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BROMECC20

Editorial

The delay to produce this 20th issue of BROMECC comes from the large number of abstracts compiled (20 in total) that we had to review. Most of them are abstracts of papers presented during the meeting of the French section of the ICOM-CC Metal WG. Proceedings should be published in the near future, but due to the quality of the presentations given we have decided to immediately translate the abstracts to make them available to the Anglophone conservation community. As a support to these abstracts PowerPoint presentations (in French though) given during that meeting can be found in folder *Other documents* of the Metal homepage of the ICOM-CC website and the folder *Coming and past events* of the **METALConsn**-info website.

One day of the meeting was specially dedicated to new research on the study and conservation of iron based artefacts. Indeed for some years France has been leading research in the field and the abstracts below clearly show the new developments in many aspects of iron conservation.

Some works on other materials are also presented. Some outcomes of the project on the conservation of scientific and technical instruments containing mercury are presented. Other abstracts relate to copper based alloys and the recurrent conservation issue of large structures made of aluminium alloys.

The protection of metals, which is one of the themes of our ICOM-CC Metal WG current triennial period, is clearly illustrated below through the presentation of results of several EU projects (EcoNET, CONSIST and PROMET).

Another important theme chosen by the Metal WG is the study and conservation of composite artefacts. Several abstracts are related to this topic.

We hope that you will find the 20th edition of BROMECC an extra plentiful issue that is more useful and interesting as ever.

Editor

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Ongoing research projects



Conservation issues for mercury in technical and industrial heritage collections (HE-ARC)

This diploma work (already presented in BROME C 16), on the theme of the presence of mercury in technical and industrial heritage collections, was performed within the scientific and technical artefacts conservation module of the HE-ARC (Haute Ecole Arc de la Chaux-de-Fonds) conservation-training programme. Here are some outcomes:

Mercury arc rectifiers from two museums of Porto city (Museum of Science and Industry and Museum of tramways) were considered as case studies. They showed that the presence of artefacts containing mercury within collections represent a high risk of intoxication for the staff and the public. Such risks are the air exposure of large quantities of mercury and concentrations of mercury vapours above safety standards and the contamination of dust and other materials. Therefore there is an absolute need to perform a detailed condition survey on such objects as soon as they enter a collection. Furthermore interventions on such artefacts require a specific approach (appropriate skills and equipment, measurement instruments, etc...), particularly in the case where decontamination is needed.

Such artefacts thereby pose significant management problems to technical and industrial heritage museums (due to the knowledge involved and costs required). The work carried out in Porto museums shows though that some interventions can be performed by a conservator having a good knowledge of mercury management (toxicity, physicochemical characteristics of the element and recommended decontamination protocols). But a preliminary assessment of the risks by an expert in mercury management is preferable and prevents any non-counteracted risk.

The conservation of technical and industrial collections containing mercury requires a specific long-term strategy (including the following steps: storage, control and identification). This strategy should include some directives (standards, recommendations) to reduce as much as possible the mercury intoxication and pollution risks. Such directives are produced by the organisations in charge of the protection of the environment and the health of workers (personal protection, handling, storage, removal of waste materials). These directives can be imposed at an international level (International Programme on Chemical Safety (IPCS), World Health Organisation (WHO), United Nations Environment Programme (UNEP)), European level (European Agency for Safety and Health at work) and national or regional levels (US Protection Agency (United States), Centre Canadien d'Hygiène et de Sécurité du Travail (Canada), Health & Safety Executive (United Kingdom) and Institut National de Recherche et de Sécurité (France), la Suva (Suisse)).

As regards the incompatibility between mercury and other materials, certain metals that are miscible with mercury (zinc, lead, tin, gold and silver) and compounds that dissolve mercury (oxidation agents, ammonia, acetylenic compounds) should not be put in contact with mercury. For other materials (considered as stable in the presence of mercury) more research is needed to assess their long-term resistance (ageing). Whatever the nature of the materials they can be contaminated with mercury (liquid or vapour state), particularly when they are porous. Therefore it is essential to develop for all materials decontamination protocols to remove all traces of mercury.

Despite the complexity of its management, mercury has to be considered as a principal component of the considered artefacts. Its monitoring represents a cost, but it is needed so that the artefact keeps its value and significance. Therefore the removal of mercury from an artefact should not be systematic and has to be performed only if no other alternatives are possible.

Contact: Antonin Torchini (HE-ARC)

Funding: no external funding

Ongoing research projects

 ATENA project: Advanced analytical techniques for the conservation of archaeological metallic and ceramic artefacts and the recovery of ancient manufacturing techniques (CNR-ISMN)

The ATENA project is focused on the application of innovative analytical techniques and the development, characterisation and testing of innovative materials and procedures for the conservation, protection and restoration of ancient metallic and ceramic artefacts.

A selected number of metallic and ceramic artefacts found in different archaeological sites in Southern Italy have been chosen for the identification of the degradation agents and mechanisms. The chemical and physical characterization has been carried out by means of the combined use of different analytical techniques, such as XRD, XPS, FEG-SEM, TGA and Optical Microscopy. The different conservation state and the different provenance of ceramic have been determined by analysing both the glaze and the ceramic body of the samples¹. The presence of chlorine on the surface of the cuprous metallic artefacts is found as the main requisite for “bronze disease” and the study of the natural “*patinas*” gives information on the corrosion phenomena during burial. The study of the mechanism of “bronze disease” is carried out in order to approach long-term reliable, safe and environmentally friendly strategies for the conservation-restoration of ancient metallic artefacts. Our innovative approach relies on the chemical synthesis of novel and reversible materials to be used as corrosion inhibitors and on the definition of a new validation protocol for their use and application on archaeological metallic artefacts. A new method for producing degraded samples for evaluating the effectiveness of conservation materials is based on the production of reference Cu-based alloys with a chemical composition and microstructure similar to that of the ancient alloys². Artificial “*patinas*”, similar to those grown on archaeological Cu-based artefacts, are produced by an accelerated method based on a chemical attack and a subsequent ageing of the sample by burial in the soil from the original archaeological site.

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Funding: MIUR, Decreto Direttoriale 9-10-2002, n. 1105/2002.

Ongoing research projects

Assessment of the environmental impact on the conservation of cultural heritage metal artefacts (IRRAP)

To minimise the alteration of cultural heritage artefacts we need to have a good knowledge of the artefact composition and their immediate environment. To achieve this objective a research project has been set up to identify the possible source of pollution (such as aggressive volatile vapours from showcases) and the presence of air particle depositions. Metal coupons (Ag, Pb and Cu) have been exposed under different conditions in various museum environments. These coupons are in fact sensors reacting quickly and selectively with certain pollutants present in the atmosphere to form a tarnishing layer. The analysis by electrochemical reduction of this layer at regular intervals gives information on the chemical nature of the products formed as well as their growth rate in a specific environment. Therefore not only the corrosive compounds might be analysed but also their synergetic effect with other pollutants and humidity can be assessed.

Contact: Virginia Costa (IRRAP)

Funding: Mission de la Recherche et de la Technologie – Ministère de la Culture et de la Communication

Ongoing research projects

Alteration of iron archaeomaterials: characterisation of chlorinated phases in terrestrial archaeological iron artefacts (CEA-CNRS/ LRC CEA/LRMH)

The understanding of the alteration phenomena of iron artefacts is essential to the conservation of cultural heritage artefacts. This alteration is often due to the presence of corrosion products containing chlorinated compounds in sudden contact with large amounts of oxygen. Indeed when recovering archaeological artefacts in equilibrium with their local environment, the change in atmospheric conditions provokes accelerated corrosion that might be destructive. To preserve these artefacts stabilisation is required. But if stabilisation treatments slow down the corrosion processes, they are not always optimised. The limitations of these treatments are due to our poor knowledge of the corrosion products containing chlorine that develop on archaeological artefacts (structure, thermodynamic stability) and of the mechanisms responsible for their formation.

Our investigation of the corrosion mechanism of iron in the presence of chlorides is based on the elementary and structural analysis of chlorinated corrosion products formed on a corpus of archaeological artefacts dating from the 12 to the 16th centuries. Recent research has revealed the presence of two different crystalline phases in the corrosion products. The oxyhydroxide akaganeite $\beta\text{-FeOOH}$ is commonly found in corrosion products of artefacts exposed to chlorinated environments. It is often considered as the species mainly responsible for the alteration of archaeological artefacts since it can release chlorides. To examine the structure of this compound, high-resolution X-ray diffraction spectra were acquired on akaganeite powder containing different amount of chlorine (between 4.5 and 12 % in weight). A preliminary result obtained is that the modification of the structure is due to the increased amount of chlorine. In addition, the study of the corrosion layers on archaeological artefacts has shown that the presence of a phase richer in chloride (15-20% in weight); the hydroxychloride $\beta\text{-Fe}_2(\text{OH})_3\text{Cl}$. This compound, which has only recently been revealed on such artefacts, plays a major role in the corrosion processes.

Based on these results, hypotheses of mechanisms explaining the formation of these phases according to the burial environment have been proposed. Chlorinated corrosion products observed at a microscopic scale on archaeological samples compared with the synthesised phases based on the combination of specific analytical techniques has allowed us to better understand the complex corrosion systems that develop in the long-term in chlorinated soils. This knowledge is an essential step to optimise the stabilisation of cultural heritage iron based artefacts.

More information can be found on the PowerPoint presentation given during the meeting of the French section of the Metal WG, Paris, 28-29 September 2006 (see folder Other documents / Meeting of the French Section of the Metal WG on the Metal homepage of the ICOM-CC website and folder Coming and past events of the **METALConsn**-info website).

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Funding: Ministère de la Recherche et de la Technologie, Ministère de la Culture et de la Communication

Ongoing research projects

Archaeological marine iron artefacts: from understanding the corrosion mechanisms to the prediction the treatment times (Arc'Antique)

Currently, it is recognised that when one plans to construct an industrial plant or a naval base made of iron-based alloys near the sea, the expected average corrosion rate of metals in seawater should be 0.1mm/year. This means that after 10 years, an iron alloy of a thickness of 10mm will loose 1mm of its original surface and that after 100 years it will have completely disappeared. Therefore, theoretically one century is enough to destroy any 10mm thick iron-based artefact that lies on the seabed. But everyday marine archaeology shows us that fortunately this conjecture is incorrect. We have then to wonder which parameters are in fact governing the corrosion rate in order to predict the condition state of iron based artefacts under their concretion crust and to estimate the treatment time to remove that crust and any chlorides from corrosion products.

From a kinetic point of view, the chronology of formation of corrosion products depends essentially on the physicochemical parameters of the medium and more particularly on the quantity of dissolved oxygen available to corrode the metal surface. Immediately after immersion of the artefact, the corrosion starts: first oxyhydroxides and oxides appear on the metal surface. During the first month it will be covered by a stratigraphy of corrosion layers that will reduce the access of dissolved oxygen. In parallel, the wreck or the site around the artefact will be covered with sand or sediments reducing too the effect of dissolved oxygen. It is then around this competition between “active” and “passive” corrosion processes that conservation experts establish their diagnostic to predict the condition state and assess the treatment times.

Today we are in a position to give some “alteration models” of marine iron artefacts that take into account the environmental parameters (physicochemical and biological) and the materials. The biological aspect is also considered.

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Contact: Jean-Bernard Mémet (Arc'Antique)

Funding: no external funding

Ongoing research projects

Visualisation of tinning on archaeological iron based artefacts (*Arc'Antique*)

Two years ago a diploma work carried out by Manuel Leroux at Arc'Antique gave some promising results on the possibility to use radiographic images to detect the presence of remaining tin on the surface of iron based artefacts (see BROMECC 3 and reference below). Traces of tin became very common in France during the Carolingian period and its analysis is therefore very important, but until recently only sophisticated analytical tools were suitable.

Since then a simple colorimetric technique has been (re)designed using cacotheline (0.5% w/v in distilled water). If all the precautions are taken as regards the storage of the solution used, this spot test is selective. Indeed it gives an immediate response showing the presence or absence of tin. The protocol conditions still have to be optimised, but the first results obtained are promising.

Beyond revealing the technological aspect that is still unknown, the positioning of tinning on iron-based artefacts is an excellent marker of the limit of the original surface on very corroded artefacts.

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Reference:

Leroux, M. & Lemoine S., *L'étamage des objets ferreux archéologiques : une présence discrète et problématique*, XIXe journées des restaurateurs en archéologie, Saint-Germain en Laye (2003), in *Conservation-Restoration des Biens Culturels* (CRBC), Paris, 20, 2004

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Ongoing research projects



A note on the detection of the original surface of marine wrought iron artefacts from observations made on marine crusts of the historic wreck, *Elizabeth and Mary* (1690), Anse aux Bouleaux, Québec (CCQ)

During the excavation of the *Elizabeth and Mary*, 400 marine crusts were discovered in close proximity of the shipwreck. They are due to the corrosion of iron artefacts (in our case wrought iron) that might be fully or partially mineralised. Corrosion products (iron sulphides produced by sulphate reducing bacteria, oxides and hydroxides, iron hydroxychlorides) have a low mechanical resistance. The interface between them and the metal (if there is still any left) is clearly defined. Their low protectiveness can lead to the full corrosion of the core metal. The void left corresponds often to the limit of the original surface of the artefact and thereby forms a good casting mould of the negative form.

The conditions of formation of marine crusts are well documented through the work of North (1976, 1981) and MacLeod (1987) (see *Studies in Conservation*), but the literature is very inadequate as regards the presence of the original surface on wrought iron artefacts in these crusts. During cleaning of wrought iron objects from the *Elizabeth and Mary*, we found under the crust a strata of almost or fully mineralised metal. This layer, which can be revealed on an X-radiograph, seems to conserve the same characteristics from one crust to another. It is not magnetic, hard and thin (1/4 to 1/2mm). Voids or iron corrosion products are found underneath.

Pneumatic hammers are used for thinning marine concretion crusts. It is a quite precise tool but it generates great vibrations that might provoke the collapse of the crust above the void left by the mineralisation of iron and the loss of the original surface (and any archaeological information held by it). To preserve the original volume, a filling compound (polyvinylsiloxane resin) and/or hydrophobic epoxy adhesive is used. After the drying of the crust, the cleaning is continued with abrasive rotating tools. This last step allows localising more decisively the strata corresponding to the original surface. In the case of full mineralisation of the metal core it is needed to use epoxy resins or pastes to mechanically reinforce the presented voids.

Composite wrought iron/waterlogged wood artefacts; essentially rifles, tools and small ship equipments are good examples of artefacts preserving important information within the crust protecting them. These kinds of artefacts are also important for North American history since they are poorly represented in the museum collections. Therefore the localisation and recovery of the profile of the original surface are essential to the understanding of 17th century North American culture.

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Funding : Ministère de la Culture et des Communications

Ongoing research projects

Fifteen years of marine archaeological iron artefact treatments: a critical review and new developments (*Arc'Antique*)

Since its creation, the laboratory Arc'Antique has treated more than 100 cannons and anchors coming from marine sites. It is therefore one of the most experienced laboratories in this field in Europe. To improve the efficiency of the applied conservation treatments (mainly based on electrochemical processes), conservation professionals involved study the materials treated and their position on site so as to predict the condition state and more significantly, their treatment time. Only afterwards can the conservation treatment follow.

We all know that the conservation of artefacts starts at the very beginning of its discovery. As regards marine archaeology, this suggestion is understood by archaeologists and usually put into practice without exactly knowing the provoked alteration processes and the further consequences of poor conservation. For many years now, Arc'Antique has developed preventive conservation strategies on site to perform the correction of mistakes unfortunately made by archaeologists.

Our protocol of treatment is now refined and used in a quasi systematic way to all marine iron based artefacts, particularly large artefacts like grey cast iron cannons. More recently the laboratory has designed a remote monitoring system that permits the performance of an electrochemical treatment on any site outside the premises of the laboratory. This new approach is currently tested on a series of cannons recovered in Saint-Malo (France) in collaboration with the regions of Brittany and Pays de la Loire. This tool not only allows us to remotely monitor the electrochemical parameters applied but also to programme them via telephone or internet. Applications of such an approach are very important and it appears as the possible solution for a good transfer of knowledge to local professionals.

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Contact : Jean-Bernard Mémet (Arc'Antique)

Funding : no external funding

Ongoing research projects



The use of sodium carboxylate as a corrosion inhibitor to protect iron artefacts (LRMH)

Atmospheric corrosion and poor conservation conditions are the main causes of alteration of cultural heritage metal artefacts (elements on historic monuments or museum objects). Conservation treatments that slow down the exchanges between the metal and the corrosive atmosphere can be applied to stabilised objects or objects in storage and exposed to uncontrolled environments. Some already exist and they have to respect ethical criteria such the reversibility or the conservation of the aspect of the artefact after application. Furthermore they should protect both the metal surfaces covered with corrosion products and those metal surfaces without corrosion products.

Within the framework of the EU-INCO-MPC1 PROMET project we developed new protection systems for metal objects exposed in the Mediterranean region. These systems are using inhibitive solutions based on carboxylic acid. These solutions are already very effective on zinc, lead and magnesium. The same solutions have been tested on bare and corroded iron surfaces. Not only are they non-toxic, but also they are cheap, easy to prepare and fully reversible. The characterisation of the surface of treated coupons has shown that the inhibiting effect is linked to the formation of a hydrophobic iron carboxylate layer on the surface of the metal.

The efficiency of these solutions has been tested using electrochemical measurements and artificial ageing in climatic chambers, simulating humid-dry cycles. The protective layer is characterised afterwards to understand the mechanism responsible for the inhibiting effect of the solutions developed and to optimise the protection.

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Funding : EU PROMET project

New research projects



EcoNET: Protection of bronze covered with patina by safe organic substances (ENSCP / DPC-BBU / ISA-DU / FCET-UZ / FFA-UZ / LISE)

Archaeological or cultural bronze artefacts on exhibition are exposed to indoor or outdoor environments. They often suffer from a substantial alteration due to increasing atmospheric pollution. Therefore it becomes necessary to protect them efficiently with patina layers or coatings. The use of clear-coatings or wax containing some corrosion inhibitors such as benzotriazole are largely employed in museums, but they modify the visual aspects and also the inhibitors employed are often noxious or even toxic. In this work, we propose the use of some harmless compounds such as corrosion inhibitors on bronze artefacts covered with patina.

The bronze used is Cu-6Sn (in wt-%). This composition was selected after a preliminary work on several archaeological bronzes found in Transylvania, Romania, dated to the Neolithic period. First, the patina has been formed on this bronze, under potential regulation, in $\text{NaHCO}_3 + \text{Na}_2\text{SO}_4$ solution, (pH 8), for three days. A light blue patina was obtained. These specimens were then dipped into an aqueous solution of various organic corrosion inhibitors for three hours. The organic compounds examined were 1mM 4-methyl-1-(p-tolyl)imidazole, 5mM 1-phenyl 4-methyl-imidazole, 0.1mM 2-mercapto-5-R-amino-1,3,4-thiadiazole, and for comparison benzotriazole. The corrosion behaviour was examined in the same solution as the patina forming solution, but the pH was adjusted to 5 by addition of H_2SO_4 . The impedance spectra collected showed (for all of them), three depressed capacitive loops. On the bases of these capacitance values, these loops were associated with the surface film with ionic conduction, the double layer capacitance with the charge transfer resistance, and the oxidation-reduction process involving the surface patina. The protective effectiveness determined from the resistance increased with the immersion duration.

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Funding: EGIDE licence number EcoNet 10 279NA

New research projects



The maintenance of Cor-ten[®] sculptures (SABKS)

Since the mid sixties to present day Cor-ten[®] steel became one of the most famous materials for outdoor sculpture. Many artists used this material because of its propagated weathering resistance. Due to unsuitable ranges of application many significant problems in the field of conservation appeared. These were surveyed in a diploma project at the 'Object Conservation' study programme at the State Academy of Art and Design Stuttgart (SABKS) with a special focus on the material and its protective rust layers, the basis for its protection, different significant damages and their causes, the potential of preventive conservation and practised interventive methods.

Although it seems to be in some way a contradiction in itself to coat weathering steel, this has often been done in hands-on conservation to overcome corrosion problems. Therefore, different coating materials already in use for outdoor metal sculptures were tested on Cor-ten[®] coupons in the framework of the CONSIST project (see BROMECC 18) in the Deutsches Bergbaumuseum Bochum (DBM). Cor-ten B[®] steel samples were covered with different coating materials such as: microcrystalline waxes, waxes used in technical corrosion protection, an acrylic and a polyurethane resin. The sheets were then weathered for two months in a climatic chamber with a relative high humidity (but also drying cycles) and a climatic chamber with a periodic changing of relative high rate of SO₂ gas and humidity using standard protocols developed at DBM in earlier projects. The effectiveness of the protective function of the coating materials will be compared and consequences for practical applications discussed.

Contact: Patrick Decker (SABKS)

Funding: no external funding

New research projects

Characterisation of corrosion layers formed during long-term exposure to atmospheric corrosion: application to the study of the reinforcing chain at Amiens cathedral (LPS-CEA/CNRS/LMC/CRCM/LADIR/LAE/LRMH)

The study of the conservation state of the original iron-based bars and clamps inserted into historic civil and religious monuments (dating from Medieval times) is part of the condition survey of built cultural heritage. Their conservation not only interests conservation professionals but experts in charge of the disposal of nuclear wastes. Indeed, France plans to conserve waste for very long periods in a vitreous matrix inserted in a container made of mild steel that is known to corrode in a uniform way. This container will be exposed to atmospheric corrosion (though sheltered) for several centuries. But if the behaviour of iron and mild steels is quite well known for exposure times below 50 years, only archaeological analogues allow an experimental study of atmospheric corrosion and its mechanisms over very long periods.

Stratmann^{1,2} showed that atmospheric corrosion of iron is controlled by a cycle called the humid-dry cycle during which the layers of the corrosion products might play a role. The objective of our work is therefore to understand whether these layers are active in the corrosion processes and how they interact with the humid-dry cycle. The morphology of the full corrosion layer has then to be determined in the case of atmospheric corrosion.

A corpus of samples dating back several centuries from the reinforcing chain of Amiens Cathedral has been considered for two reasons. First the large number of samples taken (more than 30) allows us to carry out statistical studies of the corrosion development. Secondly monitoring of the atmospheric parameters (RH, T) on site is planned for several years. These measurements will be used to create a model of the humid-dry cycle that has caused the formation of the corrosion products observed and will be used as a reference.

When observed with an optical microscope, the oxidised surfaces present a double layer³ constituted externally of lepidocrocite (γ -FeOOH) and internally of a matrix of goethite (α -FeOOH) crossed by another phase. Analysis of this phase with micro-Raman spectroscopy and Absorption of X-ray spectroscopy (XANES) indicates that it is made of more or less crystallised ferrihydrite⁴. Studies carried out on thin oxide layers by Transmission Electronic Microscope, Electron Energy Loss Spectroscopy (EELS) and micro-XRD seem to confirm these observations at nano and micro levels.

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Funding : PNR Corrosion atmosphérique / ANR ARCOR / Chim'Art

New research projects

Condition survey and diagnostic of Max Mathews' electronic violin at the Music Museum of Paris (INP - DR)

The presence of this artefact in the Music Museum of Paris collection shows the will of the museum to demonstrate to the public the diversity of currently existing musical instruments which have aesthetic, technical and acoustic interests.

The study of this object is quite complex due to the diversity of the materials considered and the special field it is related to: contemporary music creation and research. Our first objective has been to establish a thorough condition report and to understand its internal structure, its stylistic coherence and the musical thought that surrounds it. Secondly a condition diagnostic on visible alterations has been carried out. Finally and based on the diagnostic and the museographical interest of the object, we have developed conservation treatment proposals.

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Funding: no external funding

New research projects

Conservation of two libation elements from Thugny Trugny (*IRRAP*)

Two containers, used during a banquet have been conserved for display during an exhibition on Gallic people and wine at Bibracte Museum (France). They are accessories used for the preparation or collective consumption of drink. The group of objects is composed of copper and iron based band and plaque vestiges that are fragmentary and incomplete. They were recovered in the burial area of Thugny Trugny occupied between -150 and -90 BC (Tène D1a) located in Champagne in East Belgium.

A lot of traces of the technical process used to make the bands and plaques were observed on the surface of the elements during the conservation work and allowed us to propose a complete manufacturing process. Furthermore qualitative and quantitative analyses were carried out on a series of copper-based samples to determine the composition of the metals used.

All the information compiled during this conservation project was used to propose a restitution of the shape of the artefacts.

More information can be found on the PowerPoint presentation given during the meeting of the French section of the Metal WG, Paris, 28-29 September 2006 (see folder Other documents / Meeting of the French Section of the Metal WG on the Metal homepage of the ICOM-CC website and folder Coming and past events of the **METALConsn**-info website).

Contact : Jane Echinard (*IRRAP*)

Funding: no external funding

New research projects

Microcrystalline waxes for the protection of copper based alloys exposed outdoor (PPS / LRMH)

Within a university project, we have performed a bibliographic research and a survey of conservators, taking into account results of a scientific study carried out at the Laboratory of Research of Historic Monuments (LRMH).

Different issues have been revealed concerning both the products applied and the application methods; as well as the physicochemical tests to perform which require further development. The study of four microcrystalline waxes was carried out. The objective was to determine the assessment criteria that can be used to qualify the protection before and after ageing.

More information can be found on the PowerPoint presentation given during the meeting of the French section of the Metal WG, Paris, 28-29 September 2006 (see folder Other documents / Meeting of the French Section of the Metal WG on the Metal homepage of the ICOM-CC website and folder Coming and past events of the **METALConsn**-info website).

Contacts: Typhaine Brocard (PPS) and Annick Texier (LRMH)

Funding : no external funding

New research projects

■ ■ Methodology of study of mineralised organic remains. Application to the buried iron artefacts of the Middle Ages tomb of Bruckmühl, Germany (PPS)

In a funerary context, archaeological metal artefacts, particularly those made of iron, often conserve, in their corrosion crust, organic remains that decomposed and that come from elements that were in direct contact with these metals in the tomb. This explains why while examining metal artefacts conservators often find mineralised organic remains in the corrosion products. These remains were originally elements of organic fabrics or accessories. Therefore they can provide interesting information on the culture of our ancient civilisation, their funerary customs, their economy, etc... But how to collect and exploit this information, before the conservator applies to the objects appropriate conservation and restoration treatments that might destroy these mineralised organic remains?

Within this master degree project carried out at the Central conservation workshop of archaeological artefacts at Bayerisches Landesamt für Denkmalpflege (Munich) we have applied a simple methodology of study that is accessible to all and that is performed during the preliminary investigation of the artefact. Several methods have been developed in the past decades. The one proposed here is referring to them and is illustrated by the example of the iron artefacts of the tomb of the Merovingian necropolis of Bruckmühl, Bavaria. It has been developed in three steps:

- the preparation of the surface of the metal artefacts and associated organic remains to observe,
- the precise documentation of each organic layer observed through the constitution of descriptive sheets and graphic drawings,
- the use of the data collected, by compilation and reference to the archaeological context based on the data collected on site.

The coherence and the abundance of results and interpretations obtained from the archaeological information contained in the organic remains depend on several factors, and particularly on the precise description of the artefacts on site such as their orientation. It is thought then that organic remains should be studied following this methodology, at the moment when the metal artefacts are recovered on site, and the information collected should appear clearly in the conservation protocol of the artefacts.

More information can be found on the PowerPoint presentation given during the meeting of the French section of the Metal WG, Paris, 28-29 September 2006 (see folder Other documents / Meeting of the French Section of the Metal WG on the Metal homepage of the ICOM-CC website and folder Coming and past events of the **METALConsn**-info website).

Contact: Clotilde Proust (PPS)

Funding: no external funding

New research projects

The conservation issues of cleaning a 14th century eastern French water gilt, tin-plated & silvered wooden box (INP-DR)

The silvered wooden box Cl.942 is decorated with small tin plates that were cast, pierced and water gilded. It belongs to the collection of the Museum of the Middle Ages – Thermes de Cluny, Paris, since 1851 and is exhibited since 1998 in a showcase of room 12 on the ground floor of Cluny hotel. It was previously owned by a private collector. The gilding of the tin plates and the silvering of the box were restored in the middle of the 19th century.

This object does not suffer from major mechanical or chemical alteration. Still the aesthetic appearance of the artefact is not clearly legible. Indeed the box has been entirely covered with animal glue, certainly rabbit glue. This has aged with time and has suffered from climatic variations and the regular deposition of dust particles. The external layer of the glue has darkened thereby masking the reflectance of the gilding and silvering.

To solve this problem of legibility, cleaning tests have been carried out at Electricité de France – Valectra Division, with clay absorbing poultices isolated from the substrate with a cellulosic membrane to try first to rehydrate the animal glue, to distort the proteins of collagen and absorb the impurities present in the animal glue that are responsible for the darkening effect.

Contact: Aurélie Champart (INP-DR)

Funding: no external funding

New research projects



Restoration of two copper based basins from the Quend site (INP-DR)

This conservation work has been carried out on two gallo-roman copper based basins from the Quend site (Normandy) that were found incomplete and in pieces. These artefacts are now part of the collections of the Abbeville museum and were made with a similar material but differ as regards their manufacturing technique.

After testing adhesive compounds and filling materials in order to reshape and consolidate the artefacts two different conservation protocols have been proposed.

A comparison of these treatments as well as proposals of holding systems and presentations of the artefacts can be found on the PowerPoint presentation given during the meeting of the French section of the Metal WG, Paris, 28-29 September 2006 (see folder Other documents / Meeting of the French Section of the Metal WG on the Metal homepage of the ICOM-CC website and folder Coming and past events of the **METALConsn**-info website).

Contacts : Shéhérazade Bentouati & Laurence Caru (INP-DR)

Funding : no external funding

New research projects



Preservation of a DC-3 aircraft and the use of inhibitors (NSMMH / AM / AFM)

On June 13th 1952 a Swedish military aircraft, a DC-3, disappeared in the Baltic Sea. A massive search followed to recover the aircraft but three days later, on June 16, Soviet fighters shot down a Swedish Catalina participating in the search. The only object found in 1952 from the DC-3 was a lifeboat that had been damaged by grenades. These events represent an episode in the history of the Cold War well known to many Swedes through media and literature from 1952 until today.

In 2003 an independent research team found the DC-3 in the Baltic Sea in international waters. The recovery was initiated in 2003. After the forensic investigation it was decided that the aircraft should be preserved and it was turned over to the National Swedish Museums of Military History and will be exhibited at The Air Force Museum.

Although the predominant material is aluminium alloyed with copper there is also a wide range of materials not so common in more traditional marine finds. Combinations like rubber, wood and metals or leather, plastics and metals in the same object are not unusual in this case. The greatest difficulty so far has been the treatment of the composite objects. When lacking well-tested methods, preventive methods like dry air and elimination of oxygen have been ways of buying more time. The degradation of the different materials varies from total decomposition to almost untouched.

When searching for information on conservation of aluminium we discovered that it is still a relatively unknown area within the museum field. This has opened up possibilities to formulate a project searching for practical conservation methods. The conditions for the conservation of this object are somewhat unusual since it is a wreck and will remain so. It will be exhibited in a display case resembling the location on the seabed. This situation makes the line between patina and dirt hard to define. Most parts cannot be cleaned without losing patina and without cleaning they will still be chloride contaminated and highly hygroscopic. This brought up the need for suitable inhibitors to prevent corrosion. When scanning the market for products one finds that they are either hazardous to handle or the efficiency cannot be guaranteed on an object like this DC-3.

The Aluminium Conservation project is still in its planning stage. There is still time to define how tests should be performed to get the most reliable results. There is however plenty of original material left from the forensic investigation that will not be turned into museum objects which makes it possible to perform destructive tests on original material.

Contact: Christina H. Tengner (AM)

Funding: National Swedish Museums of Military History, Army Museum & Air Force Museum

New research projects



Mylar, reproductions of the alloy, its patination and conservation decisions (BM)

In 2005 Mr and Mrs R. Isaacs donated a collection of 25 Burmese lime boxes dating from the 19th and early 20th century to the British Museum (2005.01-15.1-25). During conservation of 10 of these boxes some practical problems concerning *mylar* became evident. *Mylar* is a 'black bronze' type alloy (copper with small amounts of gold, silver or arsenic and sometimes tin, lead or iron) that was produced in Burma.

The objectives for the project are to increase knowledge and experience in working with *mylar* and its patination, to identify original materials and construction of the objects that are suspected to have lost the original patina and to establish a conservation/restoration strategy for a selection of the Burmese lime boxes.

On some of the black surfaces it was found that during the conservation treatment the shine of the black surface was slightly altered. This is thought to be a result of partial removal of surface dirt/grime, or possibly a wax layer, as these would saturate the patination layer. During investigation of some untreated boxes with *mylar*, so as to establish the techniques used for manufacture (reference below), it became evident that some of the objects had lost their patina on the different alloys and that bare metal is currently exposed.

The 7 different alloys used in manufacturing the lime boxes have been reproduced (by alloying, casting, hammering, rolling/drawing and brazing) and combined in one sheet. The sheet is divided in 7 different samples for testing the following techniques/events: 2 patination techniques, stripping off patina, repatination, retarnish and coating treatments. Visual microscopic examination, colour measurements and X-ray fluorescence analyses will be carried out for all alloys from the various samples. Scanning electron microscopy and X-ray diffraction will be used on selected alloys from the various samples of the reproductions and selected objects.

Reference:

P.T. Craddock, M. van Bellegem, P. Fletcher, R. Blurton and S. La Niece. *The Black Bronzes of Asia, The 6th International Conference on the Beginnings of the Use of Metals and Alloys*, Preprint (2006)

Contact: Maickel van Bellegem (BM)

Funding: no external funding.

General information

Websites

- **ARTECH network:** http://server.icvbc.cnr.it/progetti_futuri/progetto_artech.htm. Network facilitating the access of conservation professionals to different investigation techniques of Cultural Heritage artefacts

 - **BIGSTUFF (Care of Large Technology Objects) 2004:**
<http://www.awm.gov.au/events/conference/bigstuff/index.asp>

 - **CAMEO:** website containing chemical, physical, visual, and analytical information on over 10,000 historic and contemporary materials used in the conservation, preservation, and production of artistic, architectural, and archaeological materials
http://www.mfa.org/_cameo/frontend/

 - **Cost Action G8: Non-destructive analysis and testing of museum objects.**
<http://srs.dl.ac.uk/arch/cost-g8>. Abstracts and booklets from previous workshops can be downloaded as well as announcements of future activities (Short Term Scientific Missions deadlines, training schools...).

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

 - **e-Preservation Science:** <http://www.e-preservation-science.org>. Online publication of papers in conservation science.

 - **European Cultural Heritage Network:** <http://www.echn.net/>. European network of professionals interested in the conservation of Cultural Heritage.

 - **IR and Raman for cultural heritage:** <http://www.irug.org/default.asp>

 - **LabS-TECH network** <http://www.chm.unipg.it/chimgen/LabS-TECH.html>

 - **Laboratoire Pierre Sue:** LPS PhD thesis related to the alteration of archaeological artefacts can be downloaded from <http://www-drecam.cea.fr/lps/> (in French) and go to "Archéomatériaux et prévision de l'altération."

 - **METALConsn**-info homepage: <http://rsc.anu.edu.au/~hallam/METALConsn-info.html>

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

 - **New York Conservation Foundation** website: <http://www.nycf.org/>

 - **PROMET** website: <http://www.promet.org.gr>

 - **RESTAURACION METAL SUR AMERICA:** www.restauraciondemetales.cl

 - **TEL (PhDs on line):** <http://tel.ccsd.cnrs.fr/>
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- Working Group Metals ICOM Committee for Conservation

<http://icom-cc.icom.museum/WG/Metals/>

- **Online publications of Surface Engineering Journal.** Issue addressing specifically to Metal issues: **Surface Modification Issues in Art**, Volume 17, Issue 3, June 2001. Can be downloaded

from: (<http://www.ingentaconnect.com/content/maney/se/2001/00000017/00000003;jsessionid=1xpmlw91522a3.victoria>)

- ANDRA (Agence Nationale pour la Gestion des Déchets RadioActifs)

http://www.andra.fr/interne.php3?publi=publication&id_rubrique=82&p=produit&id=5. The following documents can be ordered for free from this website : *Analogues archéologiques et corrosion* (in French only) and *Prediction of Long Term Corrosion Behaviour in Nuclear Waste Systems* (in English).

Future seminars and conference

- **2006 Conservation Science Annual** (11-16 November 2006, Sommerset, USA) organised by EAS / NYCF. A specialised seminar on the use of electrochemical techniques in conservation. More information can be obtained from the following website: <http://www.NYCF.org/eas.html>

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

- **L'homme et la matière – l'emploi du plomb et du fer dans l'architecture gothique** (16-17 November 2006, Noyon, France). Organised by the Picardie Regional Heritage Agency. For more information visit the following website: www.arpp.org or contact: contact@arpp.org

- **COST strategic workshop** "Cultural Heritage and Science: An Interdisciplinary Approach for the Conservation of Museum Objects" (5-7 December 2006, Ghent University, Belgium). For more information consult the following website: <http://www.analchem.ugent.be/ESA/chs2006/>

- **Approaches to the study of antique weapons. Lecture Series.** (16-18 January 2007, Alcalá de Henares, Madrid, Spain) Organized by IH-CSIC, IPHE and UAH. For more information, contact Marc Gener (mgener@cenim.csic.es)

- **Conservation Strategies for Saving Indoor Metallic Collections (CSSIM)** (25 February – 1st March 2007, Cairo, Egypt). Organised by the Applied Laser Spectroscopy Group (NILES, Egypt) and EU PROMET project. Both the ICOM-CC Legal Issues in Conservation and Metal WGs will contribute. For more information visit the following website: <http://www.nileslaser.edu.eg/>

- **Conservation Science 2007** (10-11 May 2007) organised by Università degli studi di Milano, ICON and the Institute of Conservation Science. For more information please contact Joyce Townsend (joyce.townsend@tate.org.uk)

- **Archaeometallurgy in Europe** (May or June 2007, Grado and Aquileia, Italy) organized by the Associazione Italiana di Metallurgia. For more information visit the following website: www.aimnet.it/archaeometallurgy2.htm

- **METAL07**, triennial meeting of the ICOM-CC Metal WG (17-21 September 2007, Amsterdam, NL). For more information visit the following website: www.metal07.org

- **Symposium 2007 – Preserving Aboriginal Heritage: Technical and traditional approaches** (24-28 September 2007, Ottawa, Canada) organised by the Canadian Conservation Institute. For more information visit the following website: http://www.cci-icc.gc.ca/symposium/index_e.aspx

Abbreviations and acronyms

AFM: Air Force Museum

AM: Army Museum

CCQ : Centre de Conservation du Québec

CNR-ISMN: Consiglio Nazionale delle Ricerche - Istituto per lo Studio dei Materiali Nanostrutturati

DPC-BBU : Dept. Physical Chemistry, Babes-Bolyai University, Cluj-Napoca, Romania

ENSCP : Ecole nationale Supérieure de Chimie de Paris, France

FCET-UZ : Faculty of Chemical Engineering and Technology, University of Zagreb, Zagreb, Croatia

FEG-SEM: Field Emission Gun Scanning Electron Microscope

FFA-UZ : Faculty of Fine Arts, University of Zagreb, Zagreb, Croatia

HE-ARC: Haute Ecole ARC de la Chaux de Fonds, CH

INP – DR : Institut National du Patrimoine – Département des Restaurateurs

IRRAP: Institut de Restauration et de Recherches Archéologiques et Paléométallurgiques

ISA-DU : Institute of Systemic Archaeology, 1 Decembrie University, Alba-Iulia, Romania

LISE : Laboratoire Interfaces et Systèmes Electrochimiques - Unité Propre de Recherche du CNRS, Paris, France

LPS-CEA/CNRS: Laboratoire Pierre Süe – Centre d'Etudes Atomiques / Centre National de la Recherche Scientifique

LRMH: Laboratoire de Recherche des Monuments Historiques

NSMMH: The National Swedish Museums of Military History

PNRC: Programme national de recherche sur la connaissance et la conservation des matériaux du patrimoine culturel

PPS: Université Paris I Panthéon-Sorbonne

SABKS: Staatliche Akademie der Bildenden Kuenste Stuttgart

TGA: Thermogravimetric analysis

XPS: X-Ray Photoelectron Spectroscopy

XRD: X-Ray Diffractometry

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Canada: Judy Logan, conservator (retired), Ottawa
Chile: Johanna Theile, conservator and lecturer, Facultad de Arte - Universidad de Chile Las Encinas, Santiago de Chile
Croatia: Goran Budija, conservator, Museum of Arts and Crafts, Zagreb
Czech Republic: Dusan Perlik, conservator, Museum of Central Bohemia, Roztoky
Denmark: Karen Stemann Petersen, conservator, The National Museum of Denmark, Copenhagen
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Romania: Dorin Barbu, conservator, Brukenthal Museum, Sibiu
Russian Federation: Andrey Chulin, conservator, the State Hermitage Museum, St Petersburg
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