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METALConsn-info

ICOM Metal working group

Bulletin of the Research On MEtal Conservation

February 2003

BROMEC5

Editorial

It is the first anniversary of our bulletin! One year ago the BROMEC was just born. Since then its development has increased a lot. From 10 countries with national correspondents we have now almost 20 and since last September the BROMEC is diffused more widely to all ICOM-CC Metal working group members.

Practically it means for all of us a better awareness of the research in metal conservation conducted all around the world. All kind of subjects are treated in our bulletin. Up to now 32 different projects have been presented. Some are completed, others are still in progress. A fraction of them have not started yet and collaborations are still wanted.

Our bulletin would not exist without the voluntary and active participation of national correspondents who gather information on research projects in their own country. The tasks of a national correspondent and the requirements to fulfil them have been discussed recently between the existing national correspondents. These information that are particularly important for members interested in becoming a national correspondent are available on request.

A lot of interesting work is conducted in Latin America. Some of you know quite well Johanna Theile. She organised in 2001 the interim meeting of our working group in Santiago de Chile. Johanna is setting up another seminar in Spring 2003 on the situation of metal conservation in Latin America (see section conference and seminar). The seminar will be in Spanish but we are planning to translate the abstracts both in English and French. In other countries the interest for research in metal conservation is as high as in Chile. In Argentina some colleagues are working for years on atmospheric corrosion of bronze monuments. These countries can then reasonably pretend to have their own national correspondents. After some discussion, it has been decided that in the future Johanna will continue to represent Chile. Blanca Rosales and Miguel Crespo will represent Argentina. National correspondents for other countries such as Brazil might be suggested later on.

In some countries some working groups are particularly active in supporting research activities in metal conservation. In France the ChimArt working group that is devoted to the study of cultural materials has organised 2 meetings in 2002 where members involved in the study of metallurgical processes, metal corrosion or the conservation of metal artefacts presented their current work. For the detail of the research projects presented please consult the “ongoing research projects” section.

The French version of BROMEC is now available. French members of the working group will receive it automatically. For other members interested in receiving this French version, please contact the editor.

The Editor
Christian DEGRIGNY

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Ongoing research projects

2002 ChimArt meetings

In the following only the titles of papers and posters presented during the meetings are given. For more information please refer to the contact person.

July 2002 (at Arc'Antique, Nantes)
Talks given:

- **D. Bourgarit & B. Mille** : Sulphide copper ores reduction during the Chalcolithic period : experimental and archaeological approaches, david.bourgarit@culture.fr
- **F. Mirambet** : Iron corrosion inhibitors with sodium carbohydrates, francois.mirambet@culture.fr
- **H. Takenouti** : Copper corrosion and passivation using amine components, ht@ccr.jussieu.fr
- **M. Aucouturier** : High temperature oxidation of bronzes, marc.aucouturier@culture.fr
- **B. Mille** : Raman spectroscopy of corrosion products, benoit.mille@culture.fr
- **M. F. Guerra** : Gold artefacts analysis using PIXE, PIGE PIXE-XRF, same email as B.Mille
- **L. Rossetti** : Lead archaeological artefacts treatments using cathodic polarisation in sulphate solution, arcantique.metaux@wanadoo.fr
- **S. Lemoine** : Tinned iron archaeological artefacts : problem related to the tin layer degradation in alkaline sulphite, arcantique.metaux@wanadoo.fr
- **R. Bertholon** : Outline of the corrosion descriptive method, regis.bertholon@univ-paris1.fr

December 2002 (at C2RMF, Paris)
Presentation of posters :

- **J. Steinmetz, E. Rocca, C. Rapin & F. Mirambet** : Temporary treatment of technical and industrial heritage, francois.mirambet@culture.fr
- **B. Chevalier, L. Fournes, F. Mirambet & A. Wattiaux** : Iron protection for industrial heritage, chevalie@icmb.u-bordeaux.fr
- **D. Neff, E. Vega, S. Reguer, E. Wasjgros & P. Dillmann** : Iron archaeological artefacts buried in clay soils : corrosion rates evaluation and corrosion forms typology, NEFF@drecam.cea.fr
- **D. Neff, R. Bertholon, L. Bellot-Gurlet & P. Dillmann** : Corrosion forms of iron archaeological artefacts, complementarity of macroscopic and microscopic approaches and analysis, NEFF@drecam.cea.fr
- **L. Beck, D. Bregiroux, S. Bosonnet, D. Eliot, S. Reveillon & F. Pilon** : Gold and silver plated Roman coins analysis, lucile.beck@cea.fr
- **L. Beck, S. Bosonnet, D. Eliot, S. Reveillon & F. Pilon** : Surface enrichment of silver coins during manufacturing processes, lucile.beck@cea.fr
- **T. Calligaro, M. Guerra, J.C Dran, J. Salomon, B. Moignard & L. Pichon** : Gold and garnets in Merovingian jewellery, Thomas.calligaro@culture.fr

For more information about ChimArt please contact the coordinator of the working group, Jean-Claude Dran at the following address: jean-claude.dran@culture.fr

Ongoing research project

A new concept for the desalination of archaeological iron artefacts in neutral solutions (***AIASCR / SVUM***)

To extract efficiently chlorides from archaeological iron artefacts containing organic remains or associated metals (such as bronze or silver), solutions with approx. neutral pH were proposed for electrochemical stabilisation (with or without external current). According the Pourbaix potential – pH diagram, pH and potential E values comprised within the area pH = 5-6 and E= - 410+/- 50 mV, covering the Fe_3O_4 stability, were considered as appropriate. At that neutral pH, chloride species concentrated at the tip of the pits should not be blocked by any iron oxyhydroxide. It is assumed then that they can be extracted in the form of soluble ferrous compounds.

The required potentials were reached either by reducing agents (mixture of phosphate buffer and ascorbic acid solutions, hydrazinbenzoate) or by cathodic polarisation in phosphate buffer and natrium benzoate solutions. The solutions were formulated also in respect of the stability of other metals and organic materials found in composite artefacts.

The desalination treatment was monitored by chloride analysis and its completion was checked by exposure of the artefacts in a humid chamber. The kinetics of the stabilisation were assessed as well as its effect on the corrosion layers during the following steps of the conservation process (mechanical cleaning).

Once the conditions of the experiments were defined on a selection of archaeological artefacts, new comparisons tests were conducted on a collection of iron artefacts dating from the same period and from the same archaeological site. Samples were given to 9 different conservation laboratories in Czech Republic where both our new protocols and traditional stabilisation techniques such as immersion in deionised water, alkaline sulphite and lithium hydroxide were tested. It was planned that the results obtained would be critically reviewed but part of these ones were lost during the floods in Autumn 2002. A workshop was nevertheless organised in November 2002 in Brno to compare the results that survived to the floods.

These first experiments showed that the new protocols offer an interesting alternative to the alkaline sulphite treatment (most effective treatment among the traditional approach). They are indeed adequate for artefacts associated to organic materials (phosphate buffer and ascorbic acid solutions work the best) or to other metals (hydrazinbenzoate is better here). In addition the stabilisation step is better controlled under cathodic polarisation. Due to the data lost during the floods some experiments have to be repeated to confirm these preliminary results.

Contacts: Alena Silhova (AIASCR) & Milan Prazak (SVUM)
Funding: Ministry for Culture of Czech Republic

Ongoing research project

Lead roofs in Denmark (***SMRH-NMD / Laboratory NKT Cables A/S/ CD-NMD***)

The predominant material for roofs on churches and cathedrals in Denmark is tile, however lead slate and copper also are common. In 1998-2002 the National Museum of Denmark, Section for Medieval and Renaissance History, has completed an investigation about church roofs made of lead. The Danish Ministry of Ecclesiastical Affairs provided financial support and analytical help was obtained from the laboratory of NKT Cables A/S.

It seems likely that lead sheets once were predominantly used as roofing on Danish churches. As curators and consultants for historical churches we found that lead roofs were being recast after only 30-60 years though it is usually expected that such roofs will last 100-200 years. Based on this observation, it was decided to examine if the quality of the lead had changed over time. This could either be as a result of the recasting process itself or as a result of the addition of so-called pure lead when recasting. The reasons given and documentation for recasting lead roofs in the years 1998-2001 were reviewed. The casting and mounting techniques of the roofs were examined and 54 samples from lead roof sheets were collected. The sheets were cast between 1702 and 2001. To have a comparative material a few samples from neighbouring countries were obtained: one from southern Germany, two from Scotland and five from England.

Lead sheets in Great Britain are produced industrially, usually as milled lead sheets, and a good quality follows a standard for the recommended quite pure lead with specific impurities (*British Standard 1178 - Milled Lead Sheet for Building Purposes*). The situation is very different in Denmark. Here the old trade of the lead caster and lead roofer is still alive, and there is no standard for a recommended lead quality. The lead which is taken down from a church roof is recast and reused for the new lead roof of the same church, and all the tasks of the process are carried out by a craftsman on his own. Some restrictions in relation to health regulations and the desire for comfort have changed the processes to a certain extent, but it remains a craft rather than an industry. Even though there is no wish to change the traditional ways, it was nevertheless desirable to secure a consciousness about the significance of the composition of the lead in use as well as mounting procedures.

At the laboratory of NKT three spectrum analyses were completed on each of the 62 samples. Spectra were made showing the content of other elements considered to be relevant. The result showed that only slight changes in the metal composition have taken place over time. Special attention was paid to the content of copper, tellurium, tin, antimony and silver in order to prove whether the cast metal actually was of a quality capable of resisting the effects of fatigue (exhaustion) and creep (slow deformation from weight). In judging this metallurgical information the author relied partly on the experience at NKT from the company's earlier work with lead cable production and the results presented by Sivaraman Guruswamy[1].

The content of tin and bismuth had risen over time while it had fallen for all other elements. The changes were minimal, and in the final report it is argued that the changes only rarely would have any significance. For many samples there were some considerations as to whether the quality was good enough. For instance, the content of copper was in some cases between the minimum and maximum limits of the British standard (0.03-0.06%), but more often the content of copper was either higher than the maximum limit or, as in most cases, lower than the minimum. It is argued that this is not significant as long as the cast metal contains other elements that also secure a resistance to fatigue and creep such as tellurium, tin, antimony and silver.

As a whole the British standards probably should be seen as a possible guideline rather than a standard for the one and only ideal composition, and this is a very important conclusion when, as in Denmark, the old craft is still alive, and the same lead is reused.

While the composition only in very few cases gave reason to consider an adjustment of the content of elements, the investigation of the reasons for recasting lead roofs showed circumstances of much more common interest. It was found that even though the number of cases in which the church authorities approve that a lead roof be recast had not increased over a period of 40 years each incident is now usually more extensive. When a number of leakages is found in one area of let us say the south side of the nave, the whole roof on the south side was recast. Often the craftsman or the architect would argue that it was most economical to recast the whole roof of the entire building, choir, nave, tower and porch, all at one time rather than at various occasions over a number of years. "It looks the best when the roof of the whole building has been recast at one time" was argued in some cases. These economic and aesthetic considerations turn out to have become important reasons why a lead roof seldom lasts more than 60 years. The good part of a roof is simply not left to serve the full period that it is fit for. In the report it is argued that a lead roof maybe should not be expected to last for 100-200 years but rather 50-300 years, provided it is recast only when the sheets have served their time and are worn out.

All churches with roofs wholly or partly covered with lead sheets were listed by the museum as a part of the research project. It showed that the roofs of more than 800 Danish churches and cathedrals were covered with lead sheets. The Danish tradition of the lead roofers has within the last 20 years been re-introduced in southern Sweden where about 30 churches have lead roofs but where the trade had died out at the beginning of the 20th century. In Denmark the 800 churches with lead roofs are attended by three companies that specialise in lead working.

Contacts: Per Nielsen (SMRH-NMD) in collaboration with Birgit-Margrete Procida (Laboratory NKT A/S) & Birgit Sørensen (CD-NMD)
Funding: Danish Ministry of Ecclesiastical Affairs

1. Guruswamy, S., *Engineering Properties and Applications of Lead Alloys*, Mercel Dekker, Inc., New York 2000

Ongoing research project

A comparative study of protective coating systems for outdoor bronze sculpture in marine environment ***(CNR-ISMAR-UOCMM)***

The main aim of the following research project is to characterise the protective properties and other qualities of some coatings applied for outdoor bronzes. Furthermore we aim also to find and discuss a relevant methodology for testing such protective systems, with a special attention to the role of natural patinas on coatings behaviour. We also address the possible applications of electrochemical methods for field assessment of conservation strategies.

The behaviour of six protective coating systems, widely applied in conservation practice, is under test: three micro-crystalline waxes (Soter LC, R21, Tromm TeCe 3534F), one organic coating (Incralac) and two double-layer systems (Incralac+ Soter LC, Incralac+ R21). Polished coupons of a cast bronze (Cu 90%, Sn 8%, Pb 2%) both unprotected and coated with the selected protective systems have been exposed to natural weathering in an urban marine environment (CNR-UOCMM exposure site inside the Harbour). In parallel, six areas with various patinas were selected on a bronze monument ("Monumento ai Mille" by E.Baroni, 1910) placed just in front of the sea, not far from the UOCMM exposure site; in those areas a number of 6 x 4.5 cm zones have been restored and treaded with the same protective systems. Several analytical techniques have been used to characterise patinas and coatings. Patina samples from the statue have been characterised by XRD, as long as patina formed on the unprotected polished coupons after 1-3-12 months weathering. A specially designed contact-probe Electrochemical Impedance Spectroscopy (EIS) measurement method is used to characterise and compare the protective performances with weathering both on coupons and on the monument. Rp (Polarisation Resistance) measurements at several weathering times have been done in order to compare the coatings behaviour on the different areas on the monument. Colorimetric data (spectrophotometric method) are under evaluation both for coupons and for test areas on the monument. A visual inspection report has been performed by a restorer after 15 months weathering on the monument.

Notwithstanding a pretty wide dispersion of data, the comparison of the impedance data values obtained for the coatings applied on the clean bronze samples and on the patinated bronze surface of the Monument suggest a different behaviour upon weathering. Further measurements are in progress for longer exposure time. The impedance values obtained on samples with no coatings enlighten the almost negligible protective properties of the bronze patinas developed in a marine environment. Nonetheless the different behaviour of the coatings on bronze samples and on the Monument suggest a not negligible role of natural patinas in the behaviour of coatings applied in conservation. This confirms similar observation obtained on artificially patinated bronze.

Further developments will include characterisation of coatings behaviour on 3,12 months weathered samples, in order to check whether this methodology allow to get results much more similar to the one obtained on the Monument. Comparison of analytical results from different characterisation techniques is in progress.

Contact: Paola Letardi (CNR-ISMAR-UOCMM)
Funding: PF Beni Culturali - no external funding at the moment

Ongoing research project

Plasma reduction, its use in metals conservation (***SNM, CC***)

Low-pressure hydrogen gas plasma reduction has been used at the Swiss National Museum in metals conservation since 1990. After a critical re-evaluation of the method in 1994 major changes have been introduced. Today it has become an integral part of the conservation procedures for archaeological iron. Its major advantages are an improved mechanical cleaning, and the speeding up of the subsequent desalination process with alkaline sulphite[2,3,4].

Further the high frequency plasma method offers an interesting alternative to common cleaning methods for historical silver artefacts. The use of plasma reduction and its effects on different silver surfaces have been investigated. It could be shown, that plasma reduction is a suitable method for silver artefacts, which are too fragile to be cleaned mechanically or chemically. An additional advantage is that inherent silver is not removed and the surface is not further compromised[5].

At the Swiss National Museum the ongoing research and further development (installation of an optical spectrometer) of the low-pressure hydrogen gas plasma reduction for metals conservation contributes to a better understanding of the processes taking place during treatment and is expected to help optimising the treatment parameters applied.

Contact: Katharina Schmidt-Ott (SNM, CC)
Funding: no external funding

2. Schmidt-Ott, K., *Applications of low pressure plasma treatment at the Swiss National Museum and assessment of the results,* Zeitschrift für Schweizerische Archäologie und Kunstgeschichte, 54(1), 1997, 45-50

3. Schmidt-Ott, K. & Boissonnas, V., *Low-pressure hydrogen plasma: an assessment of its application on archaeological iron*, Studies in Conservation, 47, 2002, *81-87*

4. Perkik, D., *The influence of low-pressure hydrogen plasma on changes in metallographic structure of iron objects*", paper presented at ICOM-CC Metal WG Congress 2001, Santiago/Chile, publication forthcoming

5. Schmidt-Ott, K., *Plasmareduktion von Silberoberflächen*, paper presented at *Exposure 2001* (International Conference on the Corrosion, Conservation & Study of Historic Metals in Situ, on Display & in Storage), Hildesheim/Germany, 7th-10th November 2001, publication forthcoming

Ongoing research project

Technological investigation of a Romanesque reliquary (***StABK / FHA / MIUW***)

The theme of this project presented in BROMEC1 and conducted as a diploma thesis at the StABK was the technological investigation and documentation of the Romanesque Vitus reliquary from Willebadessen, a former Benedictine monastery in Westphalia, Germany, next to the monastery of Helmarshausen, the working place of Theophilus, the most famous goldsmith of the Middle Ages.

Since the reliquary is made of numerous different materials such as oak wood, gilt and nielloed silver sheet as well as enamelled cooper sheet, a deep insight into the processes of work of a medieval goldsmith influenced by the school of Theophilus could be obtained.

The interdisciplinary work of conservators, scientists and art historians considered the questions of dating, provenance and authenticity of the reliquary. Various analytical technologies such as X-radiography, electron microprobe (at the MIUW), AAS, OES, GC-MS and dendrochronology were applied to answer those rising questions and the circumstances of production. Subsequently, they were discussed against the background of the technical literature of the Middle Ages (e.g. the tractatus of Theophilus, Heraclius or Mappae Clavicula).

Throughout the time of liturgical use three different states of condition which differ distinctly one from another could be defined.

Provenience and dating could be obtained by examination with non-destructive dendrochronological methods (computer tomography at FHA). The former dating established by historical examination could be confirmed. X-Radiography revealed new aspects of the matter of manufacturing and use (e. g. a former entrance inwards). Furthermore it was found that the enamels fixed to the lid were later additions to the object, perceivable by high contents of boron, inserted by the use of borax, which seems not to be used before the 17th century.

Contact: Heiner Grieb (StABK)
Funding: no external funding

Ongoing research project

Corrosion on copper, copper alloys and copper minerals caused by sulphur and reduced sulphur compounds (***StABK / ICN / MPIUB***)

The so-called `black spots`, a corrosion phenomenon first observed on archaeological bronze objects, are the subject of this work conducted as a diploma thesis at the StABK (the research project has been presented in BROMEC1). This kind of copper corrosion can be caused by the presence of elemental sulphur or reduced sulphur gases in the atmosphere, such as hydrogen sulphide and carbonyl sulphide. The spot-like growth and fuzzy structure are the main characteristics of this corrosion form. Until now, black spots were either identified as crystalline (or in rare cases amorphous) copper sulphides.

In laboratory experiments, a number of copper alloys and tin alloys containing small amounts of copper were exposed to different concentrations of sulphur and hydrogen sulphide, to learn more about the corrosion mechanisms. The corrosion products were then observed using SEM and analysed using XRF and XRD. The protective properties of different coatings on copper alloys were tested too. Surveys were carried out in museums and mineral collections in Germany and in the United Kingdom. Potential sulphur sources in the museum environment were investigated, including materials used for conservation and storage.

Some materials, which are widely used in museums are potentially harmful for objects made of copper alloys and silver, such as plastiline and vulcanized rubber. For many archaeological bronze objects it was obvious that mechanical or thermal disruption of the metal structure had caused the growth of black spots. Moreover it could be proved, that copper sulphide corrosion can occur as the main corrosion product on tin alloys with copper contents as low as one percent (pewter).

The analyses showed, that the corrosion products often consisted of a complex mixture of different phases. Numerous samples from bronze objects could not be identified with XRD at all. Some samples contained copper sulphates apart from copper sulphides plus other, unidentifiable substances, which led to the assumption, that in these cases a partial oxidation from sulphides to sulphates had taken place. It is possible, that these not yet identified phases are partially oxidised sulphides; they are either amorphous, or their crystal pattern is still unknown.

More research work and the use of alternative analysis methods will be necessary to completely characterize these corrosion products. In any case, the definition of black spots as copper sulphides must be revised.

The work was carried out in co-operation with ICN (Netherlands), The Mary Rose Trust (United Kingdom), and the Mineralogisch-Petrologisches Institut der Universität Bonn (Germany).

Contact: Maja Weichert (StABK)
Funding: no external funding

Ongoing research project

Conservation issues around the Civil War Ironclad USS *Monitor* (***MM***)

The American Civil War union ironclad, USS *Monitor* sank New Years Eve, 1862 after gaining fame by defeating the confederate Ironclad, CSS *Virginia* in the first battle of ironclads, a battle that dashed the confederacy's hopes of breaking the union's sea blockade of confederate ports, a task and hope shared by the H.L. *Hunley* currently being conserved in Charleston, South Carolina (see BROMEC4).

The *Monitor* has undergone excavation of components regularly every summer field season since 1998 when the propeller was brought to the Mariners' Museum in Newport News Virginia for conservation and exhibition. Successive field seasons have recovered the *Monitor*'s skeg, propeller shaft and packing seal, engine and engine room piping, condenser, and her 200-ton turret. Numerous other items of metal, wood, glass, textile, and a few paper items were recovered also. It is expected that the recoveries will continue for several additional years as the crew' s quarters, wardroom, administrative, and control areas of the ship are explored.

Conservation priorities to date have been centred on containing and keeping over 250 tons of metal, principally wrought and cast iron, ship components protected from corrosion while conserving small fragile artefacts and organics. Due to the very large mass of the artefacts, their complexity, and the high percentage of occluded surfaces especially in the turret, we are planning to largely disassemble major components in order to conserve them. As the turret alone has over 1200 square meters of hidden chlorides contaminated surfaces it will practically be impossible to stabilise this structure or determine conclusively that the treatment is successful. A comprehensive conservation plan for the *Monitor* has been written and is undergoing both review and revision. The plan is regarded as a living document and it is expected that it will undergo continual revision as new material is recovered from the wreck site and as we are investigating the materials.

The Museum possesses period drawings of many of the vessel's components and our archivists are actively searching for drawings and documents that will add to our understanding of the vessel, its components and its construction and use. Differences between the blue prints and the "real" *Monitor* are already obvious and these findings will probably unfold as the conservation progresses.

Plans for the future include:

- Continuing to remove encrustation build-up from inside the turret.
- Develop a plate removal and replacement strategy for the turret
- Corrosion characterization and chloride content of ferrous materials
- Development of control systems for electrolytic reduction.

It is expected that a design for research on this material will be developed as we get better controls on our existing problems and change the conservation efforts at the Mariners' Museum from organic and fragile materials into our large metal objects.

Contact: Curtiss E. Peterson (MM)
Funding : Mariners' Museum

New research project

<u>COLLAPSE - Corrosion of Lead and Lead-Tin Alloys of Organ Pipes in Europe</u> (***GOArt / ELKSJ / M&S / CUT-DEIC / AMS-UB-UCISCRM***)

The European heritage of the organ is preserved in numerous historical instruments. One major threat to this heritage is the indoor atmospheric corrosion of lead and lead-tin alloys of organ pipes. The problem has accelerated and when the pipes have collapsed there is no other way to solve the problem than replacing the historic pipes with modern ones – and a part of the sounding cultural heritage is forever lost.

There are at present no effective methods to prevent organ pipes from being corroded, and to save the valuable instruments which have already been damaged. Moreover, there is no consensus on the reasons for the increased rate of corrosion attack.

The COLLAPSE objectives are to define relevant methods and products as well as to create conservation strategies in order to combat the corrosion of lead and lead-tin alloy organ pipes. This 3 year project started in January 2003. It is coordinated by the Goeteborg Organ Art Centre (GOArt) of the Goeteborg University (Sweden) and funded by the European Commission under the 5th Framework Programme.

The research will cover the 3 following aspects:

1. Through field studies and laboratory experiments identify the factors which cause indoor atmospheric corrosion of lead-tin alloy organ pipes in order to avoid or improve corrosive environments.
2. Develop methods to clean, protect and preserve already corroded pipes from further corrosion.
3. Demonstrate the recommended conservation strategies and products in a case study using the historical Stellwagen organ (St. Jakobi church, Lübeck) severely affected by corrosion.

A European corrosion treatment guideline will be developed to contain methods, products, and materials recommended to be used for prevention of corrosion of lead and lead-tin alloys, treatment, restoration and conservation of corroded organ pipes.

Although this project has started initially between partners from Sweden, Germany, Denmark and Italy, any particular knowledge or experience in the field from Metal WG members are welcome.

Contact : Carl Johan Bergsten (GOArt)
Funding: European Commission (key action "Development of innovative conservation strategies" within the Energy, Environment and Sustainable Development Programme)

New research project

Embrittlement of silver by lead on archaeological artefacts (***LFD,SMD- NAL / DSTO***)

Fundamental studies will be made to understand the mechanism(s) by which silver is embrittled by lead on archaeological artefacts owing to long-term ageing. This research will be conducted at the Materials Engineering Department of Monash University (Melbourne, Australia) on the basis of previous research performed at the Loads and Fatigue Department, Structures and Materials Division - National Aerospace Laboratory (LFD, SMD – NAL)[6] of Emmeloord (Netherlands).

Artificial binary Ag-Pb alloys will be prepared to simulate the behaviour of archaeological artefacts. They will be aged (not above 100-200°C), subjected to mechanical deformation and fracture. Fracture characteristics will be studied then.

A possible extension of this work would be to consider alloys closer to archaeological materials such as Ag-Pb-Cu alloys.

It is hoped that this work will give more insight into the embrittlement of archaeological silver and the possible remedial measures. Moreover the outcomes of this research project will be used to understand the age-embrittlement of Al-Li alloys used in aircrafts.

Contacts: Russel J.H. Wanhill (LFD,SMD-NAL) & Stan P. Lynch (DSTO)
Funding: no external funding

6. Wanhill, R.J.H., Steijaert,J.P.H.M., Leenheer,R. & Koens,J.F.W., *Damage assessment and preservation of an Egyptian silver vase (300-200 BC)*, Archaeometry, 40 (1998) 123-137.

New research project

Research into the possibilities for the removal of tin solders on silver artefacts (***ICN, RM***)

Many silver (sterling) objects that have been repaired with tin solders (tin-lead alloy) show, upon ageing, fracture of the joint. Restoration of these fractures may include the chemical removal of the tin solder from the silver matrix using the following solutions: iron(III)chloride; fluoboric acid and hydrogen peroxide; hydrochloric acid; acetic acid and hydrogen peroxide or mechanic removal while heating the solder.

This research conducted by Maickel van Bellegem (ICN student) as his final thesis aims to find answers to the following questions:

- What are the microstructure changes in silver when treated with tin solder?
- How deep diffuses the tin or lead into the silver (and vice versa) and at what temperature?
- Can old tin solders be removed?
- Which tin solder removal treatment causes the least damage to the silver matrix?

Contacts: Bart Ankersmit (ICN) & Robert van Langh (Rijksmuseum)
Funding: ICN

New research project

Research into the stripping of corrosion layers on historical iron artefacts by acid under cathodic protection ***(ICN / RM)***

Cleaning of iron corrosion in areas that are very difficult to reach cannot be done by mechanical means. The use of acids for the removal of corrosion layers seems effective. However, acids cause etching of the underlaying iron. Cathodic protection of the metal should avoid or limit this side effect.

This research project conducted by Ilonne de Groot (ICN student) as her final thesis will address the following questions:

- Among the following parameters, which ones are important?
  - type of acid
  - cathodic potential to apply
  - treatment time
  - cathodic potential to apply during rinsing under cathodic protection

- What does the surface look like?
  - before and after treatment
  - can patinas be preserved?

Contacts: Bart Ankersmit (ICN) & Robert van Langh (Rijksmuseum)
Funding: ICN & RM

New research project

Changes occurring to archaeological iron in dry storage (***TBM***)

Dry storage is frequently used to retard the post excavation corrosion of archaeological iron. This project will assess the effectiveness of this system and ways of implementing it.

A number of freshly excavated iron objects will be monitored through the conservation and acclimatisation process. The surface will be recorded using the method devised by Bertholon[7], its mineralogy monitored with Raman, FTIR microscopy, SEM and XRD. The relative corrosivity of the site soils will be assessed by pH, soluble ions, conductivity and short term accelerated corrosion tests.

The effectiveness of silica gel for maintaining low RH in a number of different enclosures and packing systems will be evaluated as will the air exchange rates of those enclosures.

Contacts: David Thickett (TBM)
Funding: TBM

7. Bertholon, R., Robbiola, L. & Lacoudre, N., *Corrosion du Rouleau de cuivre de Qumran et localisation de la surface originelle*, Proceedings of ICOM-CC Metal 1998, Ed. W. Mourrey et L. Robbiola, James & James, London, 1998, 125-135

New research project

Comparison of galvanostatic and potentiostatic reduction for lead (***TBM***)

The two techniques will be applied to experimentally corroded lead coupon and lead artefacts corroding from storage. The degree of reduction and surface morphology and chemistry will be assessed. Half rectified galvanostatic reduced lead has a different surface structure to that reduced with full rectification and the electrolyte can also affect the structures produced. If there are significant differences in the surface morphologies then the resistance to acetic acid environments will be assessed. Although previous work has found the different corrosion resistances are overcome by storage in acetic acid concentrations into the $1000\mu gm^{-3}$ range.

Contacts: David Thickett (TBM)
Funding: TBM

New research project

Post excavation changes to archaeological iron (***BC, UL***)

Archaeological iron presents a significant challenge to conservation. The fragile information retained in the remnant metallurgical structures and mineralised organic remains are particularly susceptible to reactions generating physical changes after the iron is excavated. The conservation literature contains differing theories as to the underlying mechanism. This PhD work (conducted by the author) aims to develop and test mechanistic theories to describe this phenomena and to aid in the proper application of conservation treatments and preventive conservation strategies.

It is hoped to develop a standard material to mimic archaeological iron by accelerated corrosion. The changes occurring when this material is exposed to air will be monitored using microchemical and micro-electrochemical techniques. The model material approach will be guided by and confirmed with observation and analyses from real objects.

Contacts: David Thickett (TMB)
Funding: no external funding

General information

- Web-sites

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

- **Laboratories on Science and Technology for the conservation of European Cultural Heritage**
  http://www.chm.unipg.it/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**
  Both following addresses are correct: http://domino.datacenter.ro/cost/index.html and http://alpha1.infim.ro/cost

- Future seminars and conferences

- **20th Century Exterior Architectural Metals: design, preservation and care** (4-5 April 2003, Cambridge, Massachusetts, USA). For more information contact Technology and Conservation, 76 Highland Avenue, Somerville MA 02143, USA (Tel: 617.623.4488, Fax: 617.623.2253)
- **1st Latino-American Congress on metal conservation** (7-11 April 2003, Museum of Contemporary Art, Santiago de Chile) organised by the Conservation department / Faculty of Art of the University of Chile. For more information contact Johanna Theile (jtheile@abello.dic.uchile.cl)
- **Ethnographic & Composite Arms and Armour Seminar** (14 April 2003, Royal Armouries, Leeds, UK). Organised by the UKIC Ethnography Section. For more information contact Deborah Cane, The Conservation Centre, Liverpool (Deborah.cane@nmgm.org)
- **4th International Congress on "Science and Technology for the safeguard of cultural heritage in the Mediterranean Basin "** (April 28 – May 3, 2003, Cairo, Egypt). For more information contact cnrpfbc@tin.it
- **5th World Archaeological Congress (WAC5)** (21-26 June 2003, Catholic University of America, Washington, USA). For more information consult http://www.american.edu/wac5
- **Summer course on metallography of ancient metals** (7-11July 2003, Haute Ecole d'Art Appliqué, La Chaux-de-Fonds, Switzerland). Organised by the Western Switzerland University of Applied Sciences. Teacher: Dr. David A. Scott, max. number of participants: 14. For more information contact Valentin Boissonnas, lecturer in metals conservation, HES-SO, v.boissonnas@heaa-ne.ch
- **"Preservation of Heritage Artifacts" Conference** (14-17 September 2003, Ottawa, Canada). Organised by the National Association of Corrosion Engineers (NACE) Northern Area Eastern. Deadline for abstracts is March 1, 2003 and for completed papers is June 1, 2003. For more information contact Lyndsie Selwyn, CCI, Ottawa (lyndsie_selwyn@pch.gc.ca)
- **Archaeometallurgy in Europe** (24-26 September 2003, Milan Italy). For more information consult http://www.aimnet.it/archaeo.htm

- Abbreviations and acronyms

AAS: Atomic Absorption Spectroscopy

AIASCR: Archaeological Institute of the Academy of Science of the Czech Republic (Prague)
AMS-UB-UCISCRM: Alma Mater Studiorum - Universita di Bologna, Unita Complessa di Istituti Scienze Chimiche, Radiochimiche e Metallurgiche (Italy)
BC, UL: Birkbeck College, University of London
CD-NMD: Conservation Department – National Museum of Denmark (Copenhagen, Denmark)
C2RMF: Centre de Restauration et de Recherche des Musees de France (Paris, France)
CNR-ISMAR-UOCMM: Consiglio Nazionale delle Ricerche – Istituto di Scienze Marine – Unità Operativa Corrosione Marina Metalli (Genova, Italy)
CUT-DEIC: Chalmers University of Technology, Department of Environmental Inorganic Chemistry (Goeteborg, Sweden)
DSTO: Defence Science and Technology Organisation (Melbourne, Australia)
ELKSJ: Ev. -Luth. Kirchengemeinde St. Jakobi (Lübeck, Germany)
FHA: Fachhochschule Aalen, ARGE Metallguss
FTIR: Fourrier Transform InfraRed
GC-MS: Gas Chromatography linked with Mass Detection
GOArt: Goeteborg Organ Art Centre (Sweden)
ICN: Instituut Collectie Nederland (Amsterdam, The Netherlands)
LFD,SMD-NAL: Loads and Fatigue Department - Structures and Materials Division - National Aerospace Laboratory (Emmeloord, the Netherlands)
M&S : Marcussen & Soen (Aabenraa, Denmark)
MM: Mariners' Museum
MIUW: Mineralogisches Institut der Universität Würzburg
MPIUB : Mineralogisch-Petrologisches Institut der Universität Bonn (Germany)
OES: Optical Emission Spectroscopy
RH: Relative Humidity
RM: Rijksmuseum
SEM: Scanning Electron Microscope
SMRH-NMD: Section for Medieval and Renaissance History – National Museum of Denmark (Copenhagen, Denmark)
SNM, CC: Swiss National Museum, Conservation Centre (Zürick, Switzerland)
StABK: Staatliche Akademie der Bildenden Künste (Stuttgart, Germany)
SVUM : Society for Corrosion Protection (Prague, Czech Republic)
TMB: The British Museum
XRD: X-Ray Diffraction
XRF: X-Ray Fluorescence

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