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Metal working group

# Bulletin of the Research On MEtal Conservation

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# BROMEC19

## Editorial

Summer time is always a quiet moment for BROMEC. We are very happy though to have received some abstracts from the most recent country that nominated a national contact person: Morocco. Also two new SubWGs have recently been setup: IECO (Conservation of Industrial and Engineering Cultural Objects) and EMCN (Enamels on Metals Conservation Network) and we expect to get some interesting abstracts related to these fields in the near future. The EMCN already had its kick-off meeting on 1-2 July 2006 at Germolles' castle (France) and information is online on the METAL*Consn*-info website (SubWGs activities folder) and will be soon on the ICOM-CC Metal and Glass & Ceramics homepages of the ICOM-CC website.

In BROMEC 18 we promoted two important forthcoming events: CSSIM (Conservation Strategies for Saving Indoor Metallic Collections) that will be held in Cairo between 25 February and 1 March 2007. The deadline for sending an abstract is 1 August 2006. More information is available on the CSSIM website: http://www.nileslaser.edu.eg/. METAL 07 also has its website now online (http://www.metal07.org/). This event, the triennial meeting of the ICOM-CC Metal WG, will be held in Amsterdam and we expect you all to attend. The deadline for submitting an abstract is 15 November 2006. Do not miss this occasional opportunity to listen, meet and discuss with metal conservation colleagues!

This issue of BROMEC presents some research covering archaeometric studies (coins from Volubilis, Morocco and copper ingots from Lipari, North of Sicily), corrosion prevention (use of corrosion inhibitors on bronze alloys) and an update of the important project carried out at the Department of Analytical Chemistry, Gent University on the evaluation of the chemical and morphological changes of corroded lead artefacts after their electrolytic stabilisation. We are pleased to see too that Australia is starting a new research project on the short pulse laser cleaning of cultural heritage artefacts.

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

**Editor**
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# Contents

## Ongoing research projects

 Physical and chemical characterization of metal archaeological artefacts (***LASMAR-PD-FS-UMIM***)

The thorough study of archaeological or historical metal artefacts requires the determination of the physical and chemical properties of their constituents. It is usually carried out before any conservation or restoration work. This approach is applied within a PhD research project on antique coins.

The non-destructive physical and chemical techniques of characterization used are X-ray Fluorescence (XRF), X-Ray Diffractometry (XRD) and Scanning Electron Microscope (SEM), associated with Energy Dispersive Spectroscopy (EDS),. The data obtained are processed mathematically through multivariable statistical treatments. The results should then be correlated to the archaeological and historical data.

A first batch of Roman coins (20) excavated from the Volubilis archaeological site has been characterised by SEM-EDS at the Laboratories of the National Centre for Scientific and Technical Research (CNRST) of Rabat, Morocco. This batch will be studied then by XRF at the National Centre of Energy, Nuclear Sciences and Techniques (CNESTEN) of Morocco.

Batches from other periods and containing different alloys should be investigated in the near future.

**Contact**: Ali Allouch (LASMAR-PD-FS-UMIM)
**Funding**: no external funding

## Ongoing research projects

 Insights into the chemical and morphological changes of historical lead objects as a result of the use of electrolytic reduction as a stabilisation treatment (***DAC - GU***)

Lead artefacts corrode very badly under conditions were the humidity is high and the atmosphere contains organic acid vapours. This accelerated degradation often occurs in the display cases of museums. The materials that compose these display cases (wood, glue) indeed degrade and emit volatile organic compounds – contributing to active corrosion phenomenon. Since the showcases are closed and the air exchange is very little, the organic compounds produced can reach relatively high concentrations. Lead objects exposed to such aggressive environments have lost many surface details. If no action is undertaken, the lead object degrades further until it is transformed into a heap of powdery corrosion products constituted finally of cerrusite / hyrdocerrusite.

This study focuses on the evaluation of chemical and morphological changes of corroded lead artefacts when using electrolytic reduction as a stabilization method. Synchrotron radiation X-ray diffractometry (SR-XRD) and X-ray photoelectron spectroscopy (XPS) were used to study the chemical changes of the corrosion layer and the top (nanometre level) metal surface respectively. Neutron tomography (NT) and scanning electron microscopy (SEM) were used to visualize potential morphological changes on millimetre and micrometre levels respectively. SR-XRD data have shown that the electrolytic reduction treatment converts the corrosion products present into metallic lead. This conversion results in a surface colour change from white to a dark grey. The XPS measurements, on the other hand, reveal that, after the reduction procedure, the surface re-oxidizes, forming $Pb(OH)_2$.

Neutron tomography is shown to be a powerful technique for the study of morphological changes of corroded lead artefacts. This is due to the very different attenuation coefficient for lead and its corrosion products. The technique is a suitable non-invasive technique for the visualization of the corrosion state of an object.

Results have shown that the fine structure of the object remains well conserved after the electrolytic treatment. The resulting changes on a microscopic level are seen by a decrease in volume of the pitting corrosion structures. The uniform corrosion structures are transformed in a more porous and lamellar surface appearance. This increase in specific area could explain the re-oxidation shown by the XPS, despite the rapid drying of the object after the reduction treatment.

The results of this study have shown that the electrolytic reduction is a reliable way to stabilize and conserve corroded lead artefacts. The corrosion products are actually converted into metallic lead (that quickly re-oxidises), while the morphological changes due to the treatment are limited.

**Contact**: Annemie Adriaens and Bart Schotte (DAC - UG)
**Funding**: FWO Vlaanderen
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## Ongoing research projects

 Study of the corrosion of bronze Cu-8%Sn and the inhibiting effect of 3-phenyl-1,2,4-triazole-5-thione (LECE-FSK)

Bronzes not only constitute some of the main alloys found in cultural heritage but are largely used in industry such as in aeronautics to form engines parts or in naval engineering to form pump components. These alloys are exposed to an aggressive environment during their use, especially when they are in contact with the marine environment. Since such conditions occur on cultural heritage marine sites we expect our results to be of some interest to conservation professionals.

The objective of our research project is to study the electrochemical behaviour of bronze Cu-8%Sn in 3%NaCl medium and to test the inhibiting effect of 3-phenyl-1,2,4-triazole-5-thione (PTS) . This compound has been synthesised, purified and characterized in our laboratory.

This study was carried out by voltammetry and impedance electrochemical spectroscopy (IES). The surface state with and without inhibitor has been characterized by EDAX and Raman spectroscopy (RS).

The results obtained show that the PTS is a mixed inhibitor acting at low concentration. Its effect results in lowering of the anodic and cathodic current density. The inhibiting efficiency is 96% for 1mM of PTS and it increases with increasing inhibitor concentration and immersion time. The inhibiting effect has been confirmed by EDAX and RS that show the presence of atomic sulphur on the metal surface resulting from the action of the PTS molecule.

**Contact**: Ahmed Dermaj, Driss Chebabe, Najat Hajjaji & Abdellah. Srhiri (LECE-FS-UITK) and V. Vivier (LISE – CNRS)
**Funding**: no external funding

## Ongoing research projects

 Corrosion inhibition of bronze with *Opuntia ficus indica* stem extract (***LECE-FSK/ORL-FSK/BL-FMR***)

Bronze is used in several fields: electronic industries, sculptures, artworks… Its corrosion inhibition in several media, by the addition of organic or inorganic products is largely used. However these compounds are artificially synthesised, expensive and dangerous for the environment.

The search for naturally produced and environmentally friendly corrosion inhibitors is a priority. Our objective within this PhD research project has been to study the inhibition efficiency of *Opuntia ficus indica* seed extract to prevent the corrosion of bronze alloys. The *Opuntia ficus indica* originates from Mexico. This plant grows in semi-arid regions and is cultivated at great scale in Morocco. For our study we consider the seed extract. The bronze considered is a Cu-8%Sn bronze and the corrosion solution tested is NaCl 3%. To our knowledge the use of this cactus stem extract as a corrosion inhibitor for bronze has never been reported in the literature.

The effect of the concentration of the extract has been determined by coupling two electrochemical techniques: voltammetry (by plotting I =f(E) curves) and IES (impedance electrochemical spectroscopy). These techniques have shown that a good inhibition efficiency (82-86%) is obtained. This study is going to be continued by surface SEM and IR analysis.

**Contacts**: Hind Hammouch, Abdellah.Srhiri & Najat Hajjaji (LECE-FS-UITK) & Laila Bennaghmouch (BL-FMR)
**Funding**: CNRST

## Ongoing research projects

 Late Bronze Age copper ingots in the Central Mediterranean and the Lipari Hoard (***AGMA***)

In the Late Bronze Age, different shapes of copper ingots circulated in the Mediterranean. The best known shape is the oxhide ingots, but plano-convex ingots were also common.

The largest amount of copper ingots, discovered up to now, comes from the shipwreck found in the sea on the southern coast of Turkey near Cap Uluburun with 475 ingots (10 t of copper and 1t of tin!), the second largest one is the group of ingots from the shipwreck of Cap Gelydonia with 35 oxhide ingots and 12 plano-convex ingots. There are several finds in Cyprus - at Enkomi, Mathiati and in the Soli bay -, in Asia Minor in various sites, particularly around Antalya, in Greece, for example at Kyme, Mycenae and on the Marmara Sea, in Mesopotamia at Bogazköy, at Dur-Kurigalzu and at Göksu. However a large amount of complete pieces and fragments of ingots comes from the Central Mediterranean, in particular from the Sicily, Sardinia and Lipari islands, but also from Corsica. In the last decade several researchers tried to determine the provenance of the different kinds of ingots. Many lead isotope analyses were carried out by different scholars and the results of the analyses indicated in most cases that the copper comes from Cyprus. This is not surprising, as it is well known that Cyprus was the "island of copper" and even gave to this metal its Latin name *cuprum*. However it is quite amazing that Cypriot copper was transported to Sardinia, but it was not employed for the huge bronze production of the Nuragic civilization. Apparently, for the many Sardinian bronze artefacts only Sardinian copper was used.

The important hoard found under the wall of hut alpha on the acropolis of Lipari, the island North of Sicily, consists of 75 kg of fragments of oxhide- and plano-convex ingots, of tools, weapons and other remains and it is one of the largest hoards discovered up to now on the Italian territory. The pieces from the hoard and from the settlement, and the few ingots from Sicily have been recently studied and analysed by the author using AAS and XRF.

The results of the analyses demonstrate that there is no compositional difference in the copper used for the two ingot shapes. The plano-convex ingots that circulate in Northern Italy show a different composition. This copper seems to have been used also for the locally produced objects.

The Lipari hoard also contains objects from other Italian regions and from various Mediterranean civilisations and demonstrates that the island belonged to a wide trade network. Up to now no lead isotope analyses have been carried out on the fragments from the Lipari hoard, however the chemical composition does not contradict a Cypriot origin.

This abstract is a short overview of part of the work carried out for the volume "Oxhide ingots in the Central Mediterranean" by Lo Schiavo F., Muhly J.D., Maddin R., Giumlia-Mair A. currently in preparation.

**Contact**: Alessandra Giumlia-Mair (AGMA)
**Funding**: no external funding

## New research projects

 Short pulse laser cleaning for heritage artefacts (***AWM***)

In 2005, a group of heritage institutions joined with laser scientists at the Australian National University to put in a proposal for an Australian Research Council grant to investigate the potential of short pulse lasers for conservation cleaning. Happily, the proposal was accepted and has received funding for the next three years.

The goal of this project is to develop short-pulse, ultra-fast laser cleaning technology for selective removal of surface contamination from heritage artefacts. Short pulse lasers differ from conventional conservation lasers in that the energy of the laser breaks bonds in the contaminating material without generating heat in the substrate. This means they are free of the heat related problems of conventional lasers - such as surface melting or boiling, or thermal degradation of the substrate. They also remove material in layers of molecular thinness and can be controlled by real-time analysis and feedback to ensure that the laser stops as soon as it has reached the surface underlying the contaminant.

The project partners are
* Australian National University - Dr Ken Baldwin and Dr Andrei Rode
* Australian War Memorial - Alison Wain
* RAAF Museum (Pt Cook) - David Gardner
* Army History Unit - Capt. John Land
* Dept of Defence (Naval - Spectacle Island) - Commander Shane Moore
* Art Gallery of NSW - Stewart Laidler
* Artlab Australia - Joanna Barr

The first phase of the project will consist of setting up and configuring the laser system, followed by testing on a range of sample materials provided by the conservation partners. Later stages will involve tests on increasingly complex samples and real objects and development of a real-time analytical feedback system to control the laser. Collaboration with scientists in France is also planned, to study the possibility of using the laser to safely remove and capture radioactive material from the surface of heritage artefacts.

**Contact** : Alison Wain
**Funding** : Australian Research Council

## 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-preservationscience.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 "Archéomateriaux et prévision de l'altération."

- **METAL*Consn***-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**
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

- **French Section of the ICOM-CC Metal WG** (28-29 September 2006, INP, Paris). For more information contact Christian Degrigny (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
- **L'homme et la matière – l'emploi du plomb et du fer dans l'architecture gothique** (16-17 November 2006, Noyon, France). Organised by the Picardie Regional Heritage Agency. For more information visit the following website: www.arpp.org or contact: contact@arpp.org
- **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/
- **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
**AAS**: Atomic Absorption Spectroscopy
**AGMA**: AGM Archeoanalisi
**AWM**: Australian War Memorial

**BL-FMR**: Biochemistry Laboratory – Faculty of Medicine of Rabat
**CNESTEN**: National Centre of Energy, Nuclear Sciences and Techniques, Morocco
**CNRST**: National Centre for Scientific and Technical Research, Morocco
**DAC-GU**: Department of Analytical Chemistry – Gent University
**EDS – EDAX**: Energy Dispersive Spectroscopy
**IES**: Impedance Electrochemical Spectroscopy
**IR**: Infrared Spectroscopy
**LASMAR-PD-FS-UMIM** : LAboratory of Spectroscopy of Materials and ARcheomaterials, Physics Department, Faculty of Science, University Moulay Ismail of Meknès
**LECE-FS-UITK**: Laboratory of Electrochemistry, Corrosion and Environment – Faculty of Science – University Ibn Tofail of Kenitra
**LISE – CNRS**: Laboratoire Interfaces et Systèmes Electrochimiques, CNRS
**NT**: Neutron Tomography
**RS**: Raman Spectroscopy
**SEM**: Scanning Electron Microscope
**SR-XRD**: Synchrotron Radiation - XRD
**XPS**: X-Ray Photoelectron Spectroscopy
**XRD**: X-Ray Diffractometry
**XRF**: X-Ray Fluorescence

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