Fluorosilicates ("fluats") used in the past in the conservation of stone in Central Europe

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Key words: fluorosilicate, "fluat", consolidation, restoration of stone, SEM/EDS X-ray analysis

Introduction

In Central Europe stone sculptures were made almost from porous stone like sandstone. Relatively high porosity of the stone and strong continental climate north of the Alps caused intensive degradation of the stone surface. If the process of stone degradation could be described like loss of binding media connecting separate grains of stone, consolidation could be characterized by filling in binding media (filler).

In Bohemia and Moravia oil varnishes were used traditionally as protection of the surface of stone. Around 1850 of art historians' view of the artistic qualities of stone sculptures changed. In consequence requirements on artistic quality of the stone restoration changed too. Only pure raw stone surface was tolerated [1]. Respecting these requirements was facilitated by using new materials for the consolidation of degraded stone surfaces: First soluble glass was used as stone consolidant, but after its application some damage on the stone surface was found. This fact started using fluorosilicates (fluats) for stone consolidation and fluats were recommended by cultural heritage authorities as proved consolidants for stone sculptures.

At the beginning of the 20th century fluats were used in a similar way for the restoration of many stone sculptures in Bohemia and Moravia. For example, in 1923 then sandstone statues on the Charles Bridge in Prague were restored in this way. The process of restoration could be summarized in the following way: Statues were cleaned very well (all remainders of ancient restorations and fragments of ancient polychromy were removed). For restoration artificial stone was used as filler, bigger completions were made by natural stone. The non-cohesive surface of stone was treated ("refreshed") by fluat.

At the end of the twenties of the 20th century Karl Kuhn, conservator of cultural heritage had written: "There isn´t any universal consolidant which could be used for any type of stone. Not only theoretical assumptions but also detailed information about conservation, about climatic conditions during consolidation, about the type of degradation of stone, about its physical properties, and its petrography must be known before the final decision can be made." [2]

In the middle of the 20th century fluats were replaced by emulsions of polymers (polyacrylates) and shortly afterwards these were replaced by organosilicates, used in the consolidation of stone until now.

Content

The process of stone consolidation using hexafluorosilicates can be described in the following:

1. Corrosion of grains of quartz on the surface of stone.
2. Sintering of the layer on the top layer of stone.

Sintered layer on the surface of stone is very thin, homogenous, nonporous with the character of glass. Its thickness was established by analysis under 10 microns. The areas of stone without content of moisture and water soluble salts can be very well protected by this layer (against sudden changes of climate, against abrasion, air pollution,…). On the contrary, if this nonporous and impermeable layer covers stone with the content of moisture and water soluble salts, crystallization of salts and freezing of water below this layer causes breaking away of areas of this layer from the stone.

During the recent research work carried out on the renaissance building of Belvedere (the Royal Summer House in the Royal Garden of Prague Castle) built of sandstone and decorated with splendid, very fine stone relief, degradation of stone different in intensity and type, has been observed, especially after cleaning. Perfectly conserved large areas have also been found (Fig. 2). Evidently paler areas can be seen there – smoother sintered fluated surface – and distinctive dark areas – from which the fluated layer has broken away (probably due to pressure of crystallization). In the latter areas the stone is stripped and opened and its specific surface, in comparison with fluated surface, is huge. This fact and high air pollution result in faster degradation of stone in these areas. On the facade of Belvedere these damaged areas are clearly situated in those parts of the building where rain and salts (evolved from ancient cement restorations) penetrate into the construction.

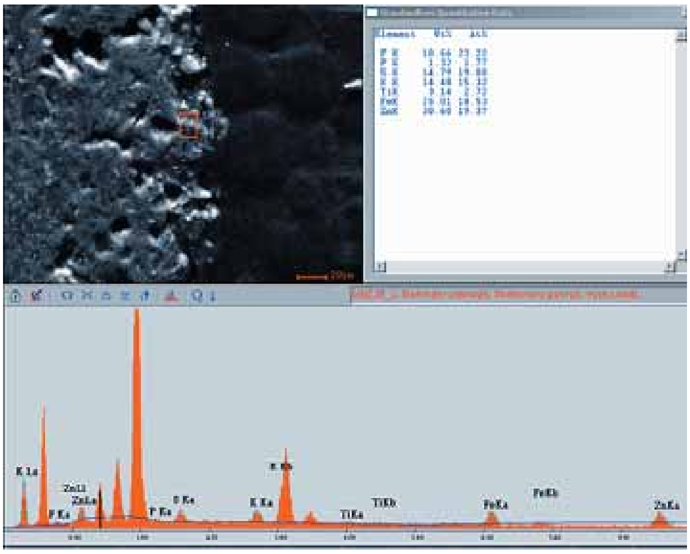

Figure 1: SEM photo of cross-section of stone and spectrum of EDS X-ray analysis Si and Al are excluded from quantitative analyses because of stricter delimitation of the fluated layer (Area in the red frame was analysed)

Last year thanks to advanced instrumental analytic technology fluorine was identified in a thin layer on the surface of the stone. Several samples of stone surface were analysed (as cross sections, in different distance from the surface of stone) by the scanning electron microscope XL 30 ESEM-TMP PHILLIPS equipped with the EDAX® multichannel X-ray spectrometer for elementary microanalysis. The ESEM® mode (i.e. environmental mode) facilitates measurement in the different vacuum level in the chamber of the microscope and different environmental conditions (wet, dry), and makes elemental analysis of non-conductive materials without metal coating possible. Due to the ultra thin window of the EDS X-ray detector this instrumentation can be used in quantitative analysis of light elements as is the case of fluorine. Fluorine was detected in a very thin layer on the treated surface of stone. The morphology of this layer is completely different from that of non-treated stone (fig. 1). The dependance of the content of fluorine on the distance from the surface of stone is documented in fig. 3.

Figure 2: Perfectly conserved areas of the surface of stone and areas from which the fluated layer has broken away

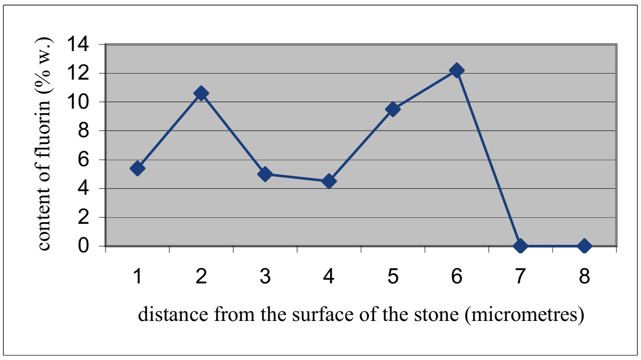

Figure 3: Relative content of fluorine in accesory elements in the top layer of the stone depending on the distance from the surface

European dimension

For a long time use of "fluats" in the conservation of stone was typical in Central European countries – Bohemia, Moravia, Austria and Germany.

Innovation and originality

A lot of damage to stone sculptures is put down to this kind of conservation, but until now using fluorosilicates has never been confirmed exactly by chemical analysis.

Impacts

Backward evaluation of the use of fluats [3] is mostly critical because a lot of stone work was damaged after this treatment (mainly the stone used in construction, especially pedestals, the parts of buildings often saturated by moisture and by water soluble salts). On the other hand, it is just to say that a lot of stone sculptures – including the excellent filigran stone decoration of the Belvedere building were partly conserved or saved due to its consolidation by means of fluats at the beginning of the 20th century…

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TESTS OF SOME ANTIGRAFFITI SYSTEMS FOR PRESERVATION OF SANDSTONE MONUMENTS

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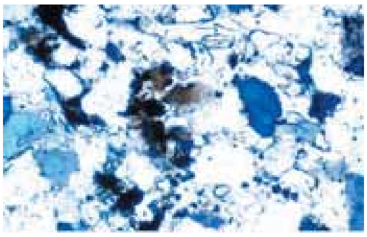
Introduction

Graffiti, which is visibly harmful to ancient monuments, is a very serious problem of major towns not only in Europe but all over the world. Therefore it was necessary to develop antigraffiti systems which would preserve surfaces of historical buildings. The aim of this research work was to compare the effectivity of different commercial antigraffiti systems in the protection of stone against graffiti.

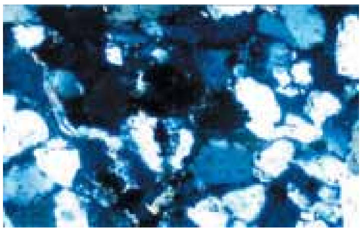
Materials

Sandstone from Podhorní Újezd quarry:

- sea Coenomanian ashlar, quartz fine-grain type of sandstone
- light grey-white or yellow colour
- the main mineral = quartz (more than 90%)
- the other minerals = feldspar, mica, glauconite
- the inter-space mass = a mixture of kaolinite, illite and quartz dust.



Sandstone in plane-polarized light (x 120).



Sandstone with crossed polars (x 120).

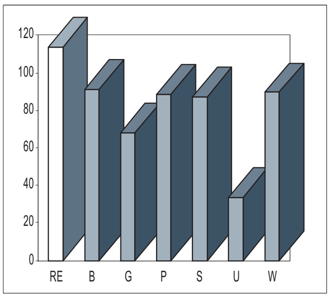
Antigraffiti systems

index	*product*	*producer*	*chemical composition*
B	BARBAKAN	Qualichem (CZ)	dispersion of polyfluorinated acrylate
G	GRS 9601	Fasco Plus (Sweden)	dispersion of wax
P	PROTECTOSIL ANTIGRAFFITI	Degussa (FRG)	solution of fluorinated siloxane
S	ANTIGRAFFITI STRIP VAPOR	Bellinzoni (Italy)	emulsion of microcrystalline wax/fluorinated acrylate
U	ULTIMA I	Fasco Plus (France)	solution of polyesters
W	WALGARD GRAFFITI BARRIER	Mapei (Italy)	emulsion of polymeric wax

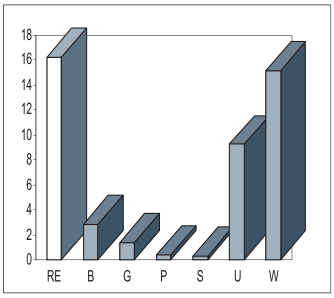
RE uncoated sample

Tests and results

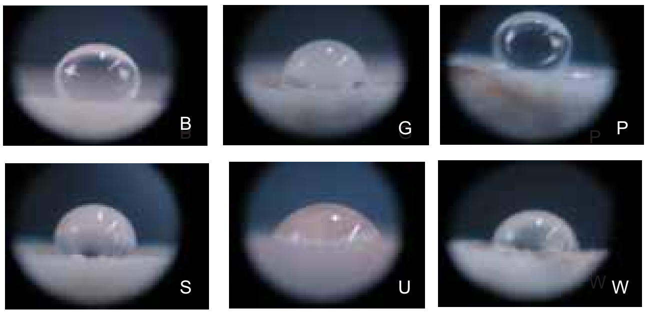
1. Water vapour permeability:
V [g/m². day]



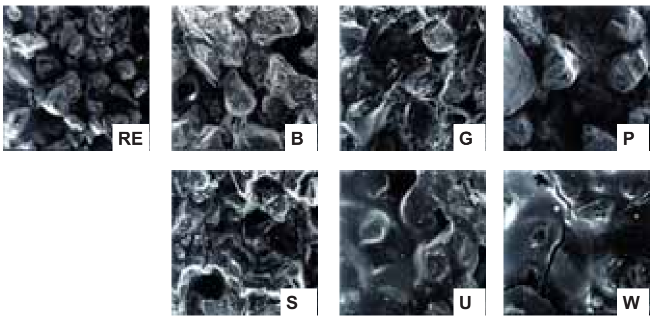
2. Karten water absorptivity:
V_{30} [l/m²]



3. The hydrophobicity of treated stone (goniometry)



4. Surface morphology of coated and uncoated stone (SEM analysis; x 240)



5. The removing of graffiti (microsandblasting – pressure 3,5 atm; corundum)

Conclusion

1. Water vapour permeability of sandstone decreased after the treatment by all antigraffiti systems, in the case of PES (U) and wax (G) noticeable.
2. Karsten water absorptivity decreased after the treatment of sandstone by all antigraffiti systems, in the case of a mixture of fluorinated acrylates and wax (S), fluorinated organosilicate (P), wax (G) and fluorinated acrylate (B) noticeable.
3. PES (U) was rather non-hydrophobic coating; fluorinated organosilicate (P) and fluorinated acrylate (B) were the most non-wettable coatings.
4. The antigraffiti coatings on the basis of PES (U) and wax (W) negatively influenced the morphology of the sandstone surface.
5. Graffiti spray was removed by a microsandblasting tool quite easy; the best results were achieved on the samples coated with fluorinated organosilicate (P) and a mixture of fluorinated acrylate and wax (S).

In the future, water absorption by capillarity and by immersing of the coated and uncoated stone samples and the resistance of the stone to salt crystallization and to frost will be assessed and changes in the surface morphology of the sandstone after the removing of graffiti will be evaluated. The samples have been placed in the open air (The Ledebour Gardens below the Prague Castle) where they will be exposed to actual out-door conditions during two years. Their considerable changes will be scanned and durability put down. According to the results of these tests, the most appropriate antigraffiti systems for sandstone monuments will be chosen.

Tests of some antigraffiti systems for preservation of sandstone monuments

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Key words: antigraffiti, graffiti, preservation, sandstone, stone

Introduction and content

Graffiti is a very serious problem of major towns not only in Europe but all over the world. This manifestation of vandalism is visibly harmful to ancient monuments [1, 2]. Therefore it was necessary to develop antigraffiti systems which would preserve surfaces of historical buildings or works of art [3]. The aim of this research work was to compare the effectivity of different commercial antigraffiti systems in the protection of stone against graffiti.

Sandstone from Podhorní Újezd quarry (natural stone – index RE) – which was commonly used in Czech historical buildings and sculptures – was chosen for this work. The sandstone is sea Coenomanian ashlar, quartz fine-grain type of sandstone in light grey-white or yellow colour. The main mineral is quartz (more than 90%); and there are very small amounts of feldspar, mica, glauconite or heavy minerals. The inter-space mass, which in fact is the chief factor in the sandstone properties, is formed by a mixture of kaolinite, illite and quartz dust [4].

Sandstone samples were coated with polymers on the basis of fluorinated acrylate (index B – Barbakan, Czech Republic), fluorinated organosilicate (index P – Protectosil Antigraffiti, FRG), polyester (index U – Ultima I, France), waxes (index G – GRS 9601, Sweden; index W – Walgard Graffiti Barrier, Italy) and polymer on the basis of a mixture of fluorinated acrylate and wax (index S – Antigraffiti Strip Vapor, Italy). Influence of selected antigraffiti coatings on the morphology of the stone surface (SEM analysis) and on water vapour permeability of the sandstone was evaluated [5], the degree of hydrophobicity of the antigraffiti systems (goniometry) [6] and Karsten water absorptivity [7] was measured. Graffiti paints were sprayed on the preserved stone surfaces and their elimination by means of a microabrasion facility was assessed [8].

The water vapour transmission rate is really the most relevant and most frequently monitored property of the coating on historical stone surfaces; therefore the extent of their permeability must be as large as possible. The measurements proved that the loss of water vapour permeability of sandstone after the treatment by all antigraffiti systems, in the case of polyester (PES) and wax noticeable: there was a 70 % decrease in PES (U) and 40 % decrease in wax (G) as against the untreated samples (fig. 1). The coatings on the basis of PES (U) and wax (W) negatively influenced the morphology of the sandstone surface (fig. 4). The hydrophilic or hydrophobic properties of antigraffiti systems depend on the polarity of the sample surface; the PES surface (U) was hydrophilic – the water contact angle being smaller than 90^o – in comparison with the fluorinated organosilicate surface (P) and fluorinated acrylate surface (B) – the water contact angle being more 115^o (fig. 2). Karsten water absorptivity decreased after the treatment of the sandstone by all antigraffiti systems (fig. 3), extremely in the case of stone coated with a mixture of fluorinated acrylate and wax (S), fluorinated organosilicate (P), fluorinated acrylate (B) and wax (G) – decrease by 98-82 %. Graffiti was removed from the coated areas of the stone by a microsandblasting tool (corundum; pressure – 3.5 atm). Thus the elimination of graffiti was quite easy. The best results were achieved on the samples coated with fluorinated organosilicate (P) and a mixture of fluorinated acrylate and wax (S).

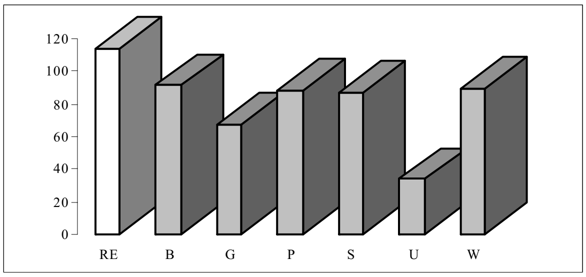

Figure 1: Water vapour permeability of the coated and uncoated samples V [g/m^2. day]

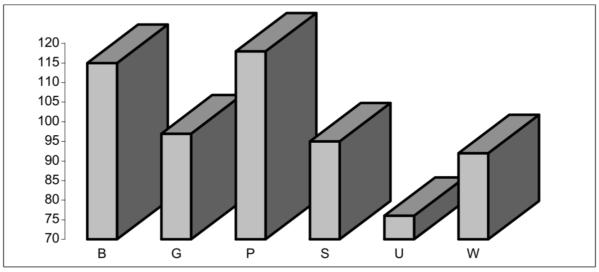

Figure 2: The dependence of water contact angle on the treated sandstone surface α [^{o}]

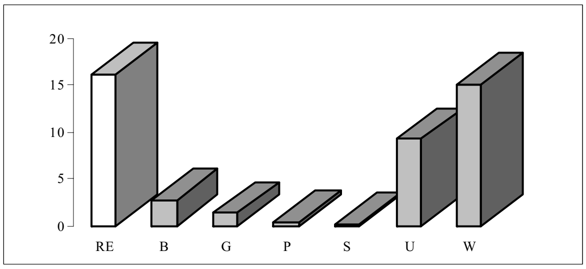

Fig. 3. Karsten water absorptivity of the coated and uncoated samples … V_{30} [l/m^2]

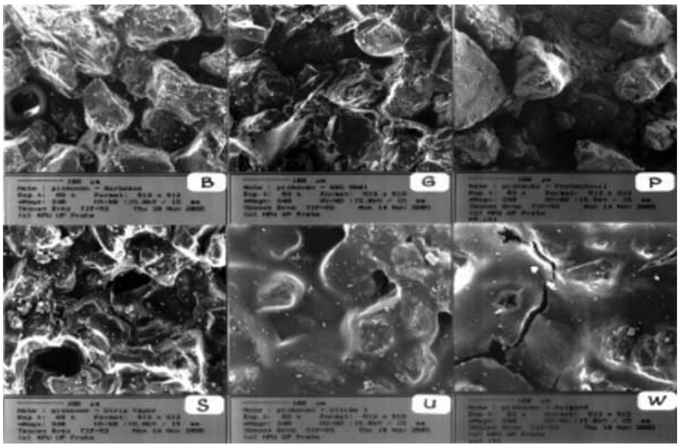

Figure 4: The sandstone surface coated with antigraffiti systems (magnification 240 ×)

Moreover, in the future, water absorption by capillarity and by immersing of the coated and uncoated stone samples and the resistance of the stone to salt crystallization and to frost will be assessed and changes in the surface morphology of the sandstone after the removing of graffiti will be evaluated [9]. The samples have been placed in the open air (The Ledebour Gardens below the Prague Castle) where they will be exposed to actual out-door conditions during two years. Their considerable changes will be scanned and durability put down [10]. According to the results of these tests, the most appropriate antigraffiti systems for sandstone monuments will be chosen.

European dimension

Vandalism, which is manifested with graffiti, is seriously injurious to European cultural heritage. That is why the theme of the preservation of monuments against graffiti is very often discussed all over Europe.

Innovation and originality

Antigraffiti systems have been developed for the preservation of surfaces of historical monuments from graffiti in the last ca twenties years. Antigraffiti materials have relatively not been researched so far and therefore their utility in the field of conservation of cultural heritage has not been too frequent. The presented work should contribute to better understanding of these materials and support their application on historical stone surfaces.

Impacts

The results of this research work will contribute to better understanding of physical-chemical properties of some antigraffiti systems and will be helpful in their application on the monuments.

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EXPERIMENTAL ANALYSIS OF COUPLED WATER AND SALT TRANSPORT IN HISTORICAL SANDSTONE

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$$\frac{\partial (wC_f)}{\partial t} = \frac{\partial}{\partial x}\left(wD\frac{\partial C_f}{\partial x}\right) + \frac{\partial}{\partial x}\left(C_f \kappa \frac{\partial w}{\partial x}\right) - \frac{\partial C_b}{\partial t}$$

Eq. 1. Boltzmann-Matano equation for 1-D salt transport

$$\frac{\partial w}{\partial t} = \frac{\partial}{\partial x}\left(\kappa \frac{\partial w}{\partial x}\right)$$

Eq. 2. Boltzmann-Matano equation for 1-D water transport

$$\kappa(z_0) = \frac{1}{2t_0\left(\frac{dw}{dz}\right)_{z_0}} \int_{z_0}^{\infty} z \frac{dw}{dz} dz$$

Eq. 3. Equation for moisture diffusivity coefficient

$$D(z_0) = -\frac{C_f(z_0)\kappa(z_0)\left(\frac{dw}{dz}\right)_{z_0}}{w(z_0)\left(\frac{dC_f}{dz}\right)_{z_0}} + \frac{1}{2t_0 \cdot w(z_0) \cdot \left(\frac{dC_f}{dz}\right)_{z_0}} \int_{z_0}^{\infty} z\left(\frac{d(wC_f)}{dz} + \frac{dC_b}{dC_f}\frac{dC_f}{dz}\right) dz$$

Eq. 4. Equation for salt diffusion coefficient

Historical masonry often contains significant amount of various salts. They can originate from several sources e.g. underground soil with water-soluble salts (in most historical buildings horizontal water-proof insulation is missing, salt solutions can be transported into materials of load bearing structures by capillary forces), sodium and calcium chlorides used for winter maintenance of pavements and footways, reactions of acid-forming gases in the air, actions of living organisms and microorganisms etc.

We were solving the problem of coupled water and salt transport in sandstone used for historical buildings. Experimentally determined salt and moisture profiles are used for determination of parameters driving the salt solution transport through the porous structure of sandstone. The mathematical analysis of experimentally determined salt concentration profiles depends on the assumed mode of salt transport in the porous material. If purely diffusion transport is assumed, common methods for solving the inverse problems for parabolic equations can be used. The simplest method makes the assumption that the diffusion coefficient is constant, the domain under consideration is semi-infinite, and the boundary condition on the remaining side of a one-dimensional arrangement is Dirichlet-type. The diffusion coefficient can be identified using the simple analytical solution of the parabolic problem with error function (e.g. [1]). The dependence of the diffusion coefficient on salt concentration can be found if some more sophisticated methods for the analysis of measured salt profiles are used. One of the methods that can be potentially used to determine concentration dependent chloride diffusion coefficients in an analogous way as moisture diffusivity or thermal conductivity is a classical Boltzmann-Matano analysis [2].

In this work, the mechanism of salt solution transport is described by Bear and Bachmat diffusion-advection model [3] taking into account both the influence of moisture flow on salt transport and the effect of bonded salt on pore walls. In the inverse analysis, the 1-D salt solution transport was assumed for simplicity. Then, the system of two parabolic equations, describing water and salt mass balance, was subjected to an inverse analysis in a similar way as for one parabolic equation, provided the initial and boundary conditions are simple enough, and the material parameters D (salt diffusion coefficient) and κ (moisture diffusivity) can be identified as functions of water content and salt concentration. The simplest possibility of such an inverse analysis is an extension of the Boltzmann-Matano treatment under the same assumptions of constant initial conditions and Dirichlet boundary conditions on both ends of the specimen for both moisture content and salt concentration where one of the Dirichlet boundary conditions is equal to the initial condition.

The arrangement of the experiment for determination of moisture and salt concentration profiles was analogous to standard water suction experiments. The samples of sandstone with the dimensions of 20 x 40 x 160 mm were first dried at 80°C and 0.1 mbar and water and vapor-proof insulated by epoxy resin on all lateral sides. Then, they were exposed by their 40 x 20 mm face to the penetrating 1M-NaCl solution. Duration of the experiment was 30, 60 and 90 minutes for three different groups of samples. After this time, the samples were cut into 8 pieces and in each piece water content and chloride concentration were measured. Moisture content was determined by the gravimetric method using weighing the moist and dried specimens. In the determination of chloride concentration, the particular samples were after drying first ground by a vibration mill so that grains smaller than 0.063 mm were obtained. Then the ground samples were overflowed by 80°C warm distilled water and leached. The chloride contents in particular leaches were determined using the ion selective electrode. On the basis of measured ion binding isotherm of NaCl, Cb = f(Cf), the profiles of bound and free chlorides were determined.

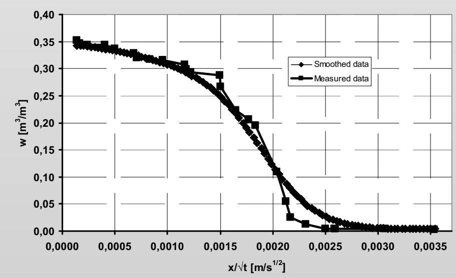

Fig. 1. Moisture profile in sandstone

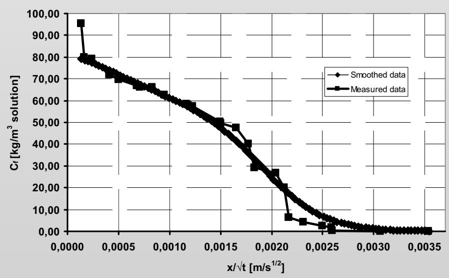

Fig. 2. Free chloride concentration profile in sandstone

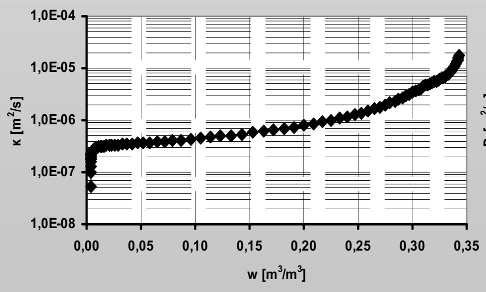

Fig. 3. Moisture diffusivity of sandstone as function of moisture content calculated using the inverse analysis

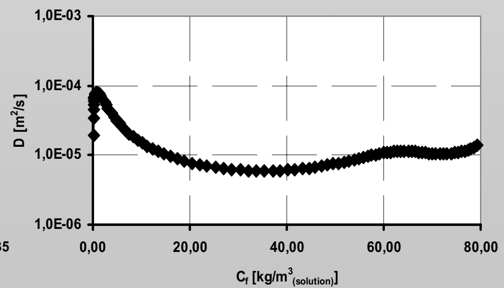

Fig. 4. Chloride diffusion coefficient of sandstone in dependence on free ion concentration

Fig. 3 shows the moisture diffusivity of sandstone as function of moisture content calculated using the inverse analysis described before. We can see that obtained results correspond to the values typical for highly capillary active materials.

Fig. 4 shows the chloride diffusion coefficient of sandstone in dependence on free ion concentration calculated using the κ(w) function in Fig. 1. We can see that from the quantitative point of view, the calculated diffusion coefficient is quite high, about four orders of magnitude higher than the diffusion coefficients of most ions in free water. Therefore, the common diffusion mechanism was probably not the only driving force for the chloride transport within the liquid phase and some other driving forces were taking place here. The acceleration of chloride transport can be attributed most probably to surface transport effects but it should be noted that this is a formal explanation only and an exact physico-chemical analysis is still needed.

The results of D and κ determination were verified by a forward analysis. In the computational simulation of wetting experiment, no salt crystallization was assumed and the Bear and Bachmat diffusion-advection model [3] was used. The computational implementation of the chosen model of coupled moisture and salt transport was performed using the Galerkin finite element method. The experimental setup presented above was considered. The results showed that the calculated moisture and chloride concentration profiles agreed reasonably well with the measured profiles.

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Experimental analysis of coupled water and salt transport in historical sandstone

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Key words: moisture diffusivity, salt diffusion coefficient, salt solution transport model

Introduction and content

Historical masonry often contains significant amount of various salts. They can originate from several sources. One of them is underground soil with water-soluble salts. As in most historical buildings horizontal water-proof insulation is missing, salt solutions can be transported into materials of load bearing structures by capillary forces. Another source of salts in masonry is sodium and calcium chlorides used for winter maintenance of pavements and footways. They can diffuse either into underground soil or directly into the masonry. Salts can also be formed by reactions of acid-forming gases in the air with basic components of building materials. Some salts can be formed by actions of living organisms and microorganisms. Water-soluble salts in the form of hydrated ions capable of transport in the porous system can also be presented in masonry materials themselves.

In this paper, the problem of coupled water and salt transport in sandstone used for historical buildings is analyzed. Experimentally determined salt and moisture profiles are used for determination of parameters driving the salt solution transport through the porous structure of sandstone. The mathematical analysis of experimentally determined salt concentration profiles depends on the assumed mode of salt transport in the porous material. If purely diffusion transport is assumed, common methods for solving the inverse problems for parabolic equations can be used. The simplest method makes the assumption that the diffusion coefficient is constant, the domain under consideration is semi-infinite, and the boundary condition on the remaining side of a one-dimensional arrangement is Dirichlet-type. The diffusion coefficient can be identified using the simple analytical solution of the parabolic problem with error function (e.g. [1]). The dependence of the diffusion coefficient on salt concentration can be found if some more sophisticated methods for the analysis of measured salt profiles are used. One of the methods that can be potentially used to determine concentration dependent chloride diffusion coefficients in an analogous way as moisture diffusivity or thermal conductivity is a classical Boltzmann-Matano analysis [2].

In this work, the mechanism of salt solution transport is described by Bear and Bachmat diffusion-advection model [3] taking into account both the influence of moisture flow on salt transport and the effect of bonded salt on pore walls. In the inverse analysis, the 1-D salt solution transport was assumed for simplicity. Then, the system of two parabolic equations, describing water and salt mass balance, was subjected to an inverse analysis in a similar way as for one parabolic equation, provided the initial and boundary conditions are simple enough, and the material parameters D (salt diffusion coefficient) and κ (moisture diffusivity) can be identified as functions of water content and salt concentration. The simplest possibility of such an inverse analysis is an extension of the Boltzmann-Matano treatment under the same assumptions of constant initial conditions and Dirichlet boundary conditions on both ends of the specimen for both moisture content and salt concentration where one of the Dirichlet boundary conditions is equal to the initial condition.

The arrangement of the experiment for determination of moisture and salt concentration profiles was analogous to standard water suction experiments. The samples of sandstone with the dimensions of 20 × 40 × 160 mm were first dried at 80 °C and 0.1 mbar and water and vapor-proof insulated by epoxy resin on all lateral sides. Then, they were exposed by their 40 × 20 mm face to the penetrating 1M-NaCl solution. Duration of the experiment was 30, 60 and 90 minutes for three different groups of samples. After this time, the samples were cut into 8 pieces and in each piece water content and chloride concentration were measured. Moisture content was determined by the gravimetric method using weighing the moist and dried specimens. In the determination of chloride concentration, the particular samples were after drying first ground by a vibration mill so that grains smaller than 0.063 mm were obtained. Then the ground samples were overflowed by 80 °C warm distilled water and leached. The chloride contents in particular leaches were determined using the ion selective electrode. On the basis of measured ion binding isotherm of NaCl, $C_b = f(C_f)$, the profiles of bound and free chlorides were determined.

Fig. 1 shows the moisture diffusivity of sandstone as function of moisture content calculated using the inverse analysis described before. We can see that obtained results correspond to the values typical for highly capillary active materials.

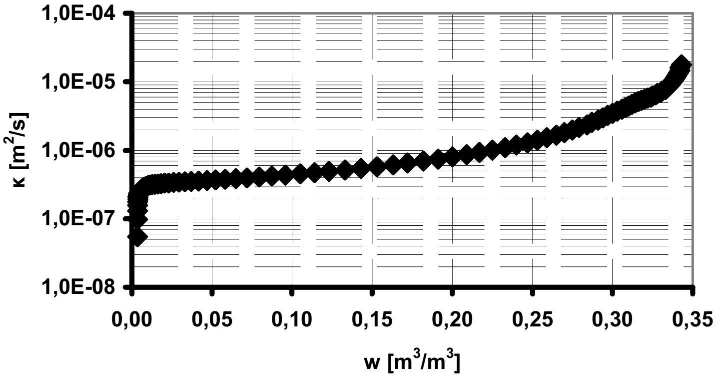

Figure 1: Moisture diffusivity of sandstone

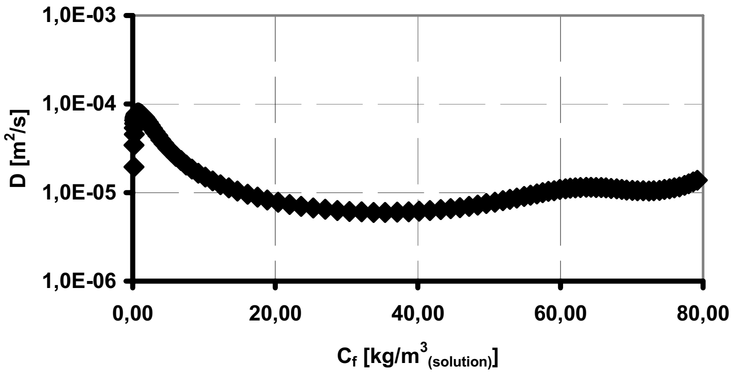

Figure 2: Chloride diffusion coefficient of sandstone

Fig. 2 shows the chloride diffusion coefficient of sandstone in dependence on free ion concentration calculated using the κ(w) function in Fig. 1. We can see that from the quantitative point of view, the calculated diffusion coefficient is quite high, about four orders of magnitude higher than the diffusion coefficients of most ions in free water. Therefore, the common diffusion mechanism was probably not the only driving force for the chloride transport within the liquid phase and some other driving forces were taking place here. The acceleration of chloride transport can be attributed most probably to surface transport effects but it should be noted that this is a formal explanation only and an exact physico-chemical analysis is still needed.

The results of D and κ determination were verified by a forward analysis. In the computational simulation of wetting experiment, no salt crystallization was assumed and the Bear and Bachmat diffusion-advection model [3] was used. The computational implementation of the chosen model of coupled moisture and salt transport was performed using the Galerkin finite element method. The experimental setup presented above was considered. The results showed that the calculated moisture and chloride concentration profiles agreed reasonably well with the measured profiles.

European dimension

The presented work was carried out in the frame of a European project dealing with prevention of salt damage to the build cultural heritage by the use of crystallization inhibitors. As the problem of salt damage is actual over the whole Europe, various institutions from Germany, Belgium, Great Britain, Spain, Greece, Netherlands and Czech Republic are involved in the project.

Innovation and originality

The approach to the determination of salt solution transport parameters given in this paper is quite unique. Many researchers dealing with salt transport mechanisms do not include in their models the influence of advection on dissolved salt transport and the effect of salt bonding on porous walls on the salt solution transport. From this point of view, the methodology (experimental and computational) described above, can be considered as an attempt towards a physically more correct solution of the problem of coupled moisture and salt transport.

Impacts

The developed model used for calculation of salt concentration profiles can find many practical applications in both technical and conservation practice. It should be helpful in the formulation of conservation procedures and methods and last but not least can be applied for predictions of salt transport and accumulation in building structures and stone monuments.

Acknowledgement

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European project details

SALTCONTROL, Contract No. SSPI-CT-2003-501571, Prevention of salt damage to the built cultural heritage by the use of crystallisation inhibitors, Co-ordinator: Prof. Dr. Patric Jacobs, Head of Department of Geology and Soil Science, Ghent University, Belgium.

The European Commission
Community Research
Fifth Framework Programme

TEAM Testing and Assessment of Marble and Limestone 2000-2005

CULTURAL HERITAGE WEATHERING PROBLEM IN NEW APPLICATIONS OF MARBLE

Katarina Malaga[1], Björn Schouenborg[1] and Bent Grelk [2]

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Key words: marble, granular disintegration, thermal expansion, bowing, field, laboratory test

Marble has been used as thin façade panels for more than 50 years. But changes with time in the strength of some marbles had led to acute safety problems and entire facades have had to be replaced at very high costs after only 30 years! The whole stone trade has suffered as a result. TEAM now presents a solution and shows that marble can be used safely if properly tested: the assessment of facades at selected study sites, using monitoring systems, risk assessment and lifetime prediction, have been used to develop a hypothesis for the observed deterioration. A methodology for inspection and corrective actions and service life prediction has been developed for buildings exhibiting problems, thus reducing maintenance costs. Research carried out on almost 100 marble types has been used to explain the mechanism of degradation and to develop European test methods. These tests can been used to identify suitable marble and determine their maximum expansion when used on a facade. Using them will help reducing the occurrence of future damage and promote the use of natural stone for cladding, thus improving employment and increasing European competitiveness in this area.
www.sp.se/building/team

The holistic approach of the TEAM project takes into consideration the fact that the problem of bowing and expanding marble and limestone is interdisciplinary in character. The phenomenon of the granular disintegration of marble is a typical weathering process observed in several cultural heritage objects therefore explanation of the relatively modern problem observed on marble claddings can contribute to solve the old problems.

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Buildings with durable marble

Buildings with non-suitable marble

Partners

Cultural heritage weathering problem in new applications of marble

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Key words: marble, granular decohesion, thermal expansion, bowing, field, laboratory test

Introduction and content

Natural stone has been used for facade applications for centuries. Originally, the stone was rather thick, when used as construction elements, and the durability was apparently good. Scientific research on properties of marble began in the late 19th century. In the years following, the thickness of natural facade stones decreased from over 1000 mm to typically 20-50 mm as a result of new cutting technologies and equipment being developed by the industry. Even though most marble claddings perform satisfactory, durability problems have begun to appear after some 50 years of using thin cladding [1, 2; 3]. Lately reports of facade failures have increased dramatically. The problem is expressed by expansion, bowing, loss of strength, and in most serious cases the detachment from the anchoring system (Fig. 1). The bowing phenomenon has also been observed in gravestones (Fig. 2). The granular decohesion of marble is a typical weathering process observed in several cultural heritage objects therefore explanation of the relatively modern problem observed on marble claddings can contribute to solve the old problems. The main objectives in TEAM were to understand and explain the mechanisms of the expansion and loss of strength and to prevent the use of deleterious marble and limestone by introducing drafts for European standards. The use of surface coating and impregnation that could prevent or diminish the degradation was tested [4]. A state-of-the-art report has been written and is based on an extensive compilation of more than 300 papers on marble and limestone deterioration dating from late 1800's to 2005. A survey of about 200 buildings has given a clear picture of the extent of the problem in geographical, geological and climatic terms. Detailed case studies of 6 buildings have resulted in a methodology for assessment of facades including monitoring system and risk assessment. Comprehensive laboratory studies including mechanical, physical and accelerated testing were compared with the results from the field studies.

It was concluded that the phenomenon of bowing of marble is actually rather common. It is observed in buildings of various ages, in buildings exposed to various weather conditions and for slabs of various thickness and dimensions and with different anchoring methods. The problem is not restricted to one type of marble or one climatic zone. It is also equally important to draw the attention to the fact that many marble and limestone claddings and pavements tend to be durable and robust, provided that the correct quality has been used. However, the facades receiving the most sunlight exhibit the highest percentage of bowing. Both concave and convex bowing can occur on the same facade with the same marble. There is a clear correlation between bowing behaviour and deterioration leading to loss of strength. It cannot be stated that non-bowing stone slabs are not deteriorating and loosing strength. There are quite a few different types of marble of different origin related to quarry areas that demonstrate the bowing behaviour. Marble types or selections from same quarry area can demonstrate bowing as well as non-bowing behaviour.

Figure 1: Bowing phenomenon observed on modern buildings

Figure 2: Bowing phenomenon observed on old gravestones, Paris

Damages and problems of other kinds than bowing and deterioration have been registered and noted. Investigations of selected buildings showed large strength loss in the order of 80 % after 35 years for one calcitic marble and 40 % for one dolomitic marble. Laboratory studies clearly indicated that there was no correlation between the amount of bowing and the loss of strength. This is especially worrying since there is a potential risk of severe strength loss without any evident bowing of claddings.

European dimension

The TEAM project consortium, represented 9 EU countries, comprised 16 partners representing stone producers and trade associations, testing laboratories, standardisation and certification bodies, consultants, building owners and care-takers and producers of fixing and repair systems. Research both in the laboratory and the field were performed on a large number of different stone types from different countries and used in different climates. A comprehensive building survey, of about 200 buildings located in different European countries, has given a very good picture of the extent of the problem both geographically and geologically. Bowing is a worldwide phenomenon not confined to one type of marble or one type of climate.

Innovation and originality

Sampling and testing of panels from the buildings have given further information about the deterioration process and its rate and, together with the inspection methodology, provided a sound basis for building a model to predict the remaining service life, including analysis of the associated risk. Laboratory testing of almost 100 different types of marble has taken us much further in our search for the mechanism and allowed us to refute many "old" hypotheses. The main extrinsic influencing factor is elevated temperature in the presence of a moisture gradient. This creates the external stresses that different marbles will respond to in different ways. The most crucial intrinsic parameter is the configuration of the grain boundaries and the grain size distribution of mineral grains in the rock. This provides different bonding strength between the mineral grains depending to the complexity of the arrangement of the grain boundary and in combination with the crystal structure. Weaker bonds will cause granular de-cohesion, resulting in sugaring of the marble and decreasing in strength.

The developed test methods have proved that every marble is unique and has a unique response to climatic stresses with its own degradation curve. The acceleration factor of the laboratory bow-test is therefore different for different marble types. Field exposures have shown that it is possible to inhibit or decrease the degradation of marble by coating the surface with a hydrophobic treatment.

Impacts

The project has established an effective mutual communication between researchers, stone producers and the construction sector and increased natural stone's position in the global stone trade. One direct spin-off of the project is the newly started in 2005 European Integrated Project: Re-engineering of natural stone production chain through knowledge based processes, eco-innovation and new organisational paradigms (I-STONE).

Acknowledgement

The authors would like to thank the European Commission for financial support of the European research project "Testing and Assessment of Marble and Limestone" (Contract no. G5RD-CT-2000-00233). The co-operation with the project partners is gratefully acknowledged.

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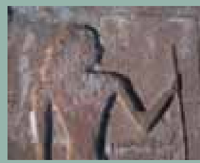
European project details

TEAM, Contract no. G5RD-CT-2000-00233., Testing and Assessment of Marble and Limestone., Björn Schouenborg, SP Swedish Testing and Research Institute, Borås, Sweden.

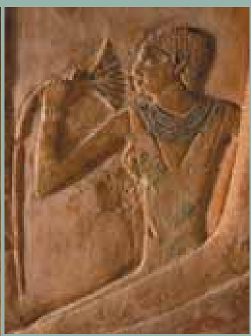
CONSERVATION WORKS IN TOMB OF INTI IN SOUTH ABUSIR /EGYPT/



Martin Dvořák

The National Institute for the Care of Historical Monuments, Prague, Czech Republic

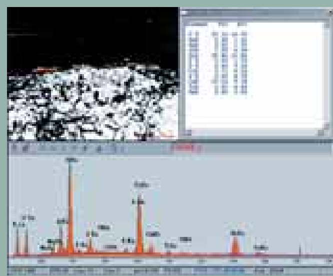
A new complex of tombs of the Fifth Dynasty was discovered at South Abusír during the expedition of the Czech Institute of Egyptology in last five years. Owner of the best preserved tomb of the whole complex was named Kar, according to the surviving inscriptions with his titles member of inner circle of the king and one of the chief justice The second well preserved tomb was tomb of his youngest son Inti adjoining to the west wall of Kar´s tomb. This poster describe the whole conservation treatment of this monument



The main scene depicts Inti, the owner of the tomb, seated at the offering table. In the upper rows Inti´s priestly and administrative titles are listed. In front of Inti a list of offerings is depicted. Another figure – his wife Merut - is depicted under a table seated at his feet and smelling to the lotus flower. Inti´s most favourite dog called Idjem is depicted in the lower part with a dwarf servant. Although incised detailing is kept to a minimum, when it is present, it exhibits a precision and delicacy.

The range of pigments used for colouring of the relief corresponds to both the customs of the period and the technical possibilities of the Old Kingdom period. The principal colours may be summarised as three main pairs: black and white , red and yellow and blue and green.

- <u>black</u> – carbon - most probably soot particles
- <u>white</u> – chalk - calcium carbonate - $CaCO_3$
- <u>red</u> – mixture of red iron oxides and red ochres - anhydrous and hydrated oxides of iron (limonite and haematite)
- <u>yellow</u> – yellow ochre, comprising iron bearing materials, notably goethite (the alpha form of FeOOH) and limonite (the yellow to brown hydrous oxide) together with varying amounts of clay and siliceous matter
- <u>blue</u> – Egyptian blue (a synthetic pigment composed of various phases containing copper and calcium. The major component is cuprorivaite $(Ca,Cu)Si_4O_{10}$, with unreacted quartz accompanied by wollastonite $(Ca,Cu)Si_3O_9$ and alkali rich glass).
- <u>green</u> - malachite - $CuCO_3.Cu(OH)_2$



For the overall deep securing of the relief, Funcosil ® KSE 500 STE was used. This material contains no solvent, is colourless, and the reaction of the making of gel is catalysed with a built-in neutral catalyst. It penetrates well into the structure of the secured stone and at the same time has a high content of eliminated gel. This means a sufficiently high degree of consolidation can be achieved, not only in the area just under the surface but also throughout the whole eroded surface, down to the undamaged core of the stone. Apart from that, it is remarkable for its resistance to the effects of weather, aggressively acidic pollutants in the atmosphere (SO_x, NO_x), and ultraviolet rays.

What is also important is that this material does not seal the pores in the structure of the stone, which, on the contrary, maintains almost entirely its original vapour permeability. The making of silica gel and therefore also the reinforcing of the eroded stone usually takes place with esters of silica acid according to the following formula:

$$Si(OR)_4 + 4H_2O \xrightarrow{catalyst} SiO_2.n\,H_2O + 4ROH$$

Repositioning of the approx. 30 fragments of decorated limestone blocks was another part of conservation treatment. A special putty Terako, developed in the State Institute for the Care of Historical Monuments, in the Czech Republic, was used to fill in surface defects.

Conservation works in tomb of Kar and Inti in South Abusír (Egypt)

Martin Dvořák

National Institute for the Care of Historical Monuments, Prague, Czech Republic

Key words: conservation, stone, polychromy, Egyptology, archaeology, indoor climate, consolidation

Introduction and content

A new complex of tombs of the Fifth Dynasty was discovered at South Abusír during the expedition of the Czech Institute of Egyptology in last five years. Owner of the best preserved tomb of the whole complex was named Kar, according to the surviving inscriptions with his titles member of inner circle of the king and one of the chief justice. The second well preserved tomb was tomb of his youngest son Inti adjoining to the west wall of Kar's tomb. In view of the state of the surviving decoration it was decided together with the Egyptian authorities represented by the Saqqara Inspectorate of Antiquities that conservation was required to stop the degradation processes and to preserve these unique monuments for the future.

Description of the state of monuments before conservation

The complex of Kar and Inti tombs was built on a low hill situated the western outskirts of the North Saqqara plateau, approx. 1 km north from the oldest pyramid complex of king Djoser. Both tombs have a simple rectangular plan, the masonry is built of local limestone blocks and the core consist of a loose filling of limestone chips and flakes of smaller blocks. The high-quality limestone was used for the places with decorated surface. The well preserved parts of decoration were in both tombs in funeral chapels and entrance corridors. Decoration of the most important parts of object (entrance corridor, decoration of walls in chapel….) were made in a classic technique of polychromed low raised relief, in which the background has been cut away and the projecting sculptural elements were subtly modelled. Other places (entrance façade, false doors…) were made in polychromed sunken relief. The best preserved part of decoration covered south wall of funeral chapel of Inti tomb. The main scene depicts Inti, the owner of the tomb, seated at the offering table. In the upper rows Inti's priestly and administrative titles are listed. In front of Inti a list of offerings is depicted. Another figure – his wife Merut – is depicted under a table seated at his feet and smelling to the lotus flower. Inti's most favourite dog called Idjem is depicted in the lower part with a dwarf servant. Although incised detailing is kept to a minimum, when it is present, it exhibits a precision and delicacy.

A *high – quality limestone* was used as a basic material for decorated parts. This is a clay organodettritic sedimentary deposit mostly composed (80-85%) from fine-grained aggregates of chemically precipitated calcite and of small amount of clay minerals. The remains of shells of the Foraminiferas epigenetic minerals – calcite veinlets – are accessory present. From results of RTG difractography is visible the presence of quartz. Thanks to its homogenous structure and relatively low–level of hardness it was the ideal material for the ancient stonemasons and sculptors when depicting a wide range of subjects; it was relatively simple to work with, down to the smallest details when using the considerably primitive tools of the day.

The *range of pigments used for colouring of the relief* corresponds to both the customs of the period and the technical possibilities of the Old Kingdom period. The principal colours may be summarised as three main pairs: black and white, red and yellow and blue and green.

- *black* – carbon – most probably soot particles
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- *green* – malachite – $CuCO_3.Cu(OH)_2$

Upon agreement with the Egyptian side it was decided to conserve all limestone blocks with decorations *in situ* and secure the whole object by concrete ceiling and safety doors and locks. The relief first had to cleansed of mechanical impurities and the remains of powdered sand and clay. This was done with brushes of various hardness and size. In addition, blowing off dirt using a low-pressure stream of air proved to be a very effective method. Special attention was paid to places with surviving polychromy, which had suffered from lack of cohesion and from flaking. On some parts of the remaining original paint layer the original binding medium for the pigment had disintegrated and weakened. These places were locally reinforced with a 5% solution of *Paraloid B 72* in toluene.

For the overall deep securing of the relief, *Funcosil ® KSE 500 STE* was used**.** This material contains no solvent, is colourless, and the reaction of the making of gel is catalysed with a built-in neutral catalyst. It penetrates well into the structure of the secured stone and at the same time has a high content of eliminated gel (about 500 grams per litre). This means a sufficiently high degree of consolidation can be achieved, not only in the area just under the surface but also throughout the whole eroded surface, down to the undamaged core of the stone. Apart from that, it is remarkable for its resistance to the effects of weather, aggressively acidic pollutants in the atmosphere (SO_x, NO_x), and ultraviolet rays. What is also important is that this material does not seal the pores in the structure of the stone, which, on the contrary, maintains almost entirely its original vapour permeability. The making of silica gel and therefore also the reinforcing of the eroded stone usually takes place with esters of silica acid according to the following formula:

$$Si(OR)_4 + 4H_2O \xrightarrow{\text{catalyst}} SiO_2.n\,H_2O + 4ROH$$

where R can be a carbon chain of various lengths (most often $-CH_3$, $-C_2H_5$........). In the case of Funcosil it is an ethyl group.

The consequent properties of the product are influenced by the size of the molecules of esters of silicic acid and the reaction time. That time depends on the kind and amount of the catalytic system used and the reaction conditions (temperature and humidity). With Funcosil KSE 500 STE softening segments are built in to the structure of the emerging gel, which give it a greater elasticity.The change in coloration was almost imperceptible after the area had dried completely.

The consolidation of the Hetepi relief was carried out with repeated coats on its whole surface (coats were applied as long as the stone accepted another consolidation, that is, five times; the average amount used for consolidation was about one litre per square metre). Upon reaching the saturation of the reinforced stone the surplus unabsorbed consolidant was wiped off, and the surface washed with toluene. (In this way, both an undesired change of colour and the emergence of shiny surfaces on the stone were avoided). A suitable temperature for the application of Funcosil is between 10 °C and 20 °C, relative humidity about 50 % and the surface of the treated stone must be prevented from heating up by exposure to direct sunlight.

Repositioning of the approx. 30 fragments of decorated limestone blocks nother part of conservation treatment A special putty *Terako***,** developed in the State Institute for the Care of Historical Monuments, in the Czech Republic, was used to fill in surface defects. According to our measurements, Terako has the tensile strength of common lime-based historical mortar, between 0.5 and 5 MPa, the permeability of a very fine lime plaster, and contains no cement and about 2 % of the weight of organic additives.

To obtain detailed information about the parameters of the indoor climate a L 3120 Comet data-logger was installed near the relief in the Inti chapel for recording temperature and relative humidity. The results of the measuring indicate clearly the changes in indoor climate.

1  2 

The main scenes from the funeral chapel depicting owner of the tomb Inti /1/ and offering bearers /2/ in technique of polychromed relief after conservation

European dimension
Conservation of monuments in framework of field archaeological expeditions support mutual understanding between European and Arabic society, between two different cultures, two different religions… Our cooperation with Egyptian experts is very important and gives a good base for co-existence our nations in future even in broader context.

Innovation and originality
We undertook the whole conservation treatment of decoration reliefs in tombs of Kar and Inti in European standard respecting all latest technologies and materials.

Acknowledgement
Author would like to acknowledge to L. Kopecký (ČVUT Prague EDAX ESEM) and colleagues from the National Institute of the Cultural Heritage (optical microscope Leica) for material analyses.

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Decoration and production of Anasazi pre-historic ceramics

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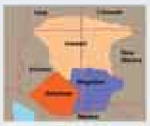
Project:

Study of pre-colombian ceramics of Nord America, specifically Anasazi tribe

Provenance of samples



Objectives:

1. Reveal the nature of phases formed during the thermal transformation of minerals in ceramic body and derive the thermal conditions of ceramic production
2. Obtain the information on nature, structure and composition of pigments used for decoration

Analytical techniques:

1. X-ray difraction – study of ceramic body
2. Raman microscpectroscopy (μ-Raman) – pigments, mineralogical phases
3. Scanning electron microscope equipped with a microanalysis energy dispersive X-ray detection (SEM/EDS)

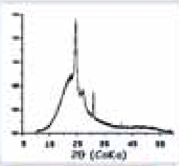
Instrumentation:

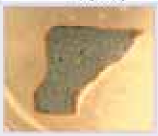
1. **Philips Analytical X-Ray PW3710**, anode Co, potential 40 kV, current 20 mA, range 2θ 10-140.005, ScanStepSize 0.015, Scansteptime 6.5 s
2. **Renishaw RM2000** – single grating spectrometer, laser: 785nm, power at sample: 0,7mW - 3mW, time: 10-100 s, spectral resolution: 3 cm^{-1}
3. **Philips 515 SEM** with EDAX Falcon system, potential 25 kV, time 100 s

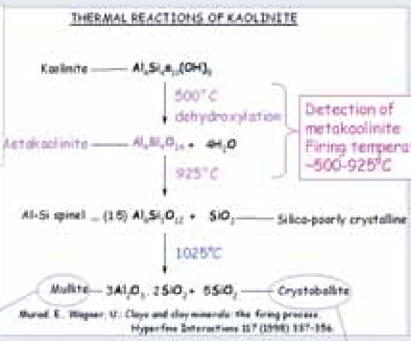
Results:

Study of ceramic body:

Principal composition of the ceramic paste determined by means of XRD – represented by minerals such as **quartz, metakaolinite, and feldspars**





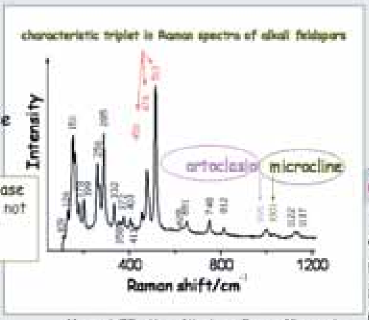


High temperature mineral phases not found
→ firing temperature not too high

K-feldspars ($KAlSi_3O_8$): structure related to the formation temperature and to the successive thermal treatment

Polymorphs: microcline, orthoclase, sanidine
- Rise in the thermal stability
- Decrease in order of crystal lattice

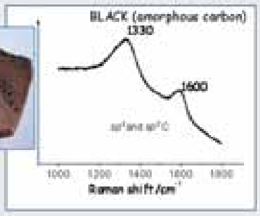
Presence of feldspars (particularly **ortoclase** e **microcline**) implies the temperature did not exceed ~900°C e the process of cooling rather slow



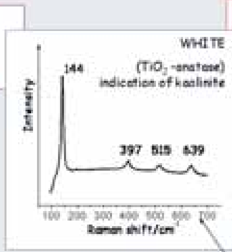
Mernagh TP.: Use of the laser Raman Microprobe for Discrimination amongst Feldspar Minerals. *J. Raman Spectrosc.* 1991; 22, 453.

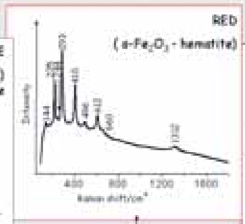
Decoration:

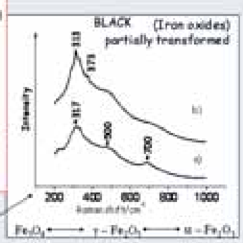
Pigments derived from materials ORGANIC

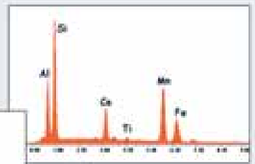


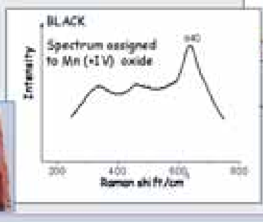
INORGANIC (iron and titanium oxides)











Confermation of presence of Mn furnished by SEM-EDX

Conclusions:

1. Raman spectra revealed that the pigments employed in the ceramic decoration derived from organic (amorphous carbon) and inorganic materials (iron, manganese oxides). Titanium oxide indicates the kaolinite to be used for the white pigmentation (confirmed by FT-IR, not shown here).
2. On the basis of results related to the present mineralogical phases one can hypothesize that the production technique employed the open bone fires in which the firing temperature usually did not overreach 800-900°C.

Acknowledgements:

This work has been supported by Marie Curie Early Stage Research Training Fellowship of the European Community's Sixth Framework Programme (contract MEST-CT-2004-504067)

7th European Commission Conference "SAUVEUR"
Safeguarded Cultural Heritage, Understanding & Viability for the Enlarged Europe, PRAGUE 31st May – 3rd June

Decoration and production of Anasazi pre-historic ceramics

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Key words: ceramics, Native American tribes, XRD, μ-Raman, SEM/EDS

Introduction

The study of decoration and production technique of Anasazi (a Southwestern Native American tribe) ceramics was pursued in this project. The ancient culture of Anasazi did not have any written history and for this reason is considered pre-historical [1]. The production of ceramics represents their most developed handcraft. Therefore the studies of these artifacts help us to understand better the materials in relation with the different production centers and the level of artistic skills of the Anasazi society**.**

Content

In our previous work micro-Raman (μ-Raman) spectroscopy, reflecting the vibrational states of the molecules, was used to provide extensive information about the nature, the structure, and the composition of the pigments utilized in decoration of Anasazi pottery. Analysis of μ-Raman spectra revealed the presence of organic-(amorphous carbon) and mineral-(pyrolusite, magnetite, maghemite, and hematite) based pigments [2].

By studying the minerals present in the ceramic body one can at least partially reconstruct the firing history to which the objects were exposed. This in turn might reflect the cultural status of the civilizations and definitely evidences their technological customs. In general, the reactions taking place upon heating of the clay matrix together with the mineral temper grains can be divided into: (i) modal reactions (formation of new more thermally stable mineral phases) and (ii) cryptic reactions (those occurring at the grain boundaries of phases with contrasting chemistry) [3]. The formation of various K-feldspars ($KAlSi_3O_8$) phases is strongly dependent on thermal conditions of crystallization and can serve as an example of modal reactions. While microcline represents a low-temperature K-feldspar polymorph with the Al-Si distribution highly ordered, orthoclase and sanidine represent the intermediate- and high-temperature ones with increasing chemical disorder in their crystalline structure [4].

The thermally-induced effects in the ceramic material were in our project traced by characterizing the phases of present minerals using X-ray diffractions (XRD), scanning electron microscopy, energy dispersive microanalysis (SEM/EDS) and μ-Raman spectroscopy. A study of X-ray diffraction patterns produced by the ceramic sections revealed mainly quartz-feldspathic-metakaolinitic compositions. The presence of metakaolin constrains the firing temperatures to fall into the thermal range from ~500 °C to ~925 °C in which the aforementioned is formed from kaolinite by dehydroxylation [5]. New phases that form at higher temperatures (e.g., Si-Al spinel phase which converts around 1050 °C to mullite and cristobalite) were not detected. The presence of feldspars was also confirmed by both SEM/EDS microanalysis and μ-Raman spectroscopy. The later allowed the microcline and orthoclase feldspathic phases to be identified, thus evidencing that the maximum firing temperature did not overreach 800 °C and rather slow cooling process.

Despite all the conveniences offered by μ-Raman spectroscopy (its non-destructiveness and non-invasiveness), the complexity of ceramic materials can require the application of various analytical methods. X-ray diffraction patterns have proven to be useful especially in detection of metakaolinite as this phase is a poor Raman scatterer.

On the basis of the results obtained one can hypothesize that the ceramic shreds studied employed the firing in open pits in which the temperature usually did not exceed 800-900 °C. Additionally, the presence of partially transformed iron-oxides found on the surface of some ceramic shreds, suggests a second firing at a lower temperature was carried out, after the paint had been applied.

European dimension

The ATHENA project trains early stage researchers on scientific methodologies for the characterisation and conservation of the cultural heritage patrimony with the aim of structuring the European research in this field. The fellows are given also the possibility of pursuing a career in conservation with a solid scientific background. The training activity in science for cultural heritage envisaged in the ATHENA project involves three European research laboratories LENS of Florence (Italy), FORTH-IESL of Heraklion (Crete, Greece), UA-MiTAC of Antwerp (Belgium) with complementary and reliable expertise as to the use of scientific techniques applied to conservation problems.

Innovation and originality

In this project a Marie-Curie fellow has been engaged with studies of artefacts belonging to a private collection of American First Nations located in Carpi, Italy. By involving broad range of analytical techniques it was possible to complement the art-historian research results of Carla Fornasari who dedicated all her life to the study and documentation of the American Indigenous People.

Impacts

The deep bound of Carla Fornasari with the currently living Indigenous tribes of American Southwest (Apache, Hopi, Navajo, and Zuñi) creates an imaginary bridge between the Native American cultures and the European ones. The studies of these artefacts are to our best knowledge unique and rare in the European framework. We are grateful for the possibility to enlarge the awareness of these ancient cultures and hope to continue the current work.

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European project details

Marie Curie Early Stage Research Training Fellowship European Community's Sixth Framework Programme contract No. MEST-CT-2004-504067, ATHENA, Coordinator: Prof. E.M. Castellucci, European Laboratory of Non-linear Spectroscopy (LENS) Florence-Italy.

THE METHOD OF CONSERVATION AND RESTORATION OF WOODEN STATUES FROM PRAGUE HOROLOGE

Marie Pacáková [1], Jiří Matějíček [2], Darina Smetánková [2], Ivana Kopecká [1] and Alena Horynová [1]

1 National Institute for Cultural Heritage. The Czech Republic

2 Specialist in conservation. The Czech Republic

Introduction

The astronomical dial with a calendar disk located on the facade of the Prague Horologe in the Old Town Square is decorated at its sides by four couples of wooden polychrome statues. The upper line of figures connected with the mechanism of the machine consists of statues of the Vain Person, the Miser and the Pleasure, which represent the dark face of mankind. Among the sinners there is also the Skeleton as the personification of death, measuring everybody's lifetime in this world. The lower line of statues represents the Chronicler, the Angel, the Astronomer and the Philosopher as symbols of education, thirst for knowledge and justice.

Restoration started in 2005 because all the wooden statues from the Prague Astronomical Clock's facade were in a very poor condition. Most of the polychromy of the statues (approximately 90 %) was missing, the wood was cracked, greyish and much degraded. This happened because the sculptures are situated outdoors, on the southern facade, where they are exposed to sunshine (UV radiation), rainfall and strong climatic fluctuations. To ensure maximum protection of the wooden statues a procedure for their conservation was carefully selected as acrylate agents used in the last restoration proved to be unsuitable due to the location of the statues. Therefore alkyd-urethane protective varnish was selected because of its very good resistance against weathering.

Condition before Restoration

Course of Restoration Works

1. Cleaning, taking out of damaged fillers and unblocking of non-cohesive connections
2. Filling of the cracks and repairing of connections – thin cut veneers and polyurethane based glue
3. Consolidation of disturbed wood and polychromy – alkyd-urethane paint
4. Filling of the missing polychromy – alkyd-urethane paint, wooden powder and pigments were used as filler
5. Unifying by means of retouching
6. Final protection – alkyd-urethane paints in three layers
7. Gilding and silvering

Condition during Restoration

Condition after Restoration

Interesting discovery in the pouch of the Miser

The method of conservation and restoration of wooden statues from Prague Horologe

Marie Pacáková[1], Jiří Matějíček[2], Darina Smetánková[2], Ivana Kopecká[1] and Alena Horynová[1]

[1] National Institute for Cultural Heritage, Czech Republic
[2] Specialist in conservation, Czech Republic

Key words: wooden plastic, conservation, restoration, Prague Horologe, alkyd-urethane varnish

Introduction and content

The astronomical dial with a calendar disk located on the facade of the Prague Horologe in the Old Town Square is decorated at its sides by four couples of wooden polychrome statues. The upper line of figures connected with the mechanism of the machine consists of statues of the Vain Person, the Miser and the Pleasure, which represent the dark face of mankind. Among the sinners there is also the Skeleton – as the personification of death, measuring everybody's lifetime in this world. The lower line of statues represents the Chronicler, the Angel, the Astronomer and the Philosopher as symbols of education, thirst for knowledge and justice. The sculptural decoration of the Horologe was probably renovated several times in the course of its existence. The last significant renovation of the statues was carried on after World War II. At that time a big fire caused severe damage of the sculptural decoration, the machine and other metal parts of the Horologe. From 1948 until the late 1970's the statues were step by step replaced by copies. Light and soft linden wood was chosen as material. Just one figure (the statue of the Angel) is made of medium hard wood – the maple. The original wooden statues dated back to the late Gothic period. The last original statues preserved until the 20th are early Baroque and are now deposited in the Municipal Museum in Prague. Nowadays their places have been taken by copies of sculptures from the 1940's to 1970's [1].

Pre-restoration research

During the last restoration in 1998-1999, which was carried out by the art company Brandl limited under the leadership of Irena Nečásková, DSc. a large-scale investigation was conducted. Composition of the statues was determined with the help of computer tomography. Analytical methods defined the materials used during in restoration in the past. All upper paints were removed and the original polychromy was uncovered. Watercolours and gouache were used for retouching. These materials were later fixed during petrification and protective acrylate painting. Six years later weather condition brought about decay of acrylate painting as well as retouching and considerable decolourization. With regard to the fact that detailed research had been conducted earlier and a restoration report with documentation was available only some additional probes were performed to find out the way the surviving original colours were treated [1].

Condition before restoration

Restoration started in 2005 because all the wooden statues from the Prague Astronomical Clock's facade were in a very poor condition. Most of the polychromy of the statues (approximately 90 %) was missing, the wood was cracked, greyish and much degraded. This happened because the sculptures are situated outdoors, on the southern facade, where they are exposed to sunshine (UV radiation), rainfall and strong climatic fluctuations. For this reason it was necessary to start the restoration. To ensure maximum protection of the wooden statues a procedure for their conservation was carefully selected as acrylate agents used in the last restoration proved to be unsuitable due to the location of the statues. Therefore alkyd-urethane protective varnish was selected because of its very good resistance against weathering. According to the plan a less resistant acrylate varnish was to be used as the final protecting layer. It was to be removed together with impurities and periodically renewed as part of regular maintenance. However, this final measure has not been realised for time reasons and will be taken within regular maintenance of the wooden statues.

Course of restoration works

The wooden sculptures were stripped of surface impurities, the copper stripes with the residue of the repellent agent were taken off and the silicone glue, which held the copper stripes to the statues was removed. The degraded acrylate paint was mechanically removed from the statue surface together with the pulverized layer of retouching. The repellent agent was removed by means of cotton wool soaked with white spirit. Non-cohesive connections in material were unblocked and damaged fillers and impurities were taken out of cracks. The cracks were filled with thin veneers and non-cohesive connections were repaired. Polyurethane-based glue was chosen to resist aggressive weather conditions. Then the surface of the statues was treated, with accent on uncovered and disturbed wood, with bright alkyd-urethane paint diluted by white spirit. This fixed the disturbed wood and polychromy. At the next step for the missing polychromy bright alkyd-urethane paint, wooden powder and pigments were used as filler. After drying the superfluous filler was cut off and the filled parts were painted again to accentuate its colourfulness and its fixation. This treatment was followed by unifying retouching. Later drying the retouching was painted with white spirit - always slightly diluted by bright alkyd-urethane paint – in three layers. In the end, to obtain a better appearance the statues were coated with semi-matt varnish.

Except for the Angel’s wings and hem of his robe the gilding and silvering of the statues and their attributes was reconstructed. Damaged gilding and silvering was removed together with acrylate undercoat. These places were covered with two layers of primary alkyd wood paint and then coated with alkyd enamel, again in two layers. Finally a 24-hour mixtion and then gold or silver leaves were applied.

The Gilded wings and robe of the Angel were restored. The gilded areas were cleaned of surface impurities, damaged places were abrased and coated with ground paint and enamel in two layers. Then a 24-hour mixtion and gold or silver plating were applied. New silver plated areas were insulated against darkening by alkyd-urethane paint [1].

European dimension

The Prague Horologe is a historical monument of extraordinary importance and fame. Conservation and restoration of the wooden statues is an important part of its protection. Planned regular maintenance will ensure long-term preservation of this part of the European cultural heritage.

Innovation and originality

Instead of classical materials, which are commonly used for the restoration of wooden statues, alkyd-urethane paints were used in the project. Classical paints are not suitable for use in outdoor places as in the Old Town Square. New materials will give much better protection and make maintenance easier.

Impacts

Application of new materials will ensure the best protection against weathering at present, and will also reduce the costs of repairs and maintenance in future.

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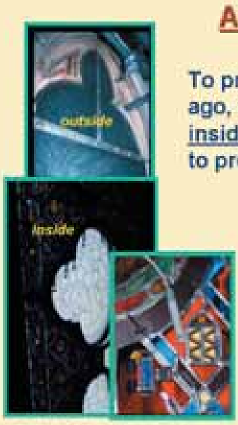
THE EUROPEAN PROJECT VIDRIO: SCIENTIFIC STUDIES AND NEW TECHNOLOGY FOR THE CONSERVATION OF ANCIENT STAINED GLASS WINDOWS

A.Bernardi
Consiglio Nazionale delle Ricerche - ISAC, Italy

Aims



Sainte Chapelle – Paris

To protect the stained glass windows some years ago, the medieval glass was moved some cms inside, and a protective glazing was put in its place to protect it against outdoor air attack.

Many open questions remained and certain reservations did still exist.

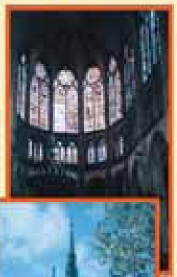
In the interspace:

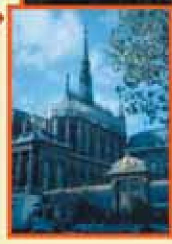
- are the *microclimatic conditions worse*?
- is there an *accumulation of air pollutants*?
- is the *growth of microorganisms increased* ?

Monuments studied

In France:

Saint Urbain Basilica – Troyes
(rural environment)
&
Sainte Chapelle – Paris
(urban environment)





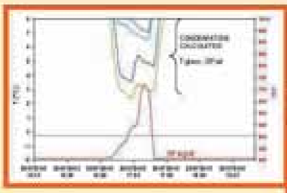
In Germany:
Cologne Cathedral

All relevant parameters for stained glass weathering were considered from a *physical, chemical and biological* point of view

Alteration of paint alteration (grisaille)

Innovation

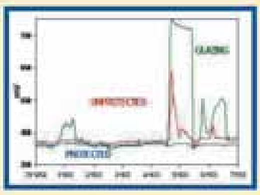
A new device (Dew Point Sensor) to detect directly the condensation on surfaces was built and patented



Condensation: comparison between direct and indirect measures (T_{glass} and air dew point DP_{air})

Dew point sensor

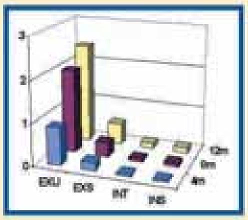
Main results



Condensation phenomena on protected, unprotected windows and glazing (Dew Point Sensor)

concerning the ancient glass

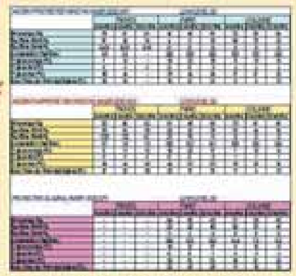
- *The protective window decreases the time of wetness on the outer surface*
- *The protective window decreases the condensation on the inner surface of the ancient window*
- *In the interspace the environmental conditions are similar to the indoor and much less aggressive than outdoor ones for:*
  - *Bioactivity*
  - *SO_2 and O_3 concentrations*
- *The protective glazing reduces the total deposited particles in the interspace and decreases the haze due to fine particles deposition.*
- *If free ventilation is ensured, the protective glazing decreases the max T° of the original glass*



Troyes: thickness of weathered layers (EXU /EXS = External Unsh. / Sheltered INT = Internal - INS = Inside; m = month)

concerning the grisaille

- *When properly ventilated the protective glazing decreases the max T° of the original glass and the thermal shock which is positive for*
  - *Paint layer conservation*
  - *Conservation products and cold paintings*
- *The protective glazing decreases the risk of condensation of the ancient window and reduces the risk of chemical deterioration of glass paint.*



All the data were finally summarised in a series of special MATRIXES to find their relationships.

Finally *the determination of the best practice* and *a series of recommendations* were done to the end users (see project web site http://www.isac.cnr.it/~vidrio)

European Project details

VIDRIO: Contract No. : EVK4-CT-2001-00045

Determination of Conditions to Prevent Weathering due to Condensation, Particle Deposition and Micro-organism Growth on Ancient Stained Glass Windows with Protective Glazing

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SCIENTIFIC OFFICER *Dr. Johanna Leissner & Dr. Michel Chapuis*

The European project VIDRIO: scientific studies and new technology for the conservation of ancient stained glass windows

Adriana Bernardi

Consiglio Nazionale delle Ricerche - ISAC, Italy

Key words: stained-glass; microclimate; chemical and biological weathering; protecting glazing, dew point sensor, condensation on glass

Introduction and content

The European VIDRIO project was a multidisciplinary project which answered to open questions related to environmental risk of stained glass windows. It was aimed at providing good solutions to the problems related to mass tourism, environmental risk and conservation of stained glass windows. Three churches, two in France: Basilica of Saint Urbain in Troyes and Sainte Chapelle in Paris and one in Germany, Cologne Cathedral, the last two included in the UNESCO's World Heritage, were the subjects. In these churches 2 stained glass windows, one with the protective glazing, another without were monitored.

The most important results have been published [1] and can be summarised as follows.

From a *microclimatic point of view* the protective glazing protects the ancient glass from the risk of condensation and from rapid temperature changes. No negative effects were associated with the greenhouse effect. The environment in the interspace was characterised by sometimes slightly higher relative humidity than inside the church The presence of the protective glazing reduced the risk of condensation on the internal side of the ancient window. A good distance and a free circulation can guarantee a higher exchange between inner atmosphere and interspace.

From the *chemical point of view* the indoors concentrations of O_3 and SO_2 resulted strongly reduced. In contrast, NO_2 revealed higher indoor concentrations where burning candles are present (Saint Urbain and Cologne Cathedral). In Sainte Chapelle only low concentrations of nitrates were observed, but a formation of $CaSO_4$-particles inside and in the interspace was detected. Soiling is much less important in Cologne Cathedral than in Saint Urbain. This trend is primarily due to a weaker deposit flux for carbon particles and to a lesser extent to insoluble ones. A decrease of haze was observed on glass samples exposed in the interspace compared with them located inside the churches. Moreover the haze of samples exposed inside is higher than for outdoor exposed glass samples again probably due to the presence of the combustion of candles. Except for the effects of the candles where present, the results proved that the glazing protects the stained glass windows against most air pollutants.

From the *biological point of view*, it was found that in all the three churches the glazing has a protective effect and there is no significant difference for the inner side of the original window in both windows protected and non protected. Good ventilation seems to have a positive effect, like a large space between glass and glazing.

Laboratory test on synthetic glass and grisaille determined the relative chemical durability of the glass of the 3 churches: Sainte Chapelle is better that Cologne Cathedral, better Than SAINT URBAIN. The exposition of sets of glass samples in positions external sheltered, unsheltered, interspace and inside the church demonstrated that the glass weathering consisting of leaching of modifiers ions (K and Ca) and formations of a hydrated glass layer. The extent of this phenomenon increases with the time of exposure and is more relevant following the scale: external unsheltered > external sheltered > interspace ~ inside. The fundamental role of water (rain, condensation, water retained on the surfaces by hygroscopic salts, etc.) and of the time of dampness was clearly evident. The neoformations of syngenite and gypsum, found especially on samples exposed in position external sheltered, indicate an important influence of the acidic contaminants in the atmosphere on the weathering mechanism (formation of iridescent layers, microfractures, severe changes of optical and mechanical properties).

A leaching mechanism was demonstrated also for the lead silicate forming the grisaille (Fig. 1) that causes the pulverisation of the paint. Several laboratory tests including thermal shock confirmed that the variations of temperature increase the instability of the fired paint and lead to the formation of microfractures and flaking of particles, a phenomenon observed in the original samples. The results indicated that the protective glazing exerts an efficient protection against the leaching of the external glass surface of the original windows and reduces the mechanical and thermal stresses that can produce the propagation of micro-cracks and the loss of the paintwork. In conclusion even with low ventilation the protective glazing protects the stained glass windows.

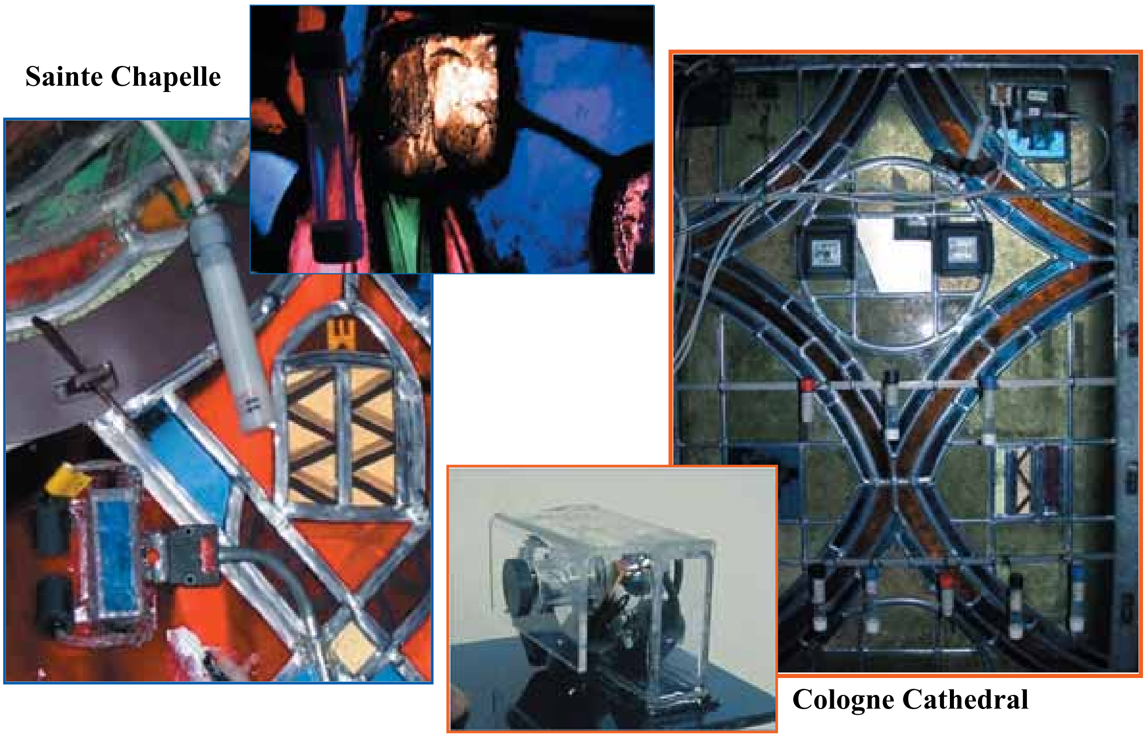

Figure 1: Installation of instrumentation in Sainte Chapelle and Cologne Cathedral. A particular of degradation of the grisaille and the prototype of Dew point sensor are also showed

Finally *the determination of the best practice* to control condensation, minimise soiling and weathering of stained glass windows and a series of recommendations were done to the end users. In a certain number of special matrixes the basic information, the identifications and values of the most important measured parameters can be found.

From the *technological point of view* a new dew point sensor (Fig. 1) to control in real time the main cause of deterioration of glass, i.e. the condensation of water, was also developed and patented. It can be used in different surfaces and in varied fields (architecture, environmental safety or transport of materials, car industry, domotica, etc).

European dimension

This project furnished general recommendations useful to all the European Community. It favored collaboration among researchers, SMEs, conservators and end-users from all Europe.

Innovation and originality

This project for the first time *drew important multidisciplinary scientific conclusions* on the conservation of stained glass windows giving important practical recommendations.

The innovation was *realise and patent a new device* to detect condensation on different surfaces.

Impacts

The project reached important scientific achievements, stimulated research and discussion, furnished important final indications to the users for the future management of the stained glass; provided useful information to built the European standards and regulations and finally cold have an economic relevance as less money is needed for future restorations.

The technological result obtained during VIDRIO project (dew point sensor) have been the object of a *Ministerial Italian Spin-off* with a collaboration between Dr. Adriana Bernardi, Tecno Penta and the National Research Council (CNR).

Acknowledgement

The obtained results came from a very good collaboration among all the involved partners in VIDRIO project and their staff, and precisely:
Dr. A. Bernardi CNR-ISAC & Dr. F. Becherini
Prof. R. Van Grieken, UIA & Dr. V. Kontozova, Dr. R. Godoi
Dr. H. Roemich, ISC & Dr. P. Mottner, Dr. G. Maas
Prof. R. Lefèvre, LISA &; Dr.H. Cachier, Dr. A. Chabas, Dr. P. Ausset, Dr T. Lombardo
Dr. M. Verità, SSV & Dr. F. Geotti Bianchini, Dr.C. Nicola, Dr. M. Vallotto, Dr. G. Sommariva
Dr. M. Bellio, Tecno Penta & Dr. G. Bassato
Prof. I. Pallot-Frossard, LRMH & Dr. M.P. Etcheverry
Dr. S. Roelleke Labor Fuer Genetische Analytik GmbH
Dr.U. Brinkmann, DBH KOLN & Mr. Gunter Hettinger, Mr. Michael Schueren

References

[1] All the numerous references produced are available in the web site of VIDRIO:
URL: *http://www.isac.cnr.it/~vidrio/* .

European project details

VIDRIO: Contract No.: EVK4-CT-2001-00045
Title: Determination of Conditions to Prevent Weathering due to Condensation, Particle Deposition and Micro-organism Growth on Ancient Stained Glass Windows with Protective Glazing
Co-ordinator: Adriana Bernardi, National Research Council-ISAC, Italy

STUDY OF HISTORICAL GLASS CHANGES DUE TO ARTIFICIAL ALTERATION IN ACETIC ACID

E.Greiner-Wronowa[1], A. Pusoska[2], D.Piasecka[1]

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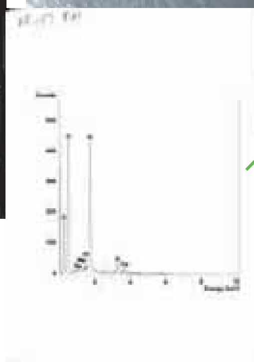
[2] The National Museum Kraków POLAND

Many historical glasses suffer and after some time their deterioration become visible . There are also many of them, which have survived for hundreds of years despite being in very severe conditions. They had to be more durable glasses, what means with better chemical stability. It was found that deterioration process depends on the composition of glass and its environment data, including physic and chemical parameters. Moreover, the stage of glass surface is very important. It is highly influented by the effects of weathering processes which occur on it.
Actually, usually surface is defected itself. It is due to the fact that all surface ions are in a state of incomplete coordination. This asymmetry of the glass surface makes abnormal interatomic distances. The space occupied by the surface ions is greater than usually, enabling to occur a replacement by ions of a layer or smaller radius. Created microporosity enables surface reaction with molecules of water, sulphur dioxide, oxygen and hydrochloric acid and another organic compounds, to reach considerable depth.
Problem of organic agents was discovered many years ago, but it was neglected in the case of glass surface activity. It was found that all organic compounds were originated from the new furnitures in museum. These chemicals are the result of the emission of damaging level of corrosive volatile compounds, mainly formaldehyde, acetaldehyde, formic acid and acetic acid from the adhesives used in the manufacturing the plywood, chipboard, harl or particleboard [3, 4, 5].
Few independent measurements of inside cabinets (or other enclosures) has been done by calorimetric and chromatography methods in museum.
The concentration of NO_2, SO_2, formic acid and acetic acid were measured in and outside of the museum showcases. Concentration of formic acid and acetic acid was detected in higher concentration within the showcases in comparison to the outside air. The results show, that the display showcases sufficiently protect the works of art from dangerous outdoor pollutants, but they accumulate dangerous organic compounds,

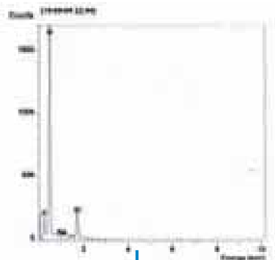
Oxide	Concentration [% weight]
SiO_2	73,94
CaO	9,26
K_2O	14,48
PbO	0,066
MnO	0,096
Fe_2O_3	0,056
Na_2O	0,84
BaO	0,14
MgO	0,59
Al_2O_3	0,065
B_2O_3	0,64

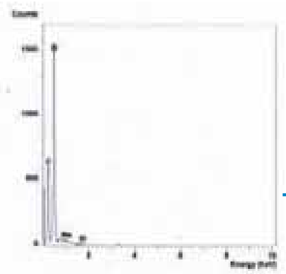
Sensor after corrosion

after 2 months in 40% acetic acid at RT and 4 h boiling



after 2 months in 5% acetic acid at RT and occasionally boiling





after 170 days in 80% acetic acid

Detected chemical components in these measurements were used as corrosive media in artificial corrosion process on chosen glass sensors. They were prepared on the base of chemical composition of the XVIII-th c. beaker from the National Museum in Kraków, with composition presented in Tab.1
This paper is focused on measurements only influence of acetic acid on glass surface at different concentrations, and for different period of time..
The need of understanding of the influence of variable quantitative is important for:

- to find level of emission for air pollution and estimate its harmful activities,
- to balance the improvements in organic compounds/air levels, which might be achieved from increased ventilation rates against the resultant higher energy requirements
- to look for material to absorb vapour organic compounds to historical objects.

To emphasize role of different surface stage of historical glass sensors used for this experiment was analysed on ground and not ground surface.
All these activities are going to make suitable restoration work and to prepare good background for susceinable conservation and to be sure that we were able to prolong our cultural heritage.

Obtaining data pointed destructive acetic acid activity on glass objects and different corrosion way than in the case of formaldehyde (in 20 and 40% concentration of solution) as well as on ground and not ground surface.
But creating silica gel layer on surface after keeping sensor in acetic acid is enough dangerous process to look for immediately protection for glass. That layer can preserve surface for a while, but actually after some time, or in the case of some unexpected changes can be collapsed and evoke further corrosion , makes damage of the historical object.

Study of historical glass changes due to artificial alteration in acidic acid

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[1] AGH – Technical University of Science and Technology, Kraków POLAND
[2] The National Museum, Kraków POLAND

Key words: glass corrosion, leached layer, organic volatile compounds, glass sensor

Introduction and content

Many historical glasses suffer and after some time their deterioration become visible. There are also many of them, which have survived for hundreds of years despite being in very severe conditions. They had to be more durable glasses, what means with better chemical stability. It was found that deterioration process depends on the composition of glass and its environment data, including physic and chemical parameters. Moreover, the stage of glass surface is very important. It is highly influenced by the effects of weathering processes which occur on it.

Actually, usually surface is defected itself. It is due to the fact that all surface ions are in a state of incomplete coordination. This asymmetry of the glass surface makes abnormal interatomic distances. The space occupied by the surface ions is greater than usually, enabling to occur a replacement by ions of a layer or smaller radius. Created microporosity enables surface reaction with molecules of water, sulphur dioxide, oxygen and hydrochloric acid and another organic compounds, to reach considerable depth [1, 2].

Problem of organic agents was discovered many years ago, but it was neglected in the case of glass surface activity. It was found that all organic compounds were originated from the new furniture in museum. These chemicals are the result of the emission of damaging level of corrosive volatile compounds, mainly formaldehyde, acetaldehyde, formic acid and acetic acid from the adhesives used in the manufacturing the plywood, chipboard, harl or particleboard [3, 4, 5].

The first indication of the detrimental environment was the corrosion of the locks of museum cabinets. Later, white crystalline efflorescence on some metal, shell and glass objects were found. The problem has been noticed when in spite of relatively good parameters kept on stable level in museum (room temperature, relatively humidity) glass objects deterioration was developing.

Few independent measurements of inside cabinets (or other enclosures) has been done by calorimetric and chromatography methods in museum.

Detected chemical components in these measurements were used as corrosive media in artificial corrosion process on chosen glass sensors. They were prepared on the base of chemical composition of the XVIIIth c. beaker from the National Museum in Kraków [6, 7].

This paper is focused on measurements influence of acetic acid on glass surface at different concentrations.

There were some relations between form of activity of the reagent (vapour or liquid) and temperature as well as the time of reaction.

Obtained results pointed that changeable parameters (inducing shocks like drastically moved sample after boiling to room temperature and after some time of exposition at room temperature once again boiling for few hours) created less visible changes than when sample was keeping at room temperature, even in the solution with low concentration, but without any drastical interaction. This phenomenon [3, 4] is known in literature as polimerization or depolimerization process. At the lower temperature the process is undergoing slowly, but consequently builds destroyed surface, which is the more affectively deteriorated.

These results were confirmed by SEM, EDS measurements and sensor surface observation in IR microscopy.

Analysis (SEM, EDS, IR microscopy) have shown that volatile organic acid plays important role in the modification of alkaline glass, especially in humid atmosphere. The increase in humidity results in an increase glass surface deterioration.

The different concentration of acetic acid solution were taken, because of differentiated concentration of organic compounds are detected in enclosures in museums. It could be explained as originality in the type of quality of ventilation as well as the age of the site. If the area is not well ventilated (i.e. rarely opened cabinets), the concentration of organic agents builds up. As the material of furniture ages, however, the amount of chemicals released decreases.

Moreover there is no information about amount of these components used for the furniture production.

The need of understanding of the influence of variable quantitative is important for:

- to find level of emission for air pollution and estimate its harmful activities
- to balance the improvements in organic compounds / air levels, which might be achieved from increased ventilation rates against the resultant higher energy requirements
- to look for material to absorb vapour organic compounds to historical objects.

To emphasize role of different surface stage of historical glass sensors used for this experiment was analysed on ground and not ground surface.

All these activities are going to make suitable restoration work and to prepare good background for susceinable conservation and to be sure that we were able to prolong our cultural heritage.

Acknowledgement

This research has been realized under financial support from the State Committee for Scientific Research (3T 08D 02730).

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[1] Newton R., *Conservation of Glass*, London 1989.
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[7] Greiner-Wronowa E., Doctoral Thesis – AGH Technical University and Science and Technology, 1999.

Silver Metal Artifacts Protection By Nano-Alumina Pigmented Coatings

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Introduction

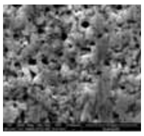
Silver metal artefacts tarnish readily in common atmospheres. Tarnishing is the formation of Ag_2S on the surface of silver when exposed to a wide range of sulphur containing environments and it is accelerated by humidity. Tarnishing is unattractive and highly undesirable and can be removed either with a silver polish or a chemical dip. In the framework of safeguarding movable cultural heritage artifacts a study on silver objects is undertaken to obtain a protective system that could be safely employed following the ethics of conservation.

Accelerated silver ageing and cleaning

Silver drawn sheet coupons as well as cast silver specimens (92.5 % Ag and 7.5 % Cu) were tarnished by different chemical methods so as to produce corrosion layers similar to the ones produced on the metal artifacts either by saline environment, containing mainly AgCl and urban environment, containing Ag_2S [1]. On the produced corrosion layers there were performed X-ray diffractometry, scanning electron and surface analysis as well as optical microscopy. The produced and thus analyzed surfaces were cleaned by an alkaline dithionite chemical method.

$CuCl_2$ aqueous solution silver ageing

Silver coupons were immersed in the hot solution of $CuCl_2$ 50 g/l (50-60 °C) for 20 min. The corrosion-patination layer developed gradually and the color changed to brownish purple. An even corrosion layer consisting mainly of AgCl and probably CuCl have been produced (Fig.1a.b).


(a)

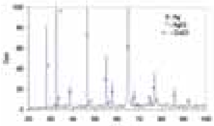
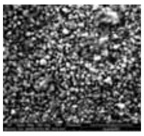

b)

Figure1. (a) SEM of the $CuCl_2$ corroded silver surface (b) XRD pattern of the corroded silver surface with characteristic AgCl and CuCl corrosion products diffraction peaks

Alkaline dithionite cleaning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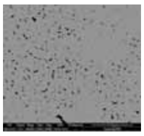

(b)

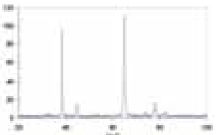
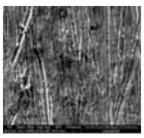
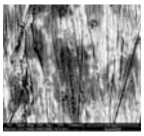

(c)

Figure 2. SEM of t*he $CuCl_2$ corroded silver surface after* the alkaline dithionite cleaning (a) SE image (b) BSE image (c) *XRD pattern reveals no presence of the corrosion products*

BaS aqueous solution silver ageing

The samples were immersed in cold (RT) BaS 5 g/l solution for 24 hours, producing a slightly uneven dark brown corrosion layer. On the sample surface it can be differentiated areas of the almost clean metal, the areas of silver rich and copper rich corrosion products. Apart from Ag_2S, on the sample surface, the presence of CuS as well as Ag_2O and Cu_2O cannot be excluded resulting by EDS analysis.


(a)


(b)

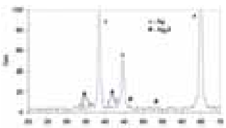
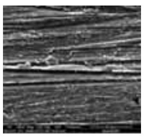

(c)

Figure3. SEM of the BaS corroded silver surface* (a) SE image (b) BSE image *(c) XRD pattern of the corroded silver surface with characteristic Ag_2S corrosion product diffraction peaks

Alkaline dithionite cleaning


(a)


(b)

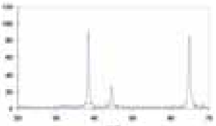

(c)

Figure 4. SEM of t*he BaS corroded silver surface after* the alkaline dithionite cleaning (a) SE image (b) BSE image (c) *XRD pattern reveals no presence of the corrosion products*

Silver protection

Clean silver coupons were protected by polymeric acrylic resins paraloid B44 and B72 systems containing Al_2O_3 nanopowder as protective pigment. Silver coupons were tested by electrochemical methods in a corrosive 0.1 M Na_2SO_4 electrolyte. The linear polarization method was employed as well as the electrochemical impedance spectroscopy to check on the integrity and protectiveness of the coating. The linear polarization results (Table 1) show that alumina pigmented paraloid B72 protective system exhibits better corrosion resistance characteristics than the non-pigmented coating.

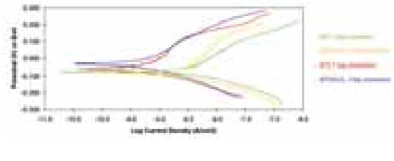
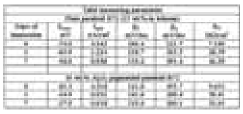


Figure 5. Tafel polarization curves of the B72 and B72/Al_2O_3 protective systems at initial condition and after 7days immersion in 0.1M Na_2SO_4solution.

Table 1. Tafel results of the paraloid B72/Al_2O_3 protective system



In Figure 6 comparative EIS spectra as Bode plots are presented of the 10% alumina pigmented paraloid B72 after 1h (initial condition), 1 and 7 days immersion in 0.1 M Na_2SO_4 electrolyte. The impedance of the plain paraloid B72 as well as the impedance of both plain B44 and 10% alumina pigmented paraloid B44 protective systems decreases with immersion time. The impedance of 10% alumina pigmented paraloid B72 increases, as it is shown in Figure 6. This can be explained by a possible development of protective reaction products by the pigment with the electrolyte, that minimizes the film defects and increases pore resistance of the system.

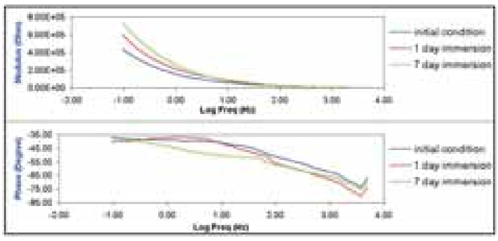


Figure 6. Comparative EIS spectra in Bode plots of 10% alumina pigmented paraloid B72 after 1h (initial condition), 1 day and 7days immersion in 0.1 M Na_2SO_4 electrolyte

Alumina pigmented paraloid B72 organic protective system is quite sufficient to protect the silver metal surface from the corrosive ions of the environment without compromising the aesthetic aspect of the metal/coating system

European dimension

The protection of silver artefacts in the museums is of primary importance since the sulphides that are in the atmosphere have a detrimental effect on the silver artefacts, tarnishing them and later when the attack continues the surface will irreversibly be altered. The existence of chlorides in the air in regions near the sea, also creates problems on the artefacts surface. Thus, the protection of the metal without changing the aesthetic aspect of the surface is of a major concern.

Innovation and Originality

The originality of this work is the employment of known polymer coatings: paraloid B72, -B44 well studied for the protection of surfaces by museum conservators as vehicle for a nano-particle Al_2O_3 pigment. The pigment enhances the protective ability of the acrylic vehicle by changing the polymer structure to a tighter one and probably prevents the silver ions diffusion to the solid/gas interface. The surface of the usually shiny coating also becomes less shiny and pleasant to the eye.

Impacts

Several methods have been developed to reduce silver tarnish which include surface treatment and a coating. A number of commercial products are available, but none of these have been assessed conclusively. Any silver protection scheme that exhibits a marked resistance to tarnishing would find acceptance and a market. The protection of silver artefacts using a reversible process might have a potential use for electronics.

Reference

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European Project Details

PROMET, Contract No. 509126, Developing new analytical techniques and material for monitoring and protecting metal artefacts from the Mediterranean region, Co-ordinator: Vasilike Argyropoulos, (T.E.I. of Athens), Ag. Spyridonos, Aigaleo - Greece 12210, Email: bessie@teiath.gr

Silver metal artifacts protection by nano-alumina pigmented coatings

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Key words: silver artefacts, protection, coatings, pigment, nano-alumina

Introduction

Silver metal artefacts tarnish readily in common atmospheres. Tarnishing is the formation of AgS on the surface of silver when exposed to a wide range of sulphur containing environments and it is accelerated by humidity. Tarnishing is unattractive and highly undesirable and can be removed either with a silver polish or a chemical dip. In the framework of safeguarding movable cultural heritage artifacts a study on silver objects is undertaken to obtain a protective system that could be safely employed following the ethics of conservation.

Accelerated silver ageing and cleaning

Silver drawn sheet coupons as well as cast silver specimens (92.5 % Ag and 7.5 % Cu) were tarnished by different chemical methods so as to produce corrosion layers similar to the ones produced on the metal artifacts either by saline environment, containing mainly AgCl and urban environment, containing Ag_2S [1]. On the produced corrosion layers there were performed X-ray diffractometry, scanning electron and surface analysis as well as optical microscopy. The produced and thus analyzed surfaces were cleaned by an alkaline dithionite chemical method.

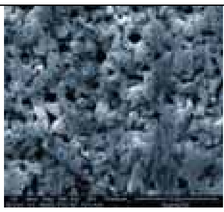
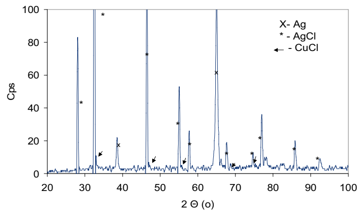
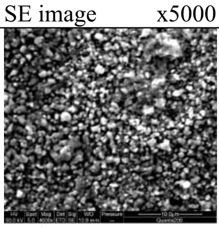
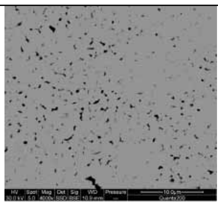
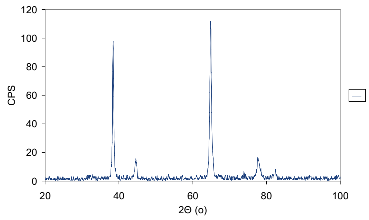
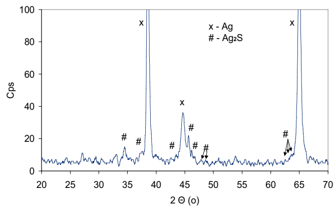
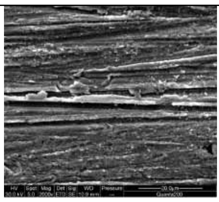
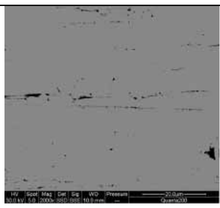
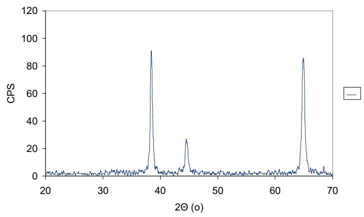
Accelerated corrosion procedure 1: Silver coupons were immersed in the hot solution of $CuCl_2$ 50 g/l (50-60 ^oC) for 20 min. The corrosion-patination layer developed gradually and the color changed to brownish purple. The samples were removed, washed in warm water and allowed to dry in air. An even corrosion layer consisting mainly of AgCl has been produced.
Accelerated corrosion procedure 2: The samples were immersed in cold (RT) BaS 5 g/l solution for 24 hours, producing a slightly uneven dark brown corrosion layer. On the sample surface it can be differentiated areas of the almost clean metal, the areas of silver rich and copper rich corrosion products. Apart from Ag_2S, on the sample surface, the presence of CuS as well as Ag_2O and Cu_2O cannot be excluded resulting by EDS analysis.
Accelerated corrosion procedure 3: The ingredients 20 g $CuSO_4 \times 5H_2O$ and 20 g $ZnCl_2$ were grinded to a thin creamy paste with a little water, using a pestle and mortar. The paste was applied sparingly to the sample using a soft brush. The surface darkened as the paste was applied. The residual paste was washed away after about an hour, and the sample was air dried. A thin even blue-green corrosion layer is formed. On the sample surface there can be differentiated areas of silver rich and copper rich corrosion products. Apart from AgCl and CuCl, on the sample surface the presence of Ag_2O and Cu_2O cannot also be excluded.

In Table 1 some SEM (secondary and back-scattered electron) images are shown as well as XRDs of silver coupons before and after an alkaline dithionite cleaning process. XRD analysis after this treatment reveals absence of corrosion products – XRDs are dominated only by the silver diffraction peaks. This is also confirmed by EDS analysis on the samples surface. On the back-scattered electron images two different areas can be observed; the gray one in which the black islands have been scattered. The black islands are areas richer in the copper content than the gray one.

Silver protection

Clean silver coupons were protected by polymeric acrylic resins paraloid B44 and B72 systems containing Al_2O_3 nanopowder as protective pigment. Silver coupons were tested by electrochemical methods in a corrosive 0.1 M Na_2SO_4 electrolyte. The linear polarization method was employed as well as the electrochemical impedance spectroscopy to check on the integrity and protectiveness of the coating. The linear polarization results show that alumina pigmented paraloid B72 protective system exhibits better corrosion resistance characteristics than the non-pigmented coating. At the initial condition (1 hour immersion in 0.1 M Na_2SO_4) alumina pigmented B44 protective system exhibits slightly better corrosion resistance properties than plain paraloid B44. However, with exposure time (up to 7 days) plain paraloid B44 offers better corrosion resistance than alumina pigmented B44. The B44 acrylic resin has denser network of cross-linking than B72, therefore, the addition of the pigment probably causes increased intrinsic stresses which makes the protective coating more susceptible to pore formation.

Table 1: SEM/EDS and XRD analysis of the silver coupons coming from the accelerated corrosion procedures (ACC 1-3) before and after alkaline dithionite cleaning

	SEM		XRD
ACC-1 Before cleaning	 SE image x5000		
After Cleaning	 SE image x4000	 BS image x4000	
ACC-2 Before cleaning	 SE image x1000	 BS image x1000	
After Cleaning	 SE image x2000	 BS image x2000	

In Figure 1 comparative EIS spectra as Bode plots are presented of the 10% alumina pigmented paraloid B72 after 1h (initial condition), 1 and 7 days immersion in 0.1 M Na_2SO_4 electrolyte. The impedance of the plain paraloid B72 as well as the impedance of both plain B44 and 10% alumina pigmented paraloid B44 protective systems decreases with immersion time. The impedance of 10% alumina pigmented paraloid B72 increases, as it is shown in Figure 1. This can be explained by a possible development of protective reaction products by the pigment with the electrolyte, that minimizes the film defects and increases pore resistance of the system.

Alumina pigmented paraloid B72 organic protective system is quite sufficient to protect the silver metal surface from the corrosive ions of the environment without compromising the aesthetic aspect of the metal / coating system.

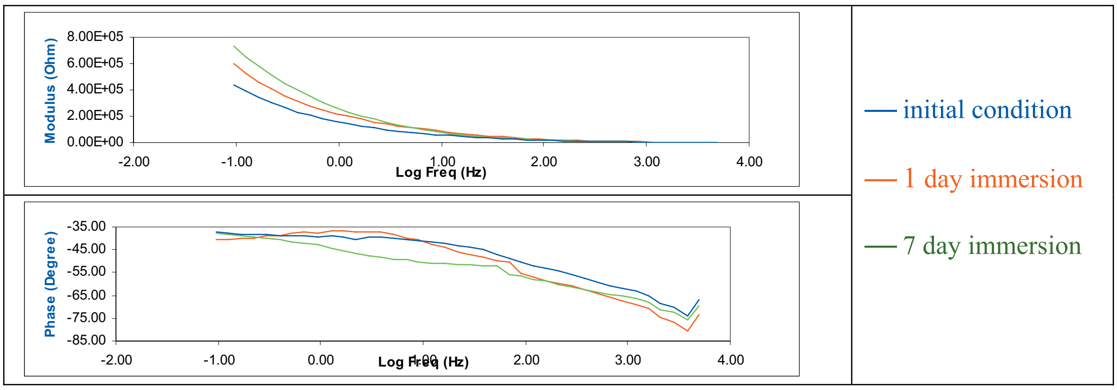


Figure 1. Comparative EIS spectra in Bode plots of 10% alumina pigmented paraloid B72 after 1h (initial condition), 1 day and 7days immersion in 0.1 M Na_2SO_4 electrolyte

European dimension

The protection of silver artefacts in the European museums is of primary importance since the sulphides that are in the atmosphere have a detrimental effect on the silver artefacts, tarnishing them and later when the attack continues the surface will irreversibly be altered. The existence of chlorides in the air in regions near the sea, also creates problems on the artefacts surface. Thus, the protection of the metal without changing the aesthetic aspect of the surface is of a major concern. Another application of the protective method can be also extended to electronics that use silver layers, which they are also affected by the same reasons as the artefacts.

Innovation and originality

The originality of this work is the employment of known polymer coatings: paraloid B72, -B44 well studied for the protection of metals by museum conservators as vehicle for a nano-particle Al_2O_3 pigment. The pigment enhances the protective ability of the acrylic vehicle by changing the polymer structure to a tighter one and probably prevents the silver ions diffusion to the solid/gas interface. The surface of the usually shiny coating also becomes more mat and pleasant to the eye.

Impacts

Several methods have been developed to reduce silver tarnish which include surface treatment and a coating. A number of commercial products are available, but none of these have been assessed conclusively. Any silver protection scheme that exhibits a marked resistance to tarnishing would find acceptance and a market. The protection of silver artefacts using a reversible process might have a potential use for electronics.

Reference

[1] R. Hughes and Michel Row, *The Colouring, Bronzing and Patination of Metals*, Thames and Hudson, London, 1982, pp. 318-332.

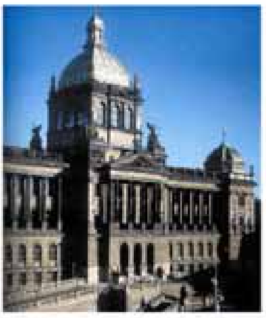
European project details

PROMET, Contract No. 509126, Developing new analytical techniques and material for monitoring and protecting metal artefacts from the Mediterranean region, Co-ordinator: Vasilike Argyropoulos, (T.E.I. of Athens), Ag. Spyridonos, Aigaleo – Greece 12210, E-mail: bessie@teiath.gr .

BRONZE ARCHEOLOGICAL OBJECTS IN NATIONAL MUSEUM OF PRAGUE – ENVIRONMENTAL MONITORING

Dagmar Knotkova[1], Kateřina Kreislova[1], Blanka Kreibichova[2], Ivan Kudlacek[3], Peter Korbel[3]

[1] SVUOM s.r.o. the Czech Republic
[2] National Museum, the Czech Republic
[3] CVUT Prague, the Czech Republic

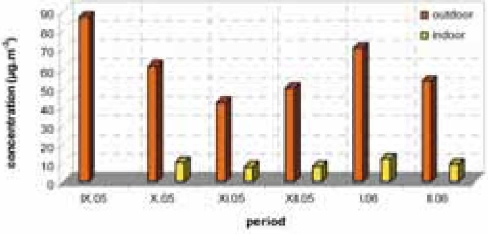


Introduction

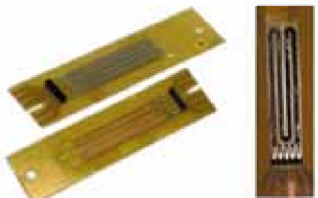
The collection of National Museum, Department of Prehistory and Protohistory, contains various copper and bronze artefacts of everyday life (vessels, spoons, tools, jewels, buttons, etc.) from Early Bronze Age to La Tène period (500 A.D.) The objects were treated repeatedly during museum exposure – in contemporary by microcrystalline wax or by Paraloid B72. The surface layers of corrosion products are very different: from fine dark layers of cuprite to volume green crust with non-uniform composition. Some of objects are covered by fine dark-green layers mixed and penetrated with conservation means.

Climatic and pollution measurement

City of Prague is one of the most polluted areas in CR. Annual arithmetic mean of SO_2 concentrations is around 10 µg.m^{-3}. The National Museum area is affected by linear sources of NO_x pollution - traffic. Instead of SO_2 this pollution is only partly reduced in buildings. Indoor concentrations of both pollutants are lower than outdoor concentration, but indoor atmospheres may be affected by non specific pollution. Temperature and relative humidity complex corresponds to low corrosive environments.
Indoor microclimates are mostly very specific and therefore the direct corrosivity derivation on standard specimens is preferred. Various methods of quantitative assessment of corrosion attack in low corrosive indoor climates were performed (mass loss of metallic standard specimens, resistance changes on copper and silver sensors, specific semi-quantitative method - linea of brightness cut).



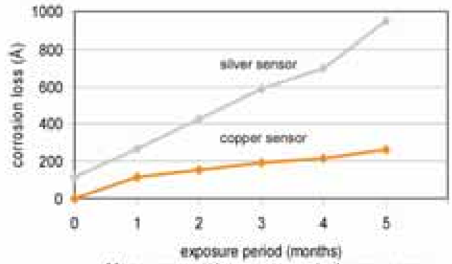
NO_x pollution measured in outdoor and indoor atmospheres



Copper and silver sensors

Corrosivity measurement by resistance sensors

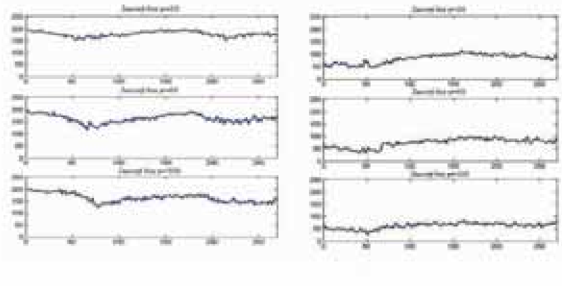
The copper and silver Rohrback sensors were placed in Depositary No 103. The sensor forms two sectors of electric circuit. The corrosion rate is measured as electric resistance changes for corroded (in direct contact with atmosphere) and protected coupon parts - *comparative method*. The results are expressed in thickness of corrosion product layer (1Å = 1.10^{-10} m). The corrosivity of Depositary is very low - degree G1 (according to ANSI/ISA S71.04) and category IC1 (according to ISO 11844-1). It can be expected the corrosion rate of copper will be r_{corr} ≤ 50 mg/m^2.a and corrosion rate of silver r_{corr} ≤ 170 mg/m^2.a.



Measurement by copper and silver sensors

Semi-quantitative measurement by brightness cut

It was elaborated specific semi-quantitative method of comparative corrosivity estimation based on computer analysis of image of corrosion attack of exposed copper and silver coupons. Comparison of optical effects in linie taken on the surface (linie of brightness cut) represents a good information on low corrosivity.



Examples of brightness cut for copper coupon
Non- exposed coupon exposed coupon

Conclusion

These methods were used for other storage rooms in National museum. The effect of position of exposition room in the large building without air condition is evident. The category of corrosivity was estimated as IC1 for typical museum depositary but IC3 for some of rooms in underground floor also used for storage of museum objects.
According to the corrosivity of microclimate the various effective protective means are necessary to apply or for the same protective mean the service life would be different.

European Project Details

MULTI-ASSESS, Contract No. EVK4-CT-2001-00044, Model for multi-pollutant impact and assessment of threshold levels for cultural heritage, V.Kucera, SCI Sweden
PROMET, Contract No. STReP-INCO-509126, Developing new analytical techniques and materials for monitoring and protecting metal artefacts from the Mediterranean region, V.Argyropoulos, TEI Greece

Bronze archaeological objects in National museum of Prague – environmental monitoring

K. Kreislová[1], D. Knotková[1], B. Kreibichová[2], Ivan Kudláček[3] and Peter Korbel[3]

[1]. SVUOM Ltd, the Czech Republic
[2]. National Museum, the Czech Republic
[3] ČVUT, the Czech Republic

Key words: museum exposures, indoor environment, monitoring, corrosivity estimation

Introduction

The Department of Prehistory and Protohistory of National Museum exhibits collection of antiquities and collection of ethnography and archaeology. At present it represents 500 000 items from prehistoric and early medieval Bohemia. The collection contains various metal artefacts (copper, bronze, iron, silver, gold) and many non metallic objects. Evaluated was collection contains copper and bronze artefacts from Early Bronze Age to La Tene period.

The aim of the work was to perform a modern environmental monitoring and estimation of the low indoor corrosivity of microclimates in agreement with international standards. Monitoring was realized in 6 typical indoor microclimates.

Climatic and pollution measurement

Monitoring of temperature and humidity was carried out at storage spaces and exposure rooms at different levels of building. Temperature and humidity were monitored by data loggers and evaluated for winter and summer season separately - Table 1.

Table 1: *Climatic parameters in various National Museum rooms measured in period 04/1999 - 05/2001*

Locality		Temperature		Relative humidity		
Floor	room	min.	max.	min	max.	average
II. cellar	2b	13,3	22,6	31	70	56
	2c	16,5	22,1	42	70	53
Ground floor	103	17,4	25,6	35	55	42
	104	16,1	26,5	32	59	47
III. floor	222	18,0	26,8	29	51	42
	276d	18,8	28,6	34	51	43

City of Prague is one of the most polluted areas in CR. Annual arithmetic mean of SO_2 concentrations is about $10 \mu g.m^{-3}$. The National Museum area is affected by linear sources of NOx pollution - traffic. Instead of SO_2 this pollution is only partly reduced in buildings. Indoor concentrations of both pollutants are lower than outdoor concentration (Figure 1), but indoor atmospheres may be affected by non specific pollution. Temperature and relative humidity complex corresponds to low corrosive environments.

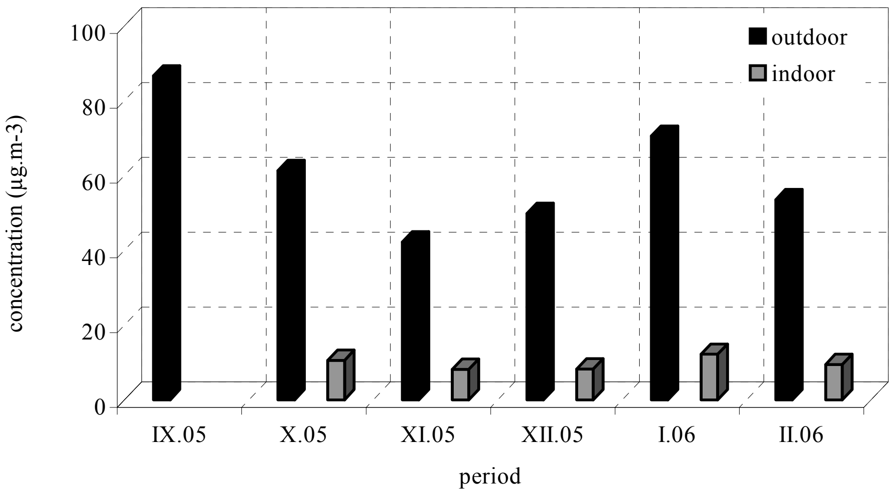


Figure 1: NO_x pollution measured in outdoor and indoor atmospheres

Corrosivity measurement by resistance sensor

Indoor microclimates are mostly very specific and therefore the direct corrosivity derivation on standard specimens is preferred. Various methods of quantitative assessment of corrosion attack in low corrosive indoor climates were performed (mass loss of metallic standard specimens, resistance changes on copper and silver sensors, specific semi-quantitative method – linie of brightness cut).

The copper and silver Rohrback sensors were placed in Depositary No 103. The sensor forms two sectors of electric circuit. The corrosion rate is measured as electric resistance changes for corroded (in direct contact with atmosphere) and protected coupon parts – *comparative method.* The results are expressed in thickness of corrosion product layer (1Å = 1.10^{-10} m). The corrosivity of Depositary is very low – degree G1 (according to ANSI/ISA S71.04) and category IC1 (according to ISO 11844-1) – Figure 2. It can be expected the corrosion rate of copper will be $r$corr ≤ 50 $mgm^{-2}.a^{-1}$ and corrosion rate of silver $r$corr ≤ 170 $mgm^{-2}.a^{-1}$.

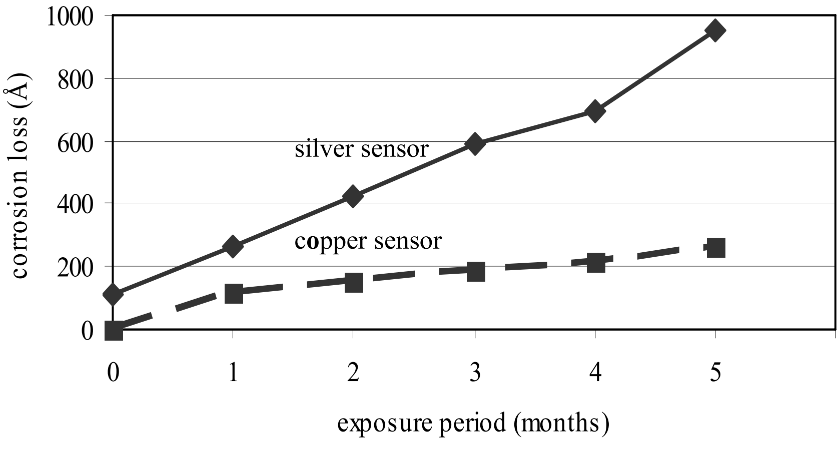
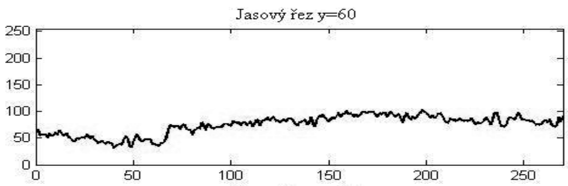


Figure 2: Measurement by copper and silver resistance sensors

Semiquantitative measurement by brightness cut

It was elaborated specific semi-quantitative method of comparative corrosivity estimation based on computer analysis of image of corrosion attack of exposed copper and silver coupons. Comparison of optical effects in linie taken on the surface (linie of brightness cut) represents good information on low corrosivity.



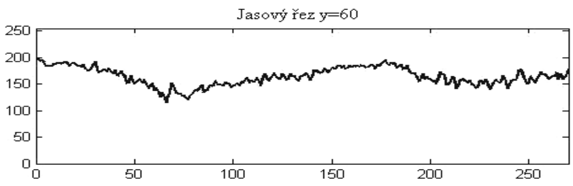


Figure 3: Example of brightness cut for non exposed and exposed copper coupons

Result of monitoring

These methods were used for different storage rooms in National museum. The effect of position of exposition room in the large building without air condition is evident. The category of corrosivity was estimated as IC1 for typical museum depositary but IC3 for some of rooms in underground floor also used for storage of museum objects.

According to the corrosivity of microclimate the various effective protective means are necessary to apply or for the same protective mean the service life would be different.

European dimension

Evaluation of corrosivity of indoor environments forms an important step in solving problems of risk in exposure for sensitive cultural heritage artefacts and choice of their conservation means.

Innovation and originality

Innovation of presented work lies in its complexity (monitoring of temperature-humidity complex and pollution components, measurement of direct corrosion effects) and in application of the new and word-wide accepted corrosivity classification standards for the corrosivity derivation and estimation.

Application of mathematical methods (computer analysis of picture of corroded surface) in relation to corrosivity evaluation represents an innovative aspect in approach for corrosivity estimation. Specific semi-quantitative method for comparative corrosivity estimation is based on computer analyse of picture of corrosion effects on copper and silver surface after one year of exposure.

Impacts

Indoor microclimates are mostly very specific and therefore a complex monitoring and standardized corrosivity determination and estimation brings valuable contribution applicable not only for museum monument care but also for sensitive equipment and museum artefact protection during storage and performance.

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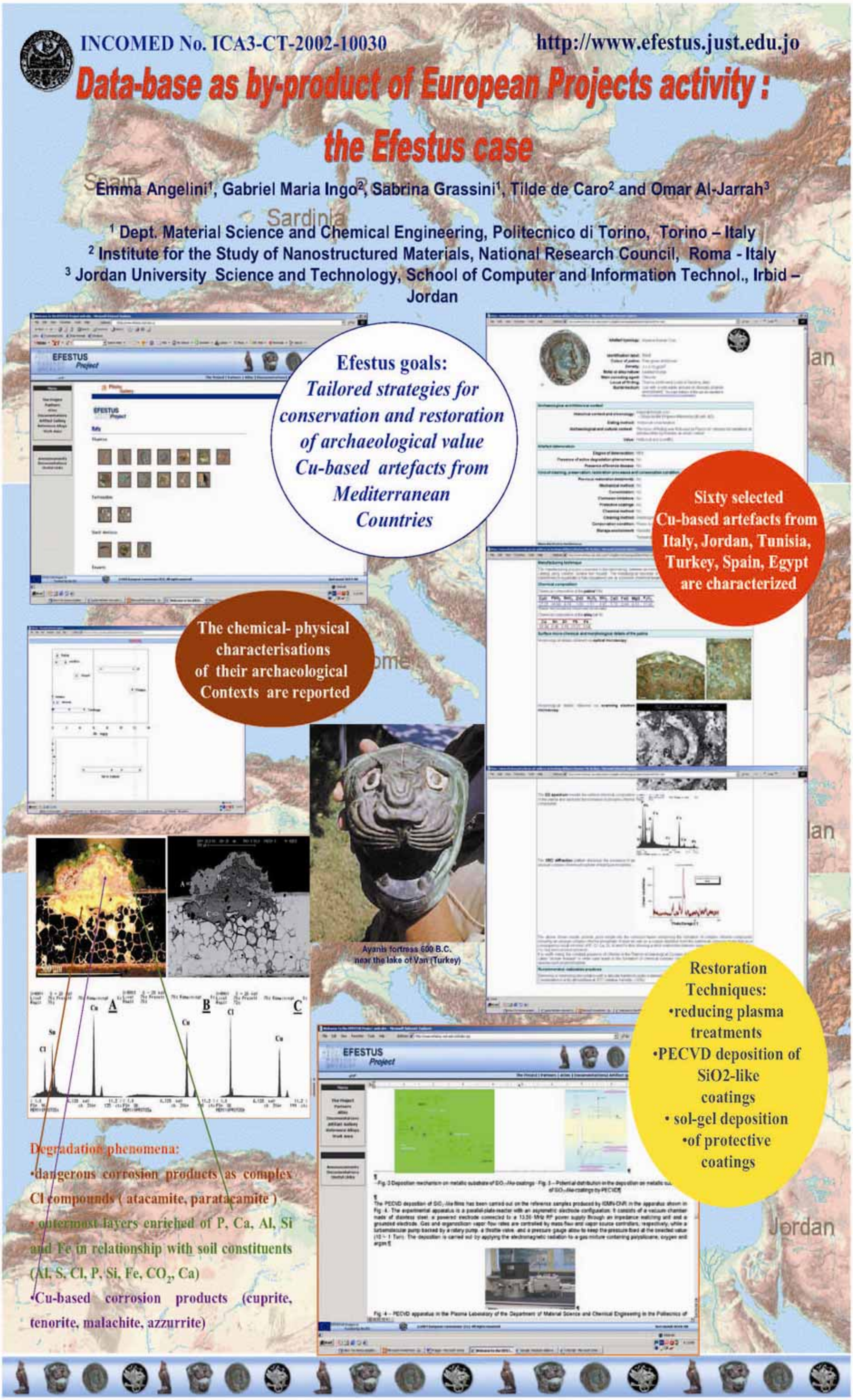
European project details

MULTI-ASSESS, Contract No. EVK4-CT-2001-00044, Model for multi-pollutant impact and assessment of threshold levels for cultural heritage, V. Kucera, SCI Sweden

PROMET, Contract No. STReP-INCO-2006- STReP-INCO-509126, Developing new analytical techniques and materials for monitoring and protecting metal artefacts from the Mediterranean region, V. Argyropoulos, TEI Greece


INCOMED No. ICA3-CT-2002-10030
http://www.efestus.just.edu.jo
Data-base as by-product of European Projects activity :
the Efestus case
Emma Angelini[1], Gabriel Maria Ingo[2], Sabrina Grassini[1], Tilde de Caro[2] and Omar Al-Jarrah[3]
[1] Dept. Material Science and Chemical Engineering, Politecnico di Torino, Torino – Italy
[2] Institute for the Study of Nanostructured Materials, National Research Council, Roma - Italy
[3] Jordan University Science and Technology, School of Computer and Information Technol., Irbid – Jordan
Efestus goals:
Tailored strategies for conservation and restoration of archaeological value Cu-based artefacts from Mediterranean Countries
Sixty selected Cu-based artefacts from Italy, Jordan, Tunisia, Turkey, Spain, Egypt are characterized
The chemical- physical characterisations of their archaeological Contexts are reported
Ayanis fortress 600 B.C. near the lake of Van (Turkey)
Restoration Techniques:
•reducing plasma treatments
•PECVD deposition of SiO2-like coatings
• sol-gel deposition •of protective coatings
Degradation phenomena:
•dangerous corrosion products as complex Cl compounds (atacamite, paratacamite)
• outermost layers enriched of P, Ca, Al, Si and Fe in relationship with soil constituents (Al, S, Cl, P, Si, Fe, CO2, Ca)
•Cu-based corrosion products (cuprite, tenorite, malachite, azzurrite)
EFESTUS Project

Data-base as by-product of European projects activity: the Efestus case

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Key words: copper-based alloys, corrosion, patina, data-base, SEM, XRD

Introduction and content

In the frame of the activities foreseen for the Efestus project financially supported by the European Commission, an interesting experience, the design and realization of a data base on the degradation and restoration of metallic artefacts, has been carried out.

The overall project is devoted to develop, validate and disseminate tailored approaches for stopping the degradation of copper-based ancient artefacts of the Mediterranean Basin and preventing further damage in Museum show boxes and deposits.

Because three European countries and seven South-Mediterranean countries are involved in the project, the number of artefacts selected as a function of the archaeological context and of the chemical composition and structure is quite large. The interesting correlations found between the different parameters evidenced the opportunity of organize all the experimental data in a data-base whose utilization will be as wider as possible.

An English-Arab web site (http://www.efestus.just.edu.jo) for the dissemination of results has been developed and all the partners have been involved in contributing to the production of the integrated information system designed to link all the characterization results, the degradation forms, the excavation context and the procedures for restoration of the artifacts, with further monitoring of the protective efficacy.

The data-base has been periodically implemented with the new results obtained by the various partners. The optimised restoration and conservation materials and procedures to be selected as a function of the different chemical composition and structure of the archaeological Cu-based artefacts as well as of the archaeological contexts are also indicated. The data-base is in continuous upgrading, also after the end of the project.

In one section more than sixty selected artefacts coming from Italy, Jordan, Tunisia, Turkey, Spain and Egypt are fully characterized with respect to: archaeological context, degree of deterioration, kind of cleaning, preservation, restoration processes and conservation condition, manufacturing technique, chemical composition [1], surface micro-chemical and morphological details of the *patina,* recommended restoration practices and materials [2]. Fig. 1 shows an example of the presentation of a Roman Coin.

In another section, the analytical data obtained from the chemical-physical characterisation of the Cu-based artefacts analized, also with portable instruments, in the different Mediterranean Countries and of the archaeological context are reported [3]. The results evidence the wide variation of the chemical composition and metallurgical features of the selected Cu-base artefacts and further, provide good insight into the nature of corrosion layers evidencing the formation of different structured degradation products characterised by various chemical composition and physical structure.

Concerning the degradation phenomena, the most dangerous corrosion products disclosed by the physical-chemical analysis are the complex chlorine compounds such as atacamite and paratacamite. It is worth noting that the presence of chlorine in the corrosion products of archaeological bronzes found in different contexts in Italy, Turkey, Jordan, Spain and Tunisia in some case induces the so called "bronze disease". In other case leads to the formation of chemical compounds that can be considered as stable species such as pyromorphite. This information is very useful because could give a good suggestion to stop the degradation phenomena as indicates that the dangerous presence of active chlorine species could be eliminated by transforming them in no-reactive species. The stabilisation is necessary for avoiding that the copper chlorides present at the interface between the outermost corrosion layers and the surviving metal is exposed and react with high relative humidity and oxygen. Indeed, these latter environmental factors induce the cyclic reaction that transforms copper chloride in paratacamite and therefore, the metal artefact in a green powdery mass whose appearance is considered as an evil by conservators. Indeed, CuCl is unstable in the presence of oxygen and moisture (high humidity) and undergoes a series of cyclic reactions leading to the rapid corrosion of the not corroded metal core. This reaction forms typical spots or patches of a light-pale green lose powder on the surface of the artefact inducing its destruction. Furthermore, the results have evidenced different corrosion behaviours with outermost layers enriched of P, Ca, Al, Si and Fe thus showing a strict relationship between some soil constituents (Al, S, Cl, P, Si, Fe, CO_2, Ca) and surface corrosion products. The other corrosion products are constituted by copper species such as cuprite, tenorite, malachite, azzurrite and different carbonates, oxides, phosphate, silicate as well as complex copper-iron sulphides.

Artefact typology:	**Imperial Roman Coin**
Identification label:	**M9-B**
Colour of *patina*:	**Pale green and brown**
Density:	**3 ± 0.15 g/cm^2**
Metal or alloy nature:	**Leaded bronze**
Main corroding agent:	**Chloride**
Locus of finding:	**Tharros (north-west coast of Sardinia, Italy)**
Burial medium:	**Soil with a noticeable amount of chlorides (marine environment). The main features of the soil are reported in the soil chemical and physical parameters**

Figure 1: Imperial Roman Coin coming fromTharros

European dimension
The Consortium is representative of the most important European and Mediterranean Countries for what concerns the ancient Cultural Heritage (Italy, Spain, Greece, Tunisia, Egypt, Algeria, Jordan and Turkey) and material science. Indeed, the expertise and the disciplines present in the involved Departments or Institutions includes archaeology, chemistry, physic, geology, computing and material science.

Innovation and originality
The aim of the effort of archaeologists and material scientists of the different Mediterranean Countries involved in this project had the was to develop tailored restoration and conservation

methods, anchored in local actions, for archaeological Cu-based artefacts selected for their historical and economical value such as coins, weapons and artistic objects. These artefacts are characterised by largely different conservation and restoration problems often tentatively solved by applying the same methodology and the same products independently of the local realities. The foreseen strategy is based on the acquisition of the knowledge of the relationship between the environmental conditions (soil nature, previous restoration and conservation treatments, external exposure, storage history, current environmental condition) and the chemical and physical properties of the artefacts, noticeable through the microchemical structure of the *patina* in order to select the best cleaning and restoration procedures via different methods.

Impacts

This project contributes to develop to the European policies regarding Cultural Heritage and its conservation, valorisation and fruition and to increase the competitiveness of the European conservation and restoration industries by creating new jobs in a wide area and by stimulating employment growth, encouraging transnationality, innovative procedures and bottom up approaches. These aspects have to be considered taking into account the possible extension of the results to all the other classes of ancient metallic objects.

The development of an integrated information system allowing communication, control and exchange of information within the partners and European and Mediterranean Museum and Conservation Institutions is of outstanding importance. As a matter of fact, in the Cultural heritage protection field, the European added value and the contribution to the implementation of the EU policies is expressed by validating the transferability of the conservation and restoration methods and materials developed in this project to other Countries.

Acknowledgement

The Authors acknowledge all the Partners of the Efestus project for their contribution: M. Genet of Consejo Superior de Investigaciones Scientificas – CSIC, Madrid – Spain; P.Vassiliou, National University of Athens, Greece; L. Bousselmi, Inst. National de Recherche Scientifique et Technique, Hamman, Lif, Tunisie, A. Cilingiroglu, Ege University, Dept. Protohistory and Near Eastern Archaeology, Bornova-Izmir, Turkey; Ziad Al Saad, Faculty of Archaeology and Anthropology, Yarmouk University, Irbid, Jordan; W. El-Saddik, Egyptian Museum, Cairo-Egypt; V. Gouda of National Research Centre, Cairo – Egypt.

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European project details

Acronym: EFESTUS, Contract No. INCOMED No. ICA3-CT-2002-10030, Title of the Project: "Tailored strategies for the conservation and restoration of archaeological value Cu-based artefacts from Mediterranean Countries", Co-ordinator: Gabriel Maria INGO, Affiliation: Institute for the Study of Nanostructured Materials, National Research Council, Roma, Italy.

Cahier des charges pour la qualification de produits de marquage applicables aux oeuvres d'art

Michel DUBUS Centre de recherche et de restauration des Musées de France et Marianne RAMAZ Laboratoire National de Métrologie et d'Essais

MERCI à Jean-Louis Boutaine et aux restaurateurs du C2RMF, aux observateurs et aux membres de la sous-commission marquage du Ministère de la Culture,
à Christophe Moulhera du Centre européen de recherche sur les textiles anciens (CERTA) à Max Billoré, Didier Bourdon, Jean-Pierre Kaminsky, Véronique Le Sant, Xavier Poisson et Jacques Weber du LNE

HISTORIQUE

20 août 1996 : création de la Commission de Récolement des Dépôts d'Oeuvres d'Art (CRDOA), présidée par Jean-Pierre Bady, Conseiller maître à la Cour des comptes
6 janvier 2000 : création de la sous-commission *Marquage* présidée par Jean-Pierre Mohen, directeur du département du patrimoine et des collections de l'Etablissement public du musée du Quai Branly, rapporteur Geneviève Ravaux.
Ses missions : identifier les œuvres par un marquage raisonné, définir une procédure d'agrément des systèmes de marquage des œuvres


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OBJECTIF

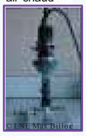
Disposer d'un marquage adapté aux oeuvres d'art sur la base d'un cahier des charges prenant en compte :

- les **propriétés** essentielles que doit présenter ce produit et résister aux agressions
- les diverses **agressions** que peuvent subir les marquages sur une oeuvre d'art

LES EXIGENCES
d'un produit de marquage

- ✓ Facilité d'application sur le support
- ✓ Lisibilité
- ✓ Innocuité vis à vis de l'oeuvre
- ✓ Durabilité
- ✓ Résistance aux tentatives d'effacement / falsification
- ✓ Réversibilité

LES METHODES D'EVALUATION

air chaud

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frottements


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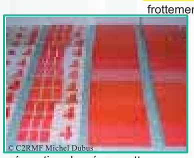
quadrillage


© C2RMF Michel Dubus
préparation des éprouvettes


© LNE Marianne Ramaz
abrasion

LES AGRESSIONS
climatiques

- ✓ Température
- ✓ Humidité relative
- ✓ Lumière naturelle derrière une vitre ou éclairage artificiel

tentatives d'effacement

- ✓ Usure, grattage, arrachage
- ✓ Agents chimiques
- ✓ Air chaud

PRESELECTION

toile / marbre / bois / laiton

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- Informations requises
  - pH / viscosité / solubilité / composition chimique / FDS
- Applicabilité
  - existence d'une notice d'utilisation
  - facilité d'application
  - pouvoir couvrant après un passage
  - temps de séchage
  - absence de bavures
- Lisibilité
  - panel d'observateurs
  - écarts colorimétriques
- Innocuité
  - test de corrosion accélérée
  - pénétrations dans le support


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Innocuité : coupe d'un marquage à la peinture acrylique rouge au dos d'une toile de lin encollée préparée. l'observation à la loupe binoculaire ne doit pas mettre en évidence de dégradation du support, ni de pénétration du produit dans le support

VIEILLISSEMENT


© LNE Max Billoré

Enceinte WEATHER-O-METER CI 4000 de type ATLAS équipée d'une lampe à arc au xénon

Conditions d'essai
valeur éclairement énergétique : E= 550 W/m²
pour 290 nm<λ<800nm
température panneau noir : 65°C ±3°C
température air ambiant : 38°C
humidité relative de (50±5)% à (65±5)%

- Programme de vieillissement par cycles de 24 heures
  - 20 heures d'exposition aux UV et HR<50%
  - 4h en obscurité et HR>65%
- Durée totale du vieillissement
  - 1000h maximum soit environ 42 jours
  - 42 cycles
- Paliers sélectifs
  - 240h (10 jours)
  - 500h (21 jours)
  - 1000h (42 jours)
- Mesures de lisibilité intermédiaires à chaque palier

SELECTION

Lisibilité
un marquage est lisible si l'écart colorimétrique calculé est inférieur à 15 et si la moyenne des notes attribuées par le panel d'observateurs est supérieure à 1.3


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Résistance aux solvants
un marquage est réversible si au moins, un des 6 solvants permet d'effacer le marquage sans dégrader le support


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Agressions mécaniques

Abrasion
un marquage est résistant à l'usure si le nombre de tours effectués par l'abrasimètre pour obtenir une apparition visible du support est supérieur à 80


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Quadrillage
un marquage résiste au quadrillage si moins de 15% de la partie écaillée par le quadrillage s'est détachée


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Frottements
un marquage est résistant si l'écart colorimétrique après 10 aller et retour est inférieur à 3


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Chaleur
un marquage ne présentant pas de dégradation sous l'action du décapeur thermique est considéré comme résistant


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CONCLUSIONS

Au total 764 éprouvettes ont été testées. Aucun produit de marquage ne répondant au cahier des charges pour tous les supports, une liste de couples certifiés a donc été établie. Un vade-mecum sera rédigé par la CRDOA en 2006. L'ensemble *liste de couples certifiés – vade-mecum - expertise scientifique du C2RMF* constituera un outil d'aide à la décision qui permettra aux professionnels chargés du marquage de choisir le produit le mieux adapté à une oeuvre ou un ensemble d'oeuvres dans un contexte donné.

Pour plus d'informations : **C2RMF conservation préventive,** Palais du Louvre, Porte des Lions, 14 quai François Mitterrand 75001 Paris michel.dubus@culture.gouv.fr

Specific requirements for qualification of cultural heritage artefacts marking

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Centre de Recherches et de Restauration des Musées de France (C2RMF), France
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This study was initially motivated in 1996 by the "Commission de récolement des dépôts d'œuvres d'art" which is chaired by Jean-Pierre Bady, Audit Office Judge. This Commission created in 2000, the Sous-Commission "Marking" chaired by Jean-René Gaborit, General Conservator, in charge of Sculptures Department at Louvre Museum and constituted of scientists and persons in charge of the Cultural Heritage security. On the initiative of the Sous-Commission, the LNE (a French national testing laboratory) with the C2RMF (the Research and restoration centre of French museums) assistance was assigned to perform a survey and qualifying tests on marking products. These studies were financed by the Department of research and Technology of the French Culture Ministry.

The aim of this study was to develop a discriminating qualification procedure based on laboratory tests to evaluate the relevancy of products available on the market. This study was done with the support of the French Ministry of Culture.

The process was motivated by 3 reasons:

- the *necessity* of marking catalogued artefacts for their identification, their management and their security
- the *increase* of the illicit trade of art objects requires secure markings for an efficient protection of these objects.
- the *need* of consistent information based on experimentation, concerning many marking systems available on the market.

Furthermore, more and more suppliers propose to Museum their marking products and services with attractive characteristics but without quality guaranty.

A protocol was designed to select the most suitable products depending on the substrates: metal, stone, canvas, wood. The study identified that the product had to *respect some essentials properties* and *resist to different aggressions* that cultural heritage may be confronted to.

Thus, the choice of the first tests of selection was done regarding the following criteria:

- the aptitude of the product to be applied on a substrate
- the resistance to obliteration or falsification attempts
- the marking readability
- the durability
- the harmlessness towards the substrate
- reversibility.

Then, the choice of the most suitable tests was done regarding the aggressions to simulate:

- aggressions from the environmental conditions as temperature, relative humidity and light

- aggressions regarding the obliteration attempts by abrasion, scraping, chemical agents, heat, striping
- and at least aggressions coming from restoration treatments with chemical agents.

The environmental tests (accelerated ageing tests) were performed in a climatic chamber in order to determine the simultaneous effects of the 3 parameters: temperature, relative humidity and UV. Interaction of the marking product within the substrate by the product penetration or diffusion in the substrate was also studied.

All together, 764 samples were tested and the results showed clearly that no universal ideal product was efficient on every material. Nevertheless, we have been able to select marking products for specific substrates using the requirements specification and the criteria defined during the study. A list of certified couples "*substrate-product*" was also constituted. In parallel, a vade-mecum was written in order to give some general information on the way to mark. Nowadays, professionals of the marking in France are in possession of three complementary elements to help them in their choice: the *list of certified couples – the vade-mecum – and C2RMF scientific skill.*

INNOVATIVE PROTECTION SYSTEMS FOR LARGE COLLECTION OF METAL ARTEFACTS CONSERVED IN THE MEDITERRANEAN BASIN - PROMET

Christian Degrigny[1], Vasilike Argyropoulos[2], Paraskevi Pouli[3], Maurice Grech[4], Katerina Kreislova[5], Mohamed Harith[6], François Mirambet[7], Andreas Karydas[8], Abeer Arafat[9], Ziad al Saad[10], Emma Angelini[11], Gabriel Ingo[12], Panayota Vassiliou[13], Emilio Cano[14], Najat Hajjaji[15], Ahmad Almansour[16] and Paola Letardi[17]

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2. The Department of Conservation of Antiquities & Works of Art, Technological Educational Institute of Athens (T.E.I. of Athens), Greece
3 Foundation for Research and Technology-Hellas (FORTH), Heraklion, Greece
4. Department of Metallurgy and Material Engineering – DMME - University of Malta, Malta
5. SVUOM Ltd. Czech Republic
6. National Institute of Laser Enhanced Sciences (NILES), Egypt
7. Laboratoire de Recherche des Monuments Historiques. France
8. Demokritos Institute, Greece
9. Royal Scientific Society, Jordan
10. Faculty of Archaeology and Anthropology, Yarmouk University. Jordan
11. Dipartimento di Scienza dei Materiali ed Ingegneria Chimica, Politecnico di Torino (POLITO), Italy
12. Consiglio Nazionale delle Ricerche, Istituto per lo Studio dei Materiali Nanostrutturati. Italy
13. National University of Athens, School of Chemical Engineering (NTUA – MS). Greece
14. Centro Nacional de Investigaciones Metalúrgicas (CSIC). Spain
15. IBN Tofail University, Faculty of Science, Department of chemistry, Laboratory SORE. Morocco
16. Faculty of Mechanical Engineering, The University of Aleppo. Syria
17. CNR-ISMAR-Sezione di Genova. Italy

Introduction

Archaeological and historic metal artefacts made of iron, copper and silver alloys from the Mediterranean are often found in museums in a poor state of conservation due to the uncontrolled environmental conditions (fluctuations of temperature and relative humidity, sea salts, rising damp), and are in urgent need of new conservation strategies. Under the auspices of the European 6th Framework priority INCO PROMET project, new innovative protection systems are being developed with the cooperation of 21 partners from 11 countries of the Mediterranean basin: Egypt, France, Greece, Italy, Jordan, Malta, Morocco, Spain, Syrian Arab Republic, Turkey and including the Czech Republic.

Most of the protection systems commonly used up to now in these countries have failed after a short time or are toxic. The lack of maintenance and/or inappropriate use of products might be the main reasons for the common failure of the corrosion inhibitors and/or coatings applied. Alternative ways to better protect metals collections are needed that are safer, more effective, reversible, and longer lasting.

European dimension

Mediterranean countries must actively participate in research to deal with their conservation problems and needs of metals collections. However, most Mediterranean and southern European countries spend their funds on research into 'hot' topics such as stone, marble, mosaics, or wall paintings due to the importance of reconstructing archaeological or historic sites for increased tourism. Thus, metal artefacts are often neglected, and great losses are incurred due to the instability of metal objects after excavation and/or storage in an uncontrolled environment. Considering the significance of the ancient and historic metals production in the Mediterranean region during Phoenician, Hellenistic, Roman or Islamic periods, its impact on European metals production is so great that losses of such cultural property must be prevented. Thus, one priority should be transnational and international cooperation for Europe and the Mediterranean region into research for the development protection systems of metal objects and creating synergy between the two for developing practical solutions.

Innovation and originality

The PROMET partners are working together on innovative protection systems such as safe corrosion inhibitors, corrosion inhibitor additives for varnish or wax coatings, and barrier films (Physical Vapour Deposition (PVD), Plasma Enhanced Chemical Vapour Deposition (PECVD) and Ion Beam Assisted Deposition (IBAD)).

The TEI of Athens began by conducting a market survey to test commercially available non-toxic corrosion inhibitor (CI) additives for synthetic waxes or varnishes not yet tested for conservation purposes as well as ready-to-use inhibiting coatings that are ecological, non-toxic, biodegradable for copper and iron alloys. The products were tested, and a selection of the top-rated ones was made according to ease to application, easy to dispose of, reversibility and aesthetic appearance. However, their long-term effectiveness remains to be determined by our research. Both TEI (Greece), LRMH (France), NILES (Egypt) and CSIC (Spain) will be involved in this testing and FORTH will determine the thickness of the coating with LIBS.

LRMH and IBN-DC are developing environmentally friendly inhibitors for the protection of iron and copper alloy metal objects. LRMH is focusing on inhibitors, composed of saturated linear carbon carboxylates of sodium of general formula $CH_3(CH_2)_{n-2}COONa$ noted NaCn, that are derived from fatty acids extracted from vegetable oil (colza, sunflower, and palm). The best anticorrosive performances have been obtained with solutions of sodium decanoate NaC_{10}. Addition of NaC_{10} solutions to an ASTM corrosive medium induces a drastic shift of the corrosion potential to higher values and a decrease of the corrosion current density (figure 1). Sodium decanoate acts as an anodic inhibitor and surface characterizations performed by Raman spectroscopy and XRD show that the inhibition effect is related to the formation of a layer of an iron or copper carboxylate on the metal surface. IBN-DC is focusing on azoles products that are tested electrochemically on copper based alloys in solution simulating acid rain and containing chlorides but cactus extracts as well. As regards iron alloys the same compounds are considered as well as surfactants such as betaines. The behaviour of bronze alloys in 3-phenyl-1,2,3-triazole-5-thione (PTS) is shown on figure 2 (96% efficiency of protection at a concentration of 10^{-3}M).

Low pressure plasmas developed by POLITO-SMIC and DMME are particularly interesting processes because of their own characteristics: low temperature processes -no bulk alterations, adaptable to any shape and material substrate, high versatility and low environmental impact. Moreover, plasma treatments can remove surface contaminants and lead to a surface chemical modification (removal of tarnish from Ag based alloy with H_2-plasma). PECVD SiO_x barrier layers on Ag-based reference alloys with H_2-plasma have been tested successfully by POLITO-SMIC and assessed using Electrochemical Impedance Spectroscopy (figure 3) [1]. After testing SiO_x coatings on steel DMME is now moving to TiO_x coatings and application of IBAD.

These protection systems are being tested electrochemically and through accelerated corrosion tests on artificially and naturally aged metal coupons that simulate the behaviour of real artefacts. Finally, the more efficient products will be tested on a selection of artefacts specifically subjected to the environmental conditions of the Mediterranean Basin.

Impact

The strategic impact of our research will provide a foundation to develop a maintenance policy for protecting and monitoring indoor metals collections from the Mediterranean region. The developing new and safe protection systems deals with one aspect of our target, and will offer alternative choices to conservation-restoration professionals for using effective products to stabilize and protect metal artefacts that are safe to use and to dispose of.

Practises developed within the project will be further discussed within international organisation such as the Metal WG of ICOM-CC (International Council of Museum – Conservation Committee).

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European Project Details

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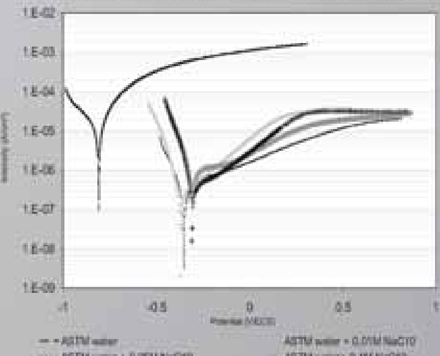

Figure 1: Potentiodynamic curves of iron after 8h of immersion in desaerated solutions

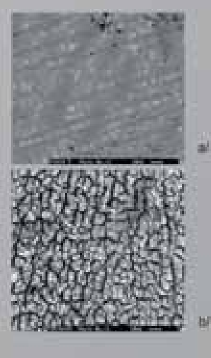

Figure 2: Appearance of a bronze surface in 3% NaCl with (a) and without (b) PTS

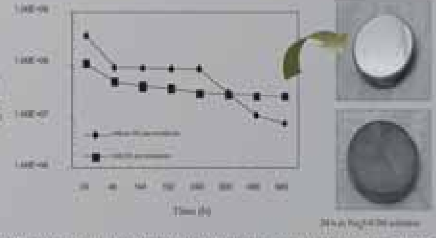

Figure 3: Electrochemical Impedance Spectroscopy measurements in 0.1M Na_2S solution showing the long term effectiveness of the SiO_x film deposited after H_2-plasma treatment

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Key words: protection systems, metals collections, museum, Mediterranean region

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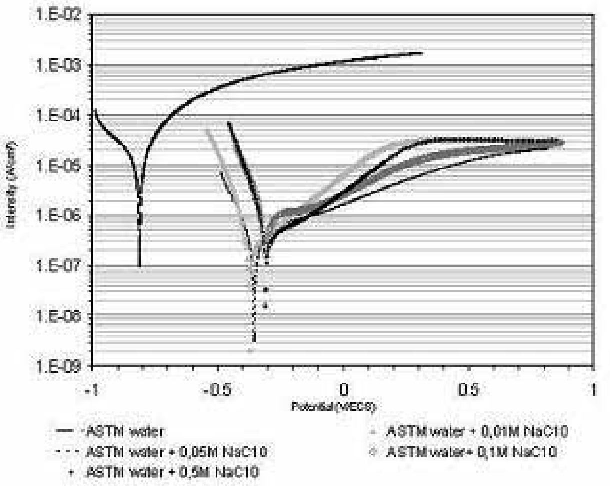

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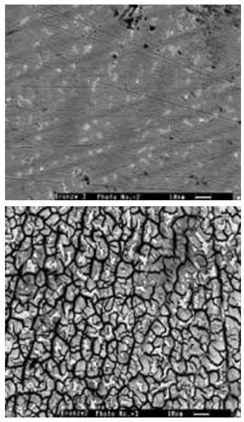

a/

b/

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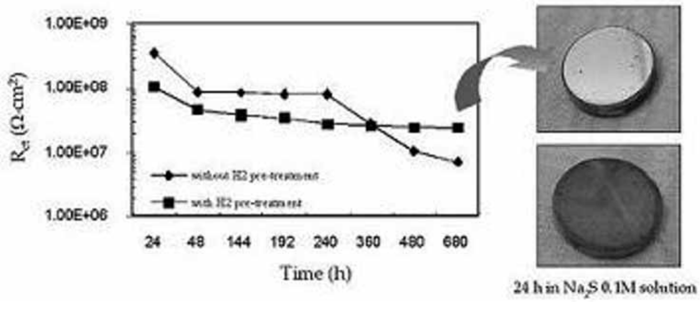

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DEVELOPMENT AND EVALUATION OF NEW TREATMENTS FOR THE CONSERVATION RESTORATION OF OUTDOOR STONE AND BRONZE MONUMENTS – JRA1

S.Bracci[1], B.Doherty[6], E.Joseph[5], M.Mach[2], M.Matteini[1], R. Mazzeo[5], C. Miliani[6], C.P.Nunes[3], D.Pinna[4], A.F.Pinto[3a], S. Porcinai[4], J.D.Rodrigues[3], B.Sacchi[1], M. Salta[3], B.Salvadori[4]

1 - Istituto per la Conservazione e la Valorizzazione dei Beni Culturali, ICVBC-CNR, Florence-Italy;
2 - Bayerisches Landesamt für Denkmalpflege, BLFD, Munich-Germany;
3 - Laboratório Nacional de Engenharia Civil, LNEC, Lisbon-Portugal – 3a : ICIST/IST;
4 - Opificio delle Pietre Dure, OPD, Florence-Italy;
5 - Università degli Studi di Bologna, Laboratorio di Microscopia TECORE, Bologna-Italy;
6 - Università degli Studi di Perugia, Centro di Eccellenza SMAArt, Dip. di Chimica, Perugia-Italy;

JRA1 objective – to Investigate new treatments based on inorganic materials defining detailed properties, advantages and limits of new conservative treatments for outdoor stone and bronze monuments, comparing new and traditional methods and encouraging their use, based on clear scientific and ethical criteria

Treatments and artifacts under study

- consolidant and protective treatments: marble, limestones and sandstones
- corrosion inhibitors and protective treatments: bronze

Topics of research

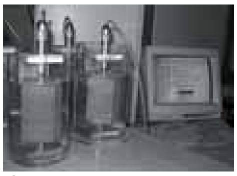
- study of the action mechanisms of treatment
- identification of the best conditions for application
- comparison of the developed treatments with the most commonly used formulation and treatments, with particular attention to the efficacy, compatibility and impact on colour
- study of the behaviour of the treatments towards simulated severe ageing conditions
- test of the experiments treatments *in situ*, on ancient outdoor materials

Stone — Main tasks done and in progress — Bronze

Materials characterisation

Stone

- Limestones
  - Lecce stone - Italian calcitic limestone
  - Ança stone - Portuguese calcitic limestone
- Marble
  - Gioia Marble - Italian
- Sandstones
  - Firenzuola - fine grained, high clay content
  - Santafiora – medium grained, low clay content



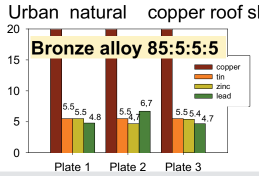
Swelling strain experiment

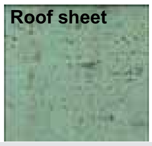
Physical, mechanical and chemical characterisation: petrographic, porosity, pore size distribution, swelling, water absorption, drilling resistance, colorimetric analysis, etc.

Bronze

Four types of bronze test substrates:

- Marine natural — cast bronze G-CuSn5Zn5Pb5 — marine exposure site
- Marine artificial — cast bronze G-CuSn5Zn5Pb5 — weathering chamber (chloride)
- Urban artifical — cast bronze G-CuSn5Zn5Pb5 — *Pichler process* patination
- Urban natural — copper roof sheet — natural patination, 80 years

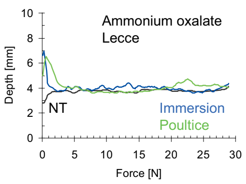




Development of new treatments and procedures

Stone

- Consolidating treatments, types and procedures:
  - Barium hydroxide - immersion and poultices
  - Ammonium oxalate - immersion and poultices
  - Modified ethylsilicate - brushing and immersion
  - Ethylsilicate - brushing and immersion
- Protective treatments:
  - Dimethylpolysiloxane - brushing
  - Barium hydroxide - poultices
  - Ammonium oxalate - poultices

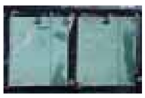


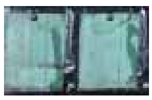
Treatment performance evaluation: strength increase, depth of penetration, colour changes, water absorption reduction

Bronze

Types of treatment and procedures, supported by inhibitors:

- Dynasilan treatments (two products)
- Protectosil (various recipees)
- VP 5035
- Various microcrystalline waxes
- Oxalate treatment by chemical deposition
- Oxalate treatment by biological deposition
- Thermal precipitation of cuprite out of complex copper solution (aqueous system)
- Thermal precipitation of cuprite out of complex copper solution (organic system)





Evaluation of some treatments water's repellence After 3months exposure

Accelerated ageing tests

Stone

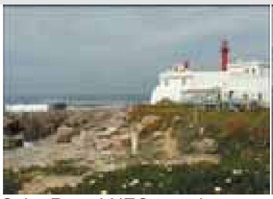
Objective: to find a suitable and quick way of producing artificially decayed stones

Ageing mechanisms tested:

- Salt crystallisation on limestones and sandstones
  - study of two degradation patterns to promote:
    - superficial degradation
    - in depth gradual degradation
- Thermal shock tested on the marble

Ançã aged by salts

Bronze



Cabo Raso LNEC test site

LNEC test chamber

The LNEC weathering procedure:

Phase 1: 3 months at 50°C, RH > 95 %

Phase 2: 6 months in salt spray chamber (5% NaCl, 38 °C)

EU-ARTECH *(www.eu-artech.org)*

Access **R**esearch and **T**echnology for the conservation of the **E**uropean **C**ultural **H**eritage, Contract No. RII3-CT-2004-506171, **2004-2009**

Co-ordinator: Brunetto Giovanni Brunetti, Uni-PG, Centro SMAArt, PG-Italy

Development and evaluation of new treatments for the conservation restoration of outdoor stone and bronze monuments

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Key words: stone, bronze, inorganic treatments, consolidation, protection, artificial ageing, durability

Introduction and content

Joint Research Activity 1 (JRA1) is one of the two Joint Research Activities in the framework of the EU funded I3 Project EU-ARTECH (Access Research and Technology for the Conservation of the European Cultural Heritage). The EU-ARTECH project consists of a consortium of twelve internationally distinguished European institutions in the field of conservation of Cultural Heritage, developing together networking activities, transnational access, and joint research activities (for details: www.eu-artech.org). The objective of the project is to work towards a permanent interoperability between the participating institutions, establishing cooperation and exchange of knowledge with other infrastructures in the field. The project, started in 2004 will last five years.

Within EU-ARTECH, JRA1 is coordinated by CNR-ICVBC and involves six institutions with the objective of developing new treatments for the conservation / restoration of outdoor stone and bronze monuments. The new treatments, based on innovative products and/or procedures, are developed, tested, and compared with other methods. The activity is devoted to compare the use of inorganic and organic materials defining detailed properties of the new inorganic applications, in the perspective of better definition of “good conservation practices” and improve knowledge on materials and methods in conservation. The developed treatments are evaluated and compared with those commonly applied today in Europe.

The JRA1 is also strictly interconnected to the other activities of the EU-ARTECH project.

European dimension

This research is undertaken in response to the pressing need, as voiced by art conservators, for new coatings and active corrosion inhibition strategies to protect outdoor monuments from polluted environments. Exposure to aggressive environments, particularly acid rain and ambient chloride salts, subject stone and bronze to chemical / electrochemical instability, usually resulting in disfiguring changes in appearance. *The various institutions already interact within the framework of common funded projects, through networks or bilateral cooperation agreements that have led to technological advances in conservation techniques over the past few decades. The community’s efforts and commitments were, however, focused primarily on verifying the validity of existing solutions rather than experimenting new methods. Therefore, there is a true need to develop and test new solutions andr to ascertain how the innovative approaches are successful on certain categories of artworks or monuments.*

Innovation and originality

There are two main approaches to face the problems of consolidation and protection of stone and metal artifacts, one is the use of organic materials, the other is the use of inorganic treatments. Both have intrinsic advantages and drawbacks mainly related to their specific nature. Also, the effectiveness of the treatments significantly depends on the material to be treated and the environmental context. The main drawbacks are evidenced in those particular situations where three conditions are associated: porous stone materials, presence of soluble salts and fluxes of liquid water and moisture. These can be also the cases of metal patinas that present a porous microstructure accessible to water and salt solutions. Joint research activity 1 (JRA1) offers the objective to clarify and define advantages and limits of new conservative treatments on outdoor monuments, comparing new and traditional methods and encouraging their use, based on clear scientific and ethical criteria (i.e. choice of methods and materials only after a careful scientific studies of the state of conservation of the artworks, using a non-invasive approach, in the full respect of their aesthetical and historical value).

Impacts

All the JRA1 partner infrastructures are institutionally involved in the conservation and study of artworks and monuments in each country. Some of them are scientific infrastructures directly interfaced to relevant European museums; some have responsibility at a national level of the safeguard and conservation of Cultural Heritage, mainly outdoor patrimony; some others are public research centres for scientific and technological studies in the field of methods and materials for the conservation of art and architectural objects. This will ensure not only the quality and reliability of the coordinated activities, but also an easy and appropriate dissemination of knowledge. In the JRA1 implementation plan the last year it is foreseen as *in-situ* demostration activity for the validation of the results of the research. For appropriate dissemination, organizations devoted to safeguards, conservation and valorization of Cultural Heritage will be involved in the final phase of the treatment set-up and all the results will be disseminated in international symposia and conferences to *restorers and to SMEs specialized in monuments restoration and maintainance at European level.*

European project details

EU-ARTECH (www.eu-artech.org)
Access Research and Technology for the conservation of the European Cultural Heritage Contract No. RII3-CT-2004-506171, 2004-2009.
Co-ordinator: Brunetto Giovanni Brunetti, Università di Perugia, Centro SMAArt, Dipartimento di Chimica, Italy.

A CONSERVATION STRATEGY FOR DOCUMENTING THE CORROSION OF OUTDOOR BRONZE MONUMENTS IN GREECE

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AIM OF THE STUDY

This poster presents the scientific research carried out on two outdoor bronze monuments, which were cast from the same model and foundry, but for the past 100 years are exposed in two very different environments in Greece. One of them is located in Athens, erected in 1904 in one of the busiest and polluted streets in the city. In the other case, it was erected in 1900 in Nafplio, a small city (150 km from Athens) only 100 m from the seaside. The aim of the study was to compare between the corrosion types found on the two monuments and correlate the observed differences to the specific exposure environments.

The monument of Theodoros Kolokotronis: Nafplio

?

Both statues were cast in parts, which were probably assembled in-*situ,* based on our inspection of the arms and feet of Kolokotronis and research into the correspondence of their sculptor (L. Sochos). Our inspection in Nafplio suggests that there are 4 parts: the head and neck of horse, upper part of Kolokotronis' body with the helmet, lower part of Kolokotronis' body together with the body and the legs of the horse and the metal base, and tail of horse and left foot of horse. In Athens, our inspection found the same 4 parts with the exception that the helmet was separately joined to the body of Kolokotronis. Obviously, the helmet was something that Sochos made as a separate piece for Athens, with the option to add and/or remove the helmet.

XRF RESULTS

The first survey of the bronze monument Theodoros Kolokotronis in Athens in 2001, using the X-ray fluorescence technique was conducted by means of a portable radioisotope – based X-ray fluorescence spectrometer. The analyses of the second monument, located in Nafplio in 2005 were conducted by means of an improved instrument based on X-ray tube excitation. The concentrations of the alloy elements in Nafplio are presented in the following Table in comparison to the Athens outdoor monument.

	XRF results Concentrations (%)	
Element	Athens	Nafplio
Fe	-	0.32 ± 0.02
Cu	91.2	90.9 ± 0.2
Zn	3.2	4.7 ± 0.1
As	Add %error -	0.15 ± 0.03
Pb	< 0.7	0.27 ± 0.02
Sn	5.6	3.6 ± 0.1

XRD RESULTS

For X-Ray diffraction, 11 and 31 samples of corrosion were taken from various locations on the bronze sculpture before treatment from Athens and Nafplio respectively and were analysed using XRD. For Athens, all 11 samples were found to contain major amounts of gypsum, and/or combinations with calcite and quartz. However, only in one sample did we find bronchantite CuSO4·3Cu(OH)2, tin oxide, and atacamite Cu2(OH)3Cl. For Nafplio, the samples that contained major amounts of gypsum were found to contain additionally minor amounts of atacamite and quartz. The samples that contained major or minor amounts bronchantite (19 occurences) also contained quartz and/or magnesium calcite, in most cases atacamite, and in some cases antlerite.

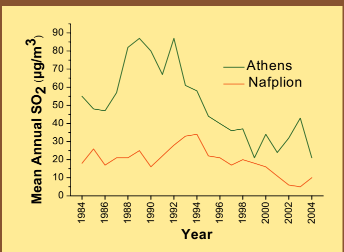
DISCUSSION

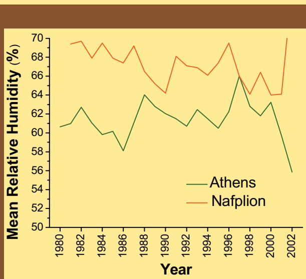
Based on the environmental findings, we can explain the corrosion types observed in the two monuments by two critical factor: in the case of Athens is the presence of gaseous air-pollutants while in the case of Nafplio, the high values of RH and chloride concentration in the salt aerosols.

During our documentation, we observed pits in the monument at Nafplion in the black patina areas, which were not apparent in Athens (see photo 1). The original surface was observed for both monuments in locations that are sheltered from the rain. It was common for sculptor's of this period to artificially patinate with sulphur of liver the bronze monument to give a shiny black appearance. Furthermore, the XRF analyses in Nafplion found that both on the black patina and green areas the presence of Cl. This was confirmed by the XRD analyses where atacamite was present in the green areas and black crust. In Nafplio we have 23 occurrences of atacamite as opposed to Athens, wherewe have only 2 ocurrences.

EXPOSURE ENVIRONMENTS

The main characteristic of the urban atmosphere in Athens is the high SO2 and NOx concentrations. As for the precipitation, it is highly acidic (50% of the rain shows pH values around 4.5). The statue located at Nafplio, is exposed to a marine atmosphere where sea-salt aerosols are abundant. The high RH values combined with the presence of NaCl result in a highly corrosive environment. The Mean Annual Precipitation is practically the same in both sites (around 400 mm per year).





CONCLUSIONS

Our scientific approach to identify the materials that constitute of the monuments tried to apply the same method for documentation and diagnostic testing for both monuments. Furthermore, the work and analyses was carried out in-*situ* and was based on non-destructive methods. The methodological approach applied to our research allows for comparative studies and the exchange of information for outdoor bronze monuments.

A conservation strategy for documenting the corrosion of outdoor bronze monuments in Greece

Vasilike Argyropoulos[1], Dimitrios Charalambous[1], Aggeliki Vossou Domi[1], Maria Giannoulaki[1], Thanasis Karabotsos[1], Kyriaki Polikreti[1], Amalia Siatou[1], Eleni Drakaki[2], Ioannis Sianoudis[2], Andreas G. Karydas[3], Charalambos Zarkadas[3] and Vasilis Perdikatsis[4]

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Keywords: outdoor bronze monuments, Greece, salt aerosols, maintenance, XRF analysis

Introduction and content

The study of the two outdoor bronze monuments, Theodoros Kolokotronis, presents a unique opportunity to enforce the conservation standard that prior to treatment, all cultural property must undergo proper documentation and diagnostic analyses, since the type of deterioration and thus treatment depends on their exposure environment. These two monuments were cast from the same model and foundry, but for the past 100 years are in two very different locations and thus exposure environments in Greece. In one case, it is located in Athens, erected in 1904 in one of the busiest and polluted streets in the city. In the other case, it is located in Nafplio, erected in 1900 in a small city (150 km from Athens) only 100 m from the seaside. The Theodoros Kolokotronis monument was created by the sculptor Lazaros Sochos, and depicts the beloved war hero from the Greek War of Independence in 1821, riding his horse, while pointing his way to victory. The first statue in Nafplio was cast in 1896 at the foundry of Thiebaut brothers in Paris. The second statue in Athens was cast in 1900 at the same foundry, but under the supervision of L. Gasne (successor of Thiebaut brothers). Inscriptions were found on the statues confirming the above details. Surprisingly, during our work in Athens in 2001, an inscription was found on the backside of the helmet's lambrequin of the second statue, with a quote from Sochos stating his objection to place the characteristic helmet on Kolokotronis. No such inscription was found on the first statue in Nafplio during our work in 2005. Both statues were cast in parts, which were probably assembled in-*situ.* Our inspection in Nafplio suggests that there are 5 parts: the head and neck of horse (up to the middle of the chest), upper part of Kolokotronis' body *with the helmet*, lower part of Kolokotronis' body together with the body and the legs of the horse and the metal base, tail of horse and left foot of horse. In Athens, our inspection also found the same 5 parts with the exception that the left foot of the horse did not comprise a separate part (the helmet did) and the helmet was separately joined to the head of Kolokotronis. Obviously, the helmet was something that Sochos made as a separate piece for Athens, with the option to add and/or remove it. The main characteristic of the urban atmosphere to which the statue is exposed in Athens is the high SO_2 and NO_x concentrations [1] (see Fig. 1). As for the precipitation in Athens, it is highly acidic (more than 50% of a rain sample-set is expected to show pH values between 4 and 5). Fortunately, the pollutants' concentrations and resulting rain acidity seem to decrease rapidly after 1992. The statue located at Nafplio is exposed to a marine atmosphere where sea-salt aerosols are abundant. The high RH values [2] (See Fig. 2) combined with the presence of NaCl result in a highly corrosive environment. The Mean Annual Precipitation is practically the same in both sites (around 400 mm per year) [2]. The first X-ray fluorescence survey of the bronze monument Theodoros Kolokotronis in Athens was conducted in 2001 by means of a portable radioisotope – based X-ray fluorescence spectrometer [1]. Due to the restricted analytical capabilities of that instrument the identification of the corrosion products consisting mainly of low Z ($Z<19$) elements was not possible. A total of 18 areas, including clean metal surfaces as well as areas with patina in place were non-destructively analyzed.

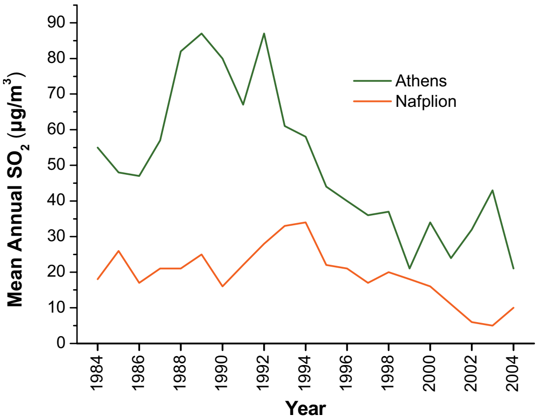

Figure 1: Mean Annual SO_2 concentrations

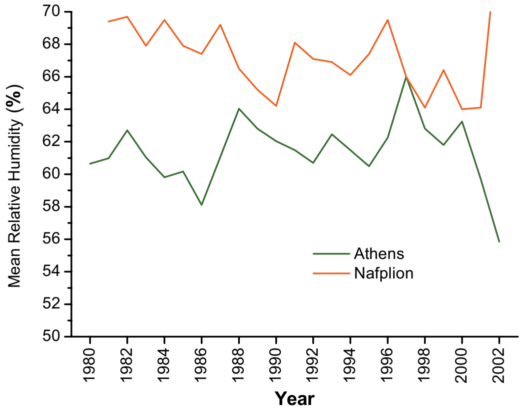

Figure 2: Mean Relative Humidity

The analyses of the second monument, located in Nafplio, were conducted in 2005 by means of an improved instrument based on X-ray tube excitation. A total of 5 different locations were analyzed utilizing two exciting modes with respect to the tube voltage and the use of filtering materials. Areas with corrosion products were measured at an operational tube voltage of 15 kV without any absorbers in the exciting X-ray beam path. At this favourable condition, characteristic S and Cl X-ray peaks could be identified, if present at least in minor amounts. For the determination of the composition of the bronze alloy, the 40 kV filtered excitation condition was employed. The concentrations of the alloy elements determined by the measurements performed in Nafplio are presented in Table 1 in comparison to the corresponding ones obtained from the outdoor monument of Athens.

Table 1: Elemental concentrations (%) determined from the cleaned areas measurements performed at the two outdoor – monuments in Athens and Nafplio, respectively

Element	Athens-monument (mean values of 4 monuments)	Nafplio-monument (left hand)
Fe	-	0.32 ± 0.02
Cu	90.3 ± 0.7	90.9 ± 0.2
Zn	4.1 ± 0.9	4.7 ± 0.1
As		0.15 ± 0.03
Pb	< 0.7	0.27 ± 0.02
Sn	5.6 ± 0.5	3.6 ± 0.1

For X-Ray diffraction, a total of around 60 samples of corrosion products were taken from various locations on the bronze sculptures before treatment from both Athens and Nafplio, and were analysed using XRD (Siemens D500), and they were identified using the software Diffrac Plus from Bruker company and the Powder Diffraction File JCPDS. The quantitative analysis was carried out by the Rietveld Method. For Athens, all of the 11 samples were found to contain major amounts of gypsum, and/or combinations with calcite and quartz, 5 samples had bronchantite $CuSO_4{\cdot}3Cu(OH)_2$, but only in one case was it a major amount. Surprisingly, 3 samples from Athens were found to contain atacamite $Cu_2(OH)_3Cl$. For Nafplio, 31 samples had enough material, but the compositions were different from Athens. The samples that contained major amounts of gypsum were found to contain additionally minor amounts of atacamite and quartz. The samples that contained major or minor amounts of bronchantite (19 occurences) also contained quartz and/or calcite, in most cases atacamite, and in some cases antlerite $Cu_3SO_4(OH)_4$. In total, atacamite was found in 23 samples, while antlerite in 4 samples. Based on the environmental findings, we expect that the critical corrosion factor in the case of

Athens is the presence of gaseous air-pollutants, while in the case of Nafplio, the high values of RH and chloride concentration in the salt aerosols. During our documentation, we observed pits in the monument at Nafplio in the black patina areas, which were not apparent in Athens. The black patina or original surface was observed for both monuments in locations that are sheltered from the rain. It was common for sculptors of this period to artificially patinate the bronze monument with sulphur of liver, to give a shiny black appearance. Furthermore, the XRF analyses in Nafplio found the presence of Cl both on the black patina and green areas. This was confirmed by the XRD analyses where atacamite was present in the green areas and black crust.
Our results are typical for such exposures, which can range from a change of the external layer of the patina to copper sulfates, formation of streaking and run-offs from the more soluble sulfates, the formation of black crusts where particulate matter accumulates and water does not wash the surface (e.g. crevices) to pitting corrosion in and around the black crusts from the presence of chlorides [4]. Furthermore, atacamite is commonly found on monuments from marine and inland areas [5], as is that case in Nafplio (23 occurrences in different samples) as opposed to Athens (3 occurrences). Thus, the presence of Cl or atacamite is abundant in Nafplio and can be attributed to the presence of salt aerosols as opposed to Athens where pitting corrosion and atacamite was not respectively observed and as abundant. However, downtown Athens is approximately 8 km from the sea, where breaking waves do occur, and atacamite on the Athens' monument may have occurred to the presence of salt aerosols.

European dimension, innovation and impact

European research into suitable coatings for outdoor bronze monuments has been a popular topic using metal coupons. However, systematic research into the study of real outdoor bronze monuments and how their condition varies across Europe has not been as favored. The type of coatings used to protect outdoor bronze monuments should depend on the environmental conditions. Our scientific approach to identify the materials that constitute the monuments tried to apply the same method for documentation and diagnostic testing for both monuments within a 5-year period. Furthermore, the work and analyses was carried out (as much as possible) in-*situ* and using non-destructive methods. The methodological approach applied to our research allows for comparative studies and the exchange of information for outdoor bronze monuments and is now routinely applied to document the condition of outdoor bronze monuments throughout Greece for their maintenance (Municipalities of Athens, and Nea Smyrni).

Acknowledgement

We gratefully acknowledge the support from the Municipalities of Athens and Nafplio.

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European project details

Athens: CLT2000/A1/GR-283, Protect our outdoor European Bronze Monuments, V. Leontari, Mun. of Athens Development Agency, Nafplio: co-funded by the European Social Fund and National Resources – (EPEAEK II) ARXIMHDHS, "Environmental consequences and protection of outdoor bronze monuments in Greece".

THE SURVEY APPROACH OF MUSEUM COLLECTIONS: A PRIORI STEP IN THE SUSTAINABLE CONSERVATION FOR METAL OBJECTS FROM THE MEDITERRANEAN BASIN-PROMET

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INTRODUCTION AND CONTENT

PROMET is a three-year European 6th Framework funded project, priority INCO, which began in November 2004 with 21 partners from 11 countries of the Mediterranean basin. The main goal of the project is ensuring the survival of metals collections housed in uncontrolled museum environments. The vast number of metal artefacts and the high cost of repeated maintenance make it impossible to simply place them in environmentally controlled areas or treat them regularly with protective coatings. One major aspect of the project is developing new strategies to assess these collections by designing survey approaches.

Surveys of metals collections housed in 12 museums throughout the Mediterranean have been carried out using: a statistical methodology in assessing the technology and condition of a large sample of objects, a data-mining technique to survey a random sample from the collection, or an in depth diagnostic investigation of the chemical and mineralogical properties of a representative number of artefacts.

Copper alloy spear shaft, Museum of Ancient Messene, Greece

Up left, Circular high tin bronze mirror (2nd c. BC) – Museum of Ancient Messene, Greece.

Up right, Steel amory of the Knights of Saint John (1530-1798 AD) - Palace Armoury, Malta.

Down left, Cast bronze lion head (672 BC) – Van Museum in Eastern Anatolia, Turkey.

THE SURVEY APPROACH FOR IRON AND COPPER ALLOY COLLECTIONS

The survey approaches developed for iron and copper alloy collections involve systematic documentation of the technology, condition, or even treatment of the objects under study.

A statistical methodology was developed by TEI (Greece) and applied to large collections, such as the collection of Ancient Messene for a pre-selected representative sample of 1000 metal objects. Two types of surveys, prior to treatment, using statistics were conducted for this collection:

A technology survey, where the variables that characterize the technological type are the morphological characteristics, as well as surface decoration, presence of plating etc. For this survey, Burt tables were created leading to classification trees containing the total number of objects according to each variable.

A condition survey, using the variables that influence the condition of objects and the value variable, was applied to predict the treatment priorities for the collection. For Ancient Messene, the following variables were considered: amount of metal remaining, type of corrosion products, burial environment, condition after excavation, amount of time prior to treatment, technology and value. Excel tables are generated with the data containing each value. Multinomial Logistic Regression (MLR) was chosen to allow the prediction of the treatment priorities: urgent to be treated, could benefit from treatment, and no need to be treated.

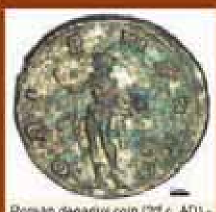
Data mining techniques were applied for two cases: first, partner JUST (Jordan) applied the technique to classify metal artefacts made of iron, copper or silver alloys, using attributes such as archaeological and historical context, burial medium, restoration method applied, chemical composition, technological processes and degradation state. Second HM (Malta) focused more on classifying the record of its past interventions, type and extent of corrosion, and method of display. The aim was to allow an evaluation of the protective systems used for the collection of the Palace Armoury in Malta.

THE SURVEY APPROACH FOR SILVER ALLOY COLLECTIONS

The applied survey was based on a detailed diagnostic investigation of the chemical-physical-morphological characteristics aimed at identifying degrading agents and phenomena.

For CNR-ISMN and POLITO (Italy), the silver based collections from the National Roman Museum-Numismatic Museum were surveyed. The survey involved first in-situ visual inspection using an optical microscope (OM). Then, some selected objects were subjected to a detailed investigation via SEM-EDS, OM, portable XRF and XRD to determine the state of conservation as well as the manufacturing features (composition of alloys and surface treatments).

NRC (Egypt) surveyed 500 silver based objects housed at the Egyptian Museum in Cairo. A representative sample of 60 objects was selected to cover all periods, value and significance. Only, non-destructive technique XRF was applied to study the composition alloys. The analysis of the condition of the artefacts is currently being carried out by means of visual inspection integrated with XRF analysis of the corrosion products.



Roman denarius coin (2nd c. AD) - National Numismatic Museum, Italy.

CONCLUSIONS-INNOVATION-IMPACT

The survey approaches developed for this project was case specific, but easy to apply to any metals collections, and necessary to help in the prioritization and decision-making for planning future treatment. These approaches were applied to 12 metals collections with a goal of establishing grounds for comparison and determining the best practices applicable to the Mediterranean region. Such a large-scale study has never been carried out before, and it is expected that the results will provide a better understanding of the conservation problems and needs for such collections.

PROMET, Contract No. 509126, Developing new analytical techniques and material for monitoring and protecting metal artefacts from the Mediterranean region, Co-ordinator: Vasilike Argyropoulos, The Department of Conservation of Antiquities & Works of Art, Technological Educational Institute of Athens (T.E.I. of Athens), Ag. Spyridonos, Aigaleo - Greece 12210, Email: bessie@teiath.gr

The survey approach of museum collections: a priori step in the sustainable conservation for metal objects from the Mediterranean Basin – PROMET

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Keywords: survey, metals collections, museum, Mediterranean region

Introduction and content

PROMET is a three-year European 6th Framework funded project, priority INCO, which began in November 2004 with 21 partners from 11 countries of the Mediterranean basin – Egypt, France, Greece, Italy, Jordan, Malta, Morocco, Spain, Syrian Arab Republic, Turkey and including the Czech Republic.

Surveys of metals collections housed in 12 museums throughout the Mediterranean have been carried out using a systematic survey approach, which involves using either a statistical methodology in assessing the technology and condition of a large sample of the objects, a data-mining technique to survey a random sample from the collection, or in the case of silver based objects in depth diagnostic investigation of the chemical and mineralogical properties of a representative number of artefacts.

The survey approach for iron and copper alloy collections

A statistical methodology was developed by TEI (Greece) and applied to collections with a large number, since for accurate hypothesis testing and for deriving parameters especially when the dependent variable (or answer) has many groups, 50 cases per independent variable used in a statistical technique is required [1]. The methodology was applied for the collection at ancient Messene, Greece, where all fragments that could not dated from the sample were removed, and the sample was reduced from 5000 objects down to 1000 objects for this type of methodology. Two types of surveys using statistics were conducted for this collection:
A technology survey, where the variables that influence the technological type are the morphological characteristics, as well as surface decoration, types of joins, etc. This survey can be compared to archaeological typologies that often use the same criteria for developing a typology, and consider relevant archaeological information. For the technological survey, Burt tables were created whereby the same variables exist in the columns and rows, and each object is counted according to occurrence for each variable. At the end, tabulation can be made according to the numbers of each variable. From here, a classification tree can be produced with the total number of objects according to each variable.

A condition survey (prior to treatment) using the variables that influence the condition of the object and its value was applied to predict the treatment priorities for the collection. For the collection at ancient Messene, the variables for archaeological iron and copper alloys were considered. Then the variables that define the deterioration state of the object and affect the condition of the object were identified. Furthermore, ‘value’ as a variable was considered to bring balance to the assessment. For Ancient Messene, the following variables were considered:

amount of metal remaining (none, little, metal core), types of corrosion products (stable or active), burial environment, conditions after excavation, amount of time prior to treatment, technology, value (cultural, utilitarian, sentimental). Under each variable there are values to define each case. Excel tables are generated with the data containing each value. Multinomial Logistic Regression (MLR) was chosen to allow the prediction of the variable (answer): urgent to be treated, could benefit from treatment, and no need to be treated? The results of this statistical assessment are given in Table 1:

Table 1: Results of the Condition Survey for the collection of archaeological iron and copper alloys objects from Ancient Messene, Greece

Treatment Priorities	Copper alloy objects	% Frequency	Iron alloy objects	% Frequency
No need for treatment	45	14	10	2
Could benefit from treatment	150	46	176	32
Urgent need of Treatment	129	40	363	66
Total	324	100	549	100

Data mining is the process of discovering meaningful new correlations, patterns and trends by sifting through large amounts of data stored in repositories, using pattern recognition technologies as well as statistical and mathematical techniques. Data mining techniques were applied for two cases: first, partner JUST (Jordan) applied the technique to classify metal artefacts made of iron, copper or silver alloys in general using attributes such as archaeological and historical context, the burial medium, the restoration method applied if any, the expected chemical composition, the technological processes and the degradation state. Second HM (Malta) focused more on classifying the comprehensive record of its past interventions (cleaning, protective coating applied), type and extent of corrosion, and method of display, which are interrelated factors and cannot be studied independently. For HM (Malta), the aim of the data mining was to find the correlation between different factors allowing for an evaluation of the protective systems used for the collection of the Palace Armoury in Malta. The application of this technique was necessary, because there were no past records, and thus some gaps in the data collected. The results of data mining applications are still being assessed and in the first case will be compared to the statistical methodogy developed by TEI (Greece).

The survey approach of silver alloy collections

The type of survey approach taken also depends on the type of objects and the subsequent diagnostic testing of those objects. For example, the survey approach carried out by CNR-ISMN and POLITO (Italy), and NRC (Egypt) of the silver based objects was different than described above. In most museum collections, precious metal artefacts are more stable, smaller in size and in numbers, and are considered higher in value than objects made of copper and iron alloys. In many cases, these artefacts had been used not only as jewels or precious decorative or artistic items but also for currency, medium of exchange and form of saving thus acquiring an historical, artistic, technical and economical value. The survey for the silver based artefacts due partly to their small size can be based on a more detailed diagnostic investigation of the chemical-physical-morphological characteristics aimed at identifying degrading agents and phenomena. For CNR-ISMN and POLITO (Italy) the silver based collections were surveyed from the National Roman Museum-Numismatic Museum, at Soprintendenza Archeologica of Cagliari and Oristano (Sardinia). The survey involved first in-*situ* visual inspection using an optical microscope (OM). Then, some selected objects were subjected to a detailed investigation via SEM-EDS, OM, portable XRF and XRD to determine the state of conservation as well as the manufacturing features. The survey found that the main degrading phenomena are the chlorine induced silver corrosion with formation of *patina* containing also soil constituents and mainly composed by chloro-argyrite, as well as “bronze disease” that affects the copper small or larger islands present in the silver matrix, and finally silver embrittlement of the alloy. Furthermore, the survey has shown that the silver based artefacts are characterised by a wide compositional nature allowing to discriminate different material classes such as nearly pure Ag, Ag-based alloys and Ag coated or Ag surface enriched artefacts. The noticeable presence of copper (as alloying element) or of the impurities coming from extractive or refining processes such as Pb or Bi have been monitored and the micro-chemical investigation has disclosed the role played by these elements in determining the mechanical and chemical properties in terms of corrosion behaviour and brittleness. Concerning the mechanical properties, the survey has indicated that some silver based objects are often found in an extremely brittle condition even though they do not show signs of heavy external corrosion and silver based alloys must have been quite ductile when the objects were mechanically worked. Sometimes these silver artefacts are easily broken with little applied force and with only a small deformation. This type of brittleness has a wide geographical and historical distribution and cannot result from corrosion, because many of these objects have not been found during archaeological excavations, but have been well conserved in mint conditions and now have become as brittle as glass probably due to an ageing process inducing a drastic change in the metallurgical and micro-chemical structure of the artefacts and therefore, in the final mechanical properties.

NRC (Egypt) also surveyed from 500 silver based objects housed at the Egyptian museum in Cairo another partner of PROMET. A representative sample of 60 objects was selected from the collection to cover all periods, value and significance, and important religious aspects, use, technology. Only non-destructively diagnostic technique XRF could be applied to study the collection and found that Ag, Au, Cu, and Sn content ranges in weight percent 83-97.5%, 0.8-2,5%, 0.5-9.5%, 0.5-2.8% respectively. Also, objects made of electrum found the Au content to range between 20-60%. The analysis of the condition of the artefacts is currently being carried out by means of visual inspection integrated with XRF analysis of the corrosion products.

Conclusions – innovation – impact

The survey approaches developed for this project was case specific, but easy to apply and necessary to help in the prioritization and decision-making for planning the conservation of these collections. The methodologies developed using a statistics approach, data mining technique or even extensive diagnostic analyses are unique may be applied to any metals collections, even in Europe. These approaches were applied to the study of 12 metals collections with a goal to establish grounds for comparison among our museum collections to derive best practices guidance applicable to the Mediterranean region. Such a large-scale systematic study has never been carried out before, and it is expected that the results will provide a better understanding of the conservation problems and needs for such collections in the region.

Acknowledgement

We gratefully acknowledge the work of Georgos Michalakos, statistician used to develop the statistical approach for the TEI of Athens.

References

1) L.G. Grimm, and P.R. Yarnold (eds.), *Reading and Understanding Multivariate Statistics,* American Psychological Association, Washington D.C., 1995.

European project details

PROMET, Contract No. 509126, Developing new analytical techniques and material for monitoring and protecting metal artefacts from the Mediterranean region, Co-ordinator: Vasilike Argyropoulos,

New Coating Materials and Strategies for the Preservation of Iron/Steel Industrial Cultural Heritage

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Motivation

Industrial development has drastically changed the economic scope of the European society. Closed down, but outstanding examples of iron and steel monuments have to be considered as important witnesses of our culture. New preservation strategies are requested for large outdoor monuments, being heavvily corroded and mechanically endangered.

The project will concentrate on the comparative tesing of established traditional, modern, and within the project developed new conservation materials and preservation strategies for industrial heritage made of iron and steel. The laboratory tests will require the application of suitable transparent compounds like traditional linseed oils and native waxes, comparing them with micro-crystalline waxes, modern resins like acrylic or epoxy-functionalised lacquers, and newly developed coatings such as the combination of isocyanato-based poly-acrylate dispersions (as silanes)and hybrid polymeric sols, leading to advanced hybrid systems by nano-scaled sol-gel preparation techniques. The influence of different degrees of surface cleaning on the protective effect of the coatings will be specified.

Pilot applications of the most promising coatings on three selected objects in Ireland, Poland, and Germany will be performed to compare the advantages of the new materials with the commercially available systems.. Management concepts for industrial heritage sites will beestablished to demonstrate the potential for economic growth through the application of new methodologies. The proposed project will provide a comparison between traditional and new materials, with will increase the preservation skills and exploitation of industrial heritage sites while ensuring adequate protection.

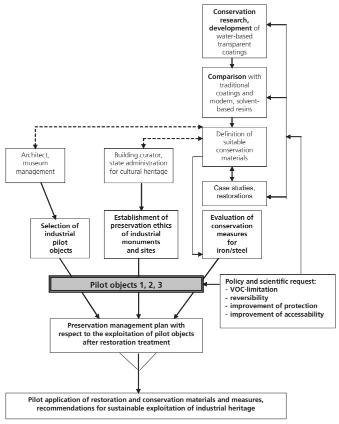
Henrichshütte, Hattingen, Germany

Jaworzyna Slaska, Poland

Objectives / Methodology

- Comparison of traditional conservation materials and technologies with modern conservation treatments, applied on iron / steel industrial monuments.
- Evaluation of the reversibility of conservation materials and measures, thus validating the re-treatability of industrial monuments.
- Development of improved conservation materials, providing long-term protection for large-scaled indooor and outdoor iron and steel monuments, with special relevance to water-based transparent coatings, produced by nano-scaled preparation techniques.
- Creation of management concepts for sustainable exploitation of industrial cultural heritage sites after conservation, taking into account the requirements of the object owners, curators, architects and administrators.

Project scheme:

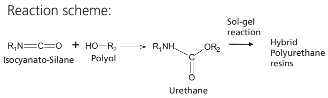


Coatings development and comparative testing

Coatings development:

Transparent ORMOCER® systems with innovative properties
- water-based resin
- application on non-ideal / corroded surfaces
- RT vulcanizing
- long-term stability
- reversible

Reaction scheme:



Comparative testing
- accelerated ageing of coated coupons
- cross cuts evaluation
- degree of rusting, tensile testing etc.
- examination by instrumental analysis (SEM / EDX etc.)

Types of resins:

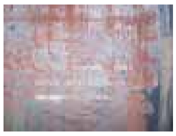
Testing of traditional and promising modern resins:
Water- and solvent-based ORMOCER®S, 1K-PUR, acrylates, PUR / acrylate combinations, (micro-crystalline) waxes, oils etc.

Pilot objects

German Mining Museum, Bochum, Visitors´ Mine

Tunneling machine

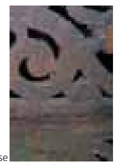
Poland: Museum of Industry and Railway, Jaworzyna Slaska, Lower Silesia

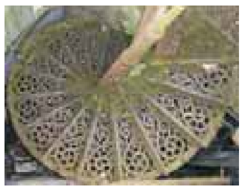


Locomotive workshop

Ireland: Iron spiral stairs of Palladian houses Castletown, County Kildare / Oldbridge, County Meath

Castletown House





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Area 8.1.B.3.6: The protection of cultural heritage and associated condervation strategies

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Duration: June 2005 - May 2008
www.consist.fraunhofer.de ➜ **www.consist.eu**

Project title: Comparison of Materials and Strategies for Sustainable Exploitation of Immovable Industrial Cultural Heritage made of Iron an Steel, **Acronym: CONSIST**

New coating materials and strategies for the preservation of iron/steel industrial cultural heritage

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Keywords: metal conservation, industrial monuments, iron, coatings, consolidants, sustainable development

Introduction / content

Industrial development has drastically changed the economic scope of the European society. Closed down, but outstanding examples of iron and steel monuments have to be considered as important witnesses of our culture. New preservation strategies and conservation materials are requested for large outdoor monuments, being heavily corroded and mechanically endangered.

The project will concentrate on the comparative testing of established traditional, modern, and within the project developed new conservation materials and preservation strategies for industrial heritage made of iron and steel. The laboratory tests will require the application of suitable transparent compounds like traditional linseed oils and native waxes, comparing them with micro-crystalline waxes, modern resins like acrylics or epoxy-functionalised lacquers, and newly developed transparent coatings such as the combination of isocyanato-based polyacylate dispersions (as silanes) and hybrid polymeric sols, leading to advanced hybrid systems by nano-scaled sol-gel preparation techniques. Room-temperature curing will be obligatory for the application on industrial heritage surfaces. The influence of different degrees of surface cleaning on the protective effect of the coatings will be specified.

The newly developed systems will be water-based and thus provide an alternative to solvent-based lacquers and natural resins available so far.

Pilot applications of the most promising coatings on three selected objects in Ireland, Poland, and Germany will be performed to compare the advantages of the new materials with the commercially available systems. Management concepts for industrial heritage sites will be established to demonstrate the potential for economic growth through the application of new methodologies. The proposed project will provide a comparison between traditional and new materials, which will increase the preservation skills and exploitation of industrial heritage sites while ensuring adequate protection.

European dimension

The project will develop strategies required to reduce the negative impact of mass tourism on the cultural heritage, by reducing the cycle of treatment, damage and retreatment. This will support sustainable development and increase competitiveness of European countries as required in the treaty establishing the European Community (implemented in 1998, see Title XVIII Research and Technological Development, Article 163). As the preservation methods developed in the project are also applicable for other industrial areas, this proposal supports the „sustainable development of economic activities“ in Europe (Article 2).

The project meets the Community Action Plan in the field of Cultural Heritage (Council Decision – O.J. 94/C 235/01), especially article 128 of the Treaty, identifying Cultural Heritage as a priority field of action (including both movable and fixed heritage) through:

- conservation and safeguarding of Cultural Heritage of European significance
- taking Cultural Heritage into account:
  - in regional development and job creation
  - tourism and environment
  - research.

The project also addresses the EC policies and agendas to support the renovation of the housing stock, measures to reduce pollution and vandalism, and the protection and improvement of buildings and open spaces in run-down areas as well as the preservation of the cultural heritage. Furthermore, it promotes equality, social inclusion and regeneration in urban areas and the preservation of the environment (Sustainable Urban Development in the European Union: A Framework for Action Com (1998) 605 final of 28.10.1998).

The conservation material development will respect standards set by conservation ethics, focussing on the reversibility and re-treatability of transparent coatings. The newly developed systems will be water-based and thus provide an alternative to solvent-based lacquers and natural resins available so far. In this respect the project will support the implementation of EC-directive 1999/13/EU, aiming at the limitation of the emission of volatile organic compounds released when using organic solvents.

Innovation

The innovative objectives can be described as follows:

- Comparison of traditional conservation materials and technologies with modern conservation treatments, applied on iron / steel industrial monuments.
- Evaluation of the reversibility of conservation materials and measures, thus validating the re-treatability of industrial monuments.
- Adaptation of established application techniques and materials to large-scaled outdoor industrial monuments with extensive surface areas.
- Development of improved conservation materials, providing long-term protection for indoor and outdoor iron and steel monuments, with special relevance to water-based transparent coatings, produced by nano-scaled preparation techniques.
- Better integration of immovable industrial monuments, buildings or equipment in the local context by improving accessibility while ensuring adequate protection.
- Creation of a management concept for the sustainable exploitation of industrial cultural heritage sites after conservation, taking into account the requirements of the object owners, curators, architects and administrators.
- Increasing the competitiveness of European SMEs by providing new conservation treatments, respecting the reglementation to reduce VOC (directive 1999/13/EU, issued by the Council of the European Union).

Originality

The project CONSIST will on the one hand identify promising traditional conservation materials and measures and will on the other hand compare these established techniques with modern materials and application skills. Moreover, the project aims to develop new transparent conservation materials, for which the reversibility and re-treatability will be investigated in laboratory experiments. This will lead to most advanced conservation strategies for the specific field of iron / steel industrial heritage.

As one of several powerful modern materials, the Fraunhofer ISC provides modern ORMOCER® conservation resins (silica-based inorganic / organic hybrid systems), especially adapted for the application on metal heritage surfaces. The most promising solution to improve the properties of these ORMOCER® resins will be a combination of the existing ORMOCER®s with other systems coming from technical applications like polyurethanes or acrylates. These water-based resins proved to be highly resistant to weathering in industrial applications on iron / steel with good adhesion and consolidation properties (e.g. in the railway or automotive sector). The functional reactive groups of these systems can be combined with available ORMOCER® systems by a nano-scaled sol-gel synthesis of isocyanato-based or succinic acid-based polymerised acrylate silanes with hybrid sols (the latter normally used as ORMOCER® precursors). The new systems will exhibit a lot of important advantages: They will be easy to apply by spraying, will consist of only one component as lacquer resin (without any primer application etc.), will show high mechanical and weathering resistance, will exhibit good adhesion and consolidation properties, and will finally be water-based instead of containing organic solvents. They will be reversible due to the content of acrylic functional groups. Curing will be performed at ambient conditions and temperatures.

Impacts

- Development of long-term stable transparent coatings, based on solvent-free sol-gel ORMOCER® resins. Market exploitation for the newly developed ORMOCER®s.
- Overall preservation documentation and action plan for European pilot objects:
  - Museum of Industry and Railway, Lower Silesia, Jaworzyna Slaska, Poland
  - German Mining Museum, Bochum,
  - Traditional Iron Stairs of Palladian Houses, Ireland
- Comparative testing of iron / steel coating resins (traditional and modern), application and cleaning techniques. Determination of most promising conservation treatments.
- General recommendations of best-practice preservation strategies and conservation materials for large-scaled iron/steel industrial monuments.

Website

www.consist.fraunhofer.de and www.consist.eu

European project details

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