and Marie-Anne Loeper-Attia (loeperattia@noos.fr)

- **SR2A 2006 workshop on Synchrotron Radiation in Art and Archaeology** (27-29 September 2006 in Berlin, Germany) organised jointly by Berliner Elektronenspeicherring - Gesellschaft für Synchrotronstrahlung m.b.H. (BESSY), Bundesanstalt für Materialforschung und -prüfung (BAM), Staatliche Museen zu Berlin (SMB) and Technische Universität Berlin (TUB). More information can be obtained from the following website: www.bessy.de/workshops/

- **Archaeological metal finds – from excavation to exhibition** (12-13 October 2006, Mannheim, Germany) organised by the Archaeological Objects WG of the Verband der Restauratoren (VDR). The AIAE sub WG will have a special session during that conference. For more information contact Martin Höpfner (martinhoepfner@gmx.de)

- **International workshop on Science for Cultural Heritage** (23-27 October 2006, Miramare-Trieste, Italy) organised by the International Centre for Theoretical Physics. For more information visit the following website: <http://www.ictp.it/~smr1778>

- **2006 Conservation Science Annual** (11-16 November 2006, Sommerset, USA) organised by EAS / NYCF. A specialised seminar on the use of electrochemical techniques in

conservation. More information can be obtained from the following website:
<http://www.NYCF.org/eas.html>

- **Matériaux 2006 - Fonctionnalisation des surfaces – interfaces** (13-17 novembre 2006, Dijon, France). For more information visit the following website : www.materiaux2006.net

- **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 contact Prof Mohamed Harith (mharithm@egypt.com)

- **Archaeometallurgy in Europe** (May or 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

Abbreviations and acronyms

DC – XJTU: Department of Conservation – Xi’an Jiaotong University

EF – UBA: Engineering Faculty, Buenos Aires University

EIS: Electrochemical Impedance Spectroscopy

FTIR: Fourier Transformed Infrared Spectroscopy

LCRR-CAV: Laboratoire de Conservation, Restauration et Recherches du Centre Archéologique du Var

SAM – PKU: School of Archaeology & Museology, Peking University

SEM-EDS (or EDX): Scanning Electron Microscopy – Energy Dispersive Spectroscopy

XPS: Xray PhotoSpectroscopy

XRD: X-Ray Diffraction

SABKS: State Academy of Art & Design Stuttgart

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

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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

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