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METALConsn-info

Metal working group

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BROMEC14

Editorial

The Metal WG continues developing networks with different continents: both Croatia, Canada and Hungary now have their national representatives and the Former Yugoslav Republic of Macedonia is represented by a few members. We are very pleased then to welcome Goran, Judy and Balazs and all our new colleagues.

As in BROMEC 13 the editors have received a similar number of abstracts. They reflect some activities in Finland forwarded by the recently appointed Finnish representative, Eero Ehanti. Two Spanish projects are also presented through Emilio Cano, Spain's representative. Hopefully, representatives from Canada and Hungary will soon inform us of research activities in their country.

Noteworthy, BROMEC 14 contains two abstracts relating to the conservation of metal artefacts by laser. These projects are performed in Sweden and Greece and cover not only all aspects of the cleaning of metal artefacts, but comparative tests with more traditional cleaning processes. Other abstracts are about the use of electrochemical techniques in conservation and the use of the most recent analytical tools to examine archaeological and historical metal artefacts.

An update on one new component of Malta's contribution to the European Union PROMET project is also given in an abstract outlining the motivation and methodology for mechanical cleaning tests of steel coupons and emphasises the need for further research in the conservation of partially corroded historic steel where aesthetics are considered paramount.

Eero Ehanti is currently working on electrolytic stabilisation of marine archaeological copper artefacts and he is raising some very interesting points in his call for the collaboration related to the modification of the appearance of the artefacts during the treatment. Any feedback on the topic would be highly appreciated.

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

In-situ conservation of grey cast iron cannon

Since 2001 a number of grey cast iron cannons have been included in an underwater corrosion survey of the wreck of the Swedish warship *Kronprins Gustav Adolf* (1788). The principal objective of the survey was to determine: the present condition of the submerged cannons after more than 200 years of immersion in seawater, and; whether the use of sacrificial anodes could be considered to protect these corroding, concreted objects *in-situ*.

The first phase of the survey involved visually selecting a number of cannons that appeared to be "fully" covered with a semi-protective layer of concretion, as well as cannons that had suffered "damage" in the form of partial concretion loss. Electrochemical *in-situ* measurements (E_{corr} and pH) were taken from the sample group of cannons in order to get a scientific confirmation of their current condition. Based on these preliminary measurements and visual observations, the most "damaged" cannon was subjected to a test in which a sacrificial zinc anode was attached to the cannon so as to facilitate cathodic protection of the corroding artefact.

In the summer of 2002, *in-situ* pH and E_{corr} measurements were taken from four pre-selected cannons, two "fully" concreted and two "damaged" ones. The average E_{corr} for these four cannons was –0.300 V vs. Standard Hydrogen Electrode (SHE) with an average pH of 7,26, indicating active corrosion (according to a modified Pourbaix diagram for this seawater) of the metal in each case. The less negative potential measured was -0,233 V/SHE from cannon AT6, which also yielded the lowest and most acidic metal surface pH of 6,97. Cannon AT6 was thus considered to be the most "damaged" object, not only based on its visual appearance, but also based on the data obtained from the electrochemical measurements, that implied this particular cannon was suffering more heavily than the others from active corrosion.

One year later a sacrificial zinc anode was attached to cannon AT6. A week after attaching the anode, the potential of the cannon-zinc system had dropped down to -0,329 V/SHE and the pH had risen to 7,20. These results indicated a change in the electrochemistry of the corroding metal towards a condition more favourable to the overall protection of the cannon. In other words, the corrosion of the cannon surface had been hindered, but the anode had not been able to completely protect the cannon against corrosion. Successive measurements 3 months and again 15 months later yielded very similar E_{corr} values, whereas pH measurements were complicated by a malfunctioning pH-electrode. Also, no notable visual changes were observed on the cannon surface during this period.

In the coming months the anode will be exhausted, before which, decisions will have to be made about the future of the project. The test can be either terminated at that point, if the data obtained is considered sufficient. Alternatively, modifications can be made to the clamp/anode unit that will aim to further increase the efficiency of protecting the cannon. More detailed analysis of the available data will therefore be of crucial importance to this particular study.

Related literature

- Degrigny, C., 2002, Bulletin On The Research On Metal Conservation (Bromec 1-3), In-situ conservation of grey cast iron cannon
- Kokko, R., 2002, Final Thesis, Evtek Institute of Art and Design, Sacrificial anodes: implications to in situ conservation on the wreck of Kronprins Gustav Adolf (1788)

Contact: Rami Kokko
Funding: no external funding

Ongoing research projects

 Conservation, restoration and technology of medieval gilded metals (***DPA-UAM***)

The metalwork workshops in medieval Spain produced gilded objects of an exceptional quality, rarely known and preserved, which must be included as a very significant part of the Metallic Archaeological Heritage, and be part of an essential legacy for the knowledge of the technological development of one of the most outstanding periods of metallurgy in the Iberian Peninsula. The aim of this 3-year (December 2004 to December 2007) project is to tackle the problems related to the conservation and restoration of these medieval objects made of gilded metal, which are usually recovered from archaeological sites in a deteriorated state and stored without any treatment. It is then proposed to research in detail with multidisciplinary collaboration and contribution, the causes which determine the singularity of the deterioration process, counting on the most accurate analyses given by the most recent scientific and technological techniques: SEM with EDXA, XRD, XRF, PIXE and PIGE. The same techniques will be used to assess the technological process of gilding, which have barely been investigated until today. From all these studies we expect to obtain a precise diagnosis of the state of conservation, in order to achieve the final objective of this project: to test and apply the most accurate and effective techniques and procedures of restoration to guarantee a good conservation of the gilded metal artefacts so they can fulfil the social function ascribed to our Archaeological Heritage.

Contact: Joaquin Barrio Martin (DPA-UAM)
Funding: Spanish Ministry of Science and Technology

Ongoing research projects

 Archaeological Heritage and conservation: application of new technological procedures to the restoration of ancient metals (***DPA-UAM***)

The main objective of the project is to tackle the serious problems that affect old iron artefacts that comprise a very important part of the Metallic Archaeological Heritage and which are usually in an unacceptable state of conservation. Therefore, it is necessary to understand the causes that determine the peculiarity of their conservation state, which can only be assessed with appropriate analytical techniques such as: SEM with EDAX, XRD and XRF. From this wide perspective and diagnosis basis it is possible to achieve the final objective: to test and apply the most suitable treatment processes to guarantee the physical consistency of the metal pieces. Special attention will be given to "avant-garde" proposals for the stabilisation of artefacts; for example, Cold Hydrogen Plasma. Through this 1-year (year 2005) project we are in line with the research themes defined by the Metal Working Group of ICOM-CC (Newsletter, March 19, 2001).

Contact: Joaquin Barrio Martin, DPA-UAM.
Funding: Madrid Regional Government

Ongoing research projects

 Cleaning of metal artefacts using pulsed lasers (***KCCCP***)

One of the important processes in conservation of archaeological metal artefacts is cleaning, in which mechanical techniques such as dental tools or micro blasting are often used. However, these methods are difficult to control and can easily result in over-cleaning of the surface. To remove aged adhesives and protective coatings prior to a re-conservation process, chemicals are often used. However, the chemical can be environmentally harmful and represent a health hazard. In extreme cases chemical residues left on the artefact can cause long-term problems.

Recent research in the cleaning of different artefacts by lasers has shown the laser as a good alternative cleaning method to minimize problems associated with traditional methods. Laser cleaning could be an effective technique for assisting in the conservation of various artefacts since it provides a high degree of control, which is essential when preserving surface details.

The project "Cleaning of metal artefacts using pulsed lasers" started in 2000 as a five-year project by the Kiruna Center for Conservation of Cultural Property in Sweden in collaboration with Luleå Technical University. The aim of this project is to develop a laser technology, which is effective and safe, for the cleaning of archaeological metal artefacts. The goal is to minimise the use of health- and environmentally hazardous chemicals while simultaneously increasing the maintenance of surface details.

In this project Nd:YAG lasers at different wavelengths (1064 nm, 532 nm, 266 nm) and TEA CO_2 laser at a wavelength of 10600 nm have been tested to clean different metal surfaces. The cleaning results have been evaluated by using optical microscopy, SEM, X-ray spectrometry and Raman spectroscopy.

Related literature
- Koh, Y.S. and Sarády, I., Removing of adhesives and coatings on iron artefacts by using pulsed TEA CO2- and Nd:YAG-lasers, in Laser Techniques and Systems in Art Conservation, SPIE Proceedings, Vol.4402, 46-53, 2001.
- Koh, Y.S. and Sarády, I., Cleaning of corroded iron artefacts using pulsed TEA CO_2- and Nd:YAG-lasers, in Journal of Cultural Heritage, Vol. 4, 129-133, 2003.
- Lee, M., Yu, J.E. and Koh, Y.S., Effect of Wavelength in the Laser Conservation of Silver Textile, in Journal of Cultural Heritage, Vol. 4, 157-161, 2003.
- Koh, Y.S., Cleaning of Metal Artefacts using Pulsed Lasers, Licentiate thesis in Engineering, Luleå University of Technology, October 2002.
- Koh, Y.S. and Sarády, I., Surface Cleaning of Iron Artefacts by Lasers, Lasers in the Conservation of Artworks (LACONA V), Osnabrueck, Germany, September 15-18, 2003.

Contact: Yang Sook Koh (KCCCP)
Funding: Norrbotten's Research Council (2000 - 2002) and The National Heritage Board in Sweden (2002-2005)

New research projects

PROMET – Corrosion product cleaning of steel coupons: original surface conservation, aesthetic values and protective system efficiency (***MCR***)

As a preliminary component of the European Union PROMET (PROtection of METals) research project that is testing the efficiency of protective coatings and inhibitors for metal cultural heritage collections in the Mediterranean basin, corrosion product (CP) cleaning tests were performed on steel coupons. The tests were designed to initiate the development of a methodology that will be implemented in 2006 after the natural corrosion of steel coupons in the Palace Armoury (PA), Malta. Steel coupons will, after 1 year of uncovered exhibition environment exposure, subsequently be tested over a second year with various coatings and corrosion inhibitors. Before testing the corrosion protection systems (coatings and corrosion inhibitors) it is imperative that an agreed level of CP removal is undertaken. To limit inapplicable results, the surface must be cleaned to the same degree that is representative of planned conservation treatments where the protection system might be used. The prerequisite to test the protection systems on surfaces that are closely representative of the artefacts' metal and CP composition/morphologies is obligatory since it is expected that the substrate (i.e. artefact surface) has a significant effect on protective coating/corrosion inhibitor efficiency. This forethought has implications for both the curatorial and conservation personnel responsible for a collection, particularly in terms of determining proper treatment methodologies *in advance* of the corrosion protection system tests. Of course, the treatment methodology must integrate the conservation ethic and aesthetic requirements expected for significant cultural heritage collections. Unfortunately, the conservation ethics of maintaining the original surface limits can contrast with aesthetic and display issues. These aesthetic requirements often do not support the preservation of some corrosion products (although considered to form a part of the original surface limit), since they "disfigure" the object due to their differing colour or form. Partially corroded metals increase this contrast in appearance. These conflicting issues are paramount in the genre of arms and armour since they were typically maintained in service with a high polish. The common expectation of a lustrous metallic suit of historic armour has and continues to significantly influence armour conservation practices. The aggressively corrosive environment in Malta further intensifies corrosion of arms and armour, a collection genre more typically associated with continental Europe and its more benign environment. It is expected, that unless balanced resolutions are found from further research, future treatments will persist where aesthetic issues associated with disfiguring CP forms and colours are minimised, while simultaneously forfeiting original surface information. This area is an ongoing point of a broader debate and relies on research and informed communication between conservators and curators. Public education is another area of required development. Resolving these issues is beyond the scope of these tests, but it is very relevant to this type of cultural heritage and the issue was incorporated into the corrosion product cleaning tests' methodology.

For the corrosion product cleaning tests, eleven simple mechanical techniques were tested on sections of partially corroded low carbon steel coupons that had corroded under accelerated conditions. The cleaning methods applied were chosen for their possible eventual replication on a larger scale on the corrosion products found on the low carbon steel armour at the Palace Armoury. Given the current, and likely near future conservation/restoration resources accessible to the large and currently vulnerable collection at the Palace Armoury, it is proposed that mechanical means of corrosion removal will be the most likely feasible approach. A variety of mechanical cleaning implements *and approaches* were trialled. The

amount and type of CPs removed was intentionally varied so results could be judged on conservation ethic, aesthetic, and protective coating/corrosion inhibitor efficiency parameters. Following the accelerated corrosion of the steel coupons the preliminary test methodology involved: describing the coupon corrosion morphology; determining a range of objectives for CP removal; performing the CP removal interventions and; finally summarising the results accompanied with suggestions for further development of the methodology. The limitations of extrapolating the performance of techniques to remove corrosion products formed under accelerated conditions with those formed under natural conditions are acknowledged, while simultaneously, the appreciable benefits of developing a universally applicable methodology is recognised.

Contact: James Crawford (DSL - MCR)
Funding: EU INCO-MPC1 Strep PROMET project

New research projects

 Environmental consequences and protection of outdoor bronze monuments in Greece (***DCAWA-TEI/LMA-INP,NCSRD/DMRE-TUC***)

The research project will establish a preventive strategy to protect and minimize possible changes that may occur to outdoor bronze monuments. The project deals directly with the problems facing a municipal and/or historical park that must manage and maintain a collection of outdoor bronze monuments. This project will develop the latest non-destructive techniques to monitor the changes to a monument and at the same time test the most effective coatings to protect the surface of the monument from effects of vandalism and the environment. Furthermore, the project's viability will be demonstrated on a collection of outdoor bronze monuments.

Our overall goal is to establish a preventive strategy to preserve and protect our outdoor bronze monuments in Greece. The approach is as follows:

-To develop state of the art portable non-destructive techniques for analyzing the surfaces of monuments so as to document any alterations that may occur with time.

-To test environmentally safe coatings for the protection of monuments from graffiti and other elements that may alter the surface.

-To develop a scientific approach for documenting the condition and materials that constitute outdoor bronze monuments, which can be applied towards a conservation strategy for their protection.

-To determine the effects of atmospheric pollution on outdoor bronze monuments across Greece.

-To produce a "Good Practice Guide" for the protection of outdoor bronze monuments that will be distributed to the municipalities of Greece.

Contact: Dimitris Charalambous (DCAWA-TEI) in collaboration with Andreas Karydas (LMA-INP,NCSRD) and V. Perdik (DMRE-TUC)
Funding: 80.000 Euros, Archimedes II program

New research projects

The application of new technologies for the cleaning of archaeological and historical metal objects. Investigation of the possibility of applying laser technology and electrolytic methods (***DCAWA-TEI/FORTH-HIESL***)

The research project will test and evaluate the application of newer technologies (laser and electrolytic methods) compared with the classical cleaning methods (mechanical and chemical) used on archaeological and historical metal objects.

Laser technology will be applied to develop a method for the cleaning of metal artefacts, with the application of Nd:YAG laser. Tests will be conducted on artificially corroded metal coupons, in order to define the parameters for the removal of the corrosion products without the alteration of the metal surface. An evaluation of the method's capabilities will also be given. Real objects will then be tested using the predefined parameters.

Another objective of this research is to apply electrolytic methods, and demonstrate the effectiveness of such methods for the conservation of metal artefacts.

Finally, the results of the research will be demonstrated to Greek conservation professionals and students of the Department of Conservation of Antiquities and Works of Art at the T.E.I. of Athens through seminars and with publication of relevant seminar notes.

Contact: Vasilike Argyropoulos (DCAWA-TEI) and Vivi Pouli (FORTH- HIESL)
Funding: 50.000 Euros, Archimedes II program

Calls for collaboration


Optimization of electrolytic stabilisation of marine archaeological copper alloys (***MMF***)

Electrolytic polarisation has been used for the stabilisation of marine archaeological copper alloy and iron objects at the Maritime Museum of Finland for some years now. The objective in every case has been to extract active chlorides from the artefacts without changing the appearance of the object or altering the information in the corrosion layers. Basic laboratory power supplies are used and the processes are controlled as closely as possible by monitoring the cathodic potential of the metal and measuring the chloride content of the treatment solutions by potentiometric titrations.

The method is working quite well, but some problems have occurred. This is notable with the treatments of copper based metals, where 1% w/v sodium sesquicarbonate has been used as an electrolyte. It is certainly an efficient solution as regards the stabilisation process, but apparently it is not very suitable for some alloys. In the case of two 16th century cauldrons, white precipitates appeared on the surface during polarisation. SEM/EDS – analyses were done on the precipitate, and the results indicate the presence of lead. Later on, the corrosion surface produced some bluish or violet patches, so the electrolysis was stopped before complete chloride extraction was achieved.

These two cases demonstrate the uncertainty we are facing with the treatments. Chloride removal is easily achieved, but the effect on the appearance seems to be a bit of a mystery every time. There are many references to unwanted patina changes with this particular solution, and more knowledge is needed on the compatibility of different alloys, electrolytes and electrolytic parameters. For example, “How do other electrolytes work? What kind of pre-treatment analytical investigations are required before starting such a conservation process?”

Of course some changes are likely to occur in most active conservation processes and stabilisation is in many cases the most important goal of a treatment, but nevertheless we feel that the effect on the appearance is an issue to take into consideration. Therefore any experience, comments or anything else related to this issue would be very much appreciated. Copper alloys are our main concern at the moment, but we are very much interested in hearing about experiences with other metals as well.

Contact: Eero Ehanti (MMF)
Funding: no external funding

General information

Websites

- ARTECH network: http://server.icvbc.cnr.it/progetti_futuri/progetto_artech.htm

- **Big stuff: Care of Large Technology Objects:**
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

- **European Cultural Heritage Network**: http://www.echn.net/

- 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."

- **M2ADL** - Microchemistry and Microscopy Art Diagnostic Laboratory is now available at the following website: http://www.tecore.unibo.it/html/Lab_Microscopia/M2ADL/

- Working Group Metals ICOM Committee for Conservation
http://icom-cc.icom.museum/WG/Metals/

Future seminars and conference
- ART'05 conference (15-19 May 2005, Lecce, Italy), 8th International Conference on "Non-Destructive Testing and Microanalysis for the Diagnostics and Conservation of the Cultural and Environmental Heritage organised by the Italian Society for Non-Destructive Testing Monitoring Diagnostics (AIPnD), the Central Institute of Restoration (ICR) and the Dept of Materials Science of the University of Lecce. For more information visit the following website: http://www.dsm.unile.it/art05.
- Metals Conservation Summer Institute 2005 (May 29 – June 9 2005, Worcester, Massachusetts, USA) organised by the Higgins Armoury Museum, the Metal Processing Institute and the Worcester Polytechnic Institute. The Metals Conservation Summer Institute is funded in part by a major grant from the Institute of Museum and Library Services, a

federal agency that fosters innovation, leadership and a lifetime of learning. For more information visit the following website www.wpi.edu/+mcsi.

- 2nd Congress Latino-American on metal conservation (25-28 July 2005, Rio de Janeiro, Brazil), organised by the Museum of Astronomy and Sciences (MAST) and the Latinoamerican Group of Metal Conservation (GLRM). For more information contact Marcus Granato (marcus@mast.br) or Johanna M. Theile (jtheile@abello.dic.uchile.cl)

- 14th Triennial Meeting of ICOM's Committee for Conservation, ICOM-CC (10-16 September 2005, The Hague, Netherlands) organised by the ICN (Netherlands Institute for Cultural Heritage in collaboration with ICOM, ICOM-Netherlands; ICOM-CC, the Netherlands Museum Association (NWV), the Dutch association of professional Conservators and Restorers (VeRes) and the Congress and Study Centre (VNG). For more information visit the following website: www.icom-cc2005.org

- **LACONA VI** (Lasers in the conservation of Artworks) (21-25 September 2005, Vienna, Austria), 6th International Congress on the Conservation of artworks by laser, organised by the Federal Office for Care and Protection of Monuments Austria-Bundesdenkmalamt and the Academy of Fine Arts Vienna. For more information visit the following website: www.lacona6.at

- RIPAM (International meeting on Mediterranean Architectural Heritage) (26-28 September 2005, Meknès, Morocco), organised by the Faculty of Science, University Moulay lamail (Meknès, M), the Interregional Centre for Patrimony Conservation and Restoration (Marseille, F) and the European network PACT "Sciences and Cultural Patrimony". For more information visit the following website: www.fsmek.ac.ma/ripam2005

- **EAS-NYCFCSAS 2005** (Eastern Analytical Symposium- New York Conservation Foundation Conservation Science Annual symposia) 2005 (14-16 November 2005, New York, USA), organized by the New York Conservation Foundation. Topics considered: deterioration of metal pipes in 16-18th Century European organs and diverse studies on Heritage in metal. For more information visit the following website: www.nycf.org/eas.html

- The Conservation of Archaeological Materials—current trends and future directions (13-17 November 2005, Williamsburg, USA), organized by The Archaeological Discussion group of the American Institute of Conservation and the Department of Conservation at the Colonial Williamsburg Foundation. For more information contact Emily Williams (ewilliams@cwf.org): program or Deb Chapman (dchapman@cwf.org): general.

Abbreviations and acronyms

CP: Corrosion Product
DCAWA-TEI: Dept. of Conservation of Antiquities & Works of Art - T.E.I. of Athens
DMRE-TUC: Dept. of Mineral Resources Engineering, Technical University of Crete
DPA–UAM: Dpto. Prehistoria y Arqueología - Universidad Autonoma de Madrid
EDS: Energy Dispersive Spectroscopy
FORTH-IESL: Foundation for Research and Technology – Hellas, Inst. of Electronic Structure & Laser, Greece
KCCCP: Kiruna Center for Conservation of Cultural Property
LMA-INP, NCSRD: Laboratory for Material Analysis, Institute of Nuclear Physics, NCSR Demokritos
MMF: Maritime Museum of Finland
PIGE: Particle Induced Gamma-Ray Emission
PIXE: Particle Induced X-ray Emission
SEM-EDS or **EDXA**: Scanning Electron Microscopy – Energy Dispersive Spectroscopy
XRD: X-Ray Diffraction

XRF: X-Ray Fluorescence

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