Editor:
Christian Degrigny

Tel: +358 9 511 9406
Fax:+358 9 823 5791
christian.degrigny@iad.evtek.fi

METAL*Consn*-info

Metal working group

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BROMEC3

Editorial

Summer time is usually a very quiet time. Permanent staff is on vacation but students are on internship. Most of the research projects presented in this issue have been partly conducted by students in different institutions and conservation laboratories.

For this third issue we got new contributions from Greece and France. You will find too some preliminary conclusions of research projects conducted in Finland by Finnish or foreign students.

Jean-Bernard Memet, conservation scientist at Arc´Antique, Nantes and **Régis Bertholon**, senior lecturer at the University of Paris Sorbonne I (Master degree in conservation of Cultural Heritage) will represent France in the future. I am very happy to welcome them among the team of BROMEC correspondents.

Some colleagues from Eastern Europe were concerned that there was no correspondent in their own country. Contacts have been taken since. Let´s hope in the near future to find motivated colleagues ready to contribute to our bulletin.

A new section has been opened for those seeking for collaborations on projects that they want to set up (see calls for collaboration).

I spent some time recently to find interesting web-sites where research in conservation of metals is mentioned. As you certainly know a lot of important research programmes are now conducted on a European level (Fifth Framework Programme – Key Action "The City of tomorrow and cultural heritage" and CULTURE 2000). For those interested in programmes funded by the European Commission, consult the following web-site: http://europa.eu.int/comm/culture/finan_en.htm. *CULTURE 2000* and *Energy, environment and sustainable development programmes* specific web-sites can be found there. The key action "City of tomorrow and Cultural heritage" can be found under the latter.

The next important event for all of us is the forthcoming ICOM-CC triennial conference in Rio de Janeiro in September 2002. William Mourey is leaving his position as co-ordinator of the ICOM-CC Metal Group and we wish him good luck in his future projects in South-Africa where he will represent CNRS. In Rio the new co-ordinator will be elected. Since I am planning to go there, I will take this opportunity to advertise our new bulletin.

I hope that you will again enjoy the reading of this new issue of the bulletin.

The Editor
Christian DEGRIGNY
Principal lecturer, Conservation Department
EVTEK Institute of Art and Design
Lummetie 2, 01300 Vantaa - FINLAND

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Applied research projects

 In-situ conservation of grey cast iron cannon (***MMF/ EVTEK Institute of Art and Design / EVTEK Institute of Technology***)

- During the 2002 summer season, the survey of the cannons on the *Gustav Adolf* wreck site was continued. The equipment needed to conduct in-situ measurements of E_{corr} and pH has been set up too. Due to the bad weather and timing problems only a few cannons could be studied. Rami Kokko has chosen two cannons partly cleaned from their crust and two others apparently still well protected. On the two first cannons E_{corr} measurements will be conducted directly on the remaining metal surface (covered with thick graphitic corrosion layer - GCL). On the two others the same measurements will require the drilling of the crust (and the GCL too). pH measurements are planned too in this latter case. Different values of E_{corr} are expected from the four cannons depending on the nature of the material surface. New measurements should be taken once a year in the future to determine whether the cannons have or not reached a stable state or are still actively corroding.

  The use of sacrificial anodes to protect the cannons (cathodic protection) will be tested on one cannon to have an idea on how effective it can be. Commercial zinc anodes will be used and a new frame has been constructed to improve the attachment of the anodes to the cannon.

- In parallel Tiina Andersson, student at the EVTEK Institute of Technology has conducted a laboratory study on the conditions of formation of the preliminary oxide-sediment layer on accidentally cleaned grey cast iron when protected with sacrificial anodes. Baltic sea, zinc anodes and modern cast iron samples are considered for these experiments.

  The influence of the sample surface and the size of the anodes on the formation of the protective layer have been studied.

Further research: In Autumn we will concentrate on the following points: 1/ simulation of the immersion of grey cast iron samples (with different surface preparations) in artificial Baltic sea water to plot E_{corr} values versus time. The objective is to compare E_{corr} values measured on site to those obtained in the laboratory. 2/ determination of a protocol for the good protection of grey cast iron using sacrificial anodes.

Contacts: Christian Degrigny (EVTEK Institute of Art and Design), Rami Kokko (Maritime Museum of Finland) & Tiina Andersson (EVTEK Institute of Technology)
Funding: Finnish Cultural Foundation, MMF and EVTEK Institute of Technology

Applied research projects

 Iron / waterlogged wood artefacts : microbiological and electrochemical study ***(Arc'Antique / ARC-Nucléart / CRCDG),***

The discovery, in 1995, of 29 marine iron / wood composite rifles of the 17th century led the French conservation laboratories Arc'Antique and ARC-Nucleart to develop a new research programme on the treatment of such artefacts. The approach, based on the concomitant use of a corrosion inhibitor and polyethylene glycol (PEG), gave excellent results as far as the iron protection and the wood consolidation are concerned.

The chosen inhibitor, Hostacor IT® is a triethanolamine associated with a carboxylic acid. Preliminary studies have consecrated this corrosion inhibitor as very effective on freshly sandblasted iron or steel [1, 2]. Thus, a new protocol was adopted for the conservation and restoration of this collection [3]. But during the storage and PEG impregnation, we have noticed the apparition, at the objects surface, of an important microbial and fungi contamination.

That is one of the reasons which led Arc'Antique and ARC-Nucléart to associate with the CRCDG in a three years research programme which began in October, 2001. The aim of this research programme is to assess the influence of the living species on both the electrochemical properties of the storage solutions and the chemical evolution of the corrosion products, with a focus on sulphur based corrosion products.

This first year consists in a two-stage research which begins, on one hand, with the description and counting of all this biomass and, on the other hand, with the selection in this total biomass of some representative micro-organisms, such as bacteria, fungi and yeast on which we will test some new biocides.

In addition, a MsS scientist, Mylène Lardoux, studies during 6 months the electrochemical and chemical interactions between the iron inhibitor and pre-corroded iron and steel surfaces.

[1] : Guilminot, E, PhD report, Ecole Nationale Polytechnique de Grenoble, France, october 2000.
[2] : Argyropoulos, V., Rameau, J-J., Dalard, F. and Degrigny, C., Studies in Conservation, 44 (1999) 49-57
[3] : Degrigny, C. and Guilminot, E., Cahier Technique ARAAFU 5 (1998) 5-10

Contacts: Nathalie Huet & Jean-Bernard Memet (Arc'Antique), Quoc Khoï Tran (ARC-Nucléart) & Malalanirina Rakotonirainy (CRDCG)
Funding: MRT

Applied research projects

 The removal of bronze spray paint from a collection of Outdoor bronze monuments in a suburb of Athens (***TEI***)

Around 5 years ago, the then mayor of Nea Smyrni decided that he would undertake the treatment of the Outdoor bronze monuments of his city, by hiring two workers to spray paint on each monument to give them a uniform bronze colour. The result upset the relatives of the deceased artist who has made the majority of the bronze monuments.

The project needs to determine the best method to remove the bronze spray paint without damaging the original surface underneath. In some instances, especially for smaller objects solvents will be used. However, for large monuments, solvents are not practical since they are toxic, and mechanical methods will have to be considered. The research proposes to determine the best method to apply for the removal of the spray paint.

Contact: Vasilike Argyropoulos (TEI of Athens)
Funding: Municipality of Nea Smyrni

Ongoing research projects

 The Conservation of historical Greek Porpi (Belt buckles) (***TEI***)

Greek costume belt buckles from the 16th century to modern day are investigated in terms of their historical significance, styles, and technological make-up. Most Porpi made for Greek costumes are made of silver alloys and nickel silver. The conservation problems in terms of corrosion and treatment are considered. Ethnographic collections throughout Greece will be considered.

Contact: Vasilike Argyropoulos (TEI of Athens)
Funding: no external funding

Ongoing research projects

 Protecting historical iron knives from persistent rust spots (***TEI, CMA***)

A collection of around 400 historic 19th and 20th century iron knives housed at the Criminal museum in Athens (CMA), Greece have been treated by the students from the Dept. of Conservation of Antiquities & Works of Art, T.E.I. of Athens. The knives are coated (with Paraloid B72 followed by Renaissance wax) for added protection, since the conditions of the museum are not controlled. However, after as little as 2 weeks around 30% of the knives show signs of active rust spots. The research proposes to find a suitable corrosion inhibitor to apply underneath the coating to help to minimise the corrosion problems encountered during the exhibition of the collection.

Contact: Vasilike Argyropoulos (TEI of Athens)
Funding: no external funding

Ongoing research projects


Iron tin-plated finds ***(Arc'Antique)***.

The aim of this project is to detect and preserve, within the corrosion products, tin-plates on archaeological iron-based artefacts. Many pieces of the Carolingian Period (9^{th}-10^{th} century to the end of the Middle Ages) examined with X-raying method are showing a particular distinctive out-lining (high density to the X-rays) in relation with their original tin-plating (or other covering metals…). That is particularly the case for small fittings and cavalry equipment.

First of all, during the conservation work, there is no external visual evidence of this finishing treatment (aesthetic and protective) because of the presence of iron corrosion products on and under the tin-plate (excepting the related cases of iron finds from the York Viking period which were less corroded).

Secondly, in some cases, we have noticed with the X-rays the disappearance of this tin-plate layer during the stabilisation treatments and particularly during the dechlorination involving an alkaline sulphite solution (Na_2SO_3 + NaOH).

This new research programme involves MsS students and is based on 3 major axes:

- The comprehension of the chemical dissolution of tin-plate in alkaline solutions,
- The detection of this layer in the attempt to get the original surface during the mechanical removal of external corrosion products.
- The development of a simple qualitative chemical test to identify tin in external corrosion products of iron.

Coordination: Stéphane Lemoine & Manuel Leroux (Arc'Antique)
Funding: no external funding

Ongoing research projects

 Examination and stabilisation of a collection of lead medals from the National Museum of Finland (***EVTEK Institute of Art and Design / HEAA, filière HES-CRAE / NMF***)

The initial objective of this project conducted by Martin Ledergerber, Swiss conservation student from HEAA, HES-CRAE Department, was to define a protocol to remove organic coatings present originally on lead medals and to preserve at the same time the corrosion layer underneath with surface information. This cleaning process should be followed then by a stabilisation treatment. Because of the powdery and loosely adherent corrosion products treatments involving mechanical contact with the surface should be minimal. Only the immersion in solvents has been evaluated during this first step.

As mentioned before the collection of the Numismatic Department of the National Museum of Finland was considered for this project. This collection has suffered recently from an exposure to high relative humidity (to 60%) and higher temperatures than usual. Due to the storage in wooden cabinets, corrosion problems occurred. A modified Oddy test (with lead coupons only) has been performed on most of the materials which are present in the storage area and most of them appeared to give negative results. Further analysis of the different corrosion products formed during the test are planned in the future. It would be quite interesting to determine which corrosion products are aggressive resulting then from an active corrosion and which ones are stable.

A preliminary survey of the collection has revealed that most of the medals are free of any protection. Only one artefact had been covered with an organic coating which has been identified by FTIR as a PVAC (poly-vinyl acetate) compound. These compounds were used indeed some years ago by the NMF. They may have favoured the corrosion processes.

During the project electrolytic measurements have been performed to assess the efficiency of the electrolytic stabilisation of artificially corroded lead coupons with or without the presence of organic protections. Different compounds were considered for the protection: natural resins, waxes, nitro-cellulose lacquers and acrylic copolymers. Similar techniques were used too to determine the optimal conditions of the cleaning process (time of immersion in solvents). Other approaches were tested as well such as the use of pigmented resins but the results were inconsistent and difficult to interpret.

At the end of this first part of the project, it appears that the cleaning of ancient organic coatings on lead artefacts is needed to ease and complete the stabilisation treatment of active lead artefacts. But the appropriate solvents have to be chosen. Optimal conditions of cleaning have to be given too. Martin is continuing his project in Switzerland (exposure of samples to solvents as vapours and use of atomic oxygen treatment). Further results are expected by the end of this year.

Contacts: Christian Degrigny (EVTEK Institute of Art and Design), Martin Ledergerber (HEAA du Canton de Neuchatel, La Chaux-de-Fonds, Switzerland) & Pia Klaavu (NMF)
Funding: EVTEK Institute of Art and Design, NMF

Ongoing research projects

Electrolytic stabilisation of marine iron artefacts in neutral solution (***EVTEK Institute of Art and Design***)

The objective of this work introduced in BROMEC 2 has been to extract electrolytically chlorides from iron based marine artefacts associated with other materials. The use of a basic solution was impossible due to the nature of these materials: paint, rubber and glass. Instead a 1% (w/v) $NaNO_3$ solution was chosen. The anode is a stainless steel grid.

The innovative part of this study was the complete monitoring of the pH of the non-buffered solution and both the cathodic and anodic potentials during the cathodic polarisation of the artefacts.

To define optimal parameters of polarisation, iron nails were first considered to simulate the behaviour of the iron part of the composite. General trends were obtained while modifying the cathodic (and anodic) potential to optimise the chloride extraction and the surface condition (polished and oxidised) of the nails. One major observation was that the pH was increasing quite fast as soon as the cathodic potential was decreasing under a certain value or the anodic potential was above another specific value. A different behaviour was observed when the nails were slightly oxidised. The increase of pH was not the general trend. Sometimes it was decreasing. But after some times the previous behaviour was observed. This difference of trend has been explained by the presence of the oxide layer. Our major concern was the behaviour of the whole system during the night where no control of the different parameters is possible. The stabilisation process lasts indeed several days, week-ends included. Thus this long term polarisation parameter has to be studied.

On archaeological artefacts the decrease of pH was on the contrary the general trend. Due to the presence of a thick GCL on the grey cast iron, it was impossible to apply such negative potentials as the ones obtained before. Polarisation was conducted this time using a constant anodic potential. Like before our objective was to maintain a constant pH for days and nights.

Chloride extraction was monitored and it appeared that by applying the appropriate potentials this extraction was effective.

Our future work will be to understand the change of pH during polarisation and the influence of the surface of the artefact considered. Electrochemical reactions taking place at the surface of the electrodes will be studied with a potentiostat.

Contact: Christian Degrigny (EVTEK Institute of Art and Design) & Ilonne de Groot (ICN)
Funding: no external funding

New research projects


Archaeological lead artefacts : case study ***(Arc'Antique)***

For the last thirty years, numerous research programmes have been developed to study the corrosion of lead and its alloys (with Sn and Sb). The major conservation problems come from the stabilisation of the corroded surface which contain the details and all the historical descriptions of the artefacts (for medals and seals for example). Five years ago Arc'Antique developed a well controlled electrolytic stabilisation technique based on the consolidating reduction of lead. This technique is now successfully used on medals and seals stored in oak cabinets and damaged by the acetic acid vapours evolved. Unfortunately, we have recently reached some limits of this reduction treatment with the conservation and restoration programmes of archaeological lead artefacts.

First, it appears to be very difficult to determine on each artefact whether the corrosion is active or not under the white crust and corrosion products (mainly lead carbonate). Secondly when the electrolytic consolidating treatments are applied, there are always some areas on each artefact which cannot be reduced.

In the case of archaeological finds, the lead corrosion products are mostly combined with some minerals which form a diffusion barrier not only for the reducing species but also for the electrolyte.

The main features of this research programme are, on one hand, to characterise the chemical composition of the corrosion products by Raman Spectroscopy and Scanning Electron Microscope coupled with Energy Dispersion Spectrometer. On the other hand, we are adapting the consolidating reducing treatment to these archaeological finds.

Contacts: Loretta Rossetti, Nathalie Huet & Jean-Bernard Memet (Arc'Antique)
Funding: No external funding

Calls for collaboration

 The conservation of Ethnographic metal collections from the Eastern Mediterranean area

Partners required: Museums with collections of metallic ethnographic collections from Eastern Mediterranean

Contact: Vasilike Argyropoulos (TEI of Athens)

Calls for collaboration

 Development of a course on the use of electrolytic techniques in metal conservation

Objective: the conservation department of EVTEK Institute of Art and Design has developed in the past years a specific course on the use of electrolytic techniques in conservation. It is dedicated to students in conservation. General concepts of metal corrosion and definition of electrochemical and electrolytic parameters are given but the course concentrates mostly on the use of these parameters to monitor the treatment of simulated or original historical and archaeological artefacts

Our objective would be to involve more speakers, particularly from abroad, to enlarge the fields of application. Specific approaches could be proposed too according to the nature of the participants (students, trained conservators). The module obtained could then be used in other training schools for conservators.

Partners required: other training schools and lecturers interested in giving lectures in the field, experts (conservation and/or corrosion scientists)

Contact: Christian Degrigny

General information

- Web-sites

Some sites offer interesting information on research applied to the conservation field. Specific studies on metals might be found.

- **5th Cultural Heritage Research: a Pan-European Challenge, Cracow (16-19 May 2002).**
  The programme of the conference + list of posters can be found on: www.heritage.ceti.pl.

- **EC Advanced study course on "Science and technology of the environment for sustainable protection of cultural heritage**
  The programme and the course materials are available on: www.ucl.ac.uk/sustainableheritage/learning/asc/index.html

- **Laboratories on Science and Technology for the conservation of European Cultural Heritage**
  http://www.chm.unipg.it/chimgen/LabS-TECH.html

- **Cost Action G8: Non destructive analysis and testing of museum objects**
  http://srs.dl.ac.uk/arch/cost-g8

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

- **Protect our European Outdoor Bronze Monuments.**
  Provide a Good Practice Guide (GPG) for the protection of Outdoor bronze monument: www.kae.gr/bronzemonuments/home.htm. Note that the GPG from the web-site is incomplete. Complete versions can be provided by the editor.

- **Corrosion source**. All kind of basic data needed when you study corrosion problems on metals can be found on that site.
  www.corrosionsource.com

- Future seminars and conferences

- **ICC 2002** - 15th International Corrosion Congress (22-27 September 2002, Granada, Spain). For more information consult http://www.15icc2002.com/intr.html

- **ICOM-CC Triennial Meeting** (23-27 September 2002, Rio de Janeiro, Brazil). For more information consult www.icom-cc.org/rio2002

- **Introduction course on the use of lasers in art conservation** (4-6 September and 20-22 November 2002, Art Innovation, Hengelo, The Netherlands). For more information contact Art Innovation (info@Art-Innovation.nl)

- **Cost action G7 meeting** + workshop: Conservators and the use of laser techniques in conservation (18 October 2002, Vantaa, Finland). For more information contact Christian Degrigny (Christian.degrigny@iad.evtek.fi)

- Abbreviations and acronyms

ARC: Atelier Regional de Conservation
CMA: Criminal museum in Athens
CRAE: Conservation-Restauration des objets Archéologiques et Ethnographiques
CRCDG: Centre de Recherche pour la Conservation des Documents Graphiques
EVTEK: Espoo-Vantaa Teknillinen Ammattikorkeakoulu
FTIR: Fourrier Transformed Infrared
GCL: Graphitic Corrosion Layer
HEAA: Haute Ecole d´Arts Appliqués
HES: Hautes Etudes Supérieures
ICN: the Netherlands Institute for Cultural Heritage
MMF: Maritime Museum of Finland
MRT: Mission de la Recherche et de la Technologie, Ministère de la Culture et de la Communication
MsS: Master of Science
NMF: National Museum of Finland
PEG: polyethylene glycol
TEI: Technological Education Institute

- Contacts

Tiina Andersson / EVTEK Institute of Technology (tiina.andersson@kolumbus.fi)
Vasilike Argyropoulos / TEI of Athens (bessie@teiath.gr)
Christian Degrigny / EVTEK Institute of Art and Design (☎:+358 9 511 9406 - christian.degrigny@iad.evtek.fi)
Ilonne de Groot / ICN (gloond@hotmail.com)
Nathalie Huet / Arc´Antique (☎:+33 2 51810940 - arcantique@wanadoo.fr)
Pia Klaavu / NMF (☎:+358 9 405 9503 – pia.klaavu@nba.fi)
Rami Kokko / NMF (rkokko@yahoo.com)
Martin Ledergerber / HEAA-HES de la Chaux-de-Fonds (martin_ledergerber@hotmail.com)
Stéphane Lemoine / Arc´Antique (☎:+33 2 51810940 - arcantique.metaux@wanadoo.fr)
Jean-Bernard Memet /Arc'Antique (☎:+33 2 51810940 - arcantique.recherche@wanadoo.fr)
Malalanirina Rakotonirainy (rakotoni@cimrs1.mnhn.fr)
Loretta Rossetti / Arc´Antique (☎:+33 2 51810940 - arcantique.metaux@wanadoo.fr)
Quoc Khoï Tran / ARC-Nucléart ((☎:+33 4 76884050 - TRAN@chartreuse.cea.fr)

- Correspondents

Australia: David Hallam, Canberra (d.hallam@nma.gov.au)
Belgium: Patrick Storme, Antwerpen (Patrick.storme@skynet.be) & Gilberte Dewanckel, Bruxelles (gilberte.dewanckel@kikirpa.be)
Denmark: Karen Stemann Petersen, Copenhagen (karen.stemann.petersen@natmus.dk)
France: Jean-Bernard Memet, Nantes (arcantique.recherche@wanadoo.fr) & Régis Bertholon, Paris (bertholon7@aol.com)

Germany: Gerhard Eggert, Stuttgart (gerhard.eggert@abk-stuttgart.de)
Greece: Vasilike Argyropoulos, Athens (bessie@teiath.gr)
Italy: Paola Letardi, Genova (letardi@icmm.ge.cnr.it)
Netherlands: Bart Ankersmit, Amsterdam (bart.ankersmit@icn.nl)
Norway: Birgit Wilster-Hansen, Oslo (b.w.hansen@ukm.uio.no)
Spain: Emilio Cano, Madrid (ecano@cenim.csic.es)
Sweden: Helena Strandberg, Göteborg (helena.s@hem.utfors.se)
Switzerland: Valentin Boissonnas, La Chaux-de-Fonds (v.boissonnas@heaa-ne.ch)
United Kingdom: David Thickett, London (dthickett@thebritishmuseum.ac.uk)
USA: Paul Mardikian, Charleston (mardikian@hunley.org)