PROGRAMME AND ABSTRACTS

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Programme and Abstracts

Edited by

Miguel Ángel Rogerio-Candelera, María J. Mosquera, M.L. Almoraima Gil

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Dear Colleagues

On behalf of the Organising and Scientific Committees, and myself, I would like to extend a warm welcome to TechnoHeritage 2017. The Conference will be held in Cadiz over three days, from 21 to 24 May 2017. During the Conference, Cadiz, which is one of the oldest cities in Western Europe, and preserves an important historical legacy, becomes a unique scenario for discussions on all aspects of Cultural Heritage. A high-quality scientific programme has been prepared, which includes new emerging topics on Cultural Heritage such as: nanotechnology, innovative monitoring and characterisation techniques, and 20th century Cultural Heritage preservation.

I would like to thank you for your scientific contribution and your attendance, which will assist in increasing the overall scientific quality of the Conference. The response to TechnoHeritage 2017 has been overwhelming. Over 200 communications of high scientific quality, from 23 different countries, will be discussed during the three days duration of the scientific programme.

I am also happy to announce the special session: "Biodeterioration: Fundamentals, present and future perspectives, a session in honour of Prof. Cesáreo Sáiz Jiménez", who recently retired. Our intention is to recognise Prof. Sáiz Jiménez's work and its impact on the Cultural Heritage conservation community, which he has helped to promote through numerous activities including, in 2011, the creation of the TechnoHeritage network.

Finally, I would like to offer special thanks to the Local Organising Committee, the International Advisory Board, and the companies and institutions participating as sponsors, for their much appreciated efforts in making this international scientific event a success.

I hope you enjoy your stay in Cadiz, and that you experience a truly valuable and memorable Conference.

María J. Mosquera

Chair, TechnoHeritage 2017

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Materials and methods for the conservation of Cultural Heritage

P. Baglioni

Department of Chemistry "Ugo Schiff", University of Florence, and CSGI-Florence, Sesto Fiorentino, Florence Italy
baglioni@csgi.unifi.it

Colloid and surface Science has always been central disciplines in many applicative areas, and fundamental knowledge from colloids has been applied across a range of industries as pharmaceutical, detergency, paint, and food industries. A precise control on structure and dynamics of colloids is required to transfer a laboratory-scale know how to field applications. This will be even truer in the near future, with the development of sophisticated hierarchically organized systems, where single components combine in a synergistic or orthogonal way to provide enhanced performances for the intended end-applications.

The Florence group has pioneered the application of soft matter and materials science to several fields, one of the most exotic is the conservation of cultural heritage that was pioneered by us. In this field, the same tenets as for the above-mentioned applicative areas hold. Art Conservation poses a formidable and exciting challenge to Colloid and Interface Scientists in two respects. First, the majority of the most performing and environmentally-safe cleaning and consolidation agents for artworks are soft matter systems. Second, the interaction of these agents with the artifact involves an exceptionally complicated range of interfacial interactions.

In this lecture I will review the most meaningful achievements of my group in this field, focusing on the application of colloidal dispersions of increasing complexity, from nanoparticles to o/w microemulsions to semi-interpenetrating hydrogels containing o/w microemulsions. These systems have been used on artifacts of the most diverse origins, from Renaissance frescoes to Picasso and Pollock. I will show how chemical and colloidal design can be implemented to meet the requirements of the end-users and how precise knowledge of structure, dynamics and interfacial interactions can contribute to overcome the traditional serendipitous approach used by conservators. Finally, I will try to summarize the main perspectives that this field can disclose for Chemistry and conservators communities.

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@No kinship is present among the authors

Smart materials for the cleaning and protection of the surfaces of culture heritage artefacts

J. Rathousky

J. Heyrovsky Institute of Physical Chemistry (Academy of Sciences of the Czech Republic)
Dolejskova 3, 182 23 Prague 8, Czech Republic
jiri.rathousky@jh-inst.cas.cz

Since early 2000s Baglioni, Dei et al. has pioneered the use of micellar solutions and microemulsions for cleaning artworks, especially for the selective removal of aged polymeric coatings from the surface of wall paintings. Inspired by their work, we have developed a generalize method, which enables to selectively remove a broad range of target substances from the surface of materials. Our approach is based on the combination of two functions which are realized by two components

- the "standard" micellar solution or microemulsion of nonionic surfactants with co-surfactants added, which is practically the same for various target substances (such as oils, waxes, polymers),
- the specific solvents selected according to the respective substance to be removed.

There are several advantages of this approach, namely the substantially facilitated formulation of the cleaning mixtures, easier preparation and better understanding of the mechanism of their action. Prospective production in larger amounts would be easier and economically more favourable. As the micelles and microemulsions are dispersed in an aqueous system, the penetration of material to be removed into the structure of cleaned artefact is maximally reduced.

According to the needs of the conservation practice in the Czech Republic the target substances include:

- resins (e.g., damara resin)
- oils
- waxes and paraffins
- water acrylate dispersions
- monomeric and polymeric hydrophobization agents.

Hydrophobization of the surface of sandstone and limestone materials is an effective method of their protection against the effects of weathering. However there are grave disadvantages of hydrophobizartion, namely a change in the original appearance of the material due to the increased deposition of dirt on the hydrophobic surface and the practical impossibility to carry out subsequent treatments particularly with hydrophilic agents. Using patented microemulsions for the controlled removal of hydrophobization it is possible to create a thin hydrophilic layer on a hydrophobized surface to ensure the uniform washing away of dirt. The procedure includes two steps

(1) the surface hydrophobization using an agent comprising alkyltrialkoxysilanes or polydimethylsiloxane polymers in an organic solvent to a sufficient depth,

and

(2) the removal of a thin surface layer of the hydrophobization, bound to the surface of the material, with a thickness of approximately 1 mm.

Another successful application of cleaning microemulsions confined in the 3-dimesionsional structure of gels was the selective detachment of damara resin layers from the surface of oil paintings as well as the rather demanding removal of unwanted overpaintings.

Film-forming gels for the removal of corrosion products from copper-based artifacts

R. Giorgi[1], E.I. Parisi[1], N. Bonelli[1], D. Chelazzi[1], G.M. Ingo[2], P. Baglioni[1]

[1]CSGI – Department of Chemistry (University of Florence) Sesto Fiorentino (FI), Italy
[2]ISMN-CNR, Monterotondo Stazione (RM), Italy
rodorico.giorgi@unifi.it

An innovative polyvinyl alcohol-based film forming system was specifically devised for a controllable and selective cleaning of copper-based artefacts, with enhanced performances in terms of both applicability and efficacy. The main advantage of this cleaning system consists in the simultaneous chemical and mechanical action, guaranteed respectively by the presence of a confined complexing agent specific for selected ions (Cu^{2+}), such as EDTA and/or polyethylene-amines.

Metallic artefacts are affected by corrosion phenomena that induce the formation of complex *patina* on their surface. Degradation causes the formation of overlapping structures, characterized by a layer of Cu(I) oxide (cuprite Cu_2O) at the interface with the metal, and by an external layer of Cu(II) carbonates, sulphates, chlorides, etc. The presence of copper oxychlorides (atacamite and its polymorphs) is usually considered as a symptom of the 'bronze disease', a cyclic phenomenon that leads to the progressive deterioration of ancient copper alloys. Cleaning procedures of these materials are traditionally performed by mechanical (vibrating or abrasive tools, micro-peening with vegetal granulates, ultra-high-pressure water, laser) and/or chemical methods (complexing agents, bases, acids). Mechanical cleaning presents some limits related to the scarce selectivity and invasiveness of this procedure, while the chemical action is generally affected by an insufficient control over the reactions involved.

The film forming cleaning system, based on polyvinyl alcohol as a polymer and loaded with a complexing agent (EDTA and polyethyleneamines), is a promising tool for the selective removal of corrosion products from copper-based artefacts, by respecting the cuprite layer. In fact, this innovative approach permits to achieve: i) improved chemical control, step-by-step, of the cleaning process, thanks to the high selectivity of the chosen complexing agent and to its confinement in the polymeric system; ii) simultaneous chemical (complexation) and mechanical action (favoured by the gentle *peeling* of the final film); iii) adjustability of the physico-mechanical properties (consistency, adhesiveness, transparency, etc.), by tuning the additives content to adapt to different substrates (non-horizontal, rough and irregular surfaces).

Two main aspects were studied over both complexing agent-loaded and not loaded systems: i) the kinetics of film formation, by investigating the evolution of the systems from polymeric dispersions towards the formation of elastic films and ii) the evaluation of the formed films properties, through the analysis of crystallinity degree.

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Removal of varnish residues and overpaints from a fifteenth century Spanish tempera and gilded panel painting with a Pemulen TR2 gel

J. de Groot[1], K. Seymour[2], D. de Man[3]

[1]University of Amsterdam, Netherlands
[2]Kate Seymour, Stichting Restauratieatelier Limburg, Netherlands
[3]University of Amsterdam, Netherlands
jazzy.de.groot@hotmail.nl, k.seymour@sral.nl, dididm@hotmail.com

Two fifteenth century Spanish panel paintings, belonging to the Seurmondt Ludwig Museum in Aachen, were brought in at the Stichting Restauratie Atelier Limburg, Maastricht, to be treated for exhibition. On a gesso ground, they were executed in tempera and parts were water gilded. Both were varnished and heavily overpainted in the past, destroying the original contrast between matt and shiny surfaces and largely covering the original paint layer. The overpaints were discoloured and darkened. After a first varnish removal, a lot of overpaint and very old varnish residues were still there. Common techniques with gelled solvents did not remove these. This paper presents a Pemulen TR2 gel to successfully remove these overpaints and varnish residues from tempera and gilded surfaces. As a result, the contrast between the matt and shiny surfaces were back and the original appearance and colours were approached in a better way.

With gelled solvents a lot of rubbing was needed for minimal removal of the residues and overpaints which was undesirable. Therefore a gel was designed with demineralised water adjusted to a pH of 7.5 and Pemulen TR2 with 10% benzylalcohol added. After cleaning, the area was rinsed with isopropanol.

Residues and overpaints were easily removed with limited rubbing from the tempera parts. Under the microscope, the original paint layer could be easily distinguished from the non-original layers. When the ground layer got exposed for a long time in damaged areas it could swell and soften because of the gel. Therefore it was necessary to use short working times for the gel, coming back to the same area several times with sufficient time between the cleaning moments. Bright, original colours were uncovered and the surface was more even and matt after removal of the varnish residues.

The gilded parts were cleaned in the same way as the tempera parts only with shorter working times for the gel because of the water sensitivity of the gilding. Original glazing and painted brocade were uncovered, revealing the original brightness of colour of the two panels. Also the gilding got shinier, giving a contrast with the matt tempera parts.

This treatment showed that the conservator can think of more unconventional ways to clean paintings when more conventional techniques fail. Dealing with a surface that was suspected to be water sensitive, because of the gesso ground and water gilding, water could be used to clean the surface using an appropriate timing.

Evaluation of cleaning procedures for the conservation of tarnished lead

T. Palomar[1,2], B. Ramirez[1], J.M. Vélix[1], E. Cano[1]

[1]Centro Nacional de Investigaciones Metalúrgicas, (CENIM-CSIC)
Avda. Gregorio del Amo, 8. 28040 Madrid, Spain
[2]Research Unit VICARTE-Vidro e Cerâmica para as Artes (FCT-UNL)
Campus de Caparica, Quinta da Torre, 2829-516 Caparica, Portugal
ecano@cenim.csic.es

The principal risk to the heritage made of lead in museums is the accumulation of the VOCs inside the cabinets, showcases and storehouses, which can induced the fast corrosion on historical lead. Lead has a good resistance to atmospheric corrosion because it forms a passive layer. However, volatile organic compounds, mainly acetic and formic acids, can break the protective layer and accelerate the degradation process. The result is the formation of a whitish, powdery and with low adhesion alteration layer on the lead. This alteration phenomenon is called tarnishing. Surface cleanings can improve the legibility and the conservation state of the objects with a severe state of corrosion, but the low hardness of lead makes it particularly susceptible to be damaged during the cleaning practices and, in addition, it requires additional security procedures due to the high toxicity of its corrosion products.

The aim of this study is to evaluate and compare the impact of different repetitive cleaning procedures for the conservation of tarnished historical lead. The assessed procedures were a mechanical cleaning (suspension of $CaCO_3$), a chemical cleaning (immersion on EDTA) and two electrochemical cleanings (potentiostatic reduction, and potentiostatic reduction and passivation). The samples were characterized before and after each cleaning by gravimetry, colorimetry, rugosity, scanning electron microscopy (SEM) and X-ray photoelectron spectroscopy (XPS).

Results show that all cleaning procedures induced chemical and physical changes on the surface of lead coupons. Mechanical cleaning produced an important mass loss and a high re-tarnishing process. It favored the recuperation of the original metallic gloss although it left occasional scratches on the surface due to the grain size of the abrasive. Regarding the cleaning efficiency, EDTA procedure was the most effective. The chemical cleaning with EDTA induced a moderate mass loss and left a completely heterogeneous surface due to the chelation of the corrosion products, although, the color and gloss of the cleaned coupons were the most similar to the original lead. The electrochemical procedures induced a negligible mass loss; nevertheless, the re-deposition of reduced lead favored the increase of the rugosity. The coupons treated by electrochemical reduction and passivation presented a flat surface because of the growth of $PbSO_4$ crystals inside the holes. The re-deposition also induced a progressive color change towards bluish and a total loss of gloss, although the re-tarnishing rate decreased.

Conservation of archaeological epigraphs on marble with laser technique

J. Barrio[1,2], M.C. Medina[2], I. Donate[2], M. Muñoz[2], A.I. Pardo[1]

[1]Departamento de Prehistoria y Arqueología, Facultad de Filosofía y Letras, Universidad Autónoma de Madrid, Calle Francisco Tomás y Valiente, 1, Campus de Cantoblanco, 28049, Madrid, Spain
[2]Servicio de Conservación, Restauración y Estudios Científicos del Patrimonio Arqueológico, Universidad Autónoma de Madrid, Campus de Cantoblanco, 28049, Madrid, Spain
maricruz.medina@uam.es

This work presents the results of the research process and the restorative intervention by laser technique on a group of four Roman epigraphs on marble of different compositions. They are dated between the 1st and the 6th centuries A.D. and were excavated in three Spanish-Roman cities. Two of the samples, made of white marble, came from the ancient Roman *municipium* of Sisapo (La Bienvenida, Almodóvar del Campo, Ciudad Real), the Visigoth altar table from the Punic-Roman site of Carteia and the *Opistodoma* inscripition from the Roman city of Valeria (Valera de Arriba, Cuenca). The last epigraph, made of veined marble, was in a very bad state of conservation, fragmented in many pieces.

The deterioration problems of archeological marbles that have been buried during many centuries are very different from those that have remained outdoors. The deterioration products of the later are due to the effect of urban pollution and are mainly black crusts, sulfate deposits, etc., while the products of the buried pieces were very hard crusts composed by carbonates, silicates, phosphates, and earths. These were difficult to remove by traditional methods (mechanical and chemical) without scratching the surface or changing the original patina, which must be conserved as it is stablished by international ethical principles of Cultural Heritage. The few restoration works on archaeological marble suggested that the laser device could be a complementary tool, offering suitable outcomes.

The epigraphs treated with laser at the SECYR laboratory have been examined under optical microscope during the whole cleaning process and studied with analytical instrumental techniques: polycrystalline X-ray diffraction and laser induced breakdown spectroscopy. The results show the efficiency of the laser technique, combining the irradiation with different wavelengths (IR and UV). They have been able to eliminate the alteration crusts and unveil the ancient graphs, without harming the original patina.

Two wavelength laser cleaning by means of Nd:YAG: its application on graffiti extraction in granitic Cultural Heritage

J.S. Pozo-Antonio[1], A. Papanikolaou[2], K. Melessanaki[2], T. Rivas[1], A.J. Lopez[3], A. Ramil[3], P. Pouli[2]

[1]Dept. de Enxeñaría de Recursos Naturais e Medioambiente. Universidade de Vigo, Vigo, Spain
[2]Institute of Electronic Structure and Laser, Foundation for Research and Technology-Hellas (IESL-FORTH), Greece
[3]Laboratorio de Aplicacións Industriais do Láser, Centro de Investigacións Tecnolóxicas (CIT), Universidade de Coruña, Ferrol, Spain
ipozo@uvigo.es, ph3776@edu.physics.uoc.gr, alina@iesl.forth.gr, trivas@uvigo.es, ana.xesus.lopez@udc.es, alberto.ramil@udc.es, ppouli@iesl.forth.gr

Graffiti is currently one of the most serious threats to the preservation of European Cultural Heritage monuments. When the graffiti paint is applied on monuments, its satisfactory extraction using traditional procedures has not been reported and also, some side effects, such as by-products and "shadows" for the chemical products and modification of the superficial roughness for low pressure mechanical procedures were reported. In this sense, laser cleaning has been thoroughly studied during the last decades; resulting to significant extraction of the paints with a minimal damage to the substrate. Most of the studies were performed in carbonate stones (limestone and marble) and only a few were based on the granitic stones, which is an important part of the European Cultural Heritage. Regarding the graffiti cleaning on granitic stones, to the best of our knowledge, different laser systems have been applied, Nd:YAG and Nd:YVO_4 being the most investigated ones. In all cases the effectiveness level achieved was dependent on the main chemical composition of the graffiti paint.

In this paper, in order to improve the graffiti cleaning, the simultaneously application of two laser beams working at different wavelengths 1064 nm and 355 nm was considered. This cleaning strategy was developed in 2002 by IESL-FORTH to remove pollution accumulations from the Athens Acropolis monuments and sculptures. In the current paper, the two wavelength laser cleaning was applied for the first time to clean graffiti on granitic Cultural heritage. Considering previous researches, three graffiti paints with different cleaning effectiveness levels, were applied in fine-grained granite. In order to demonstrate the suitability of this methodology, the cleaning of these graffiti paints was also performed with each single wavelength (1064 nm and 355 nm). The evaluation of the cleaning tests performed was carried out considering the graffiti extraction and any possible damage induced in the granitic stones ensuring that the original surface was safeguarded. The analytical techniques used were stereomicroscopy, Scanning Electron Microscopy with X-ray microanalysis, Fourier transform infrared spectroscopy and colour measurement in CIELAB space. This paper enlightens the cleaning effectiveness considering carefully the laser ablation processes for each graffiti paint and different wavelength and also the combination of both wavelengths.

Non-linear microscopy imaging for studying the process of laser removal of varnishes used in paintings

M. Castillejo[1], M. Oujja[1], S. Psilodimitrakopoulos[2], E. Carrasco[1], M. Sanz[1], A. Selimis[2], A. Philippidis[2], P. Pouli[2], G. Filippidis[2]

[1]Instituto de Química Física Rocasolano, CSIC, Serrano 119 Madrid, Spain
[2]Institute of Electronic Structure and Lasers (IESL), FOundation for Research and Technology -Hellas (FORTH), Heraklion, Crete, Greece

Laser cleaning of paintings aims at controlled removal of polymerized, degraded varnish coatings taking advantage of the high spatial resolution, accuracy, material selectivity and immediate feedback associated with the process. To circumvent the possible side effects on light-sensitive painting materials (pigments, binders, protective coatings) the laser parameters (wavelength, fluence, pulse duration, and number of pulses) have to be properly selected.

Imaging based on nonlinear optical microscopy (NLM), a technique initially developed in the field of biomedical optics, allows surface mapping and profiling of multi-layer structures (e.g. coatings) and is been increasingly applied to examine substrates of interest in Cultural Heritage. NLM imaging relies on ultrafast laser excitation (pulse duration of femtoseconds) to exploit several nonlinear optical effects that allow high contrast imaging of samples. In particular, the NLM imaging modalities of Multi-Photon Excited Fluorescence (MPEF) and Third Harmonic Generation (THG) provide non-destructive accurate determination of chemical nature and thickness within multilayer samples.

In this study we have attempted to determine by NLM the extent of photochemical damage that could be induced on underlying painting layers by ultraviolet (UV) laser removal of varnish protective coatings. This will lead to the identification of the optimal laser cleaning conditions that produce the minimum collateral damage to the painting layers. We used model samples constituted by bilayers, where the top varnish layer coats a bottom layer constituted by a doped synthetic polymer, poly(methyl methacrylate), doped with a photosensitive dye, the latter mimicking a paint layer. The aim is to determine the affected region, as a function of depth, of the doped polymer layer induced by laser ablation of the varnish. We used THG and MPEF as novel diagnostic tools and a number of laser conditions for varnish removal, namely different UV wavelengths and pulse durations. The NLM data obtained are complemented by measurements of Raman and laser induced fluorescence spectra and morphological observation by optical microscopy of the laser irradiated areas of the samples. The detailed analysis of recorded information, allows characterizing the lateral and in-depth chemical and morphological changes following laser removal of the varnish protective layer (see figure).

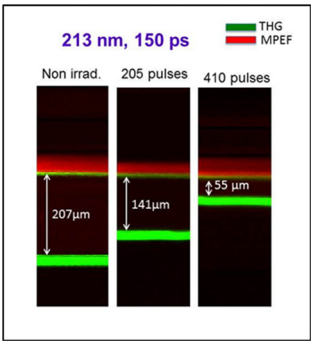

Figure. Cross sectional multimodal MPEF/THG images of model varnished painting samples. Thicknesses of varnish layer in non-irradiated and areas of the sample irradiated at the indicated laser ablation conditions are indicated.

Controlling the effectiveness of the cleaning treatments of bronze by using X-ray diffraction: equestrian sculpture of "El Cid Campeador" (Seville)

J.J. Martín-Del-Río, F.J. Alejandre-Sánchez, F.J. Blasco-López, P. Soler Núñez, C. Núñez Guerrero

Construcciones Arquitectónicas II (ETSIE, Universidad de Sevilla), Avda. Reina Mercedes nº4-A, Sevilla, Spain
jjdelrio@us.es

Copper and its alloys (bronze and brass) are materials, which are widely used in sculptures and ornamental pieces of cultural patrimony due to their capabilities to develop stable protector patina within oxidant atmosphere conditions. However, depending on the environmental conditions, they can suffer the effect of corrosion because of the pollution which is present in cities. One of the most common alterations is the so called "bronze disease", which is a cyclic corrosion produced by the presence of chlorides in it surface.

The equestrian sculpture of "El Cid Campeador" was donated by the Hispanic Society to the city of Seville (Spain). In particular, its founder, Archer Milton Hunyington, and his wife, Ana Hyatt (author), donated the sculpture for the Iberoamerican Exhibition of 1929. It is located between "Jardines del Prado de San Sebastian" and "Real Fabrica de Tabacos" in Seville, which is an urban area where atmospheric pollution is very high (SO_2, NOx, COV's, particles in suspension…). This gives rise to a high level of degradation and, because of that, in 2012 it was included within a campaign for the conservation and restoration of public monuments, which was promoted by the "Gerencia de Urbanismo de Sevilla" (Management Planning of Seville). This was the background in which this research has been developed.

The methodology which has been followed for the studies prior to any action involving the sculpture involved the chemical characterization of the bronze alloy by using FRX. Then, once the most abundant patinas were identified according to their colour tone (brown, green, yellow, white), the compounds were identified by using DRX. During the process, it was possible to differentiate between stable and instable compounds. Once the available literature was reviewed, four cleaning treatments were selected and applied to the different patinas. Their efficiency was evaluated based on the decrease in the concentration of instable compounds by using DRX semi-quantification. Finally, the stabilization of bronze was completed and a protection layer of varnish (based on an acrylic resin with antioxidant additives) was applied.

Nanomaterials for monument conservation: applications as additives in mortars, consolidants and self-cleaning protectives

P. Maravelaki-Kalaitzaki

School of Architectural Engineering (Technical University of Crete, Akrotiri University Campus)
73100 Chania, Crete, Greece
pmaravelaki@isc.tuc.gr

An important problem in the restoration sector is the reassembling of stone fragments from ancient monuments using non-cementitious mortars. The proposed adhesive mortars contain hydraulic lime or metakaolin and lime as binders, carbonate sand with grains between 250 and 63 μm and binder to aggregate ratio 1 or 2. The nano-titania as additive was employed in a binder replacement of 4.5-6% w/w. The mechanical characterization indicated that the mortars with nano-titania showed increased compressive and flexural strengths and moduli of elasticity over time, when compared to the specimens without nano-titania. The results also indicate enhanced carbonation and hydration of mortar mixtures with nano-titania. The hydrophylicity of nano-titania improves the humidity retention of mortars, thus facilitating the carbonation and hydration processes. This property can be exploited into the fabrication of mortars tailored to adhering porous limestones, where humidity controls the mortar setting and adhesion efficiency.

Three innovative strengthening, protective and self-cleaning agents for marble and calcareous stones were synthesized by using a simple sol-gel route at ambient conditions. TiO_2 nanoparticles and hydroxyl-terminated polydimethylsiloxane (PDMS) were incorporated in a tetraethoxysilane (TEOS) matrix in the presence of oxalic acid (Ox). The presence of Ox contributed to the production of both homogeneous materials and photoactive independent domains of anatase TiO_2 crystals at ambient conditions. The synthesized crack-free, homogeneous, transparent and photoactive nanocomposites provide self-cleaning, water repellency and consolidation properties to building substrates, while respecting their aesthetic qualities.

A nontoxic strengthening and protective agent for porous calcareous stones and cement mortars has been synthesized in a one-pot synthesis via the sol-gel method, incorporating nanoparticles of synthesized amorphous calcium oxalate monohydrate (ACO) in TEOS. Calcium hydroxide and oxalic acid added into TEOS produce ACO, which is then incorporated into the silica matrix, while oxalic acid also acts as catalyst for TEOS hydrolysis. The crack-free nanocomposite derived possesses a uniform microstructure with particles of approximately 7–15 nm in size. The ACO incorporated into the silica matrix gives good interfacial compatibility between the nanocomposite and building materials, such as calcareous stones and cement mortars, and improves their mechanical properties. The hybrid nanocomposite can penetrate inside the lithic substrate and acts as a strengthening agent with protective effect against environmental loading.

Study of calcium alkoxides as new conservation product for consolidation of historical limestone

M. Zuena[1], P. Tomasin[2], D. Costa[3], J.D. Rodrigues[3], L. Storaro[1], E. Zendri[4]

[1]Department of Molecular Science and Nanosystem (Ca' Foscari University of Venice) Via Torino 155, 30170 Venezia Mestre, Italy
[2]Institute for Energetics and Interphases (C.N.R.) Corso Stati Uniti 4, 35127 Padova, Italy
[3]National Laboratory of Civil Engineering, Avenue Brasil, 101, 1700-066 Lisbon, Portugal
[4]Department of Environmental Sciences, Informatics and Statistics (Ca' Foscari University of Venice) Via Torino 155, 30170 Venezia Mestre, Italy
988643@stud.unive.it

The combined action of several physical, chemical and biological factors cause the weathering of stone widely employed in the field of Cultural Heritage. These deterioration processes are well studied and the results have promoted the research and the development of novel types of consolidation treatments to overcome the limitations of traditional ones and to meet the requirements of the historic building substrates.

During the European collaborative project NANOMATCH [1], different consolidating agents for carbonate supports, as alkaline alcoxides, were synthesized and applied. In particular, calcium alkoxides are metallorganic compounds that, dissolved in an organic solvent, penetrate within the porous substrate and, reacting with moisture and carbon dioxide of the atmosphere, form a calcium carbonate coating on the pore walls [2].

In this study, calcium ethoxide with formula $Ca(OEt)_2$, is characterized, tested and applied on carbonate stone with different porosity, properly selected among those widely employed in Italian Cultural Heritage.

Its performance as stone consolidating product was investigated and compared with that of a commercial one, the nanolime Calosil E50. The kinetic of carbonation process of $Ca(OEt)_2$ was evaluated with μFT-IR and, to understand how the humidity can affect the final product, XRD was used. Preliminary results of the performance of this consolidating treatment applied on carbonate stones regarding the changing in mechanical characteristics - drilling resistance, ultrasonic velocity - and the observation of the coating - photocolorimetric measurements - are here reported and discussed.

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Canvas Consolidation Survey and Treatment Requirements for the NANORESTART project

M. Oriola, G. Campo-Francés, C. Ruiz-Recasens, A. Nualart-Torroja

Arts and Conservation Dept. (Fine Arts Faculty, University of Barcelona) Pau Gargallo 4, 08028 Barcelona, Spain
martaoriola@ub.edu

The conservation unit of the University of Barcelona (UB) is one of the partners of the NANORESTART project (European Union's Horizon 2020 research and innovation programme, grant agreement n. 646063). One of the goals for the UB described in the Work Package 3 of the NANORESTART project is the assessment and validation of the new nanoproducts developed for the strengthening of fibrous materials and in particular of the canvas support of easel paintings.

With time, the canvas support of a painting degrades and becomes fragile. Throughout history, conservators have faced the challenge of consolidating this organic-based layer by developing different treatments (impregnation, lining, loose linings, etc). The requirements this conservation intervention must fulfil have also changed along history due to a change in the governing rules of the profession. Nowadays, the minimal intervention with the least side effects is always the best option and reversibility and good ageing properties of the added materials are also very important.

In the light of this minimal intervention trend fully embraced since the two last decades, lining is seen as a very invasive treatment (while it had once been an almost routine procedure for a painting entering a conservation studio). The focus has, therefore, shifted now to new consolidation products that can consolidate the canvas layer without the need of adding a new textile that will hide forever the original canvas reverse and all the information this layer carries.

In order to know the current practices among conservators regarding the addition of a consolidant to the canvas layer and the requirements conservators would demand nowadays on new consolidants, an international survey was conducted by UB in February 2016. https://www.surveymonkey.co.uk/r/NMCGXXL

This paper analyses the answers to the survey and gives a current picture of practices in Europe regarding the topic of canvas consolidation. It also puts the results in context within the history of conservation treatments and highlights the interest of the conservation community for new better treatments. From the survey results, a prioritized list of current requirements a canvas consolidant must meet, has also been developed and this is the one that is being followed in the NANORESTART project. UB will assess the new nanoproducts developed by the project on the basis of all this new knowledge gained.

Evaluation of the efficacy of Paraloid B-72® and Nanorestore® in the consolidation of carbonated fossils

J. Pozo Canales[1], J. Romero-Noguera[2], E. Bernáldez[1]

[1]Departamento de Biopaleontología (Instituto Andaluz del Patrimonio Histórico) Camino de los Descubrimientos, 41092 Sevilla, España
[2]Departamento de Pintura (Universidad de Sevilla) Laraña 3, 41005 Sevilla, España
josepcdj5555@hotmail.com

In order to guarantee a correct preservation of the original nature of a fossil, it is necessary to establish a conservation protocol according to the most suitable criteria.

For this purpose, the efficacy and safety of the organic paleontological material of Paraloid B-72® and Nanorestore® consolidators have been evaluated. The samples studied were multiple carbonate fossil fragments belonging to the splanchnocranium, the upper jaw and the molars of a *Palaeoloxodon antiquus*, with different morphological characteristics.

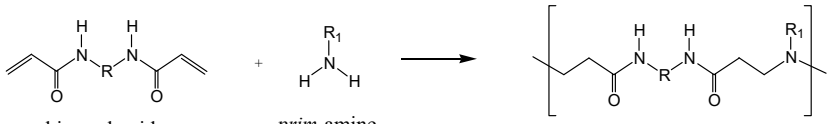
In the first assay, the penetration capacity of the studied consolidators was examined, showing better results in Nanorestore®. In a second assay, new forms of application were proposed for these two products, in order to improve their performance. In the case of Paraloid B-72® a new format has been proposed, whose penetration capacity is limited and a better reversibility is favored, whereas the adhesive capacity of Nanorestore® has been enhanced when combined with AdperTM Single Adhesive Bond 2.

Polyamidoamines as functional polymers for wood and paper protection

G. Predieri[1], C. Graiff[1], L. Bergamonti[1], C. Isca[1], P.P. Lottici[2]

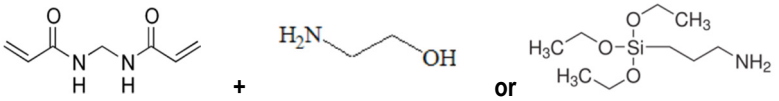
[1]Department of Chemistry (University of Parma) Parma, Italy
[2]Department of Physics and Earth Sciences (University of Parma), Parma, Italy
giovanni.predieri@unipr.it

Polyamidoamines (PAAs) are synthetic polymers obtained by the aza-Michael polyaddition reaction of *prim*-amines (or *sec*-diamines) to bisacrylamides (Scheme below). PAAs are *per se* highly functional polymers and, in addition, can be further functionalized giving rise to a variety of polymeric structures meeting the requisites for applications in such apparently disparate fields as inorganic water pollutants scavengers, sensors, drug and protein intracellular carriers, transfection promoters, peptidomimetic antiviral and antimalarial agent [1].



bisacrylamide *prim*-amine

Very recently, we have proposed the use of functionalized PAAs for the protection of human artifacts made by lignocellulosic materials (wood and paper) against environmental degradation and biodeterioration, taking advantage mainly of the intrinsically basic nature of PAAs [2]. For these purposes two kind of functionalizations have been selected endowing PAAs with different physico-chemical characteristics: the first functionalization consists in the introduction alcoholic groups in order to endow PAA with water solubility; the second one provides PAAs with grafting characteristics throughout inorganic reticulation of alkoxysilane groups. These two functionalizations have been achieved by reacting *N,N*-methylenebisacrylamide (**MBA**) respectively with ethanolamine (**EtA**) or aminopropyltriethoxysilane (**APTES**). The addition reactions and their kinetics have been followed by NMR and Raman spectroscopy [3]. Two families of PAAs have been obtained by this way, namely **PAAOH** and **PAASi**.



MBA **EtA (PAAOH)** **APTES (PAASi)**

Interpenetration of ligno-cellulosic materials by polymers has been monitored by microscopic (ESEM) and spectroscopic (μ-Raman) techniques. The alkoxysilane groups of **PAASi** give hybrid organic-inorganic networking through hydrolysis and condensation reactions (the sol-gel process) producing both hybrid wood composites with good resistance against biotic decay [2] and paper composites [4]. In the case of paper, **PAAOH** was applied in aqueous solution or vehiculated by an Agar gel mainly for deacidification purposes. Actually, the polymer acts as an effective deacidification material without altering chromatic and mechanical characteristics of paper [5].

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The efficacy of stone consolidants based on alkoxysilanes: Influence of solvent type

B. Sena da Fonseca[1], A.P. Ferreira Pinto[2], S. Piçarra[3,4], M.F. Montemor[1]

[1]Centro de Química Estrutural-CQE (IST, Universidade de Lisboa), Lisboa, Portugal
[2]Department of Civil Engineering, Architecture and Georesources (CERIS, ICIST, IST), Universidade de Lisboa, Lisboa, Portugal
[3]Escola Superior de Tecnologia de Setúbal, Setúbal, Portugal
[4]Centro de Química-Física Molecular and Instituto de Nanociência e Nanotecnologia, IST, Universidade de Lisboa, Lisboa, Portugal
senadafonseca@gmail.com

The consolidation of damaged stone-work on built heritage is often necessary, but is a challenge due to its non-reversible character and risk of harmful side effects. The chemical nature and porous media of some stones are important parameters to consider when applying alkoxysilanes-based treatments, which are the most frequently used consolidants. From other consolidants types, it is known that the nature and quantity of solvent may have a fundamental role on the overall performance of the treatments due to different evaporation rates and their role on reverse migration phenomena. It is also known that the sol-gel route of alkoxysilanes and the properties of the resulting solid materials are dependent on the solvent nature. As a consequence, it is expected an important role of the type of solvent on the overall performance of alkoxysilanes-based treatments.

To investigate such influence three similar alkoxysilane-based formulations were developed and tested with different solvents (white spirit, iso-propanol, ethanol) and a commercial solvent-free product (Silres BS OH 100) was used for comparison purposes. First, the potential for application in stone consolidation was analysed through parameters, such as the gelling times, xerogels appearance or ability to provide cohesion to calcite powder. Then, their ability to provide effective consolidation was studied by means of micro-drilling tests on treated and untreated limestone samples. The gelation kinetics, susceptibility to crack and cohesion provided to calcite powder showed to be dependent on the solvent type due to their chemical nature (Fig. 1). Thus, the formulations revealed different potentials for application. These results were confirmed by the contrasting capabilities in providing to the stone a homogeneous and effective consolidation in-depth. The formulation containing ethanol revealed to be the most suitable, since it showed an appropriate gelling time, reduced susceptibility to crack, good penetration ability and provided a uniform cohesion in-depth, as the solvent-free commercial product. The dry residue left within the pores by the formulation containing ethanol was relatively low, of around 18%, whereas the dry residue of commercial solution was of around 35%. In terms of efficiency the solution containing ethanol revealed to be the most attractive for stone consolidation purposes. The choice of the solvent medium should be considered as a control parameter in the attempting to design proper stone consolidants, as the solvent nature can modify greatly the suitability of a consolidation formulation.

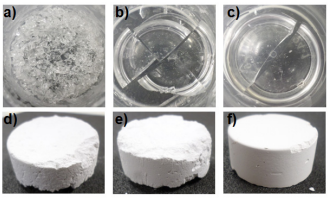

Figure 1. Appearance of the xerogels (a, b, c) and calcite powder monoliths (d, e, f) made with the formulations containing *white spirit* (a and d), iso-propanol (b and e) and ethanol (c and f).

Evaluation of the consolidation efficacy of artificially aged Italian marbles

D. Gulotta[1], F. Gherardi[1], S. Goidanich[1], L. Toniolo[1]

Department of Chemistry, Materials and Materials Engineering (Politecnico di Milano), Piazza Leonardo da Vinci 32, Milano (Italy)
davide.gulotta@polimi.it

A laboratory research aimed at investigating the consolidation efficacy of selected traditional and nano-structured consolidants was conducted in the framework of the pilot conservation site of the Renaissance façade of the Monza Cathedral (Italy). The stone surface of the façade, subjected to long-term exposition in a polluted urban environment, suffered from extensive deterioration, mainly due to mechanical and chemical erosion by rain-wash and to prolonged thermal stresses. As a result, the current state of conservation of the stone blocks and of the decorative elements is characterized by erosion with surface recession, loss of mechanical cohesion and deposits leading to crust formation, depending on the diverse exposition and orientation factors throughout the façade.

In order to set-up the most suitable preservation strategy in such conditions, four different lithotypes were studied in laboratory and fully characterized: Candoglia, Musso and Crevola marble, representative of the actual façade materials, and Carrara marble, used as reference material. Different ageing procedures, based on thermal treatments up to 400° C and chemical leaching by acid attack, were tested in order to induce a significant loss of cohesion of the freshly quarried specimens and to replicate the microstructural features of the weathered surfaces observed in real conditions.

The artificially aged specimens were consolidated by means of a reference tetra-ethyl-orthosilicate (RC 70 by Rhone-Poulenc) and by two nano-structured commercial products: an alcohol-based calcium oxalate suspension with functionalized nanoparticles (SurfaPore FX AB by NanoPhos), and an aqueous dispersion of silica nanoparticles (Nano Estel by CTS). All treatments were applied by capillary absorption in controlled conditions and cured according to the indication of the technical data sheets.

The stone characterization, the evaluation of the ageing protocol and the assessment of the consolidation effects were performed by means of a multi-analytical approach which included: optical and electronic microscopy, XRD analysis, FTIR spectroscopy, colorimetric measurements and mercury intrusion porosimetry. In addition, the microstructural changes upon ageing and consolidation were also studied by water absorption test, while a complete DRMS-measurements characterization was performed to evaluate the surface mechanical features.

The results highlighted that a single thermal treatment can be employed to induce significant damage in all the tested stone types, even though to a variable extent depending on the specific stone characteristics. The three consolidant can all be considered suitable for the stone treatment and, in particular, both nanostructured products provided results comparable to the reference TEOS in terms of increase of the mechanical cohesion of the aged specimens.

Evaluation of ammonium phosphates as consolidating agent for carbonatic stone used in Sicily

M. Martino[1], M.J. Mosquera[2], R. Giarrusso[3], G. Milazzo[1], P. Livreri[1]

[1]Master in Nanotechnologies and nanomaterials for Cultural Heritage (University of Palermo) Italy
[2]Physics Chemistry Department (University of Cádiz) Spain
[3]Geolab s.r.l. Via De Spuches, SNC - 90044 Carini (PA)Italy
martinomanu@libero.it

Most of the consolidating treatments available for the conservation of the stone artifacts still have significant limitations. In fact, there is not a single product available that satisfies, at the same time, all the characteristics researched, such as: efficacy, possibility to retreat the object, durability, compatibility and not toxicity for humans and environment. Among the products for consolidation employed in the conservation fields, the organic-polymeric are often the first choice. In the last decades is grooving the interest for the inorganic-mineral consolidate methods, more chemically and physically compatible with the substrate and more durable in time.

In this study, an innovative mineral treatment, phosphate based, was investigated as a possible consolidating agent for calcareous stones materials and compared with a commercial nanolime (Nanorestore, CTS).

Tests were conducted on two lithotypes extensively used in the historical architecture of Sicily: Marsala limestone (a highly porous calcareous limestone) and Comiso stone (calcareous stone with low porosity).

After preliminary artificial weathering with cycles of salt crystallization, each lithotype was treated with a 7% aqueous solution of DAP applied by cellulose poultice and with a solution of nanophasic calcium hydroxide dispersed in isopropyl alcohol applied by brushing until apparent refusal.

The effects of the two consolidating treatments were assessed by comparing microstructural, physical and mechanical properties of treated and untreated stones. These two treatments were evaluated in terms of effectiveness and compatibility with several tests (water capillary absorption capacity, Hg porosimetry contact angle, Drilling Resistance Measurement System, Schmidt hardness) by comparison with the untreated samples. Also the depth of the consolidating agent in the stone was investigated by Scanning Electron Microscopy with X-ray microanalysis.

From the results of this study, DAP is confirmed as a very effective consolidating treatment, that can allow a reduction of water absorption, without significantly occluding the pores, and an improvement in mechanical properties.

Considering the good performance on both lithotypes, DAP is confirmed as a promising consolidating treatment, also thanks to its high water solubility, absence of toxicity, and very low solubility of the reaction product, calcium phosphate.

Methodological proposals on GPR techniques

L. Lagostena Barrios[1], J.A. Ruiz Gil[2]

IVAGRO, University of Cadiz, Campus de Puerto Real, Spain

The experience of one year GPR application and the realisation of several projects for local authorities are our aim in this work for introducing two ideas about new methodological proposals. We want to remark the changes concerned to the GPR application, we aren't but humanistic professionals operating it. Our researching targets are historic and archaeologic that is an obligatory condition. We consider the GPR techniques not auxiliary or secondary but more important. In our opinion the next technological boundary for archaeological analysis is the non-invasive archaeology. In other words, we understand technological advances (remote sensing) like substitute or complementary tools of the archaeological excavation.

Following this principle, we can propose one advance for enhancing the Archaeological Maps. In fact, we were working in the *Carta Arqueológica de Medina Sidonia* (2012), the first experience in an archaeological map with archaeological sites and settlements georeferenced by GPS. Now we want to adde the DGPR analysis for management and heritage protection of bigger singular localisations.

In the other side, the GPR application in urban context may be an adjusted method if we combine the Stream X GPR for streets, squares and huge spaces with HiMod in houses, rooms, gardens, and small spaces. This possibility with our projects is open for doing it.

Policies for conservation of Cultural Heritage. The *almenara* towers of Cádiz province

M.P. Gallego Pérez

Universidad de Sevilla, Spain
pilargallego@us.es

Cádiz coast enjoys an enormous appeal thanks to the richness of its natural and cultural values but it also constitutes a fragile scene that it's worryingly being degraded by the pressure imposed by the expansion of urban, industrial, port and tourist centres of the coast.

Cultural Heritage is relevant, in terms of sustainable growth, because of identities assertion, social cohesion and economic development that it implies, but it is also a resource at risk, that requires protection in its conciliation with urban growth.

This research proposes the study of the abundant Cultural Heritage in our geography, such as the defence and territory control architectures, that illustrates the close relationship between the cultural goods and the natural values of the environment where they are inserted. In particular, this study focuses on the analysis of the *almenara* towers of the Cádiz province, which form a defensive system along the coast. These entities form a Cultural Landscape that identifies the territory and though they represent an opportunity for its revitalization, they also withstand the pressure that the coast suffers, so its effective protection must be established from the conservation policies at a regional scale. In this sense, what is proposed is a model of analysis that can be extrapolated to similar cases, to offer solutions at three levels: formulas to allow the Planning to treat in detail the cultural values of the territory, through specific and qualified guidelines and recommendations; new protection figures from the legislation on Cultural Heritage that guarantee the preservation of these goods in their individual and contextual dimension, and, finally, proposals to preserve the Cultural Heritage that allows the revitalization of the territory and its enjoyment, regardless of their cultural values.

Combined application of Multi-Channel 3D GPR and Photogrammetry from UAVs for the study of Archaeological sites

J. Vallés, T. Chapa, J. Matesanz, M.A. Maté

Centro de Apoyo a la Investigación de Arqueometría. Universidad Complutense. Facultad de Geografía de Historia. Prof. Aranguren 2. 28040 Madrid (Spain)

The application of 3D multi-channel GPR equipment to the detection of buried structures in archaeological sites has meant a qualitative leap compared to traditional 2D systems. In the same way, orthoimages obtained from Drones allow the elaboration of photogrametries and digital elevation models of very high precision with a significant saving of time. The combination of both methods provides crucial information for documentation, research and management of archaeological sites. The CAI of Archaeometry of the Complutense University has used for this purpose a Stream X of the company IDS and a Microdrone MD4-1000. In this work we present their joint application to different archaeological examples, pointing out how the morphological, sedimentary and lithological features of each one can affect the quality of the obtained results.

Non-destructive assessment of weathering in granite blocks of historical buildings: in situ gamma-ray spectrometry (GRS)

J. Sanjurjo-Sánchez[1], M. Couto[2], C. Alves[2,3]

[1]*Instituto Universitario de Xeoloxía "Isidro Parga Pondal", University of A Coruña, A Coruña, Spain*
[2]*Lab2PT (FCT UID/AUR/04509/2013; FEDER COMPETE POCI-01-0145-FEDER-007528)*
[3]*Earth Sciences Department, School of Sciences, University of Minho, Braga, Portugal*

Rock surfaces suffer weathering processes when exposed to atmospheric agents. This occurs at higher rates on stone blocks of historical buildings in urban environments due to several pollution sources. Increased weathering rates on monumental stone are a major cause of decay due to the induced changes in the structure, mineral and chemical components of rocks. This occurs in all rock types, including granite. However, weathering and its causes are not easy to assess in building stone due to the restricted sampling that hinder the use of destructive analytical methods. Thus, the use of non-destructive methods has been encouraged in the last years. One of the problems of them is the rock heterogeneity, above all in some rocks such as granites that causes important scattering of results and ambiguous conclusions, when spot analyses are performed.

Some geophysical techniques have been applied to assess physical weathering processes (e.g. tomography), but they do not allow assessing chemical weathering. Gamma-ray spectrometry (GRS) is usually used for geological mapping. *In situ* GRS allows assessing the radioisotope content of rock surfaces. 40K, 238U and 232Th and the daughter isotopes of their decay chains are the major radionuclides present in rocks. Their content can be non-destructively assessed by in situ GRS from the gamma-ray emission from rocks. However, this technique has never been used to *in situ* assess the decay of building stone. This is mainly due to some requirements of the technique (it requires plain surfaces and some minimum rock thickness) and the poor knowledge of the changes occurred in the radioactive content of some rock types due to weathering. In this work, we have applied *in situ* GRS to assess stone weathering on buildings of A Coruña (NW Spain) and Braga (NW Portugal). Such buildings were constructed with two types of granite rocks taken from quarries identified in the outskirts of both cities. Quarry samples with different weathering degrees (from fresh to completely weathered) were taken and analysed by other geochemical methods and laboratory high resolution gamma-ray spectrometry to precisely assess their content in radioisotopes, while rock surfaces were measured by *in situ* GRS and results compared. These tests allowed checking the changes in the given radioisotopes with weathering. Afterwards, *in situ* GRS was used to assess and compare weathering in buildings constructed with the same rock types.

In situ gamma-ray spectrometry (GRS) use for non-destructive archaeological exploration

J. Sanjurjo-Sánchez[1], C. Arce Chamorro[1], C. Alves[2], J.C. Sánchez Prado[3], R. Blanco-Rotea[3]

[1]*Instituto Universitario de Xeoloxía "Isidro Parga Pondal", Universidade da Coruña, A Coruña, Spain*
[2]*Lab2PT (FCT UID/AUR/04509/2013; FEDER COMPETE POCI-01-0145-FEDER-007528) and Earth Sciences Department, School of Sciences, University of Minho, Braga, Portugal*
[3]*Landscape, Heritage and Paleoenvironment Laboratory, University of Santiago, Spain*

Geophysical prospection methods are used in archaeology to locate features of archaeological sites before excavation. Among geophysical methods, those mostly used in archaeology are seismic methods, electromagnetical surveys, and georadar. All of them allow assessing properties of soil, sediment and/or rock, providing cross section of soil properties that can be related to buried archaeological structures and objects. Gamma-ray spectrometry (GRS) is a technique used for different geological purposes including mineral exploration and mapping. However, it has not been applied in archaeology: the only study case known by the authors was successful (Moussa, 2001) but no later reports or more extensive studies have been found.

In situ GRS is a non-destructive method that allows direct assessment of potassium-40 (^{40}K), uranium-238 (^{238}U) and thorium-232 (^{232}Th) and daughter radionuclides of their decay chains on rock outcrops and soils. Such radionuclides are ubiquitous in most rocks and soils and the main causes of natural gamma radiation. The technique allows assessing their concentration in topsoil, being of potential use for archaeological exploration but two assumptions must be made: the archaeological buried objects must contain a different concentration of radionuclides than the surrounding sediment or soil, and they must be buried in the topsoil (25-30 cm depth). Thus, it is potentially applicable for exploration of shallow structures or objects. However, it does not provide cross-sections of the ground, but maps of the structures and objects buried.

In this work, we have tested *in situ* GRS in an archaeological site that was partially excavated. In the site, remains of walls made of stone have been excavated, being buried in other parts of the site, but near the ground surface, being the top of the structures at 10-30 cm depth. We have tested in situ GRS in small parcel of 10 x 7 m, located beside nearby excavated areas which wall remains are partially buried in the studied parcel. The purpose of the study is to assess if the technique is reliable for the exploration of structures. Rocks used as building materials in the walls are mostly metamorphic rocks of very low radionuclide content with negligible ^{40}K. However, the sediment that buries the structures contains significant amounts of K, U and Th radioisotopes. Results showed reliable results for surface exploration where shallow structures exist, despite the low radioactive content of the archaeological materials in the site.

Digital Heritage on SW Spain: The UCA Agenda

J.A. Ruiz Gil, L. Lagostena Barrios

IVAGRO, University of Cadiz, Campus de Puerto Real, Spain

On 2006 a group of Humanities professors created Agustin de Horozco Seminar for Economics Studies in Ancient and Medieval History. In this moment the focus of the research was on Geographical Information System (GIS) and Global Position System (GPS) for spatial georeferencing of historical events. This framework was co-financed by the ERDF (European Regional Development Fund).

The main projects were RIPARIA and AQVA DVCTA. The former is a Researching Project about SW Spain wetlands in Ancient and Medieval times. It was funded by National Fund of Economy Ministry of Spain. Aqua Ducta was a punctual study about the roman waterway to Gades (nowadays Cadiz) funded by Agriculture Authority of regional Autonomous Government. Hence from this basis in 2015 the Seminar participated on a new proposal for technological framework of Spanish Economy Ministry. Our aim was reinforcing the GPS system with the Differential GPS (DGPS), joint a GPR (Ground Penetrating Radar).

The focus in this case pretends a step more in spatial knowledge: the creation of the UCA Georadar Unit. Since the spring of 2016 our team has worked with two GPR Systems, the Stream X and HiMod. In the first case sixteen antennas worked in a whole carry on a 4x4 vehicle, fifteen kilometres per hour in the best conditions. The DGPS is included from Leica Geosystems. And the results explained in radiograms are possible to translate in 3D images. The software we use for this is GPR Slice. In the second we work without DGPS and we need to design a grid for locate the HiMod position. We display the images with the OneVision software, from IDS Corporation, like the full of the GPR advices.

After the respective training courses the Stream X was applied in the Phoenician settlement of *Castillo de Doña Blanca*, for testing the results in a known local. Then we tested the equipment in the *Manchon del Hierro*, an unidentified site. In both sites the results were astonished. The first Season of Georadar activity was implemented at *Mesas de Asta* site. The HiMod did it first activity in Puerto Real Maior Church, searching graves and funerary structures in the subsoil.

Unmanned aerial systems as research tools in archaeology and cultural heritage

L. Barbero, J.A. López-Ramírez, L. Talavera

CEIMAR, Universidad de Cádiz, Campus de Puerto Real, Spain
luis.barbero@uca.es

Unmanned aerial systems (UAS) are becoming popular tools in research in different areas, and particularly in archaeology and cultural heritage preservation and conservation, as they provide with very stable platforms where to place a variety of sensors with the purpose of obtaining new data.

One of the main purposes of using aerial survey in archaeology is to integrate data from a series of photos to produce a detail photogrammetric product that can be an ortho-rectified photograph, a digital surface model, or a digital 3D point cloud of the archaeological site. This can be done on a variety of scales. On the other hand, the generation of these high quality photogrammetric products has become very time and cost-effective, thus resulting in a revolution in the way archaeology research is done in the XXI century.

Low weight and size sensor are being developed to be implemented in UAS. The most popular one are digital RGB cameras which provide with photographs for photogrammetry but other sensors could be place on board mainly for prospecting purposes. These include thermal cameras which use in archaeology is based on the fact that materials cropping out or near bellow surface reflect the infrared radiation depending on its composition, moisture content and density. On the other hand, these differences in composition, moisture and density of the near surface materials in an archaeological site may result in either different vigor of the plants growing on top or even in the appearance of different species. These can be detected by a multispectral camera on a UAS which can measure the difference in adsorbance of the active photosynthetic spectral region (visible and near infrared) of the plants. Indexes such as the NDVI (Normalized Difference Vegetation Index), GNDVI (Green Normalized Difference Vegetation Index) or RVI (Ratio Vegetation Index), among others, are produced and can reveal a vegetation pattern, the development of which could be related to the nature of the near surface materials, including buried archaeological structures.

UAS in archaeology also provide an effective way of recording 3D models of large areas, or even constructions or small artifacts, archiving georeferenced models for future studies in case of destruction or disappearance. Another advantage is the reduction of fieldwork time and the enhanced identification of detailed structures and features (even at millimeter scale) that are not easy to identify in normal ortho-photographs.

LiDAR technology applications for the study of Roman mining landscapes: The case of river Sil upper basin (León, Spain)

R. Rubio Díez

Universidad de Salamanca (Departamento de Prehistoria, Historia Antigua y Arqueología)
C/Agricultura, 2 5ºA 37004 Salamanca, Spain
cuspasante@hotmail.com

The application of LIDAR technology for archaeological contexts is a recent concept still under development. The fact that LIDAR flights are available for most of the Spanish territory creates a remarkable tool for the analysis and management of the archaeological heritage. By allowing a better visibility of the archaeological remains, this technology expands both research opportunities and protective measures. Regarding archaeological surface surveys in mountain and forest areas, the application of LiDAR technology gives us a major advantage by being able to penetrate the vegetation and present a detailed imaged of the actual terrain topography. By doing so, this new technology can be a prime source for field work planning.

With this paper, I will present the results obtained in the river Sil upper basin (León, Spain) in a surface field survey carried out within a research project focused on landscape and social evolution between the Early Iron Age and the Late Roman Period. The LiDAR archives were a fundamental tool to detect topographic anomalies which, with their following on-spot verification, allowed identifying new archaeological sites, primarily, Roman gold mines.

Due their morphology and location, mining areas are very hard to detect and enclose, and so they have been traditionally left out of several of the province's archaeological inventory revisions. By supporting research with LiDAR technology, it was possible to identify record and protect a great number of previously unknown archaeological sites. These findings also help to understand the workings of Roman gold mines and further explain the historical process behind the Roman conquest of the Hispanic northwest. The data available so far shows the complexity and standardized basis in which Roman mining took place during the Early Imperial period in this high mountain ridge.

Environmental pH monitoring with optical sensors at the Monastery of Santa María la Real de Nieva (Segovia, Spain)

J. Peña-Poza[1], S. San José[2], C. Gil[3], M.A. Villegas[1]

[1]Instituto de Historia, CCHS-CSIC. Calle Albasanz, 26-28. Madrid, Spain
[2]FCNV. Real Fábrica de Cristales. La Granja de San Ildefonso, Spain
[3]Univ. de Valladolid, Campus María Zambrano. Segovia, Spain

The knowledge of current environmental conditions in which Cultural Heritage is preserved is a key factor to establish appropriate actions for its future conservation. One of the factors that most influences Heritage items deterioration is environmental acidity, which is connected with increasingly high pollution levels.

The Monastery of Santa María la Real de Nieva (Fig. 1) has a front and a cloister that are Goods of Cultural Interest (Bienes de Interés Cultural). Consequently, the environmental acidity monitoring of these spaces results of great interest to evaluate environmental conditions to which they are subjected to assess if they are adequate for a correct conservation.

To carry out the environmental acidity monitoring, chemical sensors synthesized by the Sol-Gel technology and with optical response to environmental acidity were installed in different spaces of the Monastery, either in the cloister (Fig. 2) or in the church. These sensors show a qualitative response through a colour change. In addition, they are also able to give a quantitative response by using a portable measuring unit developed and patented by the research team. The second option was employed in this contribution.

Figure 1. Aerial view of the Monastery

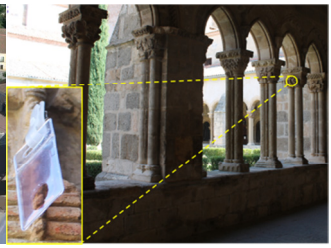

Figure 2. Sensor installed in the cloister.

The environmental acidity monitoring consisted of undertaking two sets of measurements, each set concerned with a distinct period of activity. The first one corresponded to a normal period of visits and religious activities, while the second one corresponded to a period of high flow of people connected with the main feast of the religious patron.

On the whole, resulting data showed pH values little harmful for conservation of cultural goods. However, those sensors installed in the cloister exhibited higher acidity levels (lower pH values) than those installed inside the church. Higher acidity levels were also determined in the period of high flow of people with respect to the pH levels determined in the normal period of visits. Temperature and relative humidity measurements were accomplished as well to complete the study of environmental conditions.

3D Laser scanning applied to diagnosis in vaults

A. Tirado, R. Ortiz, P. Ortiz

Department of Physical, Chemical and Natural Systems, University Pablo de Olavide. Carretera de Utrera Km 1, ES-41013 Seville, Spain

Nowadays, the use of new technologies to evaluate changes in the conservation of cultural heritage is a crucial issue. The laser scanner is a tool with enough precision to describe the existing reality, with which certain aspects can be quantified in order to evaluate objectively the conservation status of cultural heritage. The laser scanner provides us, with a clear and accurate diagnosis, of the processes that have occurred on the historical buildings in order to determine the most appropriate actions.

A Leica ScanStation C10 laser scanner has allowed obtaining the planimetry of the Real Parroquia de Santa María de la Magdalena (Seville, Spain). This church was carried out by Leonardo de Figueroa between 1691 and 1709, in baroque style.

The generated model is a high density point cloud in true magnitude, with the degree of detail of a millimetre, from which metric calculations can be performed, as well as obtaining drawings, cuts or sections, vectorizing and shaping 2D/3D elements. Additionally, the reflectance value of the materials is registered, that is the rebound intensity of laser light beam in each and every points.

In order to evaluate the damage of the vaults, length and width measurements of the cracks and fissures found in the temple under investigation were conducted with the purpose of analyzing objectively the potential damages produced over time. This is possible considering that each point has coordinates that allow locating it. Cracks and fissures are indicated by the disturbances that can be seen in a point cloud's plane. They are detected by a gap in the aforesaid cloud.

Measurements were performed thanks to Leica Geosystems HDS Cyclone 3D Point Cloud Processing Software. The model allows detecting cracks between 2-20mm and length up to 7.2 m. The monitoring of these fissures with 3D Laser scanning allows analyzing the vulnerability and the damage evolution of monuments, and it could be a very useful tool to forecast the preventive conservation.

The use of Micro-computed Tomography as a means for studying the Cultural Heritage

B. Notario, M.I. Sarró-Moreno

Consorcio del Centro Nacional de Investigación sobre la Evolución Humana (CENIEH) Paseo Sierra de Atapuerca 3, 09002 Burgos, Spain

The goal of this work is to describe an X-ray based non-destructive or non-invasive imaging method to study archaeological objects and cultural heritage.

Non-Destructive Testing (NDT) covers a wide group of techniques used both in science and industry to analyze the properties of a material without producing damage [1]. Among NDT methods, X-ray computed tomography arises as a powerful technique for studying archaeological objects. This method allows not only 2D images acquisition, but reconstruction of 3D real structures. Since "tomos" is a Greek word meaning slicing, tomography gives a description of a slice of matter within a bulky object based on several images collected at different angles.

The use of this technique in the field of archaeology and cultural heritage is very useful, since it is a non-destructive technique, the process does not damage the sample. On the other hand, once the 3D reconstruction is obtained, anyone can work on the piece and analyze all the parameters they want from all over the world. Likewise, this method is also useful for restorers allowing them to know how much they have to remove the residues present in the piece.

Nowadays, the National Research Center of Human Evolution (CENIEH) has a micro-computed tomography equipment (GE Phoenix v/tome/x s 240) composed of two x-ray tubes (the nano-focus (up to 180 KV) and the micro-focus (up to 240 KV)) that achieves resolutions up to 500 nm (in the case of the nano-focus) or 1 micron (in the case of the micro-focus).

Since its purchase in 2015, more than 300 scans have been carried out in different materials such as modern-day teeth from reference collections, fossils, microfauna and foraminifera, among others.

During the presentation, the equipment as well as the most interesting results obtained with it, will be presented and explained in detail.

[1] E. Solórzano et al., *Polymer Testing* 32, 2013, 321-329.

3D Multispectral Imaging

B. Campanella[1], E. Grifoni[1,2], S. Legnaioli[1,2], G. Lorenzetti[1], S. Pagnotta[1], V. Palleschi[1,2]

[1]Applied and Laser Spectroscopy Laboratory, Institute of Chemistry of Organometallic Compounds, Research Area of National Research Council Via G. Moruzzi, 1, Pisa, Italy
[2] National Interuniversity Consortium of Materials Science and Technology (INSTM) Via G. Giusti, 9, Florence, Italy
b.campanella89@gmail.com, egrifoni@hotmail.com, s.legnaioli@pi.iccom.cnr.it, a_lorenzetti@hotmail.com, stefanopagnotta@yahoo.it, vincenzo.palleschi@cnr.it

In recent years, the documentary survey of Cultural Heritage has experienced an enormous boost thanks to the optimization of 3D *Reality Based Modelling* that brings documentation and preservation of CH to a more computational oriented approach.

Generally, the use of *Digital Photogrammetry* is consolidated for all those works of art that are inherently three-dimensional, such as sculptures, buildings and archaeological artefacts. On the contrary, the most widespread tendency is to consider the paintings as 2D objects on which apply all the different imaging techniques ignoring the depth information. Their planar nature just partly justifies this approach. However, the reverse side of the paintings can be highly informative for conservators. Consequently, it would be useful to obtain a spatially resolved image in different bands of the electromagnetic spectrum.

The 2D Multispectral digitization and the 3D modelling of easel paintings provide complementary information (spectral *vs* spatial). Integrating the analysis of radiometric contents using 2D multispectral images and the 3D morphometric details of a painting in a single coordinate system can obviously enhance the potential insights into data analysis. Indeed, the usefulness of a 3D model morphometrically correct and well detailed in the Infrared spectral band, to obtain a multiplicity of structural and spectral information in a single digital representation has been proved.

Generally, most of the already proposed combined systems lack flexibility because they acquire data related to the same object by different sensors or in different modes that require complex and time-consuming operations of registration.

Bringing together in a single solution the instances above mentioned, a specific variant of 3D RBM integrated with the *Multispectral Imaging* technique will be introduced. The 3D modeling procedure directly based on multispectral images that we propose is a good compromise in terms of flexibility, cost and precision. The conceptual assumption is that MSI is an extension of color imaging. Thus, the Structure from Motion strategy is a more flexible and easy way to render the different spectral bands, because there is no need for proceed neither to the registration nor to know the calibration parameters of the devices used.

With this same method, it is also possible to obtain a single 3D model starting from a variety of input images.

Because of its suitability for the specific needs of the technical testing, a 14th century panel painting signed by Barnaba from Modena (preserved in the Museum of San Matteo in Pisa) was studied.

Analysis of materials during the restoration of *Tota Pulchra* by Giuseppe Cesari

A. Kriznar[1,3], A. Gómez Morón[2], L. Nuñez Casares[2], E. Fernández Ruíz[2], L. Martín[2], M.A. Respaldiza[1,4]

[1]Centro nacional de Aceleradores – Universidad de Sevilla (CNA-US), Seville, Spain
[2]Instituto Andaluz de Patrimonio Histórico, Seville, Spain
[3]Departamento de Escultura y teoría de las Artes Plásticas, Facultad de Bellas Artes, Universidad de Sevilla, Seville, Spain
[4]Departamento de Física Atómica, Molecular y Nuclear, Facultad de Física, Universidad de Sevilla, Seville, Spain

Giuseppe Cesari (1568-1640), was an Italian Mannerist painter, very much valued in Rome by the Popes and other important clients. He developed a personal style shown by strong colours and chiaroscuros and was known as a fresco and as a canvas painter. Most of his works are conserved in Italy, however one is in the collection of the *Real Academia de Bellas Artes de Santa Isabel de Hungría* in Seville. It was painted around 1600 in the technique of oil on canvas and presents a *Tota Pulchra*. In the spring of 2016 the painting was sent to the *Instituto Andaluz de Patrimonio Histórico* for its restoration and material research.

In general, the conservation state of the painting was very degraded, principally due to a fracture in the lower part of the canvas, but also due to natural processes of ageing of the materials and to some unfortunate interventions in the past. Therefore, the restoration was principally directed towards the removing and repairing of the existing damages but also to return to the painting its aesthetic presentation.

During its restoration, material analyses were carried out, in order to identify pigments and painting preparation used by the artist. For this purpose, invasive and non-invasive techniques were used, such as UV light to distinguish later interventions, radiography to see the internal structure of the painting, and X-Ray Fluorescence (XRF), used for the identification of inorganic materials. The XRF was carried out directly *in situ*, in the restoration workshop. Different colours and tonalities were selected, in order to get the best overview of the materials applied by the artist. The XRF results revealed the use of Ca based preparation, probably chalk (identified by Ca peaks) with a thin layer of reddish priming, carried out as a mixture of red ochre (Fe) and vermilion (Hg). In the painter's palette we can also find lead white (Pb), used also for highlighting, yellow ochre (Fe) and lead-tin yellow (Pb, Sn), azurite (Cu) and smalt (K, Co, Ni, As) for blues and a copper based green pigment, being not possible to identify it with more precision by XRF; for dark colours umber and bone black were used. Also later interventions were confirmed with the help of the UV light and XRF, which identified the existence of modern pigments (20th century) as titanium white (Ti), cadmium yellow and cadmium red (Cd).

Were Late Prehistoric stelae painted? Digital image analysis-based research of the Late Prehistoric stelae of Mirasiviene (Lora del Río, Sevilla) and Montoro (Montoro, Córdoba), South Spain

M.A. Rogerio-Candelera[1], L. García Sanjuán[2], M. Diaz-Guardamino Uribe[3], D.W. Wheatley[4]

[1]*Instituto de Recursos Naturales y Agrobiología de Sevilla (IRNAS-CSIC), Sevilla, Spain*
[2]*Departamento de Prehistoria y Arqueología, Universidad de Sevilla, Sevilla, Spain*
[3]*Cardiff University School of History, Achaeology and Religion, Cardiff, United Kingdom*
[4]*Department of Archaeology, University of Southampton, Southampton, United Kingdom*
m.rogerio@csic.es

The dictionary defines a stela as "a usually carved or inscribed stone slab or pillar used for commemorative purposes". Despite the vague commemorative idea implicit in the concept, we are currently far from having an unambiguous interpretation of Iberian late prehistoric stelae.

A formal question periodically updated in Iberian archaeology is that of the surface treatment of the late prehistoric stelae. These stone monuments, usually engraved following several models, could have been painted, as various apparent colours randomly detected suggest. A complete study on a wide series of stelae would clarify the question, but due to different factors (mainly of an economic nature, but also linked to the need of sampling in order to perform most analytical techniques), this kind of study has not yet been conducted.

This contribution presents the methodology and results of the study of the external appearance of two engraved Spanish stelae: Mirasiviene, which is a typical Late Bronze Age stela from the southwestern Iberian Peninsula, and Montoro, a probably pseudo-epigraphic stela from the Iron Age. These stelae remain unpublished, although the complete publications of both them are currently under preparation. The image analysis protocol implemented on these stelae was designed from an extensive previous experience in rock art recording and involved the decorrelation of standard RGB images by means of Principal Components Analysis.

Application of traditional Japanese technology in large formats 20th century paper

G.M. Contreras

Institut Valencià de conservació, restauració e investigació. IVC Generalitat Valenciana
C/ Pintor Genaro Lahuerta 25, 3ª. Valencia, España
contreras_gem@gva.es

Paper was used from great painters to do sketches. People considered sketches as minor art works, but they are the first and fresher expression of the artist, as painters materialize their ideas and regrets. The Hispanic Society of America preserves an important collection of large sketches that Sorolla drew for the Library's project in this institution. The IVCR restored 32 of 170 sketches with traditional Japanese method.

Sorolla used a low quality paper to do this work and he made collages of his own sketches. The technique used was gouache and this made difficult the restoration process because water can dilute the pigments. In the other hand, these drawing had an additional challenge for the research, a cotton textile support which deformed them because cotton and paper have different behaviour with humidity.

Sorolla's sketches were studied by microphotography, IR reflectometry, UV images to assess the damages and X-ray Fluorescence, SEM/EDX and FTIR to recognize pigments and adhesives (AAVV. *Sorolla íntimo. Bocetos de vision de España.* Fundación Bancaja 2015). Adhesive found was wheat starch and the pigment employed were soluble in water, so it was necessary to research a new restoration method that was non dangerous for the sketches but necessary removable. The cellulose ethers commonly employed in paper restoration have not the warranty to preserve paper for centuries. So we decided to employ traditional Japanese technology to restore these sketches. Traditional Japanese technology is based on the use of wheat starch and handmade paper of vegetable fibres that reduce the stress on the lamination's drawings. These Japanese methods began to apply in Europe in 2000, and in these case, the difficulty of this research was the applications in large format. We studied one by one the sketches to adapt the method because the stress of fibres was enlarged with the sketches sizes. In the ten smaller sketches a tension smoothing and a laminate to counterfibre, while in large sketches (150 x 200 cm) a double lamination to counterfibre and paper fibre was carried out. This adaptation of the Japanese treatment allows stabilizing the tensions in the large format works for its exhibition and storage. These works have been exhibited in Valencia, Alicante, Castellón and La Coruña, which has allowed verifying the effectiveness of the method to stabilize the deformations in the large formats.

Thanks to the HS and the restorers: Ángel Calderón, Patricia Real y Marisa Ferrando.

Impact of dry cleaning conservation techniques on electrophotographic prints

S. Ruiz de Diego[1], E. Antón García[2], S. Muñoz Viñas[2]

[1]Museo Internacional de Electrografía, Universidad de Castilla La Mancha, Cuenca, Spain
[2]Instituto de Restauración del Patrimonio, Universidad Politécnica de Valencia, Spain

Around the second half of the 20th century, a breakthrough in printing technologies took place. A wide range of printing systems and devices were developed, and rapidly adopted by mass market and experimental artists. Electrophotography, also known as xerography, really stands out from other techniques. These prints have become common in modern art collections and archives.

Nowadays, the conservation and preservation of electrophotographic prints are becoming concerns for conservators and institutions dealing with this type of prints, since these have begun to show some signs of deterioration. However, very little literature has focused on this topic.

In order to better address these issues, we have studied the impact of traditional treatments on these prints. As part of our research, we conducted a series of experiments in which a set of replicas were subjected to traditional dry cleaning treatments. After the cleaning procedure, we evaluated changes on the image artwork through naked-eye and with magnification tools such as optical microscopy and scanning electron microscopy (SEM).

Through any of these means, slight changes on the surface and overall look of the print may be observed. Furthermore, significant changes may take place if small fragments of the eraser are left on the surface. These residues, in the form of crumbs, in contact with the image, can get stuck to the ink in just one hour. In turn, the eraser residue may stick to other materials in contact with the print. In our experiments, this phenomenon took place in most of the electrophotographic prints treated with plasticizer-containing erasers. This effect can be related to the so-called vinyl offset.

Vinyl offset is the result of the interaction between the thermoplastic resins used in most electrophotographic inks and the plasticizer often found in polyvinyl chloride (PVC) plastics. When they are in contact for a period of time the ink may soften and adhere to the PVC surface. This problem affects many electrophotographic prints kept in PVC envelopes. As we have found out, some commercial erasers common in paper conservation practice include plasticizers in their formulation. If residues from plasticized erasers are left on the print, vinyl offset is likely to occur.

In conclusion, this research shows that is highly recommendable avoiding the use of plasticizer-contain eraser on electrophotographic prints. If the use of such eraser is unavoidable, or when in doubt, the conservator should make sure that no residue is left on the print.

The Spanish civil optical telegraphy network. An opportunity for study and conservation

A. Alonso Durá[1], S. Tormo-Esteve[2], P. Bértolo Valero[3]

[1]Dept. of Mecánica de los Medios Continuos y Teoría de Estructuras.
Universidad Politécnica de Valencia, Spain
[2]Dept. of Construcciones arquitectónicas. Universidad Politécnica de Valencia, Spain,
[3]Máster Universitario en Conservación del Patrimonio Arquitectónico.
Universidad Politécnica de Valencia, Spain
santores@arq.upv.es

The network of towers of optical telegraphy in Spain conceived by the Colonel of the General Staff Jose Maria Mathé, conforms a unique system built in the mid-nineteenth century. The reasons for its implementation were the government's needs to ensure the communications of the state capital with the cities of the peripheral regions of the Spanish peninsular territory in a fast and safe way.

The political, economic and social instability in a territory in transition from the old regime to a modern state was the motivation to need an alert system that would allow a rapid response. Although optical telegraphy was being replaced by electric in the most advanced nations, in Spain it was decided to implement a system of optical telegraphy inspired by the French system of engineer Chappe, which had 50 years of experience and in our territory had not been used.

The singularity of Mathé's system of civil optical telegraphy consists of adding 50 years of progress in modern telegraphy to a tower conceived as a veritable fort, where telegraphers and soldiers lived together. This construction was considered like a piece of defensive architecture with the most advanced technology for the military strategy. The system was to transmit a codified message from one tower to another using a code of signals and alerts. The most important conditions were a good visibility and a strategic situation.

The telegraph system stopped being used after a decade of its construction, being the towers as only testimony of the past. This communication explains the different types of buildings that still exist in the eastern part of Spain, specifically, the line from Madrid to Valencia. The situation of deterioration is analysed with a hypothesis of general action to maintain its conservation.

The main conclusion of this research is to study an unknown and few divulged heritage technological system. The need for action is necessary and is determined by the urgency of preserving this testimony in this period of the history of communications and defensive architecture of Spain.

Technological proposals for recycling industrial wastes for environmental applications

L. Esquivias[1], I. Romero-Hermida[2], V. Flores-Alés[3], V. Morales-Flórez[1], A. Santos[4]

[1]Dpto. Física de la Materia Condensada, Universidad de Sevilla, Av. Reina Mercedes, s/n, 41012, Seville, Spain
[2]Dpto. Química-Física, U. de Cádiz, Av. República Saharaui s/n, 11510 Puerto Real, Spain
[3]Dpto. Construcciones Arquitectónicas II, U. de Sevilla, Av. Reina Mercedes 4, 41012 Sevilla, Spain
[4]Dpto. Ciencias de la Tierra, U. de Cádiz, Av. República Saharaui s/n, 11510 Puerto Real, Spain
luisesquivias@us.es

In this work we have tested the viability of the indirect carbonation of phosphogypsum (PG) wastes by caustic dissolution with soda and liquid waste of the aluminum anodizing. Both processes started by the addition of phosphogypsum in a caustic dissolution in a ratio 0,5 kg of PG/L of dissolution under room conditions, resulting in the precipitation of the sequestration agents (portlandite (P) or katoite (PGA)), which were separated by centrifuging the suspension at 3000 rpm (all the liquid phases in the methodology were discarded). The carbon capture efficiency was tested by two different experimental procedures: (1) bubbling pure CO_2 into an aqueous suspension of the sequestration agent and (2) by the weathering pools procedure capturing atmospheric CO_2 . XRD, XRF, TGA and SEM were used to analyze the different phases of the procedure. Alkaline liquid waste contained mainly Na (110 ± 2 g/L) and Al (52 ± 2 g/L). The analysis of samples P and PGA confirmed the complete dissolution of the original gypsum and the precipitation of portlandite and katoite ($Ca_3Al_2(OH)_{12}$). The thenardite (Na_2SO_4) was easily removed by simple washing with distilled water. The TGA confirmed weight losses in a process between 250 ºC and 400 ºC (of two steps in the case of the katoite), which can be explained in terms of the reported two-step dehydration of the P and PGA phases. The analysis of the samples after the carbonation experiments confirmed the good efficiency of both carbon sequestration processes. The XRD analysis of the samples confirmed calcium carbonate as almost the exclusively crystalline phase. In addition, the corresponding aluminium compounds phases are present. TGA showed a mass drop of 20 wt.% from 400 ˚C to 750 ˚C due to the decarbonation of the different calcium carbonate polymorphs. Considering these results and the XRF analysis, the carbonation efficiency is estimated above 80%. The XRD analysis of weathered samples revealed the presence of calcium carbonate, thenardite and some traces of quartz. In the case of katoite, an aluminium hydroxide (bayerite, $Al(OH)_3$) resulted. In both cases, the carbonation efficiency was of 100%. A former work, confirmed that toxic trace elements and radioactive species present in the original PG were generally transferred to the solid precipitated phase. The procedure presented in this work represents an environmental proposal to jointly manage the controversial phosphogypsum stockpiles with, eventually, the aluminum industry caustic waste, enabling an efficient technology of carbon dioxide sequestration.

To evaluate one of the obtained precipitates, preliminary studies for the application of the portlandite (lime paste) as construction material, has been carried out. Different mixtures of lime/sand and and water/lime have been tested to obtain a normal consistency, determined according to the procedure described in UNE 83-811-92. For the preparation of the specimens ratios lime/sand = 1:3 and water/lime = 0.5, by weight, was used. Four specimens (4x4x4 cm^3) were made. For the preparation of the mortars, it was used silica sand CEN EN 196-1 (SiO2 content, 99% by mass). The preservation of the specimens was followed according to the standard procedure. For the preservation of the specimens they were placed in a polyethylene bag for 5 days, then the molds were removed and stored in the bag for 2 days, after that time they were kept in a humidity chamber with a humidity of 65 ± 5% for 21 days. Then, the compression test was performed on the flat faces

of two of the specimens and the remaining two were left in contact with the atmospheric CO_2 for a fast carbonation. A month later, the remaining specimens were subjected to the compression test, the results obtained are within the values of other types of pasta limes at these ages; at 28 days was 0.6N / mm^2 and at 59 days was 0.8N/mm^2. After fracture, the phenolphthalein test was carried out to check the mortar carbonation degree. From the outer to the inner of the mortar, it was observed that its carbonation took place only in a thickness of few mm. Thus, the carbonation process is incomplete and considerably higher mechanical strength could be expected for longer aging times.

Furthermore, lixiviation assays are in progress on the different samples: PG, P, PGA and mortars.

NanoRestArt - Nano-materials for the Restoration of works of Art: Cleaning of contemporary art cellulosic supports

E. González[1], S. Marras[1], I. Lozano[2], E. Sánchez[2]

[1]Laboratorio de materiales, Área de investigación y Formación
[2]Servicio de Conservación y Restauración de Patrimonio Bibliográfico, Documental y Obra Gráfica, Instituto del Patrimonio Cultural de España (IPCE)
C/ Pintor El Greco, nº 4. Ciudad Universitaria. 28040 Madrid, Spain
analisis.materiales.ipce@mecd.es

The Spanish Cultural Heritage Institute (IPCE) takes part in NANORESTART project focusing on paper based artifacts. Its mission, among others, is the research of new technologies applied to conservation and restoration fields. The main purpose of this investigation is the implementation of nanotechnologies to the Cultural Heritage, with a focus on contemporary art. This goal will be achieved by formulation of environmentally friendly nanostructured fluids. The IPCE is involved in the assessment of the effectiveness of nano-based materials in cleaning (WP2) and consolidation/reinforcement (WP3) of cellulosic support. This research will extend current cleaning and reinforcement methods offering a valid alternative to traditional restoration techniques. This contribution presents the objectives, methodology and first results of WP2.

IPCE focused its investigation on the assessment of new tools for the removal of different kinds of dirt (artificial soiling, fatty stain and water stain) that in many case could be harmful for the paper support. In order to achieve a representative selection of papers, techniques and alterations mockup models and real cases have been selected and prepared. The formulation developed by CSGI (Centre for Colloids and Surface Science) for the project are highly retentive hydrogels based on PVA (poly(vinyl alcohol)) and PVP (poly(vinyl pyrrolidone)) networks. These gels are transparent, have excellent mechanical properties, allow great control on diffusion, and are environmental friendly. Their assessment will be achieved by evaluation of application, long-term behavior, interaction and compatibility with the different art materials considered. The work methodology employed implies several steps: 1.Bibliographic research; 2. Preparation of models; 3. Aging; 4.Products application; 5. Long term behavior evaluation; 6.Testing of the methodology on real models; 7.Elaboration of application protocol. Analytical characterization is performed before and after each operative phase. Different analytical techniques are employed depending on the information needed (Fourier Transform Infrared - Attenuated Total Reflectance (FTIR-ATR) Spectroscopy, Scanning Electron Microscopy (SEM-EDX); CAMAG DigiStore Documentation system; Colorimetric measurement.-NCS Colour Scan 2.0 CAPSURE.)

The mockups to be used for the study have been realized in duplicate; one set destined to natural aging, and the other one to accelerated aging according to ISO 11341. In this paper just the results concerning the testing of the products on natural aged set are reported.

Nanotechnologies for contemporary art conservation: some applications on plastics

M. Gomez,[1,2] D. Reggio,[1,2] I. Rodriguez Arias,[2] M. A. López Quintela,[2] M. Lazzari[1,2]

[1]Center for Research in Biological Chemistry and Molecular Materials (CIQUS), University of Santiago de Compostela, 15782 Santiago de Compostela, Spain
[2]Dept. of Physical Chemistry, Faculty of Chemistry, University of Santiago de Compostela, 15782 Santiago de Compostela, Spain

This paper describes the contribution of the University of Santiago de Compostela (USC) to the Horizon 2020 NanoRestArt project (NANOmaterials for the RESToration of works of ART). NanoRestArt aims to provide the contemporary art museum community with a platform of conservation treatments and characterization methods based on the most advanced nanotechnologies. Plastics used in artworks are often highly perishable and their preservation is a challenging issue for scientists and conservators. Our specific aim is to develop novel sampling devises able to address the deterioration of polymeric surfaces, such as those of design objects and modern paints. Furthermore, we are testing the reproducibility and sensitivity of the Surface Enhanced Raman Scattering (SERS) technique and its potentials for *in situ* and non-destructive analyses. Many weathering phenomena are being explored within the project; however, we focus on the identification of early indicators of polymer ageing. As far as conservation is concerned, we also aim to develop novel active plastic coatings based on radical scavengers made out of metal clusters supported by metal nanoparticles.

Prototypes of SERS-active substrates are being optimised with different metal coatings, polymeric supports and nanostructures. Namely, we fabricate perfluoropolyether-based [1] and Ormocers©-made substrates by nano-imprint lithography which are coated with different thickness of SERS active metals. To date the aluminium coating by vapour deposition allows the best performance on thermal and photo-aged references such as linseed oil and commercial polyisoprene and ABS, as well as historic plastics from museum collection. To validate the SERS results, we characterise the samples through FTIR-ATR spectroscopy, differential scanning calorimetry, gas chromatography-mass spectrometry and SEM. As a second objective, we prepare metal cluster-based composites to protect the plastic surfaces. Metal clusters can act as electron transporters with modulated band gaps [2] that deactivate the radicals formed during the ageing of polymers. The 'radical traps' are applied on the plastic surfaces through tailored salts-bearing solutions, and by the end of the project we aim to offer new transparent, residue-free, and long-lasting post-processing stabilizers.

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Identification of polymers in the cast sculptures from museum collection

A. Klisińska-Kopacz[1], B. Łydżba-Kopczyńska[1,2], P. Frączek[1], A. Kłosowska-Klechowska[1], M. Obarzanowski[1]

[1]National Museum in Krakow,al. 3 Maja 1, 30-062 Krakow, Poland
[2]University of Wroclaw, Faculty of Chemistry, Cultural Heritage Research Laboratory, F. Joliot-Curie 14, 50-383 Wroclaw, Poland

Contemporary art and design are an important part of our cultural heritage. Increasingly large percentages of museum, library, and archive collections are composed of objects that are in part or entirely made from synthetic polymers. Due to the inherent instability of the materials, as well as artistic experimentation with additives many heritage objects made from synthetic polymers are degrading at an alarming rate. The lack of conservation expertise lead to the application of inappropriate treatments that have, in some cases, resulted in the increased degradation of objects.

The aim of this research was to develop the methodology for identification of the polymers used in museum objects. Tadeusz Kantor and Alina Szapocznikow's cast sculptures were the subjects of our research. First a review of historical recipes of polymers mixed by the artists were done. The polymers and additives composing the body of the sculptures were identified and characterised with portable Raman (785 nm, Inspector Raman, DeltaNu), micro-Raman (514 nm, Jobin-Yvon T64000) and FTIR (IR Affinity-1, Shimadzu). Fillers and inorganic colorants were characterised and identified with XRF (Artax 400, Bruker), and SEM-EDS (ProX, Phenom). In order to evaluate the state of preservation, non-invasive analysis were performed: VIS, near IR, UV photography and X-ray radiography (Dix-Ray).

The identification of the materials is the first step to the creation of recommendations for the care and display of resin cast and plastic objects in museum collections. The development of the best way to analyze polymers in museum collection was recognized. It is an element of respect and care of the cultural heritage of the nineteenth through twenty-first century. Through gaining a better understanding of the materials used, the effect of artist's additives and conservation treatments, it will be possible to propose ways to limit the objects' degradation, advise on their care and display, and help to ensure their continued presence and display in the nation's collection.

Following the natural degradation of caoutchouc: Material analysis of a diving suit from the turn of the 20th century

E. Gómez-Sánchez[1], N. Ferrer[2], D. Kirchner[1], C. Larrue[3], V. Saisnith[3], S. Seidel[4], J. Fey[4]

[1]Material Science Laboratory, Deutsches Bergbau-Museum Bochum
Herner Str. 45 44787 Bochum, Germany.
[2]Centro Científico y Tecnológico de la Universidad de Barcelona, Spain
[3]École Nationale Supérieure de Chimie, Lille, France
[4]Conservation Department Deutsches Bergbau-Museum Bochum, Germany
elena.gomezsanchez@bergbaumuseum.de

Extensive material analyses, among them FTIR in the MIR and FIR spectral ranges, GCMS and REM-EDX, were performed on samples of a turn of the century diving suit (19th-20th, Fig. 1). The object is part of the collection of the Deutsches Bergbau-Museum Bochum (German Mining Museum).

The present work aimed at investigating the materials, especially its polymeric components, and state of conservation of the object, with the purpose of supporting the conservators when planning conservation measures before the suit can be exhibited again.

The study allowed discovering a range of caoutchouc materials used in the diving suit with different purposes, and produced with a range of manufacture processes using different additives, as seen e.g. in REM-EDX. Caoutchouc could be found as lining in waterproofing layers in the textile (Fig. 2), as sealing material in the helmet and in three-dimensional caoutchouc elements.

In the object, a wide range of conservation states for caoutchouc are present, notably in the waterproofing textile, ranging from brittle material to that still maintaining its elasticity. The detailed FTIR study allowed to follow the degradation process and to link certain features to the conservation state of samples with very different infrared spectra, which corresponded in fact to the same material and served the same purpose in different parts of the object. A good correlation can be found between the FTIR spectrum and the qualitative mechanical properties of the samples in the course of the degradation process. The FTIR changes in the spectrum of caoutchouc during natural ageing and the low molecular weight compounds appearing in the process, as analysed with GCMS, will be compared with literature data from artificial ageing.

Fig. 1. Diving suit. (Picture: J. Fey)

Fig. 2. Cross-section of a sample from the diving suit.

Comparative study of protective coatings for the conservation of Urban Art

S.A. Ruffolo[1], A. Macchia[2], L. Rivaroli[2], E. Palermo[1], M.F. La Russa[1]

[1]Università della Calabria, Dipartimento di Biologia, Ecologia e Scienze della Terra (DiBEST)
Via Pietro Bucci, 87036 Arcavacata di Rende (Cs), Italy
[2]YOCOCU, Youth in Conservation of Cultural Heritage
Largo dei Quintili 21, 00175 Roma, Italy

In recent years, the new conservation challenge consists to preserve contemporary mural paintings by Graffiti vandalism or tagging. Contemporary mural paintings are complex artworks for several reasons, including the heterogeneous materials used, the variation of varnishes, and the different types of substrate. Currently we are developing a scientific research to define the issues of long-term care and maintenance of mural paintings and to evaluate the performance of different categories of protective coatings on these artworks. Currently we are exploring the possibility to use antigraffiti agents as protective coatings for urban mural paints. In this paper is focused the on preliminary results related to: a) the study of the interaction of antigraffiti on common synthetic varnishes; b) the testing of effectiveness and efficiency of several commercial products used as antigraffiti, those products are based on the mixture of chemical such as polysiloxane, fluorinated polymers, and microcrystalline waxes); c) the definition of the best procedure to remove vandalism spray without damaging the painting. Laboratory tests have been carried out on specimens; performance has been evaluated by optical and electronic microscope observations, as well as by colorimetric measurements.

The Problem of Dating of 20th Century Russian Oil Paintings: FTIR Microspectroscopy and Numerical Simulation

I.A. Balakhnina[1], N.N. Brandt[1], A.Yu. Chikishev[1], Yu.I. Grenberg[2], I.A. Grigorieva[3], I.F. Kadikova[2], S.A. Pisareva[2]

[1]*Faculty of Physics and International Laser Center, Lomonosov Moscow State University, Leninskie Gory 1, Moscow 119992, Russia*
[2]*State Research Institute for Restoration, Ministry of Culture of the Russian Federation, bldg. 1, 44 Gastello Street, Moscow 107114, Russia*
[3] *The State Hermitage Museum, Dvortsovaya Naberezhnaya 34, St.-Petersburg, 190000, Russia*
brandt@physics.msu.ru

The aim of the work is to test applicability of the FTIR microspectroscopy to the dating of paintings using time-dependent variations in the oil media of zinc-white paint in the paint layer of the 19th-20th-century Russian paintings.

We studied 493 samples of white paints of 230 paintings from several Russian museums and private collections. The paintings have authentic signatures and dates and known provenances. In the experiments we used 219 samples of white paints in which only zinc-white paint was identified using XRF.

We do FTIR micro measurements using a Hyperion 1000 (Bruker) microscope with Tensor 37 IR spectrometer (in the transmission mode, a spectral interval is 600-4000 cm^{-1}, a spectral resolution is 4 cm^{-1}, a lateral resolution is 20 μm).

For spectra processing we subtract linear background in a spectral interval of 2000-3700 cm^{-1} in each spectrum and employ normalization of the entire spectrum by the integral intensity in the interval 2780-3020 cm^{-1}, which we denote I_1. It is commonly accepted that the integral intensity in this spectral interval is insensitive to aging and can be used for normalization of spectra. Then, we calculate the integral intensities in spectral intervals of 1570-1610 (I_2), 1700-1790 (I_3), and 3050-3700 cm^{-1} (I_4). In spite of significant spreads of experimental data, we observe tendencies toward an increase in ratio I_2/I_1 and a decrease in ratio I_3/I_1. A clear tendency is absent for ratio I_4/I_1, which can be due to either close rates of variations in the intensities or weak dependences of the intensities on age.

The experimental results do not make it possible to determine the functional dependence of the aforementioned intensity ratios on age. In this regard, the construction of approximation curve is an incorrect procedure. Moreover, a theoretical model of the intensity changes can hardly be formulated due to possible time-dependence of integral intensity I_1, effect of storage conditions on ageing, presence of various impurities, etc.

The further analysis consists of two parts. First, we propose a procedure that makes it possible to perform threshold estimation of the age of painting based on the measured intensity ratio of spectral bands. Second, we perform numerical simulation of ageing to assess reasons for significant spread of experimental data.

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Modern concrete and its evolution from the standpoint of the built heritage

M.T. Blanco-Varela, J. Murcia

Instituto de Ciencias de la Construcción Eduardo Torroja, CSIC
Serrano Galvache 4, 28033 Madrid, Spain

The industrial manufacture of portland cement in the mid-nineteenth century is regarded as the starting post for modern concrete. In a little over a century and a half, concrete development and improvements in its bearing capacity, durability and workability, along with the application of appropriate structural and construction techniques to the product, has driven exponential growth in the number and type of works that can be built with this material. As noted below, many of such structures are today regarded as part of the built heritage.

Since its inception, concrete has varied significantly in its characteristics and properties, in line with changes in cement manufacturing technology, the energy crisis and the environmental concerns arising in the last quarter century. Concrete production technology has also undergone substantial modification, not only to adapt to the new cements but also to enhance its industrialisation, with the inclusion of admixtures that improve fresh and hardened concrete properties, the development of new construction techniques and so on.

At the outset concrete was used primarily in civil works and only much later in building construction, among others because it was regarded as a scantly aesthetic material apt, in buildings, for the foundations only. Esteem for concrete as a building material came with the advent and expansion of rationalist architecture (Le Corbusier, Mies Van der Rohe, Niemeyer and Spanish engineer Eduardo Torroja, to name a few), which recognised the sculptural dimension and countless possibilities of fair-faced concrete for very attractive plastic solutions. Early on, then, exposed concrete architecture and concrete sculpture were next-of-kin, thanks to ongoing innovation in the material itself and in construction processes.

Prestressed concrete came into practical use in the late nineteen twenties. Given the significant progress attendant upon its structural, constructional and economic, not to mention formal advantages, it was extensively applied after World War II, particularly in Europe.

Today, in addition to sculptures made of this material, many (bulk, reinforced and prestressed) concrete structures are more or less explicitly deemed to be heritage assets, if not necessarily aesthetic elements, by a number of professional communities. The works so regarded include buildings, bridges, viaducts, aqueducts, dams and thin shell roofs, as well as industrial and communications towers and huge wind generators with their prestressed concrete shafts.

The swift expansion of this abundant heritage makes its conservation a growing challenge that will demand ever greater efforts on the part of scientists, engineers, architects, restorers and society at large.

Centennial concrete structures

J.P. Gutiérrez Jiménez, R. Piñeiro Martínez de Lecea, L. Echevarría Giménez, S. Martínez de Mingo

Eduardo Torroja Institute for Construction Science (IETcc-CSIC)
C/ Serrano Galvache, 4. Madrid. Spain
l.echevarria@csic.es

The reinforced concrete structures built in the first half of the 20th century, both in edification and civil works, are about to finish their service life (if they haven't finished it yet). Several of these structures are already centennial and have started to be rehabilitated with modern intervention techniques.

A rational planning of the interventions, repair, reinforcement or even of demolition needs a previous analysis of the real state of the structure. This analysis results in a complex process due to the great amount of parameters involved that are not known.

In order to analyze the structure, it must be assumed that it has been built with the same regulations that are valid at the moment of realization of the project and construction. That is why it is necessary to firstly carry out a normative investigation in order to know the characteristics of the original design, the materials used and the actions considered in the calculation, as well as the constructive systems employed during the construction and the details applied to the design.

In documentary research it is common not to be able to locate the plans of the original structure, which will make necessary a previous survey of its dimensions. In addition, for the characterization of the materials it is necessary to carry out tests on samples drawn from the structure itself, the results of which will give an indication of the materials used in the construction period.

This paper shows the research of several singular structures of reinforced concrete which antiquity has motivated an evaluation of their state in order to be able to keep them in service or for their possible reuse with different intervention solutions. It describes the inspection methodology, the frequent pathology that affects these structures, the several tests carried out on materials, the structural evaluation and the solutions and recommendations applicable to their recovery.

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Measurement of water content and salinity index in concrete by evanescent field dielectrometry

M. Bouichou[1], E. Marie-Victoire[1], H. Jourdan[1], B. Thauvin[2], R. Queguigner[2], R. Olmi,[3] C. Riminesi[3]

[1]Laboratoire de Recherche des Monuments Historiques, Ministère de la Culture et de la communication, Sorbonne universités, CRC-LRMH, CNRS-USR 3224, 29 rue de Paris, Champs-sur-Marne, France
[2] Cerema, Direction territoriale Ouest, Saint-Brieuc, France
[3] CNR, Florence, Italy
myriam.bouichou@culture.gouv.fr

Water and chloride ions are key parameters in corrosion processes of reinforced concrete. Furthermore, rebars corrosion is the first cause of decay in historical monuments made of concrete. Thus to develop new techniques to be able to detect or quantify water and chloride ions seems to be an interesting approach in the diagnosis of cultural heritage reinforced concrete buildings, especially if these new techniques are non-destructive.

The technique SUSI-R© is a non-invasive microwaves system based on the evanescent field dielectrometry technique. In particular, the SUSI instrument is equipped with a resonant termination able to probe the material until 2 cm in depth. Water content and salinity index are calculated from the resonance properties of the probe, which are a function of the material permittivity. Initially developed to quantity the moisture content and to detect the presence of salts in mural paintings, SUSI-R© was considered in this study for concrete.

In a first phase; the SUSI-R© technique was tested to follow the moisture and salts content in reinforced concrete slabs, made with CEM I or CEM III cements, after their semi-immersion in water or in a sodium chloride solution. Several series of measurements were then realized before and during the rise of the imbibition front. In the second phase, the calibration of SUSI-R© was made in laboratory on prisms made with the same concretes as those used for the slabs, and that had undergone the same curing conditions. The resonance parameters were correlated to the moisture content contained in these samples, with various saturation rates, in water and salted water.

The first results of this study showed that the technique allows to follow the hydric changes of the material but also to differentiate the type of imbibition solution: water or salted water. Different evolutions of salinity index were also distinguished according the type of cement. The calibration in laboratory allowed to connect the resonance parameters of the probe with values of moisture content, and so to quantify the moisture content of the concrete slabs investigated during the first phase of the study.

Advances in the monitoring of electrochemical chloride removal in corroded reinforced concrete. Application for the rehabilitation of historic buildings

S. Ramos-Cillán, I. Martínez, M. Castellote

Eduardo Torroja Institute (IETcc), Spanish National Research Council (CSIC)
sara.ramos@csic.es

Existing experience on electrochemical methods for the rehabilitation of corroded reinforced concrete structures shows that chlorides can be removed from these structures and that carbonated concrete can be realkalised. Historic buildings, no matter whether they are famous monuments or so called "minor", represent an important part of our cultural heritage. An appropriate use of these treatments in Historical Heritage can help in forecasting the future behaviour of the structure as well as an appropriate rehabilitation of the same.

However, the current state of know-how has advanced sufficiently to dissipate doubts about the efficiency of electrochemical chloride extraction (ECE) in the majority of the cases, (excluding structures in which additions such as slag has been used for partial cement replacement.); doubts appear to determine the evolution and the final of the treatment. Actually, the way to define the efficiency implies the extraction of concrete cores from the structure to analyse the chloride content. In this way, monitoring the treatment by non-destructive electrochemical techniques is a promising evolution for the application of these rehabilitation treatments in historic buildings.

The intention of this work is to make the checks in a bigger scale of the achievement in a previous work (http://dx.doi.org/10.1016/j.electacta.2015.06.005), in which was possible to monitor the ECE process using different electrical and electrochemical parameters and the determination of passivity indicators to be measured during the treatment, which show consistent differences between repassivated and non-repassivated steels in small mortar specimens.

The present work attempts to find an experimental effective way of monitoring trough electrochemical techniques desalination treatments in concrete elements (slabs contaminated with chlorides). So, it means a change of the scale in the specimen size. In this case, very high quantities of ion chloride were added in the mixing water (up to 12% of chloride by weight of cement), precisely to treat to take to the limit the treatment; in some cases would not be effective and so see differences that permit to calibrate our indicators for this kind of treatment.

ECE treatment was monitored through different electrochemical techniques: accumulated electric charge density (s), instant off potentials (Eoff), polarized and depolarized potentials (Epol, Edep), Polarization Resistance measurements (Rp) registered before, during and after the treatment, electrolyte resistivity measurements (Rx) and its variation during the process (Rx/Rini), and electrochemical impedance spectroscopy (EIS). Core samples were also analysed after treatment to determine the chloride concentration profiles and its coherence with the passivity indicators proposed.

Results suggested that the variations detected for the different parameters at laboratory scale in the previous work have been corroborated in this last phase, being the evolution of Rx /Rini and polarized potential variation (Epol) the more appropriate parameters to be considered as passivity indicators.

In all cases, a very good reproducibility of the tests carried out with two types of contaminant (NaCl and CaCl2) is observed when performing the scale jump, following the results the same variation. Other parameters such as those based on EIS or potential depolarization values could also be considered.

Conservation of ancient reinforced concrete: problematics and challenges

E. Marie-Victoire, M. Bouichou

Laboratoire de Recherche des Monuments Historiques, Centre de la Recherche sur la Conservation, Ministère de la Culture et de la communication, Sorbonne universités, Unité de Service et de Recherche du CNRS, CRC-LRMH CNRS-USR 322429, rue de Paris, 77420 Champs-sur-Marne, France.
elisabeth.marie-victoire@culture.gouv.fr

Concrete is a major building material of the 20th and 21st centuries. However the epic history of actual concrete began in the 19th century with the natural cements production. Then the Portland cements and the metallic reinforcements appeared, leading to nowadays multiplicity of cements and concretes. This history is marked by innovations and patents, followed by regulations and standards. But in between, when architects and builders did learn how to use concrete and experimented a lot, numerous construction defects were made. In addition, concrete is a porous material, sensitive to its environment. All the conditions were therefore gathered to, on the one hand produce incredible architectures, and on the other hand to generate defects and decays that are now to be cured. As a consequence, concrete is now recognized worldwide as a cultural heritage material as evidenced by the recent UNESCO listing of the famous German Bauhaus architecture, the Polish Centennial Hall in Warsaw, the Dutch defence line of Amsterdam, or the French Le Havre city centre rebuilt by Auguste Perret. There is therefore a clear need to quantify this cultural heritage, but also to identify its specific decays and more crucial to develop new restoration and conservation treatments and strategies in accordance with the Venice charter, which means, among other criteria, to preserve a maximum of the original material and aspect.

In France a recent inventory lead to a list of 830 concrete monuments, with a predominance of domestic and sacred architecture. The majors decay mechanisms affecting these monuments were identified as superficial sulphate reaction combined with black dirt deposits, biological covering or erosion. But the most represented and also the more deleterious was carbonation-induced-corrosion. So for two decades, the French ministry of culture, in association with industrial sponsors, and European supports, is developing research activities on ancient concrete decays understanding and characterization, but also on new conservation treatments. If the problematics of cleaning either black crusts or biological covering is now quite apprehended, the question of targeted carbonation-induced corrosion treatments is still open. After several years of research on realkalisation treatments and migrating corrosion inhibitors, with quite limited results, the thematic of water-repellent is now under exploration. In parallel, if non-destructive testing is generally favoured in the field of historical monument, due to the intrinsic seasons impact on the corrosion processes a new field of research is emerging: permanent moisture and corrosion monitoring, the idea being to develop warning sensors and strategies to be able to plan restorations before major losses of original material.

Preserving concrete thin shells. The case of Dietingen sud station by Heinz Isler (1968-1969)

F. Albani[1], C. Dusi[2]

[1] *Department of Architecture and Urban Studies, Politecnico di Milano*
Via Bonardi 3, 20133 Milano, Italy
[2] *Accademia di architettura, Università della Svizzera italiana*
Largo bernasconi 2, 6905 Mendrisio, Canton Ticino, Switzerland
francesca.albani@polimi.it

After World War II the research about the double curavature structures in reinforced concrete was a frontier in the field of typological, spatial and expressive innovation. New materials, new technologies and new production systems supported research into shape-resistant structures that led in various directions. The landscape between the Twenties and Seventies is complex and varied. Among the principal leading figures was the swiss engineer Heinz Isler with his methods called "form finding" based on the use of physical modelling to determine the form and subsequently investigate its stability. When a concrete shell is shaped using a hanging-membrane model, it assumes an ideal form using a minimum of materials, with minimal deformations and compression only. This is only the first step in finding the form. Then one has to do the exact structural analysis, the layout of the reinforcement and prestressing elements, and the detailing, to deal with constructional problems, and finally to carefully observe the structure in use. Heinz Isler's research certainly entered an interesting phase with construction of the dome of Deitingen sud station built in 1968-1969.

The paper intends to investige the case of Deitingen sud station shells restored in Nineties by Heinz Isler himself. The problem of the conservation of this type of structure is not only a question of decay, but it is also a question of the significance and values that acquires (or loses) over time. It might appear that, given the peculiar features of these structures and the authority of the engineers who made them, their fate was to become valued objects, with care and attention lavished on them. In some cases this is true and in others less so.

If the question of the understanding and perception of the architectural, experimental and technical significance of these structures is surely the central factor affecting their future, it is, however, possible to find a specific set of issues related to the morphology of these structures and the construction method by which they were made, which plays a fundamental role in the maintenance and repair project. Among the principal, and most obvious, were their slender cross sections which failed to guarantee sufficient thicknesses of concrete cover to protect the reinforcement rods for long periods, while the methods used to build the roof were incapable of keeping moisture from entering.

Buildings for hydroelectric power plants in N.W. Italian Alpine valleys. An open problem of maintenance, conservation and re-use

S. Fasana, M. Zerbinatti

Department of Structural, Geotechnical and Building Engineering, Politecnico di Torino, Corso Duca degli Abruzzi, 24, 10129, Torino (Italy)

First decades of the 20th Century saw the grown-up of numerous hydroelectric power-plants, diffused in the largest part of Italian Alpine valleys.

As these architectures are representative of technical innovation and can also represent new economical chance for local communities, they are generally characterized in their image by evocative significance: often planned by famous architects or engineers of the Eclecticism (like Piero Portaluppi or Carlo Ceppi) and emphasized by the amazing natural surroundings.

This industrial heritage is actually exploited by numerous interesting local initiatives that connect it in cultural paths. In fact, they are expressive of different construction techniques: technical solutions, stylistics, formal and aesthetical elements are partially based on traditional constructive techniques (stone bearing wall, particular finishing surfaces of decorative stones and external renders, e.g.) often integrated by innovative ones (reinforced concrete structure frames, steel trusses, e.g.), built by able builders (Società Ing. Porcheddu, with Hennebique system, e.g.).

Depending on different elements, such as location, hydraulic head, power produced and technical management requirements, each power station could include different buildings, either in number than in destination; these can be shortly distinguished in *technical* and *complementary. Technical buildings* consist essentially in the proper power plant, were swirl are located, penstock, intake works, transformation cabins; *complementary buildings* generally consist of office buildings and caretaker's houses. These buildings could be located in different places at different altitudes, otherwise could represent a unitarian site for energy production.

The present paper focuses on the complexes of hydroelectric power plants of western Alpine arch, in Piedmont and Aosta Valley regions. Until the second half of the past century, main intervention on *technical buildings* consisted in updating of mechanical or electric apparatus, in order to ameliorate the efficiency or to conform it to new specific norms and acts; *complementary buildings* generally did not require intervention, unless routine maintenance. Recently, some impressive changes, like automation in management, suddenly caused the abandon of many office buildings and caretaker's houses.

Starting from a) the analysis of documents reached from archives (executive drawings, yard documentation, historical photos), b) the analysis of local materials, used and nowadays available, and c) the material degradations phenomena observed on site, the study search appropriate technical solutions for maintenance, restoration and recovery interventions. The main objective is to define guidelines oriented to harmonious recovery projects in relationship with the peculiarity of the buildings, the aims of the Properties, the tourist vocation of the places.

Sculptural ensemble "Hombre y mujer" of May Cavestany: materials and deterioration

A.M. Barberena-Fernández[1], M.T. Blanco-Varela[2]

[1]Escuela Superior de Arte del Principado de Asturias, Plaza de Camposagrado s/n., 33400 Avilés, Spain
[2]Instituto de Ciencias de la Construcción Eduardo Torroja, CSIC Serrano Galvache 4, 28033 Madrid, Spain

The sculptural ensemble "Hombre y mujer" is a schematic and expressionist figurative representation of two linked human figures located on a pedestal, created by the artist Margarita Cavestany in 1958 for a front of building in Avilés (Asturias), currently being restored in the Escuela Superior de Arte del Principado de Asturias.

The objective of this work is to characterize the materials that compose it and to study the state of conservation of the mentioned artwork. The ensemble is a high relief of zinc formed by several pieces, individually made with a casting technique, assembled with lead and tin welds, rivets and steel bars. The hollow back side has been reinforced in parts: with a lime, plaster and sand bastard mortar and ceramic bricks in the lower extremities and with plaster paste inside the upper extremities for fastening the steel reinforcements that are located inside or as a rest of the casting technique.

The ensemble displays among other damages: fissures, generalized corrosion, loss of volume, deformations and separation of pieces by vandalism.

Samples were taken from the surface, obverse and reverse of the sculptures as well as their fillings and welds and were studied through scanning electron microscopy with microanalysis (SEM/EDX), X-ray diffraction (XRD) and infrared spectroscopy (FTIR). The results have allowed to characterize the nature of the different fillings and welds (lead and tin), a grout present in the torso of the man (calcite and an organic additive) and to identify different degradation products from zinc.

Thus, in the interior zones in contact with gypsum, zinc sulfate heptahydrate ($ZnSO_4 \cdot 7H_2O$) is identified, also present in highly corroded areas of the surface as a white powder. On the back there are also deposits of hydrozincite ($Zn_5(CO_3)_2(OH)_6$), as well as hydroxides, phosphates, arsenates and hydrated zinc / copper sulfates. Many of the crystalline phases referred to are the result of surface corrosion to form a patina, while others more unstable come from the interaction with plaster filling and atmospheric pollutants.

Mechanical and durable properties and sustainability evaluation of polymer-modified mortars for structural reparations

A. González Lucas[1], J. Fernández Gómez[2], M. J. Rubio Encinas[2], A. Moragues Terrades[2], P. Villanueva Llauradó[2]

[1]Sika S.A.U., Carr. De Fuencarral 72, Alcobendas, 28108 Madrid, Spain
[2] Departamento Ingeniería Civil: Construcción, ETSICCP, UPM C/Profesor Aranguren 3, 28040 Madrid, Spain

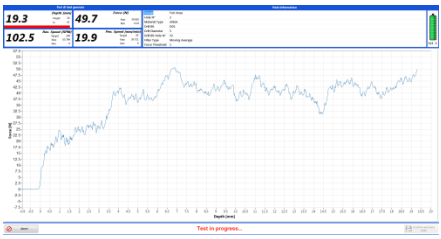
This paper presents an experimental investigation on cement-based mortars for reparation of concrete structures, in order to assess the impact of the inclusion of polymers on the long-term performance and Life Cycle. The investigation was undertaken considering the properties regulated by the European standard UNE-EN 1504, which indicates the minimum requirements that repair mortars must provide for structural categories. Two cement-based mortars, one with polymer and one without polymer, were designed in order to obtain mechanical properties that fulfilled the requisites of structural reparation R4 as presented in UNE-EN 1504. Tests to characterise mechanical properties consisted of compressive strength, flexural strength and adhesion by pull-off. The durable properties of the mortars were evaluated by carrying out tests including depth of carbonation, capillary suction and adhesion by pull-off tests after 50 freeze-thaw cycles. In addition, the microstructure of the mortars was analysed through mercury intrusion porosimetry at the ages of 28, 60 and 90 days. Results from porosimetry tests, depth of carbonation and capillary suction were coherent and indicated that the polymer enhanced long-term performance of the mortar by means of refining its porous structure and by hindering the penetration of aggressive agents. A significant finding was that adhesion after freeze-thaw cycles, which is determinant for repair applications, was also improved by the refinement of the mimcrostructure. With these results, the service life of reparations made with each mortar was calculated according to the Spanish Code EHE-08. The expressions of EHE-08 take into account initialization and propagation of carbonation; both aspects were observed by assessing the carbonation speed in the tests and given an average thickness of 10 mm for repair coatings. It was observed that the inclusion of polymers led to an extended service life of 62.62 years (with a IIb exposure) compared to that of 25.31 years with traditional mortars, and thence sustainability of mortars was compared regarding their renovation frequency. For evaluating different criteria regarding the mortar's sustainability, a Life Cycle Assessment (LCA) tool was developed with the software ACV GaBi 6.3. The results of the Cradle-to-grave analysis included the total energy demand, the global-warming potential and the photochemical ozone creation potential. From the LCA it was concluded that, for reparations with a service life greater than 50 years in a normal environmental exposure, polymer-modified mortars optimise the sustainability of the repair solution. This justifies the inclusion of polymers in cement-based repair mortars from performance-oriented and environmental approaches.

Portable device for Drilling Resistance Test method

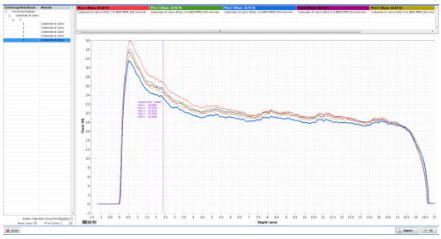
E. Valentini, A. Benincasa

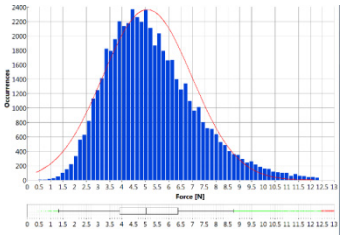
SINT Technology S.r.l, Via delle Calandre, 63 - 50041 Calenzano (Florence), Italy
www.sintechnology.com info@sintechnology.com

The Drilling Resistance Test Method can be used for the characterization of historic masonry materials, both on site and in laboratory. It allows to obtain detailed information concerning the mechanical properties of materials and to evaluate, for example, the performance of consolidation treatments. The test consists in drilling a small hole at a set constant rotational speed and penetration rate in order to measure drilling force versus depth. The Drilling Resistance Measurement System (DRMS) is an useful portable tool that continuously measures the required force to drill the hole in the investigated material during all the testing process.



A dedicated software performs a real-time data acquisition from the instrument and provides advanced features for data analysis. The software also produces filtering functions in order to separate the desired signal from the noise (drill bit rotation, vibrations, etc.). After the data acquisition, it's possible to elaborate each hole result in relation to the other measurements acquired by the software.





Due to the high fluctuations in the drilling resistance around the mean value of some materials (e.g. mortars and clay bricks), the average parameters are not enough to characterize them. In these case it's advisable to use indices that take into account the non-uniformity of the material (e.g. mode, standard deviation, etc.). The results of the statistical analysis are provided by the DRMS acquisition and calculation software that returns statistical parameters (Standard Deviation, Kurtosis, Skewness, box plot and histograms) from the drilling resistance measurements. The analysis is complemented by graphic contents that enable a rapid comparison between the calculated statistical indices (related to the specific material) and an ideal Gaussian distribution. It's also possible to export acquired data into different format files to allow the elaboration with third-part software programs.

Synthesis and analytical characterisation of $Ca(OH)_2$ nanoparticles / (Poly (EMA/MA) nanocomposites for consolidation of ancient Egypt carbonate stones

S.M. Ahmed[1], S.S. Darwish[2], M.A. Adam[2], M.A. Al-Dosari[3], N.A. Al-Mouallimi[4], N.A. Elmarzugi[5]

[1]The grand Egyptian Museum (Ministry of Antiquities) Cairo, Egypt
[2]Department of Conservation (Faculty of Archaeology, Cairo University) Giza, Egypt
[3]National Nanotechnology Research Center (King Abdulalziz City for Science and Technology-KACST), Riyadh, Saudi Arabia
[4]Saudi Nano Information Center, Jeddah, Saudi Arabia
[5]Faculty of Pharmacy (Tripoli University & National Nanotechnology Project, Biotechnology Research Center, LARST), Tripoli, Libya
sayedmansour32@yahoo.com, nelmarzugi@gmail.com

Ancient Egypt carbonate stone monuments (lime-based wall paintings, calcareous stones) undergo unwanted changes due to the exposure to many physical and chemical deterioration factors. The aim of this study was to evaluate the effectiveness of inorganic compatible treatments, based on nanosized particles of calcium hydroxide (slaked lime) as a consolidation and protection material dispersed in acrylic copolymer, poly ethylmethacrylate/methylacrylate (70:30) (Poly (EMA/MA), for calcareous stone monuments and painted surfaces affected by different kinds of decay, thanks to the conversion of lime into calcium carbonate. Calcium carbonate is, as a matter of fact, very compatible with many carbonatic lithotypes and architectonic surfaces, because its characteristics are very similar to those of the materials to be restored.

The synthesis process of Ca $(OH)_2$ nanoparticles/polymer nanocomposites have been prepared by in situ emulsion polymerization system. The prepared nanocomposite containing 5% of Ca $(OH)_2$ nanoparticles showed obvious transparency features and represent nanocomposites coating technology with hydrophobic, consolidating and well protection properties.

Some tests are performed in order to estimate the superficial consolidating and protective effect of the treatment; the obtained nanocomposites have been characterized by TEM, while the penetration depth, re-aggregating effects of the deposited phase and the surface morphology before and after aging was examined by Scanning electron microscopy (SEM), Improving of stone mechanical properties were evaluated by compressive strength tests, Changes in water-interaction properties were evaluated by water absorption capillarity measurements and colorimetric measurements were used to evaluate the optical appearance.

All the results converged in individuating these nanometric particles of slaked lime as an innovative, completely compatible, and efficient material for the consolidation of artistic (lime-based wall paintings) and architectural (limestones) surfaces, a $(OH)_2$ /polymer nanocomposite enhanced the durability of limestone toward thermal aging and improved the stone mechanical properties compared to the samples treated with pure acrylic copolymer without Ca $(OH)_2$ nanoparticles.

Preconsolidation prior desalation on granitic rocks. A new approach to evaluate the most suitable treatment

I. de Rosario[1], T. Rivas[1], J. Feijoo[1], R. Benavides[3], M.J. Mosquera[2]

[1]Dpt. Ingeniería de los Recursos Naturales y Medio Ambiente (E.T.S.I. Minas. Universidad de Vigo), Campus Lagoas Marcosende, Vigo, Spain
[2]TEP-243 Nanomaterials, Dpt. de Química-Física, Facultad de Ciencias Universidad de Cádiz, Campus Universitario Rio San Pedro, Puerto Real, Cádiz, Spain
[3]Tomos Conservación Restauración, S.L.
irosario@uvigo.es

The soluble salts are one of the most aggressive deterioration factors in granites used in architectural and archaeological heritage, being responsible for the formation of sand disaggregation and scales [1]. Similarly, soluble salts are one of the most difficult problems to be solved on site. The most frequent intervention is desalination with poultices, although the desalination is almost never completely effective given the difficulty of eliminate the source of the salts. During in situ interventions of granite suffering sand disaggregation or scales derived from salt crystallization, conservators need to perform, prior to desalination with poultices, a consolidation of the surfaces in order to avoid the loss of material which can be derived from the contact of the altered surface with the poultices. This consolidation must be performed in order to increase de cohesion of the rocks but without compromising the effectiveness of the poultices to extract the salts. Another problem arising during in situ interventions is the need to choose the suitable consolidant and poultice for the rock to be treated through a previous evaluation in laboratory with the same rock used in the monument; this is derived from the high influence of the textural an mineralogical properties of the rock in the effectiveness and durability of the consolidants [2] and also on the effectiveness of the desalination poultices [3].

In this study, a specific protocol aimed to identify the proper consolidant and type of poultice to respectively preconsolidate and desalinated the North façade of the Cathedral of Ourense, an emblematic example of Galician Romanesque, is presented. Using the same rock of the façade, the approach consisted on: 1) the effectiveness and harmful effects evaluation under laboratory conditions, of two consolidants, one of them a nanoconsolidant based on silicon oligomers modified with n -octylamine (UCAD-2o); 2) the same evaluation in selected areas of the façade, by means techniques adapted to be applied on monuments and with the aim to confirm the results obtained in laboratory; 3) evaluation of the desalination effectiveness of different types of poultices and application procedures in the preconsolidated areas of the façade, comparing the results with data obtained for untreated areas of the monument.

The results showed that: 1) the evaluation made in situ and in laboratory conditions showed the same results regarding effectiveness; both consolidant allowed to reduce the porosity of the granite and to increase de superficial cohesion; 2) the type of poultice and the desalination procedure that allowed a greater efficiency of desalination of chloride and sulfate (the salts found in greater quantity) was one that favored the desalation by means advection; 3) the nanoconsolidant showed a better behavior in order to desalinate the rock in situ, because this product reduced to a greater extent the capillary pores and, in consequence, allowed to obtain a higher desalination effectiveness. These results allowed to identify, on the basis of scientific knowledge, the proper consolidant product and the type and procedure of desalination for the rock of the façade, and confirmed the need to perform an evaluation of the effectiveness of consolidation and desalation

specifically designed to the rock of the building and to the active deterioration process, in order to obtain the maximum effectiveness and the lowest harmful effects on the stone.

Acknowledgments: To the Dirección Xeral de Conservación e Restauración de Bens Culturais, of the Galician Autonomous Government which allowed to dispose these data to be published. J. Feijoo's research is supported by a FPU grant from the Spanish Ministerio de Educación, Cultura y Deporte.

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Carbonation of lime mortars in high CO_2 environment

D. Ergenç[1,2], R. Fort González[1], D. Sanz Arauz[2]

[1]*Institute of Geosciences (CSIC-UCM)*
[2]Conservation and Restoration of Architectural Heritage Program, ETSAM (UPM)
C/ José Antonio Novais, 12, 28040 Madrid, Spain
duyguerg@ucm.es, rafael.fort@csic.es

For the conservation and sustainable restoration of the archaeological sites and historic buildings, the importance and the need of using lime based mortars rather than cement is already accepted. Nonetheless, the carbonation of the lime can be last for years and the researchers, therefore, have been trying to find the way of acceleration of this process [1-3]. Apparently, CO_2 concentration is one of the crucial factor affecting carbonation and thus the durability of mortars [1,2].

In this research the mortar samples were cured at high-CO_2 atmosphere in the climatic chamber in order to accelerate the carbonation of mortars. For this aim, two types of lime mortars were prepared; lime putty and standard sand (M1) and lime putty, standard sand, ceramic dust and fragments (M2). After the two weeks setting in a humid environment, the mortars were demoulded and half of the samples were placed into the climatic chamber in which the temperature (20˚C), relative humidity (60%) and CO_2 concentration (1600 ppm) were constant during the experiment for 6 months, and the others were left in laboratory conditions.

The carbonation of the samples was observed in 28, 90, 120 and 180 through the microstructure, physical, hydric and mechanical properties by means of X-ray diffraction (XRD), thermogravimetry (TGA-DSC), optical microscopy, phenolphthalein test, scanning electron microscopy (SEM-EDS), mercury intrusion porosimetry (MIP), ultrasonic pulse velocity (UPV), surface hardness (equotip), air permeability, water absorption and capillary absorption, compressive and flexural strengths. Note that mechanical tests were conducted in the 90,120 and 180 days.

The evolution of the physical, mechanical, and microstructural properties during the carbonation of M1 and M2 mortars in the climatic chamber in comparison with the control samples is investigated and also the applicability to the conservation field is discussed.

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Superomniphobic coatings for the protection of stone monuments

I. Karapanagiotis

Dept. of Management and Conservation of Ecclesiastical Cultural Heritage Objects (University Ecclesiastical Academy of Thessaloniki) N. Plastira 65, 542 50 Thessaloniki, Greece
y.karapanagiotis@aeath.gr

Bioinspired surfaces of special wetting properties, from superhydrophobicity to superhydrophilicity (Fig. 1) have recently attracted considerable attention because of their numerous potential applications ranging from coatings for biomedical devices and windows/solar cells/mirrors for self-cleaning, to coatings for the preservation and protection of monuments of the cultural heritage, against rainwater induced decay.

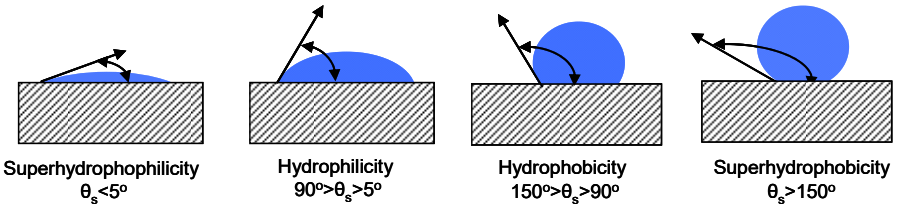

Figure 1. Wetting regimes.

We report that the wetting properties of the surfaces of polymer films changed dramatically from the usual inherent hydrophobicity (or slight hydrophilicity) to superhydrophobicity (static contact angle, θ_S > 150º) by embedding oxide nanoparticles into the polymer matrices. The desired hierarchical roughness at the micrometer and nanometer scale was induced in various polymers and polysiloxane materials used in modern conservation science, by adding oxide nanoparticles, ranging from 7 to 70 nm in mean diameter. Particles were added in the polymer solutions which were afterwards sprayed on substrates such as sandstone, marble and mortar which can be found in monuments of the cultural heritage. It is stressed that superhydrophobicity was accompanied by water repellency, as evidenced by the low contact angle hysteresis (CAH < 10º). Therefore, the simple method, devised to change the wetting properties of polymer/siloxane films thus achieving extreme nonwetting is flexible as it can be effectively applied using different materials, including polymers and oxide nanoparticles of low cost. Moreover, the method can be easily used for the treatment of large and various surfaces-substrates such as buildings and monuments.

The effects of the (i) concentration and size of the nanoparticles, (ii) chemical nature of the polymer matrix and (iii) treated substrate, on the wetting properties of the films were investigated and interpreted using Scanning Electron Microscopy (SEM). Furthermore, it will be shown that depending on the color of the underlying substrate, the superhydrophobic water repellent polymer/siloxane-nanoparticle films may have a negligible effect on the aesthetic appearance of the treated substrate. The effects of the nanoparticles on the vapor permeability and water absorption by capillarity will be elucidated.

Finally, it will be demonstrated that with careful selection of the polymer material and the concentration of nanoparticles, protective coatings are produced which can repel virtually any liquid with surface tension between that of water (=72 mN/m) and oil (=29 mN/m). Superomniphobic coatings can provide enhanced protection to buildings and monuments often exposed to urban air pollution.

Electrochemical methods in conservation of Cultural Heritage

T. Rivas

Dpt. Natural Resources and Environmental Engineering, School of Mine and Energy Engineering, University of Vigo, Spain
trivas@uvigo.es

In this talk, a review of the current state and of the potential of electrokinetic methods in the conservation of the archaeologic, architectural and artistic heritage is made. The scientific and technological progress for its application in the desalination of materials, such as bricks, sedimentary carbonate rocks and, more recently, granites is exposed, as well as its advantages over the conventional methods of desalination (poultices) and the challenges to be addressed for its implementation in situ. Also, the promising results for the consolidation of porous materials are described, highlighting the contributions regarding the design of the devices that allow a homogenous consolidation across the area affected by the electric current but also the limitations regarding the chemical nature of the consolidants and their compatibility with the materials. As potentialities, this technique could be adapted to be applied in situ, in order to waterproof the walls affected by capillary rise, thus reducing on the materials the risk of chemical and physical alteration of water or soluble salts.

Effectiveness of a novel consolidant/hydrophobic nanomaterial applied on archaeologic stones: Durability Assessment after three years of in situ exposure

F. Elhaddad, M.J. Mosquera

TEP-243 Nanomaterials Group (Physical-Chemistry Department, University of Cadiz) Campus Universitario Rio San Pedro 11510 Puerto Real (Cádiz), Spain
farid.elhaddad@uca.es

The archaeological monuments are subjected to different environmental decay, resulting in damage and deterioration of building stones. The archaeological site of Baelo Claudia (Cádiz) was founded by the Romans in the late second century. The continuous exposure to marine aerosol has produced a severe weathering of the Baelo Claudia building stone. The aim of this study was to assess the durability of a novel consolidant/hydrophobic nanomaterial applied on the Baelo Claudia sandstones after three years of exposure to conditions of this archaeological site. For comparison, two commercial products were also evaluated: Silres BS290 (hydrophobic product) and Silres BSOH100 (consolidant product). The following evaluations were carried out: porosimetric distribution, vapour diffusivity, hardness Vickers test, drilling resistance, contact angle tests, measurements of water absorption by capillarity and colorimetric test. We also observed the changes in morphology of the stone by SEM. Finally, we measured the penetration depth of the products under study by contact angle evaluation.

The results showed that the product synthesized in our laboratory has maintained its consolidant effectiveness for three years due to the combined effect of the surfactant and the PDMS, creating a crack-free coating in the surface of the sandstone. In the case of the commercial consolidant BSOH100, a crack coating was produced. The hydrophobic proprieties of the UCA product were also maintained for three years due to the formation of a continuous crack-free layer on the sandstone surface and to its higher penetration depth than that produced by the hydrophobic commercial product. Specifically, BS290 produces a superficial and discontinuous coating, being completely altered by environmental agents after the three years exposure.

Acknowledgements: This work has been supported by the Spanish Government/ FEDER-EU (MAT2013-42934-R).

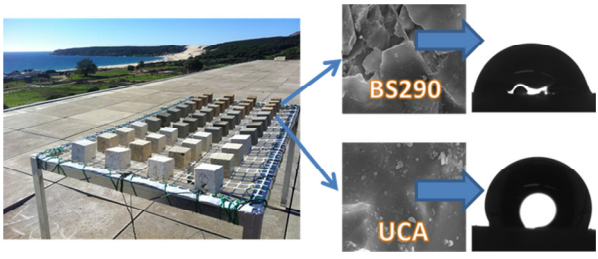

Figure1. SEM images and contact angles of the treated stones after three years exposure to conditions of Baelo Claudia archaeological site.

Effectiveness of a new consolidants generation on sedimentary rocks

M. Remzova[1,2], L.A.M. Carrascosa [3], M.J. Mosquera[3], J. Rathousky[1]

[1]*J. Heyrovsky Institute of Physical Chemistry (Academy of Sciences of the Czech Republic) Dolejskova 3, 182 23 Prague 8, Czech Republic*
[2] *Department of Physical Chemistry (University of Chemistry and Technology) Prague, Technicka 5, 166 28 Prague 6, Czech Republic*
[3]*TEP-243 Nanomaterial Group (Physical-Chemistry Department, University of Cadiz) 11510 Puerto Real (Cadiz), Spain*
mon.remzova@gmail.com

Monumental stones are exposed to weathering processes, which have a negative effect on their mechanical properties. Therefore, restauration and protection of these weathered materials by application of suitable consolidants is an important challenge.

Silicon alkoxides have frequently used as consolidants for the weathered silicate materials due to their chemical compatibility. However, their physical properties are not ideal. Their drawbacks, the shrinkage and cracking, can be reduced by the use of mesoporous consolidants or by their modification with nanoparticles (NPs). In order to suppress the formation of micropores and subsequently, preventing cracking, organic amines are employed as structure-direct agent of consolidants. Thus, the role of primary amines with an alkyl chain is more complex than that of mere catalysts. In the case of the NPs, they can increase the mechanical resistance of the material and produce larger pores.

In this work, a consolidant product was synthesized by the following sol-gel route: a silica oligomer was mixed with n-octylamine in an alcoholic solution. In addition, polydimethylsiloxane or hydrophobic silica NPs were added in order to provide hydrophobic properties. Alternatively, a product using an organometallic catalyst instead of n-octylamine was prepared to stablish comparisons. The prepared sols were applied on Lecce Stone, which is a biocalcarenite with an open porosity around 35 %. A lot of Monuments in the southeast of Italy have been built with this stone. The evaluation of the mechanical properties by means of Drilling Resistance test showed an enhancement of the consolidation properties for all the treated samples. Regarding to the samples treated with the products containing hydrophobic components, the water protective properties were evaluated by measuring static and dynamic contact angle values. Indeed, a water absorption by capillarity test (WAC) was carried out. Finally, the possible negative effect induced by the consolidant products on the stone were tested. Specifically, colour change and vapour permeability were evaluated.

The best consolidant performance was obtained for the products containing n-octylamine because of cracking is prevented. WAC data showed that the hydrophobic products significantly decreased water absorption. The contact angle values measured after the WAC test showed that the hydrophobic preserved their water protective properties, whereas they were completely lost for the other products. All the products induced colour difference values (ΔE^*) ≤ 5, being negligible for human eye. Regarding to vapour permeability, all of them caused reduction lower than 25 %.

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Protecting clay mortars through water-proof techniques

A. Karozou[1], K. Matziaris[2], M. Stefanidou[1]

[1] Laboratory of building Materials, Civil Engineering Department, Aristotle University of Thessaloniki, Greece
[2] R&D Uzin Hellas, Thessaloniki, Greece
stefan@civil.auth.gr, uzin@otenet.gr

Clay–based materials have been proved to be sustainable and environmental friendly. As an important number of our cultural heritage is made by clay, these materials should be studied and protected. The main pathology of clay materials is attributed to the different forms of humidity (rain water, condensation, capillarity) which disintegrate the clay structure and provokes the loosening of the material's cohesion.

The aim of this paper is to study the protection of clay mortars by increasing their hydrophobicity. Clay mortars were produced and two approaches were followed in order to increase their durability. The first refers to the use of additives in the form of redispersible powders which were added in 5%w/w of the clay. The aim was to promote the cohesiveness, the hydrophobicity and the workability of the matrix. Additionally, the surface of the mortars was covered by a siloxane-based polymer which in one case was nano-modified using nano-SiO_2 in 1.5%w/w.The surface treatment was applied by brush.

After treatment the specimens were subjected to physical tests such as, water absorption, by Karsten tubes and capillarity as well as the water drop test in order to measure the static contact angle on the surface. In parallel, durability tests in wetting-drying cycles as well as in salt cycles were performed. The results show that the water-proofing treatment was sufficient and important improvement of the hydric behaviour of clay mortars was observed in all cases. Significant and durable improvement was observed in the cases where the combination of the redispersible powders with nano-modified siloxan polymer was used.

The results of this paper can be used by restorers and researchers dealing with the preservation of the vernacular architecture.

Long-lasting superhydrophobic coatings for stones

L.A.M. Carrascosa, A. Gonzalez-Sanchez, M.L.A. Gil, M.J. Mosquera

TEP-243 Nanomaterial Group (Physical-Chemistry Department, University of Cadiz) 11510 Puerto Real (Cadiz), Spain
luis.martinez@uca.es

Stones have been widely used as building materials because of their mechanical properties. However, their exposure to outdoor environment may causes stone decay due to action of different factors, such as: wind, temperature changes and especially water that produces: salt crystallization, ice swelling or biodecay.

In order to obtain superhydrophobic surfaces, it is necessary to combine a reduction of surface free energy (by chemical modification of the surface), and create a roughness characteristic of a Cassie-Baxter state (where water remains on the top of the peaks of the roughness, improving repellence). Although the development of superhydrophobic coatings on stone has been previously investigated, their durability under outdoor conditions remains as a challenge. Therefore, it is necessary to produce coatings with high chemical and mechanical resistance.

We prepared asuperhydrophobic coatings by mixing a silica oligomer, in the presence of n-octylamine, with hydrophobic silica nanoparticles (NPs). The NPs are treated with hexamethyldisilazane (HMDS). Thus, they play a double role: (i) to reduce surface energy and (ii) to produce Cassie-Baxter roughness. The effect of NPs content was studied. These sols were applied onto low-porous limestone samples by spraying. The measurement of static and dynamic contact angle values confirmed that superhydrophobic surfaces are produced. Indeed, a topographic analysis by Atomic Force Microscopy (AFM) and Scanning Electron Microscopy (SEM) showed the creation of Cassie-Baxter roughness. Finally, the treated stones were subjected to three durability tests: absorption by capillarity followed by contact angles evaluation, rain-simulation, and a peeling test. The coating containing the highest NPs content showed the best long-lasting performance. After peeling test, an in-depth investigation of the surfaces was carried out by AFM and SEM. The images obtained showed that Cassie-Baxter topography is exclusively achieved for the highest NPs content product.

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Superhydrophobic coatings with self-reparability properties for application on building materials

N. Badreldin, L.A.M. Carrascosa, M.J. Mosquera

TEP-243 Nanomaterial Group (Physical-Chemistry Department, University of Cadiz),11510 Puerto Real (Cadiz), Spain
nabil.badreldin@gmail.com

Water is the main factor of decay for building materials by means of mechanisms such as: erosion, scaling, biological colonization, cracking and salt crystallization. Therefore, their protection against water is a fundamental requirement. Superhydrophobic coatings, which are produced by combining a decrease of surface energy and a Cassie-Baxter roughness, are able to prevent water penetration and produce repellence, giving rise to self-cleaning properties. A drawback of these surfaces is associated to organic pollutants adhesion that produces a significant loss in superhydrophobic properties.

In this work, superhydrophobic nanocomposites with self-reparability properties have been developed and applied onto two different building materials: granite and concrete. The coatings were prepared by a sol-gel route by using a fluoroalkylsiloxane and TiO_2 nanoparticles. The fluoroalkylsiloxane was used for decreasing surface energy whereas titania nanoparticles played two roles: (1) to create Cassie-Baxter topography, and (2) to produce a photocatalytic effect able to degrade organic pollutants. In order to stablish comparisons, a product containing silica nanoparticles, instead of titania, was also evaluated.

The obtained results permit to conclude that the two coatings under study produce superhydrophobic surfaces (static contact angle values higher than 150° and hysteresis lower than 10°). Moreover, the coatings containing TiO_2 are able to self-repair the superhydrophobic coatings after staining with olive oil. This effect is due to the photoactivity of TiO_2 nanoparticles.

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Superhydrophobic marble by combining of sol-gel coating and laser ablation

M. Botana-Galvin[1], L.A.M. Carrascosa[2], F.J. Botana[1], M.J. Mosquera[2]

[1] TEP-231 Corrosion and Protection Group (Materials Science, Metallurgical Engineering and Inorganic Chemistry Department, University of Cadiz) 11510 Puerto Real (Cadiz), Spain
[2] TEP-243 Nanomaterials Group (Physical-Chemistry Department, University of Cadiz, 11510 Puerto Real (Cadiz), Spain
marta.botana@uca.es

The interest on superhydrophobic surfaces has increased during last years because of their numerous applications, such as: self-cleaning, anti-icing, separation of liquids and anti-corrosion. These surfaces are characterized by a water contact angle value higher than 150° and a hysteresis angle lower than 10°. In order to obtain superhydrophobic surface it is necessary to decrease the surface free energy and producing a Cassie-Baxter roughness on the surface. This roughness can be obtained by: (i) top-down methods, in which some material from the surface is removed to produce roughness and (ii) bottom-up methods, in which a new surface with the appropriate roughness is created over the original one.

In this work, an innovative process to produce superhydrophobic coatings on building materials has been developed. This process combines the two procedures previously described. Specifically, the superhydrophobicity is produce on marble samples from Macael quarry (Almería, Spain). Firstly, the stone samples were treated with a hydrophobic coating in order to decrease the surface energy (bottom-up method). In this route, which has been previously developed by our research group, a silica oligomer is mixed with polydimethylsiloxane in presence of n-octylamine [1].

After coating drying, the treated marble surfaces were ablated by using a nanosecond pulsed UV laser to produce the desired roughness (top-down method). After laser processing, the treated surfaces were characterised by measurement of dynamic and static contact angles, surface roughness and morphological study by SEM. The results permit to conclude that laser fluence values above150 J/cm^2 at 50 mm/s scan speed lead to superhydrophobic surfaces.

Acknowledgments: This work has been supported by the Spanish Government/FEDER-EU (MAT2013-42934-R).

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Degradation phenomena in copper-based works of art and innovative approaches for a reliable and safe protection

G. Di Carlo[1], C. Giuliani[1], E. Messina[1], M. Salzano de Luna[2], M. Lavorgna[2], G.M. Ingo[1]

[1] Institute for the Study of Nanostructured Materials (ISMN), National Research Council (CNR) Via Salaria km 29,300, 00015 Monterotondo (Rome), Italy
[2] Institute for Polymers, Composites and Biomaterials (IPCB), National Research Council (CNR) Piazzale E. Fermi 1, Località Granatello, 80055 Portici (Naples), Italy
gabriella.dicarlo@ismn.cnr.it

Copper-based alloy artefacts are affected by degradation processes leading to the formation of alteration products and reactive compounds (as chlorides, hydroxychlorides, sulphides and sulphates), which can significantly modify the object surface appearance and compromise the conservation status of valuable works of art. The degradation phenomena in copper-based objects represent a critical issue and in particular the "bronze disease", induced by chloride species, moisture and oxygen, is extremely harmful for the artefacts since it is based on a cyclic copper corrosion process that can continuously transform the alloy in a greenish powder of copper hydroxychloride polymorphs, such as atacamite. The degradation products lead usually to the formation of naturally grown surface patinas, whose composition can be complex, depends on several parameters, such as alloy composition, metallurgical features and environmental conditions, and can affect the chemical-physical stability of the artefacts. At present, concerns related to the degradation of both ancient and modern copper-based works of art are still relevant and the most effective protective materials are based on the use of commonly toxic corrosion inhibitors and large amounts of organic solvents. Therefore, innovative approaches to fulfil the protective, aesthetic and safety requirements are demanding.

In this context, we have focused our attention on the development of nanostructured polymer coatings able to provide an active protection of copper-based works of art by using safer procedures than benchmark products. The attention has been focused on active protective systems based on the use of low toxic of corrosion inhibitors, environmentally friendly polymers obtained from renewable sources and not toxic solvents for their application and removal. These protective systems are based on an approach similar to the drug delivery, since they contain nanocarriers loaded with corrosion inhibitors which are released under external stimuli related to the beginning of corrosion processes. The controlled release of inhibitors allows to hinder degradation phenomena and to obtain long-lasting protective coatings. The nanostructured polymer coatings developed by our group are optically transparent, easily removable and effectively preserve the surface characteristics of bronze substrates during accelerated corrosion tests (Figure), and thus represent a promising solution for the safe and long-lasting protection of Cu-based alloy artworks.

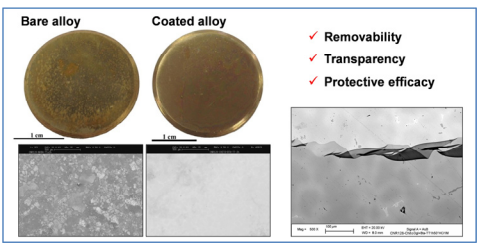

Figure 1. Cu-based alloy disks without and with protective coating (on left and right, respectively) after accelerated corrosion treatments. On the right, the scanning electron microscopy image of treated coated disk after partial removal of the coating.

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Saturated long chain sodium monocarboxylates for inhibition the corrosion of lead objects in atmospheric conditions and in acetic acid corrosive solution

E.A.A. Mohammed, A. Adriaens

Department of Analytical Chemistry, Ghent University, Krijgslaan, 281-S12, B-9000 Ghent, Belgium
elbeshary.ahmed@ugent.be

Many metallic heritage objects, including lead, are in open display cases in museums, where the environment cannot be fully controlled. Temperature and humidity fluctuations often cause these objects to experience cyclic wet and dry periods and to suffer atmospheric corrosion [1]. Hydrolysis of the wood of the display cases, for instance, releases organic acids. These released organic acids, particularly acetic acid, result in an active corrosion which can lead to the loss of these objects [2]. Similarly, the lead metal parts of the pipe organs, an important part of the cultural heritage of Europe, corrode by the organic acids which are emitted from the oak wooden wind chest resulting in the degradation of the pipe structure through pitting and cracking [3]. One way to protect these objects from corrosion is by using a protective coating.

In this study, sodium salts of saturated linear carboxylic acids with the general formula $CH_3(CH_2)_{n-2}COONa$ (n = 14, 18)—labeled NaC_{14} and NaC_{18}—were used to inhibit the corrosion of metallic lead. The salts were dissolved in water/ethanol 1:1 (*V*/*V*) mixture at 50 °C to increase their solubility. Lead coupons were immersed in the resulted solutions for 24 h. Consequently, the coatings were characterized by scanning electron microscopy, Fourier transform infrared spectroscopy, X-ray diffraction, and X-ray photoelectron spectroscopy. The corrosion inhibition properties of the hydrophobic layer of lead carboxylates were examined by linear sweep voltammetry and electrochemical impedance spectroscopy in a corrosive solution simulating atmospheric conditions and in acetic acid corrosive solution.

Results show that the coatings have higher charge transfer resistances and low corrosion current values comparing to the uncoated sample, which proves the inhibition efficiency of these coatings against the lead corrosion. A comparison between the various coatings show that the inhibition efficiency increases by increasing of the carbon chain length where the $Pb(C_{18})_2$ coating has exhibited the highest charge transfer resistance and lowest corrosion current values.

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Ion exchange resins as a solution against atmospheric degradation of CorTen steel

P. Ruiz, J. Aramendia, K. Castro, N. Prieto-Taboada, J.A. Carrero, G. Arana, J.M. Madariaga

Department of Analytical Chemistry (University of the Basque Country-UPV/EHU), P.O.Box 644, E-48080 Bilbao, Spain
kepa.castro@ehu.eus

CorTen steel is a type of weathering steel which, in contact with compounds present in the atmosphere in which it is exposed, develops a protective layer that prevent access of mentioned compounds (such as oxygen and moisture) reducing the corrosion rate. Due to this fact it is a very used material, among others, with artistic aims, and it is due to its appearance that it is in vogue among modern artists, being some of these structures part of Cultural Heritage. However, the anticorrosive action depends on the exposure conditions of the metallic surface. In spite of the fact that acid gases are necessary for the development of the protective layer, if they are in high concentration, they can increase the corrosion rate by forming soluble salts such as sulfates, nitrates or chlorides.

In order to prevent the resulting damages due to the increase of the corrosion rate, in this research work the use of the ion exchange resins is proposed with the aim of removing the mentioned soluble salts. Purolite A-100 is a macroporous polystyrenic weak base anion resin having tertiary amine functionality and it is developed to adsorb specifically chlorides, nitrates and sulfates. Moreover, it can be re-used several times reducing the environmental impact. Therefore, it is a very suitable material for the problem that is wanted to be faced.

For this study, a special type of CorTen A steel pieces were exposed outdoors during 6 weeks. They were exposed in a site which is located in the mouth of a river, at three kilometers far from many industries and at the access to the beach. Therefore, due to the environmental conditions, a wide variety of anions were formed in the steel surface. To evaluate the effectiveness of the resin as a solution for the steel damages, it was necessary to quantify the salts present in the steel pieces before and after resin treatment. This quantification was carried out using a Dionex ICS 2500 ionic chromatograph with a suppressed conductivity detector ED50. The results showed (Fig. 1) that the quantity of the anions that were causing the steel damage decreased after the resin treatment. Moreover, sulfate, which was in higher concentration and for that reason it was the most harmful compound, was the anion which decreased more. As conclusion, it can be affirmed that the proposed solution is valid, and consequently that problem, was solved.

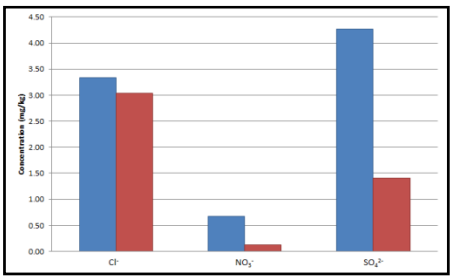

Figure 1. Results obtained by ionic chromatography.

Lanthanum-Silica Sol-Gel coatings for protecting metallic materials in museums: approaches to copper, steel, and lead substrates

J. Peña-Poza[1], F. Agua[1], J.F. Conde[1], C. Gil[2], M.A. Villegas[1], M. García-Heras[1]

[1]Instituto de Historia (CCHS-CSIC) Calle Albasanz, 26-28. 28037 Madrid, Spain
[2]Univ. de Valladolid, Campus María Zambrano. Plaza de la Universidad, 1. 40005 Segovia, Spain
mariangeles.villegas@cchs.csic.es

Museums with objects and collections made from different metals and alloys face the difficult challenge of slow down as much as possible their processes of corrosion, not only in exhibition rooms and inside the showcases but also in their holdings.

Within the framework of a research project funded by the Spanish Ministry of Economy and Competitiveness (MAT2015-65445-C2-2-R, MINECO/FEDER), some novelty solutions are being applied to the field of protection of metallic materials from museum collections based on silica Sol-Gel coatings doped with lanthanum compounds. The use of lanthanum compounds has proved to be very effective against corrosion in other metallic substrates such as aluminium or magnesium alloys.

Transparent and colourless coatings were prepared from sols composed of tetraethoxysilane (TEOS) and/or methyltriethoxysilane (MTEOS) as precursors, distilled water to undertake the hydrolysis, ethanol as solvent, and an acid as catalyst of the hydrolysis. Lanthanum acetate was added as doping agent, while L-cysteine was also added in a set of sols as corrosion inhibitor. Following these formulations, Sol-Gel coatings were deposited upon common glass slides, as well as upon metallic plates from 1.0 to 1.5 mm in thickness. Application of coatings on both types of substrates was accomplished by the immersion-extraction procedure at a constant speed under controlled temperature and relative humidity. The metallic plates selected were copper, steel, and lead, since these metallic substrates are among the most common metals used in Cultural Heritage items of museum collections. Once coatings were deposited the remaining sols were gelified at 60-100 °C for 4-96 h and then powdered to be characterized by Fourier transformed infrared spectroscopy (FTIR) and differential thermal analysis (DTA) and thermogravimetry (TG).

In order to evaluate the behaviour and resistance of the coatings some tests of accelerated aging were carried out in the laboratory either in climatic or Kesternich chambers. In addition, they were subjected as well to an atmosphere saturated with organic acids and also to UV irradiation. Simulated conditions tested were undertaken to approach real conditions of use inside a conventional museum showcase. The microstructure of the coatings before and after accelerated aging tests was observed through optical and field emission scanning electron (FESEM) microscopies.

First resulting data on copper, steel, and lead substrates indicated that these multifunctional coatings can be a fruitful preventive conservation avenue to effectively protect historic metal items exhibited in museum collections.

Chemical equilibria in deacidified corroded manuscripts including Iron Gall ink

J. Matas[1], H. Bagan[1], E. Marin[1], C. Sistach[2], J.F. García[1]

[1]Department of Chemical Engineering and Analytical Chemistry, University of Barcelona. Diagonal 645, 08028 Barcelona, Spain
[2]Archive of the Crown of Aragon, Almogàvers 77, 08018 Barcelona, Spain
jfgarcia@ub.edu

Manuscripts are one of the most spread cultural heritage objects. To preserve the information they include, it is of paramount importance to maintain their physical integrity. Many manuscripts were written using iron gall ink which is, in fact, the origin of their instability. Degradation processes are based on the acid hydrolysis and on the oxidation of the cellulose as consequence of the generation of sulphuric acid and the presence of metallic ions. Both processes have a limited development when the pH of the manuscripts is around neutral values. In order to achieve this pH range, several deacidification procedures including a variety of products have been proposed.

The objective of this study is to contribute to the basic chemical knowledge of the deacidification processes applied to corroded manuscripts in order to understand their capabilities and limitations.

The study was developed on real XVII century rag paper manuscripts written with Iron gall ink. These are administrative manuscripts without historical value. They are in a quite important corroded stage with pH values around 4-5.

Several equivalents sheets of these manuscripts have been treated by using GEOL dissolution (gelatine in an hydro alcoholic media) including different alkaline compounds usually applied for d deacidification purposes: calcium carbonate, calcium propionate, magnesium oxide and magnesium ethoxide. In addition, the solution included in the commercial bookkeeper® product has also been applied.

Application has been performed manually by brush to both sides of the sheet covering the entire surface.

Determinations performed in all cases, untreated and treated manuscripts, were: kinetic study of the pH evolution, total acidity and total alkalinity.

The most interesting results were obtained from the kinetic studies. For untreated manuscript fragments including ink, kinetics shows a quick decrease of the pH followed by a stabilization of the acid value. For the different treated fragments of manuscripts also including ink, the behaviours found show some similarities. In the cases of Magnesium ethoxide and Magnesium oxide, pH decreases abruptly and then starts to increase slowly. That means that acidity remains and it is quickly transferred to the dissolution, whereas the alkaline compounds are slowly dissolved. In the case of calcium carbonate and calcium propionate, there is a little or any (respectively) decrease of pH followed by a medium or quick (respectively) increase of pH. These behaviours are related to the solubility of both compounds. Thus, a question arises, what is more convenient for manuscripts preservation an alkaline reserve that is a little or a lot soluble in water?

Identification of the evolution of indigo blue by multispectral imaging

N. Tello Burgos[1], A. López Montes[1], X. Shao[2], E.M. Valero[2], J.L. Nieves[2], M.R. Blanc[3]

[1]Dpt. Painting, Faculty of Fine Arts, University of Granada, Avd. Andalucía s/n 18071 Granada, Spain
[2]Dpt. Optics. Faculty of Sciences, University of Granada, Avd. Fuentenueva s/n 18071, Granada, Spain
[3]Dpt. Analytical Chemistry, Faculty of Sciences, University of Granada, Avd. Fuentenueva s/n 18071, Granada, Spain

Indigo is a particular blue color due to its nature because it can be considered as pigment or colourant; organic dye from vegetal (*Indigofera tinctoria* plant) insoluble in water which does not need mordant to color, settling as microscopic particles between the support´s fibers [1]. At present indigo is a material very studied by conservators and chemists because it has been used as dye or pigment for the manufacture of many historical and artistic pieces as well as pictorial layers of mural and panel painting, colourant for textiles and tinting of papers.

Most of these studies are focused on the development of methods for the characterization and identification of the original material [2,3]. But we could not find any research on the evaluation of the changes that can occur as a result of the aging process by external agents (temperature, humidity and light). For this reason our research team is working in the identification of compositional variations and degradation products that could appear [4].

A comparative study between standard samples and samples aged in a controlled climate chamber under extreme conditions of humidity, temperature and light was carried out. In this occasion, multispectral imaging in the visible and NIR spectral ranges was used to identify the evolution of degradation of indigo blue. The spectral images have been captured with a 16 channels filter wheel multispectral camera from Pixelteq, US. The camera responses for the 16 channels were used to train a Support Vector Machine and classify the samples according to their ageing phase into four different groups. The multispectral imaging data were comparatively analyzed with the results of the other techniques (UV-visible spectroscopy, capillary electrophoresis with diode array detector (CE-DAD) and fluorescence spectroscopy) and we found good correlation between the classification based in spectral data and the fluorescence and spectroscopic data and good accuracy in the SVM-based classification, which emphasizes the feasibility of using a spectral camera as a non-invasive technique for characterizing the ageing phase of indigo samples.

It is important to acknowledge that the identification of aged dyes can be difficult due to the possible changes that their physical and chemical characteristics could have undergone with time. Scientific knowledge of the art materials is required to carry out their identification and to comprehend the evolution of techniques used for their manufacture and dating.

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Noninvasive investigation of common, painted and glazed Islamic pottery (9th-11th centuries) from the cities of Mértola and Évora (Portugal) using portable XRF spectrometry

M. Beltrame[1], S. Gómez Martínez[2], L.J. Gonçalves[7], J.R. Ribeiro dos Santos[4], F. Branco[6], A. Candeias[5], J. Mirão[3]

[1]CIDEHUS, Interdisciplinary Centre for History, Culture and Society - UNESCO Chair in Intangible Heritage - HERCULES Laboratory, University of Évora, Évora, Portugal
[2]Archaeological camp of Mértola, Mértola, Portugal - Centre of Study in Archaeology, Arts and Cultural Heritage Sciences, Lisbon, Portugal
[3]HERCULES Laboratory and Geociences Dpt., School of Science and Technology, University of Évora, Évora, Portugal
[4]CIDEHUS, University of Évora, Évora, Portugal - Municipality of Évora, Évora, Portugal
[5]HERCULES Laboratory and Chemistry Dpt., School of Science and Technology, University of Évora, Évora, Portugal
[6]CIDEHUS - History Dpt., School of Social Sciences, University of Évora, Évora, Portugal
[7]Faculty of Fine Arts, University of Lisbon, Largo da Academia Nacional de Belas Artes, Lisbon, Portugal
massimo@uevora.pt susanagomez@sapo.pt jmirao@uevora.pt jr.ribeiro.santos@gmail.com candeias@uevora.pt fbc@uevora.pt luisjrg@gmail.com

This study presents the preliminary results of an analytical program carried on Islamic pottery from 10th -13th centuries, recovered in urban area of the Mertola and Èvora towns of (Centre-South of Portugal). For this purpose 36 samples of Islamic ceramics were analyzed. Mostly of the samples are classified as honey and manganese or green and manganese glazed ceramics and were recovered in the urban area of the towns of Évora and Mértola covering a chronological framework comprised between the 10th and the first half of 13th centuries. The study also included the analysis of several samples of common and white painted ceramics, 2 samples of red painted ceramics as well as of 7 kiln rods, partially covered by green glaze, recovered in a production context in the urban area of Mértola. These materials were utilized as "standard" of local ceramic productions.

The main goal of the study is to understand pottery characteristics in term of raw material employed for the preparation of the clay paste and of the glaze. This will allow getting information about the ceramic dissemination in the Islamic domination of Gharb al-Andaluz, especially in the towns of Évora and Mértola, assessing if the two towns were inserted in the same commercial circuits and evaluate the hypothesis of glazed ceramic production in the town of Mértola. For this purpose a portable XRF spectrometer has been used for the analysis of the ceramic samples. The analysis is completely noninvasive, fast and allows the direct semi-quantitative data evaluation in the field or in museums. The present results showed that different technological solutions were employed for the production of common/painted ceramics and for glazed ceramics. Glazed ceramics were produced using Ca rich raw material and they are not compatible neither with the kiln rods from Mértola nor whit the common and painted ceramics from the two towns. Moreover glazed ceramics from the two towns have different iron and titanium ratio. Regarding glaze characteristics, ceramics were decorated using silica lead glaze or with tin opacified silica lead glaze. Black, green and yellow glazed decorations were obtained adding manganese, copper and iron oxides respectively. To conclude the towns of Mértola and Évora pertain to different commercial circuits but glaze technology was very similar suggesting the existence of different centres of production.

Raman microspectroscopy of blue-green historical beads: comparative study of undamaged and strongly degraded samples

I.A. Balakhnina[1], A.A. Mankova[1], I.G. Shpachenko[1], E.A. Morozova[2], T.V. Yuryeva[2], V.A. Yuryev[3], A.Yu. Chikishev[1], N.N. Brandt[1]

[1]*Faculty of Physics and International Laser Center, Lomonosov Moscow State University, Leninskie Gory 1, Moscow 119992, Russia*
[2]*State Research Institute for Restoration, Ministry of Culture of the Russian Federation, bldg. 1, 44 Gastello Street, Moscow 107114, Russia*
[3]*A.M.Prokhorov General Physics Institute of the Russian Academy of Sciences, 38 Vavilov Street, Moscow 119991, Russia*
brandt@physics.msu.ru

Degradation of blue-green historical beads is a significant problem for storage of historical items even under controlled museum conditions. Almost undamaged and strongly degraded beads can be located at distances of several millimeters from each other on a single artifact. In this regard, it is expedient to study the reasons for degradation of historical beads. The practice of restoration works in Russian museums shows that blue-green historical beads exhibit the strongest degradation. Such a phenomenon must be interpreted with respect to conservation of artifacts and optimization of restoration procedures.

Surface chemical reactions can be the reason for degradation of beads. A relatively high concentration of potassium oxide may lead to the formation of potassium silicates that cause corrosion and destruction of beads due to surface hydrolysis. However, archeological beads with a relatively low content of potassium oxide of no greater than 7 wt % also exhibit significant degradation.

Raman spectroscopy is a helpful tool in the study of glass items including historical artifacts. The method makes it possible to identify impurities and dyes in glass and characterize glass structure. Raman microscopes allow measurements at micron spatial resolution and Raman imaging.

Raman spectroscopy proves the presence of Potassium antimonyl silicate ($KSbOSiO_4$) (KSS) crystals in the historical beads. Charcoal ash or antimony oxide that had been added as opacifiers in the course of manufacturing may serve as sources of antimony. The KSS crystals could be formed immediately due to quenching or in the course of long-term storage. The KSS crystals, the sizes of which are no greater than 2-3 μm, are nonuniformly distributed inside the samples, and the nonuniformity is significantly higher for strongly degraded beads. Strongly degraded beads exhibit regions in which Raman spectra substantially differ from each other in the interval of the Q^n bands (860-1250 cm^{-1}). This circumstance indicates variations in the content of (non)briged oxygens in a unit cell and, hence, local changes of glass structure. The main spectral changes are a decrease to almost zero of the Q^3 intensity and an increase in intensity of Q^2. In addition, Raman data indicate a local decrease in the relative content of alkali or alkaline earth oxide and/or an increase in silica content in strongly degraded beads.

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How analytical techniques are able to address archaeological questions: a case study of a painted ceramic

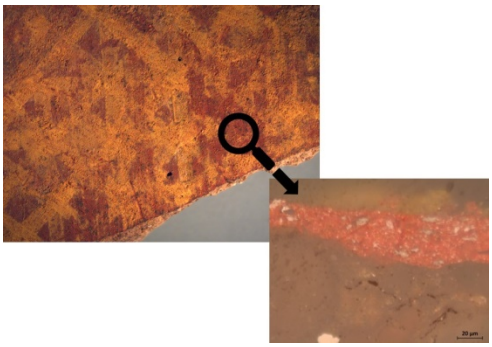
I. Donate[1], M. Medina[1], S. Celestino[2], E. Rodríguez[2], C. Pascual[3], P. Recio[3], J. Barrio[4], A.I. Pardo[4]

[1] Servicio de Conservación, Restauración y Estudios Científicos del Patrimonio Arqueológico, Universidad Autónoma de Madrid, Madrid, Spain
[2]Instituto de Arqueología de Mérida, Consejo Superior de Investigaciones Científicas, Mérida, Badajoz, Spain
[3]Instituto de Cerámica y Vidrio, CSIC, Madrid, Spain
[4]Departamento de Prehistoria y Arqueología, Facultad de Filosofía y Letras, Universidad Autónoma de Madrid, Madrid, Spain

Application of instrumental analytical techniques has become essential when approaching the study of archaeological materials, as they provide information which can help to answer certain questions that are still unknown. Thus, this article presents the results of an interdisciplinary research conducted on a painted ceramic, whose fine and unusual decoration, of red and yellow colors raised doubts about the technological features and raw materials. The ceramic appeared incomplete and fragmented on the foundations of a circular hut that was demolished to build on it a rectangular building, in *Cerro Borreguero*. It is a site located in *Zalamea de la Serena* (*Badajoz*, Spain), from the transition period between the end of the Bronze Age and the beginning of the Iron Age. Specifically the piece, of indigenous production, dates from the end of 8th century BC.

Non-destructive and micro-destructive analytical and examination techniques were employed: reflected-light optical microscopy, field emission scanning electron microscopy for microstructural characterization of ceramic paste and painted layer, energy dispersive x-ray spectroscopy to determine elemental composition of materials and polycrystalline X-ray diffraction to identify the main crystalline compounds. The obtained data reveal the use of non-calcareous clay, with a medium content of iron. This and an oxidizing atmosphere during firing would explain the reddish colour of the paste. And, regarding the decoration, the study confirms the application of a post-firing polychromy, employing natural ochres of iron oxides and hydroxides, which is uncommon in archaeological contexts, due to its difficult conservation.

In addition, analyses performed with laser induced breakdown spectroscopy on rocks found in the same site prove the presence of natural ochres in the zone. Therefore, the pigments utilized to decorate the ceramic could come from a nearby area where the piece was found.



In situ evaluation of outdoor sculpture with a gel polymer electrolyte cell

B. Ramírez Barat, A. Crespo, E. Cano

Centro Nacional de Investigaciones Metalúrgicas. Consejo Superior de Investigaciones Científicas. Avda. Gregorio del Amo 8, Madrid 28040, Spain

In the past few decades, development of new analytical techniques applied in the field of cultural heritage has been focused on the development of non-invasive techniques and portable instrumentation. The availability of handheld techniques, that can be directly applied in situ and without sampling opens a lot of new possibilities in the field of heritage studies and conservation science.

Focusing in the field of metallic cultural heritage, besides general analytical techniques, electrochemical methods are of particular interest for conservation assessment. Electrochemical techniques such as electrochemical impedance spectroscopy (EIS) can give information on corrosion processes and/or corrosion rates and on the protective properties of coatings and inhibitors used in conservation treatments. In situ application of electrochemical techniques have to deal with some practical difficulties, being the one of the main challenges how to put an electrochemical cell filled with a liquid electrolyte in the irregular surface of a sculpture. To overcome this problem we have developed an electrochemical cell, with a classical three-electrode design, in which the liquid electrolyte has been gelled with agar.

The electrolyte is composed of an artificial rain solution, to imitate the environment in which sculptures corrode, ten/fold concentrated to have enough conductivity, to which 3% w/v of agar has been added. The agar concentration has been selected after evaluating the performance of the electrolyte at different concentrations on electrochemical measurements on bronze coupons. The cell has been tested in different materials (bronze, corten steel) on laboratory coupons and in field measurements, and used for monitoring the evolution of patinas and coatings with time. Some of these results are presented, showing the applicability of the gel polymer electrolyte (G-PE) cell for the conservation assessment of metal outdoor sculpture.

Scientific and technical study of glasses of a possible Venetian mirror from the *Virgen de la Encina* Basilica at Ponferrada (León, Spain)

J. Peña-Poza, F. Agua, J.F. Conde, M. García-Heras, M.A. Villegas

Instituto de Historia, CCHS-CSIC. Calle Albasanz, 26-28. 28037 Madrid, Spain

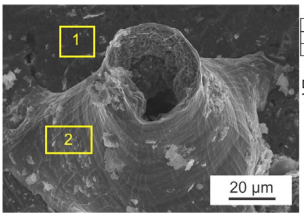
Recent restoration works accomplished on a Venetian style mirror conserved in the *Virgen de la Encina* Basilica at Ponferrada (León, Spain) raised the question if the mirror was actually produced in Venetian glass factories or could have been produced in other place copying the well-known and imitated Venetian or *façon de Venice* style glasses.

With the aim of mainly answer this question a scientific and technical study of glass materials was accomplished. The study was focused on the following aspects: 1) determination of the chemical composition of materials; 2) microstructural and microanalytical study of such materials; 3) determination of their state of conservation; and 4) identification of chemical species or chromophores responsible of glass colouring.

Selected glass samples, encompassing the variety of the mirror materials, were taken to undertake such study. These samples included: two colourless flat glass samples with quicksilver-like remains in one of their sides, three colourless cylindrical and twisted glass samples (two of them with an inside cordon of blue glass), and one sample of a flat blue glass. All these glass materials were characterized by the following chemical-physical techniques: low magnification binocular glass, X-ray fluorescence spectrometry (XRF), field emission scanning electron microscopy (FESEM) equipped with energy dispersive X-ray microanalysis (EDS), and UV-Vis spectrophotometry.

The chemical composition results obtained by XRF determined that all the samples were soda lime silicate glasses. However, three groups were established. One group composed of the two colourless flat glass samples, another group composed of the three colourless cylindrical and twisted glass samples and the last one composed of the unique flat blue glass. The first two groups resulted compatible with glasses produced in Venetian glass factories during the sixteenth and the seventeenth century: flat glasses with the so-called “Venetian common” and cylindrical and twisted glasses with the so-called “Venetian cristallo”. The identification of a mercury or quicksilver amalgam in the flat glasses is also in agreement with this chronology. The presence of a notable content of arsenic oxide in the flat blue glass indicated that it was not from Venetian origin and that it was produced later in time, probably at the end of nineteenth century or early twentieth century.

The blue flat glass contains Co^{2+}-ions, while the cordons of blue glass inside the cylindrical and twisted glasses contain Cu^{2+}-ions as chromophores. In terms of the conservation state, glasses showed a light superficial dealkalinisation which could be due to continuous exposure to humid environments.



Area	Si	Sn	Hg	O
1	0,4	78,1	n.d.	21,5
2	0,5	77,9	n.d.	21,6

Detail of irregular structures from the mirror layer of sample EV-2. Table shows EDS microanalyses results (n.d. not determined).

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Rising damp in Heritage buildings hygro-regulated wall base ventilation system

A.S. Guimarães, V.P. de Freitas

CONSTRUCT-LFC, Faculty of Engineering (FEUP), University of Porto, Rua Dr. Roberto Frias, 4200-465 Porto, Portugal
anasofia@fe.up.pt, vpfreita@fe.up.pt

The conservation of historic buildings has become increasingly important in recent years. Rising damp in historic buildings can be considered one of the most important manifestations of moisture, leading to deterioration of materials like stone due to freeze/thaw cycles and the presence of salts associated with processes of dissolution/crystallization.

The treatment of rising damp in historic buildings is of great complexity, due to the high weight and the heterogeneity of these walls. Traditional techniques used to deal with these problems present limitations that justified the need to find new approaches.

The Building Physics Laboratory – LFC of the Faculty of Engineering of the University of Porto – FEUP has been developing experimental research relevant in the field of rising damp based on a hygro-regulated wall base ventilation system. The system has been validated, featured and designed. The technique consists on circulating air around the base of the walls with steam pressure conditions conducive to drying. The ventilation of walls increases evaporation, which reduces the level achieved by the damp front.

The characterization of the hygro-regulated systems' operation were made based on experimental studies developed in laboratory which allowed the influence of the velocity of the air, condensation risk and the possibility of salt crystallization. It was also measure a church in the North of Portugal in which this system were implemented, with the purpose of validating its operation and establishing criteria for programming the ventilator.

It is considered important to understand that those buildings presents some unique aspects that show the importance of develop investigation in this specific area. This contribution is just a step but it is important to continue this investigation to get all the characterization and the design of this new technique. It is necessary to model and see the real behaviour of the system and optimize its performance.

3D Characterization of Arqueological Ceramics

M.F. Martins Costa[1], W. Magalhaes[2], M.A. Alves[2]

[1]Centro de Física, Universidade do Minho, Portugal
[2]Museu de Arqueologia e Etnologia, Universidade de S. Paulo, Brazil

Optics and optics and photonics based inspection tools and methods had expensively proven their invaluable importance in the preservation of cultural heritage and artwork. The non-invasive inspection of the 3D shape of objects and of the micro-relief structure of its surfaces can be of high importance in the characterization process required in most works of restoration or preservation of archaeological artwork. In this communication we will report on a method of optical non-invasive microtopographic characterization of the surface of archaeological ceramics. The samples used in this study are pre-historical and pre-colonial ceramics and pottery of tribes in the Paranaiba valley in Minas Gerais, Brazil. The pottery found is decorated with incisions with different geometric distributions and levels of complexity corresponding to two periods of indigenous Indian occupations: one from a period dated at 1,095 ± 186 years ago and another of the early nineteenth century dated between 212 ± 19 years and 190 ± 30 years ago seemingly corresponding to the occupation of the territory by southern *Kayapós* tribes.

Deterioration caused by dimensional change in stone (EPS pathology): The role of the organic matter - pore network - salt combination

J. Gisbert Aguilar[1], O. Buj Fandos[1], B. Bauluz Lázaro[1], F. Peddis[2], F. Cuccuru[3]

[1]Dpto. Ciencias de la Tierra Facultad de Ciencias. Universidad de Zaragoza 50009 Zaragoza Spain
[2]DICAM Alma Mater Studiorum Università di Bologna 40131 Bologna (Italy)
[3]Dipartimento di Ingegneria Civile, Ambientale e Architettura, University of Cagliari 09123 Cagliari (Italy)

We study pathology of dimensional changes in Miocene lacustrine limestones of the Ebro's basin (middle and high sections) with very low content in clays. The studied samples come from blocks of stone from Burgos and Tudela Cathedrals and their respective original quarries. The pathology, known as "EPS" causes extreme dimensional changes both in moistening and drying. The process owns a fast and catastrophic activity, with characteristic features.

In previous works the pathology was replicated using magnesium salts associated to the processes of moistening and drying. In this works, we obtained evidences of the existence of an important dimensional change that was not due to salt crystallization In this study we realized tests to evaluate that change when salts are present and when they are not, measuring the dimensional variation in the three space axis (X,Y,Z). Significant changes in the rock only with the moistening-drying with distilled water have been measured. However, the process is very irregular and there are problems of repeatability, essentially because sculpted test tubes from the same block show different behaviors to the same stimulus, in spite of we have been working with universe samples of hundreds of test tubes. The lack of repeatability reaches maximum levels in fresh quarry test tubes, being mitigated in samples of monument whose availability is, unfortunately, very limited.

The phenomenon that is better documented (for its repetitive occurrence) has been the oscillating pulses of contraction-expansion of test tubes during a continuous process of water loss (drying). EPS pathology has also been detected in other rocks and we carry out here a comparative petrographic analysis of them all. In its original composition the presence of organic matter (most of it from algal origin) coincides with a porous system with predominance of sizes inferior to 1 μm. In the catastrophic demonstration of the process magnesium salts are always involved.

We conclude that in dimensional changes without salts, the agent that causes them is an organic matter close to alginite. The peculiarities from organic matter are the only ones that can explain the set of experimental facts and its irregularity. This last phenomenon would be associated to the variability/complexity in the evolution of organic matter in the rock and its partial oxidation. Hypothetically it is also necessary that organic matter forms part of the rock skeleton, being this aspect a "key" both for dimensional changes in case salts are present or not. In catastrophic dimensional changes when salts are present, the porous system and magnesium salts are also relevant elements for the development of the phenomenon.

Marble sculptures cracks fixing by metallic staples

J.M. Gallardo[1], E. Díaz-Gutiérrez [2], J.A. López[3]

[1]Departmento de Ingeniería y Ciencia de los Materiales y el Transporte, Universidad de Sevilla, Camino Descubrimientos s/n, 41092 Sevilla, Spain
[2] Asociación de Investigación y Cooperación Industrial de Andalucía, Camino Descubrimientos s/n, 41092 Sevilla, Spain
[3]Departamento de Construcciones Arquitectónicas I, Universidad de Sevilla, Reina Mercedes 2, 41012 Sevilla, Spain
josemar@us.es

Twelve marble figures representing lions are the main motto of a decorative fountain at the Court of Lions, in Alhambra Palaces, in Granada, Spain. They are more than 8 centuries old from carving and were severely deteriorated. Because the cold winters in Granada, water use to freeze in the Lions mouth, what served as spring of the fountain. Also the channels carved in the left front leg, shoulder and tongue suffered from ice expansion associated to the frizzing of water. As a consequence, complete cracking of the lions front half were experienced. Even though adhesives technology have been incorporated in the restoration, it was considered convenient to maintain metallic staples used up to nowadays. In this paper, the characterization of old staple material and the selection of new materials to be used in the staples are described.

Deterioration Analysis of Hydraulic Mortars Pavements

L.J. Fernández Carrasco, D. Torréns Matín, J.LL. Zamora i Mestre

Departament d'Enginyeria Civil i Ambiental, Universitat Politècnica de Catalunya, Carrer Jordi Girona 1-3, Barcelona, Spain
lucia.fernandez@upc.edu

An hydraulic mosaic is a decorative tile formed by pigmented cement in the upper material. This HP has been traditionally used as pavement for both interior but also exterior ambient. This type of architectural element was developed in the south of France in the XIX mid-Century, being used as pavement until 60s. The fabrication process is characterized by the use of metallic molds for the color application, and fixed to the cement base by means of hydraulic press [1]. Due to their properties the cement is the main material used in the mosaics manufacturing, giving strength and stability to the pieces. The pigments are colorant additives that are used to give the adequate color without affecting the mechanic properties of the material [3]. Different pigments are used but not always in pure estate, and sometimes have a pretreatment or mixed before it.

These types of tiles have been used widely as pavements in houses at final -Century XIX and early-Century XX. They are now a great part of historical buildings from these years, examples of this can be seen in the Gaudi Houses. Therefore the knowledge about their conservation and reparation is important for keep this part of the cultural heritage. One detected problem seen in hydraulic mosaics has been the appearance of stains on these pavements, mainly those sited in very affluently of public. This phenomenon produces a deterioration of the pavement and suggests a possible discoloration of the tiles.

The scientific literature about this material is scarce, reduced to a few academics papers. Therefore this work tries to advance in the technological knowledge of this material and in the analysis of superficial detected damages. In order to achieve this aim, we have performed an experimental research studying hydraulic mosaic samples both, in situ and in the lab. The samples were analyzed by different microcopies optical microscopy and Scanning Electron Microscopy (SEM) with coupled Energy Dispersive X-Ray spectroscopy (EDX) before and after of some treatments developed to determinate the nature of certain discolorations (Figure 1). The experimental data showed some carbonation processes of the samples that lead to the discoloration of the hydraulic mosaic.

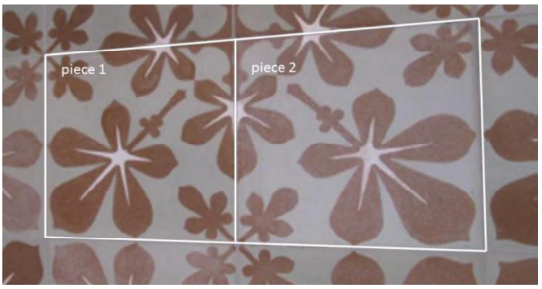

Figure. Hydraulic mosaic tiles, piece 1 without discoloration and piece 2 with discoloration.

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The Problem Stone Progressive Survey Technique (ProSt-ProST). A Pilot Study at The Bell Tower, Tower of London

M. Michette[1], H. Viles[1], C. Vlachou[2], I. Angus[3]

[1]School of Geography, University of Oxford, UK
[2]Historic Royal Palaces, London, UK
[3]Carden & Godfrey Architects, London, UK

This paper presents the Problem Stone Progressive Survey Technique (ProSt-ProST), an integrated approach to diagnosing stone decay mechanics at vulnerable built heritage sites. The Bell Tower at the Tower of London is chosen as a suitable example for piloting the technique, given its large stock of Reigate Stone. Reigate Stone was widely used in medieval London and is presently in a condition of advanced deterioration at a number of important sites. Whilst it has been the subject of past research, underlying mechanisms of decay are poorly understood. The pilot study tests the initial stages of a proposed methodology, linking the results of metric surveying, stone mapping, decay mapping and portable non-destructive techniques in order to progressively define and assess specific Reigate Stone conditions. Stone mapping located extant Reigate Stone and was useful for investigating structural and historic parameters in present day condition. Decay mapping recorded diverse Reigate Stone weathering patterns and intensities, categorised according to the *ICOMOS* glossary. Two distinct patterns were analysed with a Portable Petrographic Pilot Pack (PoPePiPa), consisting of an *Equotip Piccolo* to measure surface hardness, a spectrophotometer to assess glauconite content, an electric resistance moisture-measuring device and a thermal imaging camera. Devices were chosen to test initial hypotheses on Reigate Stone deterioration, based on findings of the mapping stages and previous research. Results suggest the tested stages are appropriate for designing environmental monitoring strategies and selecting representative samples for more detailed petrographic analysis.

Chemical composition of embalming substances found in 17th century burials at Miguel de Cervantes' tomb. Effects of boiling on oxidation of several biomarkers

E. Parra-Crego[1], M. Martín-Gil[1], A. García-Rubio[2]

[1]Instituto del Patrimonio Cultural de España (Área de Investigación y Formación) C/. Pintor el Greco 4, 28040 Madrid, Spain
[2]Departamento de Antropología Física, Sociedad de Ciencias Aranzadi
enrique.parra@mecd.es maria.martingil@mecd.es almugarciarubio@yahoo.es

Funerary rites are part of the cultures and have a close relationship with the religious beliefs of the people. For this reason they are of interest in archaeological and anthropological studies. Within them, embalming is a common rite. The rite of embalming and the materials used for it can be focused as a process of temporary preservation of the body for mourning or as a permanent preservation of the body (mummification).

The procedures and materials used, however, are common and have varied little, from periods as old as those of Egyptian mummies. This is so, until the appearance of formaldehyde and polymers and synthetic products, as early as the nineteenth-twentieth century. Thus, based on the formulas based on the pine resin of such mummies, mixed many times with other products such as Arabic gum and essences like camphor or others, we arrive to the middle Ages. There are recipes that tell us of the deposition of the bodies in tables with plaster to desiccate the gutted bodies, as well as the use of alcohol of camphor, rosemary and resins (rosin).

This practice, which has sometimes been banned, as well as cremations (for example during the early years of Christianism) has been investigated from a material point of view, thanks to the collaboration of the IPCE and ESCRBC Madrid with the team of archaeologists and forensic investigators. They have carried out the studies in the burial places of the Trinitarias' Church (Madrid) in search of the tomb and the body of D. Miguel de Cervantes. Our contribution to the research has been the analytical study of remains of substances used for embalming found in ancient glass bottles of the seventeenth century or later, found within several niches. This has been carried out by combining Fourier Transform Infrared spectroscopy (FTIR) with gas chromatography coupled to mass spectrometer (GC-MS). The result of the chemical analysis is that the samples have compositions with ingredients as sandaraca resin (cypress), resin of rosin (pine), animal fat of waxy consistency and composition compatible with spermaceti wax, essential oils with compounds such as camphor and related monoterpenes. They differ in the proportions of the other components, but it is clear that they do not depart much from the compositions described in medieval recipes. The effects of boiling, following the original recipe, produces oxidation and degradation of several biomarkers.

European Research infrastructures for Heritage Science: from IPERION to E-RIHS

E. Cano, B. Ramírez Barat

Centro Nacional de Investigaciones Metalúrgicas-CENIM (Consejo Superior de Investigaciones Científicas-CSIC). Avda. Gregorio del Amo 8, Madrid 28040, Spain
ecano@cenim.csic.es

Tangible cultural and natural heritage are key components of the European identity. The study and preservation of this heritage is a global challenge for science and the European society at large. Heritage Science is a cross-cutting domain embracing a wide range of research disciplines supporting these aspects of tangible and intangible heritage conservation, interpretation and management. It is founded on the interdisciplinary combination of knowledge from arts and humanities (conservation, archaeology, history, art history, ethics etc.), and from science and technology (chemistry, physics, mathematics, anthropology, biology, geology, computer sciences and engineering, etc.).

Excellent science needs excellent infrastructures. Heritage Science is not an exception, and the high level research carried out by the European scientific community in this field has brought about the need of structuring the net of infrastructures operating throughout Europe. Several European projects have been funded in this domain though FP5, FP6 and FP7. Labs-Tech, EU-ARTECH and CHARISMA have been the predecessors of the current H2020 research infrastructures project IPERION CH, the *Integrated Platform for the European Research Infrastructure ON Cultural Heritage* (H2020-INFRAIA-2014-2015, G.A. 654028). IPERION CH provides access to European scientists to fixed (FIXLAB) and mobile (MOLAB) instrumentation and scientific archives (ARCHLAB) of recognized excellence in the field of Heritage Science. But the main constraint of these projects, as well as other similar ones, (e.g. ARIADNE in the field of Archaeology) is their temporary nature. To tackle this limitation, E-RIHS has been launched.

E-RIHS, the *European Research Infrastructure on Heritage Science*, aims to establish a stable pan-European distributed infrastructure to support research on heritage interpretation, preservation, documentation and management. E-RIHS has been included in the European Science Forum for Research Infrastructures (ESFRI) roadmap in 2016, under the coordination of Italy, and the support of other 11 countries, amongst them Spain. It will be organized in a star-design structure, with a central hub and headquarters in Florence (IT), and national hubs in the participating countries. E-RIHS aims to seamlessly continue and enlarge the activities of IPERION-CH, providing access to FIXLAB, MOLAB and ARCHLAB, and the new platform DIGILAB (for digital contents) to European scientists working in the field of Heritage Science.

E-RIHS is now in the preparatory phase, starting in 2017, with the support of a CSA of H2020 and contributions by the participant countries. The aim of this phase is to address legal status, the business plan for long-term sustainability and management/governance organization, leading to the establishment of an ERIC (or other suitable legal form) in 2020. In parallel, the national hubs will be structured and organized in each country.

Air tightness and RH control in museum showcases: concepts and testing procedures

M. Perino

Department of Energy, Politecnico di Torino, Torino, Italy
marco.perino@polito.it

The control of the Relative Humidity (RH) is a key factor for assuring a proper conservation of artworks. In the majority of museums/archives the collections are kept at a very stable and controlled RH by means of traditional air conditioning systems (HVAC systems). Nevertheless, the demanding requirements as far as the acceptable variation of RH is concerned (frequently less than 5 %), pose a lot of challenges and, frequently, it is hardly possible to achieve the desired goals by just using air conditioning systems. As a result, even highly sophisticated HVAC systems are, in many cases, not able to guarantee a satisfactorily constant and controlled hygric environment and, when they succeed, they give rise to significant energy consumptions (which can represent a non-sustainable cost for the museum structures). Furthermore, the museum/archive exhibition halls often contain and display the so-called "mixed" collections, that is, a number of objects constituted by various materials are kept together in the same environment. These objects may require to be preserved at different RH levels (e.g. metals at low RH values, organic material at RH values around 50 %) and it becomes impossible to satisfy such condition by using full air conditioning systems (HVAC systems can only provide a uniform RH level throughout the whole room volume). A possible solution to these problems is represented by the adoption of museum (conservative) showcases.

A showcase allows realizing a "box in box" configuration (being the first box the room of the building and the second the showcase). With this approach a first and rough climatic control is exerted by a usual HVAC system (which does not need to be particularly sophisticated nor powerful) while the "finer and local tuning" of the RH is achieved by means a passive control inside the showcase (using e.g. "buffer materials"). However, such approach reveals to be effective only if the showcases have sufficiently good air/gas tightness and a suitable capacity in smoothening the indoor air temperature and relative humidity.

In this paper, the concepts that allow the control of the RH by means of conservative showcases will be presented and critically discussed. The behaviour of the showcases will be analysed relating their air/gas tightness with the capability of controlling the indoor environmental conditions.

The combined effect of gas diffusion and convection on the showcase microenvironment, with particular emphasis on the RH control, will be discussed and testing procedures (e.g. pressurization tests, tracer gas measurements and temperature/relative humidity response tests) will be described.

Specifically, the results of a number of laboratory measurements (done on experimental/real showcases) will be shown and an analysis of the influence of the air tightness and gas permeability on the passive control of the RH inside the showcase will be developed. Furthermore, application of the proposed testing methods on real case studies, in actual museum conditions, will be illustrated and the results of medium to long term monitoring of the temperature and RH inside showcases before and after their retrofit, will be critically examined.

Finally, laboratory and field measurement results will be critically analysed in order to abstract general recommendations about: (i) how to test the showcase air tightness; (ii) how to assess the suitable air tightness of a showcase in relation to the desired level of control of the RH; and (iii) how to assess the suitable quantity of buffer material (for the RH control) in relation to the air tightness of the showcase.

Risk management in collections: An innovative approach to methodological analysis and technological planning in Museo Nacional Centro de Arte Reina Sofía

P. Montero[1], J. Pinto[2]

[1]Department of Painting-Restauration, University Complutense of Madrid, Madrid, Spain
[2]Museo Nacional Centro de Arte Reina Sofía, Madrid, Spain
mp.montero@art.ucm.es

The Museo Nacional Centro de Arte Reina Sofía (MNCARS) houses a unique collection in the world which comprises indispensable works of modern and contemporary Spanish art, as well as extraordinarily relevant artworks by international authors. The museum's insignia artwork, the *Guernica* by Picasso, which has transcended generations, has become a symbol of our most recent past, and a reference point of Spain's political and cultural position worldwide. Conserving and transmitting this cultural heritage to future generations is not only a legal but also a moral obligation. Unfortunately, in the current socio-political and cultural context no institution within this category is free from suffering emergency situations, either anthropic (vandalism, theft, terrorism…) or natural episodes (circumstances worsened by the climate change: floods, earthquakes…). The aim of this paper is to show a comprehensive model able to manage and protect efficiently the MNCARS collection in case an emergency might arise which affects the artworks. With this purpose in mind, an innovative approach to methodological analysis and planning technology will be explained, along with an ensemble of means and dynamic technological methods able to store, manage, update, manipulate, recover, analyse, show and transfer special data (GIS, and BIM) and characterisation of the collections in order to prevent and minimise the scope of vulnerabilities and obtain maximum protection, as well as to manage the whole operating process in case an emergency may arise and a contingency plan for the artworks protection needs to be deployed. This project's innovation lies, therefore, in the creation of an innovative analysis methodology which will allow us to implement georeferencing technologies to the protection of artworks in case of emergency.

Optimizing damage and colour fidelity in museum illumination with a mathematical model

D. Vázquez, A. Alvarez

Optics Department, Complutense University, Av Arcos del Jalón 118,28037 Madrid, Spain
dvazquez@ucm.es

Heritage preservation and exhibition of art goods are social, cultural and economic needs that show opposing requirement. The intelligent use of new light sources should allow the development of systems that combine both requirements and allow making these art goods available to the next generations according to sustainability principles. The goal of this research is to develop light systems and sources with an optimized spectral distribution. The optimization implies to maximize the color fidelity reproduction and the same time to minimize the photochemical damage. In this way the perceived color under these sources will be similar (metameric) to technical requirements given by the restoration team uncharged of the conservation and exhibition of the goods of art. On the other hand, depending of the fragility of the exposed art objects (i.e. spectral responsivity of the material) the irradiance must be kept under a critical level. Therefore, it is necessary to develop a mathematical model that simulates with enough accuracy both the visual effect of the illumination and the photochemical impact of the radiation. Spectral reflectance of a reference painting (*The woman in blue* of Picasso) has been measured with a high resolution non-contact spectrophotometer. A light source has been modeled as four LEDs (red, green, blue and amber), those intensity will be varied from 0 to 100. The mathematical model is based on a merit function that optimized the individual intensity of the LED-light sources taking into account the damage function of the material and color space coordinates. Moreover the algorithm used weights for damage and color fidelity in order to adapt the model to a specific museum application.

A new approach for lighting energy management

B. García-Fernandez[1], A. Álvarez Fernandez-Balbuena[1,2], D. Vázquez-Moliní[1],

[1] *Department of Optics, University Complutense of Madrid, Faculty of Optics, Madrid, Spain*
[2] *Department of Physics Applied to Natural Resources, School of Forestry Engineering, Polytechnic University of Madrid, Spain*
bgarciaf@ucm.es

Lighting of cultural heritage is one of the area's most challenging and complex because of the multiplicity of objectives that should be pursued. There is a need of protect and preserve the works of art fulfilling objectives like energy conservation and pollution reduction, meanwhile the exhibition of the art is suitable for the correct visual recognition. The use of Hollow Prismatic Light Guides (HPLGs) offers advantages as the possibility of reduce the risk of damage in materials with the benefit of reduce energy consumption providing good quality and optimal colour reproduction. In this work, we present an optical system compound of HPLGs with a customizable elbow to illuminate spaces bending contours for a wide range of angular configurations with high efficiency. In addition, a mathematical model is presented to determine transmission efficiency in the optical system. The new approach can be used in natural and artificial lighting solving architectural and lighting designs restrictions with high colour reproduction.

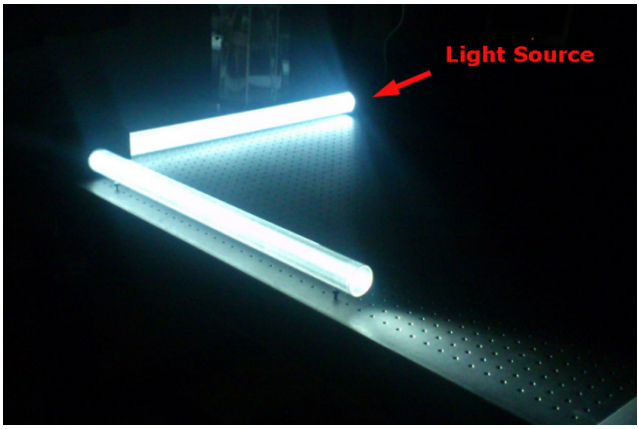

Figure. Customizable high efficiency optical system for guide of light (Experimental setup).

Nanoscience and nanotechnology applied to cement-based materials

J.S. Dolado

TECNALIA R&I
C/ Geldo-Parque Tecnológico de Bizkaia-Edif. 700, Spain
jorge.dolado@tecnalia.com

Over the last decades there has been an intensive research activity devoted to explore the capability of nanomaterials and nanotechnology to improve cement-based materials. This effort has comprised (i) new simulation strategies like atomistic simulations which implicitly take into account the complex nanostructure of cementitious materials, (ii) new synthesis pathways, like the ones offered by the Supercritical Fluid Technologies (SCF) which enable ultra-fast synthesis of nanoparticles, or even (iii) the advent of new family of nanoparticles like the C-S-H nanoseeds or CSH nanofibers which have been considered as the "ultimate" additions and fibers for concrete. This paper aims to illustrate some the ongoing progress on these topics and it will pay special attention to address how these new methodologies and products can be employed to improve the ageing and durability of cement-based materials.

New composite structures for rehabilitation and new constructions: expansive concrete filled tubes

J.P. Gutiérrez Jiménez, S. Martínez de Mingo, L. Echevarría Giménez, A. De Diego

Eduardo Torroja Institute for Construction Science (IETcc-CSIC)
C/ Serrano Galvache, 4. Madrid. Spain
l.echevarria@csic.es

A study on the use of controlled expansion concrete for the filling of structural steel tubes is presented in this paper.

In the last decades, the use of composite systems formed by an outer steel tube filled with conventional concrete (known as CFT, that stands for "concrete filled tubes") has become very common.

The structural performance of this system improves when combined with the use of a controlled expansion concrete, due to, basically, the ease with which a state of tri-compression is obtained in the inner concrete: The concrete tries to expand, but the steel tube restricts the expansion of the concrete, and consequently generates a state of compression in the concrete. This state of confinement is beneficial to the structural element, as it increases its strength.

In addition, the confinement allows these composite systems to resist all or part of the longitudinal shear stresses that takes place between the two elements, outer metal tube and inner concrete, when subjected to compressive stresses or bending moments without the need to provide any amount of connect connectors or, if applicable, a minimum amount.

That is why the systems formed by steel tubes and controlled expansion concrete are very interesting in rehabilitation works. For instance, in constructions where it is necessary to replace or add new columns with elements of small section; or in civil works, for the extension of boards in arch bridges. They are also used in new construction in both building and civil works.

For practical purposes, it is essential to be able to quantify the generated confining pressure. This work presents an approximate approach that allows to estimate the confining pressure generated due to the expansion of the concrete and to study the effect of different variables in this pressure, such as thickness and outside diameter of the tube, the relation between the thickness and the diameter, strength and elasticity of the materials, the expansion deformation of the concrete, the amount of longitudinal inner reinforcement and the axial load level.

Acknowledgements: This work is part of the BIA Project 2013-49103-C2-1-R: "Design and characterization of special concrete", granted by the Ministry of Economy, Industry and Competitiveness.

Structural analysis model of GFRP bars to reinforce Heritage Buildings

A. Alonso-Durá[1], A. Almerich-Chulia[1], S. Tormo-Esteve[2], V. Llopis-Pulido[1]

[1]Departamento Mecánica Medios Continuos y Teoría de Estructuras Universitat Politècnica de València, Camino de Vera S/N, Valencia, Spain
[3]Departamento Construcciones Arquitectónicas, Universitat Politècnica de València, Camino de Vera S/N, Valencia, Spain
santores@arq.upv.es

Glass Fiber Reinforced Polymer (GFRP) has become more and more popular as material in technology for the Conservation of Cultural Heritage. It is due to its advantages of corrosion-resistance, high strength, nonmagnetic properties, fatigue-resistance...

Over recent years, the study of GFRP bars as internal reinforcement for structures has grown. The research has been developed to get a kind GFRP bars for work as internal reinforcement of structures; both in tensile and compression, and their mechanical properties (strength, elasticity modulus, bond, ...).

The use of Glass Fiber-Reinforced Polymers bars in the restoration of architectural heritage is very versatile. One application is to use GFRP bars as internal reinforcement in traditional structures, masonry, stone, lime concrete… GFRP bars do not show the type of expansive corrosion exhibited by steel reinforcing bars and they have coefficients of thermal expansion that improve their compatibility with masonry, stone. GFRP bar reinforcement embedded in these structures result in longer service-life

In addition, nowadays, structural analysis models of heritage buildings are done. These have allowed us to know their structural behaviour against different actions. One of these is the study of seismic vulnerability of the Cathedral of Valencia. Its research presents that the most vulnerable structural volume is the dome, obtaining its collapse mechanism.

When compared to a new model of numerical structural analysis that introduces the GFRP bars as a reinforcement, the results show an improvement of the structural response obtained against an earthquake.

Pathology of masonry brick façades. Applications and repairing solutions

J.P. Gutiérrez Jiménez, R. Piñeiro Martínez de Lecea, S. Martínez de Mingo, L. Echevarría Giménez

Eduardo Torroja Institute for Construction Science (IETcc-CSIC) C/ Serrano Galvache, 4. Madrid, Spain
l.echevarria@csic.es

The general typology of façades of fairface masonry bricks, that has been developed during the second half of the twentieth century and widely used in Spain until nowadays, consists on a ½ foot wythe of fairface brick, mortar, air chamber (ventilated or not) , thermal insulation and plaster coat. Besides this solution, other special typologies exist, based on ceramic bricks used in singular buildings.

Damage frequently appears in this type of systems. The main problems are related to humidity, the lack of sufficient support of the enclosures, the strains due to thermal and moisture expansion, the structural deformation, the rheology of the materials (creep and shrinkage), damp expansion due to humidity of the bricks, freeze-induced cracking and the appearance of other types of defects and damages related to efflorescences and scaling of different source (physical, chemical or mechanical).

Many of these problems adopt the form of fissures and cracks, instability or buckling of whole sections of wall and occasional shifting or detachment of siding on structural members. These problems are aggravated with the use of inadequate constructive solutions which can be decided during the design or the construction.

In this paper it is described the frequent pathology of these practices, a methodology of work to be followed for its research and the study of intervention solutions.

Several mechanical tests on ceramic and mortar pieces, studies of the chemical composition of the constituent materials and theoretical researches of the resistant behavior of the bricks and block walls under different states of load are also analysed.

After the study of the origin of the defects, several solutions of reparation and restitution are studied by conducting tests in order to find the optimum solution to perform the repair that, keeping the formal composing of the façade, the strength and durability of the system, is economically and constructive feasible. Finally, an application on a façade of a singular building of the 20th century made with fairface hollow bricks with a singular geometry is included, where all the evaluation process is defined and the repair proposals are described.

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Two decades using molecular techniques to study biodeterioration of cultural heritage: an amazing biotechnological development

G.Piñar[1], K.Sterflinger[1]

[1] Department of Biotechnology, VIBT-Vienna Institute of BioTechnology, University of Natural Resources and Life Sciences, Vienna, Austria
guadalupe.pinar@boku.ac.at

In the last two decades, molecular techniques have developed at a fast pace and have complemented classical microbiological methods to study microbial diversity in cultural heritage. The fusion of cultivation and molecular strategies has delivered complementary results enabling a much better understanding of the diversity and the role that microbial communities play in biodeterioration processes.

Recently, new methods have evolved for different applications, enabling the study of microorganisms from their DNA, RNA and proteins and the ongoing scientific and technological progresses led to meta-genomics, -transcriptomics and -proteomics, which give a complete overview of the present microorganisms, their activity and the expressed proteins in an specific environment. These state-of-the-art methodologies are now developing at a very fast pace and Next Generation Sequencing (NGS) methods are becoming applicable in the field of cultural heritage. Nevertheless, new challenges are arising to adapt NGS protocols properly to the special requirements of cultural asset samples, as DNA/RNA extraction and amplicon protocols, as well as the combination of different strategies to overcome the limitations given by non-invasive or minimal-invasive sampling.

This review shows an overview about the amazing development that molecular techniques have undergone in the field of biodeterioration in the last two decades and, in addition, suggests some future perspectives. To this end, some exemplary molecular studies, focused to investigate two well-known biodeterioration phenomena, and carried out in collaboration with the working group of Prof. Cesareo Saiz-Jimenez, have been selected. First, we review the microbiota associated with well-investigated monuments affected by the "rosy discoloration" phenomenon. This phenomenon is widely observed on monuments located in central and south Europe and has an effect on diverse materials, as stone, wall paintings, buildings and burial-related materials. The affected monuments may be exposed to different climatic conditions and diverse UV irradiations, but, as a common denominator, all of them have constructional problems that enable water infiltrations. The migration of water, mainly through the walls, produces further crystallization of salts on the surfaces leading to the formation of saline environments that offer optimal growth conditions for halophilic microorganisms. These halophilic microorganisms have shown to be similar in all investigated monuments, even if they are in different geographical locations. Second, we show an overview of the microbiota associated with macro-colonies covering the surfaces of different caves. Results also show an intriguing similar microbiota in geographically distant caves. Future perspectives are suggested.

Detecting cells with low RNA content colonizing artworks non-invasively: RNA-FISH

R. Vieira[1], M. Pazian[1], A. Pereira[1,2], A. Candeias[1,2], A.T. Caldeira[1,2], M. González-Pérez[1]

[1]*HERCULES Laboratory, Évora University, Largo Marquês de Marialva 8, 7000-809, Évora, Portugal*
[2]*Chemistry Department, School of Sciences and Technology, Évora University, Rua Romão Ramalho 59, 7000-671, Évora, Portugal*
ricardo.o.vieira89@gmail.com

There is a need to enhance the methods for signalizing the microorganisms associated to biodeterioration of Cultural Heritage (CH) materials. An RNA-FISH in Suspension protocol was previously proposed by us as an alternative for *ex situ* analysis of the microbial colonizers from microsamples [1]. However, since: i) the low RNA content of the target cells has been previously reported as a possible limitation for RNA-FISH application in environmental and CH samples; and ii) the use of non-invasive sampling methods is preferred in CH field; the aim of this work was to investigate the capacity of this RNA-FISH protocol to detect cells with low RNA content and the possibility of adapting it for application in samples collected by non-invasive techniques.

Universal probes for targeting Eukaryotes (EUK516) and Bacteria (EUB338) labeled with Cy3 and 6-FAM dyes were used for all the assays. Cells with low RNA content (checked through RNA extraction and spectroscopic quantification) of bacteria and yeast strains isolated from biodegraded Cultural Heritage objects were used to simulate those colonizing artworks. For evaluating the possibility of the protocol to become a non-invasive approach, wood and stone slabs artificially inoculated with biodeteriogenic yeast and bacteria cells were prepared and a low invasive sampling was performed by swabbing or by an impression method with filter paper, nitrocellulose and two types of membranes. The cells were recovered from the samples and the RNA-FISH protocol was applied in the resulting suspensions. Regarding the detection of cells with low RNA content, the results showed that, for all the microorganisms tested, using the specific probes for the target microorganisms labeled with the Cy3 dye satisfactory signals were observed. However, low intense or undetectable signals were detected with 6-FAM labeled probes. This revealed the potential of the RNA-FISH In suspension protocol to detect bacteria and yeast cells with extremely low RNA content and evidenced the need of using dyes with high quantum yields for avoiding false negatives.

On the other hand, when the sampling was performed by swabbing or by the impression method and this RNA-FISH approach was applied: i) the cell recoveries obtained for all the methods before FISH application were acceptable; and ii) good FISH signals were detected without background interference.

Thus, whereas more tests are required, the non-invasive RNA-FISH methodologies presented in this work seem to be good alternatives for analyzing the potential biodeteriogenic microorganisms thriving in CH objects overcoming the drawback of background fluorescence.

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Studying colonization of stone surfaces: what can we learn from model biofilms growing in flow-through chambers?

A. Gorbushina[1], F. Villa[2], F. Capitelli[2]

[1]Department of Materials and the Environment, BAM Federal Institute of Material Research and Testing, Berlin, Germany,
[2]Department of Food, Environmental and Nutritional Sciences, Università degli Studi di Milano Italy
anna.gorbushina@bam.de

Soil formation on weathering rock surfaces is intrinsically connected with the development of primary microbial colonization at the atmosphere-lithosphere interface. A great number and variety of microorganisms is involved in these microbial communities, which are dominated by fungi, algae, cyanobacteria and heterotrophic bacteria. Rock-inhabiting life is ubiquitous on rock surfaces all around the world, but the laws of its establishment, and more important, quantification of its biodeterioration and geological input are possible only in well-controlled and simplified laboratory models. Here we would like to compare two model rock biofilm consisting of the heterotrophic and the phototrophic interacting partners.

In the present work the growth of these model biofilms on diverse materials with different physical and chemical properties was investigated under well-controlled laboratory conditions. To clarify the role of environmental factors, the parameters temperature, light intensity and relative humidity were varied in growth test series. For accelerated substrate colonization and to increase the biomass yield different flow-through chambers systems with semi-continuous cultures have been applied, simulating weathering conditions like flooding, desiccation and nutrient input. The biofilm development was studied by (i) confocal laser scanning and electron microscopy and (ii) qualitatively and quantitatively with respect to cell forms and biomass. A correlation between the presence of the model biofilm and mineral surface alteration as well as geochemical tracers of weathering were followed on various rock substrates (with differing geochemistry, porosity etc.) exposed in another flow-through chamber, filled with crushed rock material. Under mentioned environmental conditions different types of flow-through chambers have been used and will be compared.

Primary bioreceptivity of limestones to phototrophic microorganisms: a laboratory-based stone colonization experiment

A. Z. Miller[1], A. Dionísio[2], M.F. Macedo[3], C. Saiz-Jimenez[1]

[1]*Instituto de Recursos Naturales y Agrobiología de Sevilla (IRNAS-CSIC), Av. Reina Mercedes 10, 41012 Seville, Spain*
[2]*CERENA, Instituto Superior Técnico, Universidade de Lisboa, Av. Rovisco Pais 1049-001 Lisbon, Portugal*
[3]*VICARTE, Departamento de Conservação e Restauro, Faculdade de Ciências e Tecnologia, Universidade Nova de Lisboa, 2829-516 Caparica, Portugal*
anamiller@irnas.csic.es

The conservation of historic buildings and monuments from cultural heritage is a major issue in modern societies, both from economic and cultural viewpoints. This study aimed to evaluate the primary bioreceptivity of limestones widely used as building materials in Mediterranean countries to further establish an index of bioreceptivity. The experimental set up relied on: i) molecular and culture characterization of photosynthetic-based biofilms collected from five limestone monuments from Portugal, Spain and Italy, to select the most adequate culture to be used as inoculum for laboratory-based bioreceptivity experiments; ii) inoculation of five limestone types with the phototrophic culture: *Ançã* limestone (CA), *Lioz* limestone (CL), *San Cristobal* stone (SC), *Escúzar* stone (PF) and *Lecce* stone (PL); iii) incubation for 90 days within a growth chamber and monitoring of photosynthetic biomass using different analytical approaches.

DNA-based molecular analysis revealed that the biofilms from Orologio Tower (Lecce, Italy) and Santa Clara-a-Velha Monastery (Coimbra, Portugal) were dominated by microalgae, particularly *Chlorella*, whereas the cyanobacterium *Chroococcidiopsis* was the dominating genus from Ajuda National Palace (Lisbon, Portugal). The biofilms from Seville and Granada Cathedrals (Spain) were mainly composed of the cyanobacterium *Pleurocapsa*. DGGE analysis of the cultivated biofilms revealed a remarkable stability, of the microbial components from the Coimbra biofilm, which was further used as inoculum for the laboratory-based bioreceptivity experiment.

The results from the petrophysical characterization of the lithotypes and from microbial growth monitored along the course of the bioreceptivity experiment were statistically analysed by means of PCA and ANOVA in an attempt to determine the primary bioreceptivity of the five lithotypes to phototrophic microorganisms and to evaluate the direct relationships between stone bioreceptivity and petrophysical properties. The limestones PF followed by SC showed the highest bioreceptivity, contrasting with the lowest bioreceptivity of CL. The CA and PL revealed moderate bioreceptivity.

The petrophysical characteristics, water absorption by capillarity, surface roughness, as well as open porosity and water vapour permeability, were the keys for the microbial development on the stone samples. The high values of water absorption by capillarity and open porosity obtained for PF, SC and PL indicate great susceptibility to biodeterioration, which render them unsuitable for very humid outdoor environments if preventive treatments, such as the application of hydro-repellents, are not taking into account. The relative low values of water vapour permeability and open porosity of CA renders this lithotype less bioreceptive for microbial colonisation. The very compact nature of CL and its extremely low capillarity coefficient, open porosity, surface roughness and water vapour permeability constitute an impediment to microbial growth. The diffusion of these data to end-users (e.g. conservators/restorers, engineers, architects) may contribute to decision-making on the lithotypes to apply in future building constructions and to choose the best conservation strategy based on the potential bioreceptivity characteristics of the materials used in monuments.

Why is it so difficult to prevent biodeterioration?

M. Hernández Mariné

Department of Biologia, Sanitat i Medi Ambient, University of Barcelona. Avda. Joan XXIII s/n Barcelona, Spain
marionahernandez@ub.edu

Knowledge concerning the effects of abiotic factors on cave dwelling microorganisms is essential, both from ecological and economic standpoints, to ensure the sustainability of show-caves and monuments. Terrestrial microbial populations have been thriving for billions of years. Each genotype has evolved in a slightly different way, and each has a unique geological and biological story. The strategies that they all adopt to perpetuate their lines could be considered from the human point of view as helpful or annoying. Regarding cultural heritage, organisms colonizing the substrata are disruptive and their effect is named biodeterioration. First, microorganisms living in natural or artificial materials can obscure rock paintings and speleothems due to their own pigments. In addition, their metabolism causes biochemical action resulting in stone dissolution or salt crystallization. Finally, some of them are able to enter preexisting holes and cracks, dwelling in crevices and pores or actively boring, causing mechanical pressure during growth. Moreover, microorganisms generally assemble in a multi-species complex, known as biofilm, which self-segregates a complex and protective matrix. This biofilm mode of life provides them with increased resistance to environmental stresses compared to independent life as individuals. Communication by means of chemical signals and collective behaviors, in response to environmental cues, are other reasons for their resilience. In order to prevent their development, various weapons, based mainly on chemical substances, have been used. Biocides attack and destroy individual organisms, but have little effect on communities in the long term. The next step must be based in prevention and friendly alternatives to prevent or slow down the development of biofilms.

The aim of this review is to summarize recent findings that improve our understanding about biodeterioration and advance the fight against it. The review higlights the implication of Prof. Dr. Cesáreo Sáiz Jimenez as a leader in the improvement of knowledge. Dr. Sáiz Jimenez has been a key figure in this field, which cannot be accomplished by any one individual or research group but only by a network of groups. Technoheritage, the multidisciplinary taskforce that he conceived and built, and which assembles most of us, has been key to providing a correct and complete framework where many disciplines have come together to produce mutually beneficious results. We are thankful for his contribution.

The biodeterioration of Cultural Heritages: the need to know, preserve and prevent

L. Bruno[1], F. Marano[2], V. Valle[1], E. Viaggiu[1], F. Valentini[3]

[1]Dept. of Biology University of Rome "Tor Vergata".Via Cracovia 1, 00133 Rome, Italy
[2]Dept. of Earth Sciences Sapienza – University of Rome. Piazzale Aldo Moro 5, 00185 Rome, Italy
[3]Dept of Chemistry, University of Rome "Tor Vergata", Via della Ricerca Scientifica 1, 00133 Rome, Italy
laura.bruno@uniroma2.it

Cultural Heritage is the set of Goods that allow us to reconstruct the origins and evolution and to characterize human cultural and artistic expressions. Thus, there is the need to be preserved and enhanced. However, the activity carried out for the conservation of cultural heritage in order to maintain their integrity and identity are often in contrast with those carried out for their enhancement aiming to improve the knowledge and to increase public enjoyment.

The possibility to visit valuable sites like the Roman Catacombs or archaeological and paleontological remains exposed *in situ* (i.e. fossil bones) is an added value to our knowledge and fruition of cultural heritage. However, the environmental conditions present *in situ* can cause biodeterioration's problems. Phototrophic biofilms are widespread on Cultural Heritage exposed to natural or artificial light in outdoor and indoor environments and represent a threat for their conservation. These biological patinas consist in complex communities formed by bacteria, cyanobacteria, microalgae and fungi that develop on different substrata causing discolorations, crust formation, exfoliation and precipitation of secondary minerals. Nowadays, the actions carried out to restore and conserve these sites, based on the use of mechanical interventions coupled with the employment of chemicals, are often invasive for the substratum and dangerous for humans and the environments.

A study with several microscopy techniques was undertaken in order to characterize the phototrophic biofilms that develop on the walls of the Catacombs of S. Callistus and the fossil bones exposed at the site of La Polledrara di Cecanibbio, one of the richest palaeontological sites of Quaternary period of Europe. The cyanobacteria present in these biofilms appeared as particularly biodeteriogenic due to the ability to mobilise minerals from the lithic substrata or to penetrate inside the superficial cortical portion of the bones for more than 50 μm causing mechanical damages. Moreover, small bone fragments colonized by biofilms were analyzed to evaluate the possible damage induced by the biofilm growth to the fossil remains.

In order to develop new non-invasive conservation strategies different approaches were proposed: besides the control of environmental conditions *in situ*, the nanomaterial graphene oxide and essential oils were evaluated as new biocompatible, eco-sustainable compounds as an alternative to the classical biocides. The tests were carried out on phototrophic biofilms collected *in situ* and grown on agarized medium and the effect evaluated as the ability to inhibit the growth and to reduce the photosynthetic activity measured with PAM.

Microorganisms and monuments: Forty years of Heritage conservation

B. Hermosin, L. Laiz, V. Jurado, A.Z. Miller, M.A. Rogerio-Candelera

Instituto de Recursos Naturales y Agrobiología de Sevilla (IRNAS-CSIC), Avda. Reina Mercedes, 10; 41012 Sevilla, Spain.
hermosin@irnase.csic.es

From the seminal studies about the problems of conservation of Vazquez Diaz's mural paintings "Poema del Descubrimiento", during the final 1970's until today, the research trajectory of Cesáreo Sáiz Jiménez encompasses almost 40 years of continuous effort addressed to understand and help in the conservation of Cultural assets, especially of built heritage (historic buildings and monuments as well as archaeological sites) and subterranean heritage (with an especial dedication to caves, with or without rock art, and subterranean necropolis).

This long and continuously updated research trajectory reached multiple goals, as could be the assessment of deterioration processes, the description of new species of microorganisms for the science, or the *rendez-vous* of different research groups by means of multiple collaborative initiatives. In the meantime, he also contributed to the formation of a human capital that integrated a multidisciplinary research group, continuously enriched by different approaches and techniques.

The purpose of this contribution is to enlighten the role of Dr. Sáiz Jiménez along almost four decades dedicated to the applied investigation on the conservation of Cultural Heritage.

Fungal contamination of paintings and wooden sculptures inside the storage room of a museum. Thoughts on the adequacy of current norms and established reference values

H. Paiva de Carvalho[1], N. Mesquita[1], J. Trovão[1], A.C. Pinheiro[1], S. Fernandez-Rodriguez[2], V. Gomes[3], A. Alcoforado[3], F. Gil[4], A. Portugal[1]

[1]Centre for Functional Ecology, University of Coimbra, Coimbra, Portugal
[2]AEROUEX- Aerobiología en Extremadura, Department of Construction, School of Technology, University of Extremadura, Cáceres, Spain
[3]MNMC – Museu Nacional Machado de Castro, Coimbra, Portugal
[4]Centre for Studies of X-Ray Diffraction Material, University of Coimbra, Coimbra, Portugal
hugopaivacarvalho@gmail.com.

Biodeterioration of cultural heritage is a topic of ever-growing concern. A torrent of scientific work has been published during the last decades on the identification of different damage types on different materials, the responsible organisms, their direct and indirect physico-chemical effects on materials, possible treatment methods and other related topics; Nonetheless, although an extensive knowledge has been acquired, current recommendations concerning architectural and HVAC (*Heating, Ventilating and Air Conditioning)* requirements for art conservation purposes are still lacking. Most of the current norms concerning air-quality in repositories focus human safety essentially, and the recommended temperature and humidity values sometimes disregard the existence of micro-niches and the extremophilic character of most microbial biodeteriogens. We address this matter through a case study within the storage room of the Machado de Castro National Museum in Coimbra, Portugal.

Fungi are one of the most aggressive contaminants in objects of art. The presence of fungal colonies was detected on wooden sculptures and paintings, stored inside a painting storage room in the Machado de Castro National Museum in Coimbra, thus making this site an excellent case study. Since this occurrence was unexpected in a recently constructed art repository, these contaminated objects were sampled for fungal isolation and identification, along with indoor air sampling for each season, during a one-year period. Molecular biology methods complemented with morphological observation were used for the identification of fungal organisms.

Direct object sampling allowed the retrieval of 10 fungal isolates (3 different genera and 4 different species) from 8 contaminated paintings. Also, 19 fungal isolates (5 different genera and 9 different species) were retrieved from 7 contaminated sculptures. The air sampling process provided a total of 153 isolates (24 different genera and 43 different species), from which the most common genera were *Aspergillus*, *Cladosporium* and *Penicillium* and the most frequent species were *Aspergillus versicolor*, *Cladosporium cladosporioides* and *Penicillium copticola*. Although the number of airborne CFU's was considerably low in all seasons, some fungal species with known biodeteriorating capability and adverse human health effects were present.

The relevance of air contamination monitoring as a single tool for biodeterioration risk assessment is discussed, as well as currently available norms and recommendations. Preventive measures are advised and considerations are made regarding possible future, more effective approaches.

Green strategies in the Spanish *National Research Plan in Cultural Heritage* (PNIC). Technologies for the early detection of biological contaminants in display cases.

M. Bueso[1], D. Durán[1], F. Gaztañaga[1], I. Herráez[1], A. Manrique[1], M. Martín-Gil[1], J. Montero[1], C. Muro[2], B. Sánchez[3], N.N. Valentín[1]

[1]Área de Investigación y Formación, Instituto del Patrimonio Cultural de España (IPCE). C/ Pintor El Greco, nº 4. Ciudad Universitaria. 28040 Madrid, Spain
[2]Área Científica. Dpto. de Restauración del Museo Nacional Centro de Arte Reina Sofía. C/ Santa Isabel, 52, 28012 Madrid, Spain
[3]Dpto. Energía, Centro de Investigaciones Energéticas, Medioambientales y Tecnológicas (CIEMAT). Avda. Complutense 40. 28040 Madrid, Spain
daniel.duran@mecd.es

The National Research Plan in Cultural Heritage (*Plan Nacional de Investigación en Conservación,* PNIC), is a key coordination and development tool for initiatives in research of cultural heritage –conservation sciences- between the State Administration, Autonomous Communities and other agents. This specific science needs such a framework as it gathers interests from traditionally separated fields such as science and humanistic, without forgetting its purpose of providing solutions to real problems that are raised to restorers and curators during the implementation of their practice of guarding cultural assets. The *Conservation and environmental program* has been defined under the PNIC framework in parallel to European and global green policies that seek sustainable research. The Program main objectives are among others the promotion of research focused on the prevention of cultural heritage risks implemented with environmental and human health best practices; the definition of new strategies to avoid toxic and/or expensive products traditionally used and the optimized use of them.

Under this context, the main outcomes of the project titled "Development of technologies for the early detection of biological contaminants in display cases and containers with air and oxygen-free atmospheres" will be presented. Display cases are a common element in most of museums and there is a great deal of unresolved questions about its preventive conservation and maintenance. Inert-gas-filled, hermetically sealed display and storage cases have been successfully used to preserve sensitive organic and mineral materials and are a particular case that deserves a special attention.

The presentation is focused on the use of bio-sensors as early warning of biological contaminants and on the design requirements needed for the oxygen-free display cases to keep these elements. Concerning bio-sensors the concept and basic techniques are introduced along with the latest improvements achieved.

Regarding to the second aspect an experimental anoxia display case was built and indeed it was finally installed in the MNCARS to hold a collection of objects by Salvador Dalí, including a small piece made out of chocolate. That was possible thanks to the donation of a set of spare materials from the Getty Museum and the help of the environmental engineer Mr. Shin Maekawa, staff member of the museum and experienced designer of that sort of show cases.

Some other aspects covered are the building and installation processes together with the physical principles, construction details, specific problems arising from air tightness, and finally some key maintenance considerations.

Light4Heritage: Lighting-based strategies to control biological colonization in built heritage

P. Sanmartín[1], D.Vázquez-Nion[1], M.C. López-Rodríguez[2], J. Arines[3], S. Calleja-Vaquero[1], L. Cabo-Domínguez[1], B. Silva[1], B. Prieto[1]

[1]Universidade de Santiago de Compostela. Departamento de Edafoloxía e Química Agrícola. Facultade de Farmacia. 15782 - Santiago de Compostela, Spain
[2]Universidade de Santiago de Compostela. Departamento de Botánica. Facultade de Bioloxía. 15782 - Santiago de Compostela, Spain
[3]Universidade de Santiago de Compostela. Departamento de Física Aplicada. Facultade de Física. 15782 - Santiago de Compostela, Spain
patricia.sanmartin@usc.es

The Light4Heritage project aims to develop innovative and safe strategies based on urban ornamental lighting in order to inhibit/enhance growth of microorganisms and chromatically integrate biological colonization on built structures. To our knowledge, no previous studies have investigated the use of light quality and intensity to control biodeterioration in outdoor habitats. It therefore seems appropriate to address this question by taking advantage of the current trend for using LED lamps to illuminate outdoor cultural heritage monuments in urban centres. The lighting provides greater visibility to stone structures and showcases different features. Furthermore, coloured LEDs (red, green, yellow, blue, etc.) are often favoured over white LEDs to create different effects on buildings or monuments. As a preliminary approach to developing lighting-based control strategies, we carried out a study to evaluate how coloured cellophane film affects the quality and intensity of light and, therefore, the growth and colour of biofilm-forming photosynthetic microorganisms. We used red, yellow, green and blue cellophane film (rather than coloured LEDs) to generate different light qualities (by cancelling the spectral components in certain bands of the visible electromagnetic spectrum) at different photon flux densities. We then used the coloured cellophane to cover phototrophic cultures, derived from natural biofilm growing on a historic granitic building and mainly comprising green algae and cyanobacteria, in order to promote specific physiological responses. The blue cellophane inhibited growth of the test culture. By contrast, the yellow cellophane did not significantly decrease the biomass, pigment or EPS content relative to uncovered, control cultures. The different coloured cellophane covers also generated colour changes in the culture; e.g. the red cellophane produced notable greening, whereas the green cellophane enhanced the redness of the culture. To follow up on this research, we compared the effects of blue, green, red, cold white and warm white LED lamps on phototrophic cultures. We determined changes in biomass, pigment and carbohydrate content, biofilm architecture, and diversity and abundance of species. Phototrophic biofilms thrived well under blue LEDs, whereas green and red LEDs had a weak biostatic effect. Phototrophs responded differently to exposure to the lamps: the biofilms developed under blue light predominantly comprised chlorophyta, and those exposed to red and green light mainly comprised cyanobacteria. These findings contribute towards developing new conservative technologies for controlling biological colonization integrated with lighting projects for cultural heritage buildings and monuments.

Action protocol against termites in urban areas

J. Galván[1], D. Lorenzo[2], M. Gajú[3], C. Villagrá[1], M.T. de Troya[4]

[1] Eduardo Torroja Institute for construction Sciences, Departament of Construction. Serrano Galvache nº4, 28033, Madrid, Spain
[2] PEMADE. Santiago University. University Campus, s/n, 27002, Lugo, Spain
[3] University of Cordoba. Department of Zoology. Motorway A4 Madrid - Cádiz, Exit 396 A, 14014 Cordoba, Spain
[4] National Institute for Agricultural and Food Research and Technology, Forestry products Departament. Motorway A6 Madrid - La Coruña, Exit 8, 28033, Madrid, Spain
j.galvan@csic.es

Wood, together with stone, is the oldest material used in construction, the evolution in its technology makes possible that today we can found technical wood products for construction, with an environmental quality, due to its organic origin. Its origin makes wood susceptible to the attack of xylophages organisms (fungi and insects) that cause different pathologies in the timber structures.

Currently the Spanish real estate has about one and a half million houses with wooden structures, which by their construction ¿date? are usually located in the historical city centers. In addition, most of the buildings that make up our cultural heritage have wood as part of their structure, and most of them has some kind of intervention related to the attack of xylophages organisms. Underground termites are a problem of the Mediterranean countries since their climatology favors their development.

In Spain, termite attack is very important in cultural heritage and even in new construction, as they can cause serious damage to structural elements (pillars, beams, roofs, etc.), carpentry (doors, windows, etc.) and wooden goods (furniture, paintings, libraries, etc.), causing not only the economic losses resulting from the rehabilitation but also losses in the cultural heritage and legacy of our country.

Currently there are many types of treatments against the attack of subterranean termites, however in Spain, there is not a methodology that allows to control the damages. The current ¿regulation? on urban planning proposes the replacement of the Technical Inspection of Buildings (ITE), by the Building Evaluation Report (IEE), incorporating the presence of xylophages organisms as one of the parameters to be measured, but does not describe in any part of the text how to carry out such evaluation.

Subcommittee 4 of the Technical Committee on Standardization (CTN) 56 "Timber and Cork" has established a group of termite experts who are developing a technical action protocol to systematize the pest control of subterranean termites in urban areas, both in buildings and in their environments, by specifying basic procedural guidelines.

Self-cleaning and de-polluting stone surfaces

R. Zouzelka

J. Heyrovsky Institute of Physical Chemistry, Academy of Sciences of the Czech Republic
Dolejskova 3, 182 23 Prague 8, Czech Republic
radek.zouzelka@jh-inst.cas.cz

Deterioration of stone surfaces caused by deposits of dust and dirt particles from polluted air is one of the most serious problems facing conservation today. Titanium dioxide (TiO_2) has become a promising photocatalytic material due to its ability to protect the surfaces against darkening. Moreover, highly porous TiO_2-based coatings exhibit very good permeability and protect the substrate (natural or painted) against the degrading effects of the ultraviolet radiation contained in daylight—prolonging its lifespan and protecting against changes in color (fading). The main advantage of photocatalytic TiO_2-based coatings is their applicability to various construction materials used in buildings, pavements, walls and tunnels, amongst other surfaces. Anti-noise barrier in in Prague's Barrandov District located in the close proximity of some very busy roads (20-30,000 cars pass by daily) was coated with TiO_2-based coating. Even after only two years, a difference in colour can be seen between areas where the protective coating has been applied and those where it has not. The results will be discussed.

Stone cultural properties in Europe, particularly buildings and statues made of marble, limestone, and sandstone are considerably affected by acid rain that is formed by reaction with nitrogen oxides (NOx) in the atmosphere. Therefore, it is a necessary to substantially reduce NOx concentration. This reduction can be achieved on photocatalytic active surface. Experiments on concrete as a support for photocatalyst were carried out in two types of reactors with laminar and turbulent flow under "real world setting" conditions of temperature, relative humidity, irradiation and pollutant concentrations. The decrease in the total concentration of nitrogen oxides on contact with the photocatalytic surface reached 20-50%, i.e. at a concentration of 100 ppb the decrease in NO and NO_2 was 20-50 ppb. The results showed that photocatalytic process significantly reduced both nitrogen oxides in the air.

Au-TiO_2/SiO_2 photocatalysts for application as self-cleaning and de-pollutant coatings on building materials

M. Luna[1], J.M. Gatica[2], H. Vidal[2], M.J. Mosquera[1]

[1] TEP243 Nanomaterials Group (Departamento de Química Física, Universidad de Cádiz)
[2] FQM110, Solids Chemistry and Catalysis Group (Departamento C.M., I.M. y Química Inorgánica, Universidad de Cádiz) Facultad de Ciencias, Campus Universitario Río San Pedro s/n. 11510 Puerto Real, Cádiz, Spain
manuel.luna@uca.es

Nowadays, pollutants concentration is significantly high in big cities and industrial environments. Atmospheric aerosol pollutants produce visible stains on building surfaces. Specifically, small particles and greasy deposits are adhered to building surface by organic binders such as hydrocarbons and fatty acids. This promotes a significant change in the aesthetic of historic and modern buildings of our cities and subsequently, it is responsible of great investments in buildings conservation.

The use of photoactive building materials provides a possible solution because they can decompose organic compounds deposited on their surfaces towards H_2O, CO_2 and other harmless species by the exclusive action of the sun light. In addition, these materials could help in the depletion of atmospheric pollutant such as NOx since TiO_2 photoactivity was discovered, it has become the most used photocatalyst for several reasons: stability, availability, low cost, lack of toxicity and great efficiency. The most important drawback of TiO_2 for application on building and monuments is that its absorption is exclusively localized in the ultraviolet range that only constitutes 3-5% of solar light. Since 45% of solar light is in the visible range, enhancing the visible absorption of TiO_2 is an important challenge. The use of nanostructured noble metals, which has a great localized surface plasmon resonance (LSPR), is one of the most extended choices to improve TiO_2 photoactivity.

In order to fulfil this objective, we incorporated gold nanoparticles (NPs) to commercial TiO_2 NPs by means of three different methods, so as to improve the Au-TiO_2 interaction. Next, Au and TiO_2 NPs were incorporated to a starting sol containing silica oligomer and n-octylamine. The Au-TiO_2-SiO_2 photocatalysts were applied as sols on wide range of common materials employed in cultural heritage, such as granite, limestone, marble and concrete. The photoactivity and self-cleaning properties of the coatings were by degradation tests of a model dye (methylene blue) and atmospheric pollutants (NO) in order to confirm the best Au-TiO_2-SiO_2 preparation procedure and their versatility as coating for different building materials

The sols prepared, having low-viscosity, with low-viscosity penetrated into the pore structure of the building substrates and they gelled, in situ, producing crack-free Au-TiO_2-SiO_2 nanocomposites. The integration of Au-TiO_2 NPs into the silica matrix produced a well-adhered and continuous coating on the building material surface, promoting a high durability. The addition of Au to the photoactive nanocomposite significantly increased the self-cleaning and de-pollutant properties of the material.

Acknowledgments: We are grateful for financial support from the Spanish Government MINECO/FEDER-EU: Project Mateco (MAT2013- 42934-R) Manuel Luna would also like to thank the Spanish Goverment for his pre-doctoral grant (BES-2014-068031).

Photocatalytic nanocomposites for the protection of European Architectural Heritage

F. Gherardi[1], M. Roveri[1], L. Niccolai[2], J. Weber[3], L. Toniolo[1]

[1]Department of Chemistry, Materials and Chemical Engineering "Giulio Natta", (Politecnico di Milano), Piazza Leonardo da Vinci, 32, 20133, Milan, Italy
[2]Colorobbia Consulting S.r.l., Via Pietramarina, 53, 50053, Sovigliana Vinci, Florence, Italy
[3]Institute of Arts and Technology/Conservation Sciences (University of Applied Arts Vienna) Salzgries, 14/1, A-1013, Vienna, Austria
francesca.gherardi@polimi.it, marco.roveri@polimi.it, lucia.toniolo@polimi.it, niccolail@colorobbia.it, johannes.weber@uni-ak.ac.at

In recent years, promising results were obtained by using nanostructured materials for built heritage conservation. In particular, in the field of stone protection, the introduction of inorganic nanoparticles such as TiO_2, ZnO and Ag can enhance the protection efficacy of traditional treatments, as well as giving them additional properties (photocatalytic, antifouling, antibacterial). The self-cleaning and depolluting properties of photocatalytic treatments can be employed as a preventive strategy towards stone degradation, with a reduction of maintenance activities and costs for historic buildings.

In the framework of the EU-Horizon 2020 project "Nano-Cathedral", nanostructured photocatalytic protective treatments were formulated by using different TiO_2 nanoparticles, solvents and silane/siloxane systems in the blends. The innovative products were applied on 6 lithotypes (Ajarte fossil limestone, Balegem sandy limestone, Obernkirchen and Schlaitdorf sandstones, St. Margarethen calcareous arenite and Apuan marble), selected among the stones used in five medieval cathedrals (Vitoria-Gasteiz, Ghent, Cologne, Vienna and Pisa) and a contemporary opera theatre (Oslo Opera House), considered as representative of different exposure conditions in the European context.

The stone specimens were tested before and after the application of the products to evaluate the effectiveness of the treatments, following a screening protocol of laboratory tests which includes microscopic observations, VIS reflectance spectrophotometry, water absorption test by contact sponge, rhodamine fading test and monitoring NOx reduction to assess the photocatalytic activity of the applied treatments. A specific characterization of the new materials has been carried out with spectroscopic and microscopic analyses.

The treatments show promising results in water absorption reduction, preserving the surface color of each lithotype, except for the TEOS-polydimethylsiloxane-based treatment which leads to ΔE^* values higher than 5. Laboratory tests proved different behaviors as photocatalytic and depolluting properties of the treatments according to microstructural differences and the products characteristics.

The same innovative materials have been preliminary applied on the stone materials on-site, at the aim of setting-up the application methodology on deteriorated substrates. The promising results obtained so far will be confirmed in lab and on-site in the future tasks of the Project for an improved knowledge of the complex system "treatment/stone substrate".

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Heterogeneous photocatalysis as a self-cleaning and anti-graffiti technology in cultural heritage conservation

E. Jiménez-Relinque, F. Rubiano, M. Castellote

Eduardo Torroja Institute-IETcc (Spanish National Research Council [CSIC]), Spain
eva.jimenez@csic.es

Among other problems, cultural heritage conservation in large cities faces two important problems mainly related with the aesthetics of the surfaces: on one hand, airborne particulate matter emitted by the exhaust of motor vehicles that cause deterioration and dirt the surface, and on the other hand, the events of vandalism with graffiti. Traditional cleaning methods on these structures are costly and may themselves cause further damages to the materials. Thus, photocatalytic technology arises as a promising way to reduce the impact of dirt from pollutants and graffiti on these historical constructions.

Photocatalysis is classified as an advanced oxidation process. Through light activation, the nanoparticulated photocatalyst, usually TiO_2, generates redox species which may degrade organic and inorganic pollutants on the photocatalyst surface (self-cleaning properties). Beside this, due to the photo-induced hydrophilicity, dirt and stains on surfaces should be easily removed due to rainwater soaking between the adsorbed substance and the TiO2 surface.

In this work, the efficiency for self-cleaning, removing different dyes, and graffiti of different colours has been undertaken. Three different commercial TiO_2 based photocatalyst placed on the surface of two different substrates typical of buildings of the European cultural heritage, natural stone and brick, have been tested in accelerated conditions in the lab using a lamp simulating the solar spectrum. Additionally, efficiency for self-cleaning and graffiti is being tested in real conditions at the environment of Madrid in paving slabs at a technical scale of pilot plant as part of the project Life-Photoscaling (LIFE13-ENV/ES/001221).

The results are critically discussed in the light of the differences in the reaction mechanisms based on the characteristics of the substrate and composition of dye or graffiti.

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Evaluation of antigraffiti products on ornamental stones

C. Ricci[1,2], F. Gambino[2], E. Matteucci[2], M. Nervo[2], A. Piccirillo[2], T. Rivas[1], J.S. Pozo-Antonio[1]

[1]Dept. de Enxeñaría de Recursos Naturais e Medioambiente (Universidade de Vigo), Vigo, Spain
[2]Centro Conservazione e Restauro La Venaria Reale, Piazza della Repubblica,Venaria Reale, Torino, Italy
cricci@uvigo.es, francesca.gambino@centrorestaurovenaria.it, enrica.matteucci@unito.it, marco.nervo@centrorestaurovenaria.it, anna.piccirillo@centrorestaurovenaria.it, trivas@uvigo.es;ipozo@uvigo.es

The use of antigraffiti products on ornamental stones employed in architecture was evaluated by a multi-analytical protocol. Both sacrificial and permanent antigraffiti were tested on five different lithotypes: granite, diorite, travertine, limestone and gneiss. These lithotypes were selected according to their different genesis and composition, as well as different chemical-physical properties. All these ornamental stones are employed for the architectural heritage in the city of Turin (Italy).

The analytical protocol proposed aims to evaluate the changes induced on the stones and the behaviour after the application of the antigraffiti coatings.

Moreover, the effectiveness of the cleaning procedure recommended by the antigraffiti manufacturer and the consequent level of removal of the paint were evaluated.

Changes of the stone surface were studied by optical and electron microscopies and by means of measurements in the CIELAB space; also, the low-pressure water absorption was evaluated with the contact sponge method.

In order to evaluate the advantages in the use of antigraffiti products, the same protocol was applied on untreated stones.

In addition, a possible increase in bioreceptivity due to antigraffiti products was considered.

The methodology described aims to determine the suitability of antigraffiti products employed on different kinds of stones and graffiti paints.

Photocatalytic self-cleaning coatings for limestones by N-doped TiO_2

L. Bergamonti[1], F. Bondioli[1], G. Predieri[2], Y. Paz[3], L. Fornasini[4], P.P. Lottici[4]

[1]Dept. of Industrial Engineering (University of Parma) Parco Area delle Scienze, Parma, Italy
[2]Dept. of Chemistry (University of Parma) Parco Area delle Scienze, Parma, Italy
[3]Dept. of Chemical Engineering (Technion-Israel Institute of Technology) Haifa, Israel
[4]Dept. of Physics and Earth Sciences (University of Parma) Parco Area delle Scienze Parma, Italy
giovanni.predieri@unipr.it

The main forms of deterioration of stone buildings and monuments are related to the accumulation of pollutants and to soiling processes. Photo-catalyzed oxidation methods can be used for the decomposition of various environmental pollutants. TiO_2 based photocatalysts are widely employed for self-cleaning coatings which can preserve the original appearance of the artefact [1]: the development of visible-light active TiO_2 photocatalytic materials by non-metal doping is of great current interest [2].

Different N-doped TiO_2 nanoparticles were synthesized by sol-gel methods starting from titanium(IV) isopropoxide or titanium(IV) oxy-sulfate using urea, ammonium fluoride and nitric acid as complexing agents or peptizers and have been investigated for self-cleaning photocatalytic coatings on different types of limestones among the most frequently used in historic buildings. A comparison was made with TiO_2 commercial P25 (@ Evonik).

The dried nanocrystalline powders were characterized by X-ray Diffraction (XRD), Raman, Diffuse Reflectance Spectroscopy (DRS) and X-ray Photoelectron Spectroscopy (XPS). The properties of the coatings were examined, according to the UNI-Normal protocols, by measurements of capillary water absorption, of surface wettability (static contact angle) and of colorimetric parameters. The photocatalytic oxidation of methyl orange (MeO) and Rhodamine B (RhB) under solar lamp irradiation, with and without UV component, was used as indicator of the activity of the different N-doped TiO_2 coatings.

XRD and Raman results indicate crystallite sizes in the range 4-10 nm (Figure 1). Band gap evaluation by DRS suggests a light shift toward lower energies of the N-TiO_2 samples with respect to the commercial product. XPS measurements indicate that the N-doping procedures have different effects on the nitrogen chemical state within the titanium dioxide particles. The self-cleaning TiO_2-based treatments do not introduce colorimetric changes compared to the untreated limestones and do not alter the properties of the stones as determined by measurements of the water capillarity absorption and wettability tests.

The photocatalytic activity on both dyes of N-TiO_2 coatings on the limestones was found better or comparable with that of P25.

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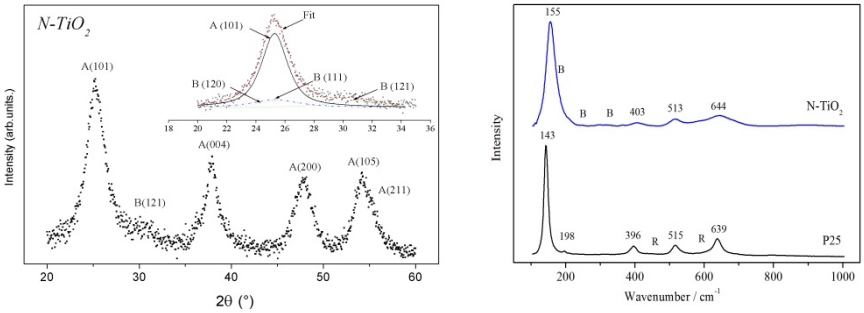

Figure 1. XRD and Raman spectra of N-doped TiO_2

Photocatalytic activity of TiO_2/AuNRs - SiO_2 nanocomposites applied to building materials

A. Truppi[1,2] M.J. Luna Aguilera,[3] F. Petronella,[2] R. Comparelli,[2] M.J. Mosquera[3]

[1]CNR-IPCF, Istituto per i Processi Chimici e Fisici, U.O.S. Bari, Bari, Italy
[2] Università degli Studi di Bari–Dip. Di Chimica, Bari, Italy
[3] TEP-243 Nanomaterials Group. Facultad de Ciencias, Univ. Cádiz, Puerto Real, Cádiz, Spain
r.comparelli@ba.ipcf.cnr.it

Atmospheric pollution is notoriously a serious problem with an evident impact on structures and urban buildings. Stone is among the most widely used building materials since ancient times. However, stone surfaces may deteriorate over time due to several source of damage as for example the increase of polluting gases and fine particulates, the crystallization of soluble and insoluble salts inside the porous network or the action of acid rains that give rise to the so-called "black crusts". Mesopouros photocatalytic TiO_2 - based nanocomposites deposited on the surface of stone and other building could provide self-cleaning and air-purifying properties due to photocatalytic processes initiated by light activation. Unfortunately, pure TiO_2 wide band gap limits its photoabsorption to the UV region only ($\lambda < 390$ nm), representing just a small fraction (4%) of the whole solar spectrum, thus limiting the possibility to exploit natural sunlight. One of the most promising solutions to these problems are plasmonic nanostructures in combination with TiO_2.

The goal of this work is to set up the synthesis of visible light-active Au nanorods (NRs) modified TiO_2-SiO_2 nanocomposites (namely UCA-TiO_2Au), for potential application in building materials. The photocatalytic properties of UCA-TiO_2Au mesopouros composites prepared by a simple and low cost technique, by mixing ethoxysilane oligomers and TiO_2/AuNRs in presence of non-ionic surfactant, were investigated. We have tested 3 types of TiO_2/AuNRs nanostructures in order to evaluate the effect of synthetic conditions on the photocatalytic activity of coating. Self-cleaning properties of these materials deposited as coatings on the surface a popular building limestone were evaluated by the degradation of a target compound (methylene blue, MB) under direct exposure to simulated solar light using TiO_2 P25 Evonik as a reference material. Moreover, these coatings upon irradiation by simulated solar light were successfully employed for the photocatalytic oxidation of Carbon soot. The experimental results pointed out that UCA-TiO_2Au 450°C sample was the best performing coating in MB bleaching being even able to catalyse a 25% soot removal after 340h of simulated solar light. In addition, the obtained nanocomposite provides effective adhesion to limestone, crack-free surface coating, improve stone mechanical properties and give rise to hydrophobic and self-cleaning properties.

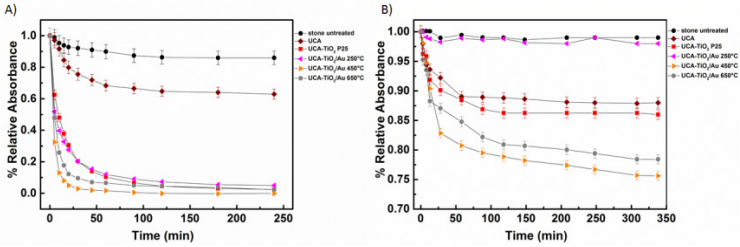

Figure 1. A) Evolution of photocatalytic degradation of Methylene Blue (MB) and B) photocatalytic soot oxidation for each material under study. Each data point is the mean of three replicates.

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Effectiveness of Innovative Nanomaterials with Consolidant, hydrophobic and photocatalytic properties on "Pietra di Noto"

G.M.C. Gemelli[1], F. Elhaddad[1], F. Fernandez[2], M.J. Mosquera[1]

[1]TEP243-Nanomaterials Group (Dept. of Physical-Chemistry, Faculty of Sciences, University of Cadiz), 11510 Puerto Real, Spain
[2]Faculty of Architecture and Industrial Design (University San Raffaele), Via Val Cannuta 247, 00166 Rome, Italy
gemelligmc@gmail.com

The "Pietra di Noto" is a yellowish biocalcarenite widely used in the baroque monuments of the Noto valley (Sicily, Italy). It has been recently included in the Unesco's world heritage list. This stone is very sensitive to the action of chemical agents and in particular, to salt crystallization due to its high water capillarity absorption. For this reasons, three innovative nanostructured products with consolidant, hydrophobic and photocatalytic properties, developed by University of Cadiz, were tested on samples from "Pietra di Noto" quarry. Our objective was to evaluate compatibility, effectiveness and durability of these products. For comparison, we also evaluated a commercial consolidant "Estel 1000" from CTS.

The UCA consolidant contains a silica oligomer and an aqueous solution of n-octylamine, which catalyzes the sol-gel process and prevents cracking due to the formation of mesoporous xerogels. In addition, we prepared a consolidant with hydrophobic properties by adding a polydimethylsiloxane (PDMS) to the starting sol. A consolidant with photocatalytic properties was also prepared by adding TiO_2 and Au nanoparticles to the sol.

The effectiveness of the consolidant products were evaluated by different tests according to UNI-EN standards, including: colorimetric test, measurements of water absorption by capillarity, salt crystallization, hardness Vickers test, drilling resistance. Hydrophobic properties were mainly evaluated by contact angle tests and the photocatalytic activity was evaluated by a methylene blue degradation test. The obtained results demonstrated the higher effectiveness of UCA products compared to the commercial product. Specifically, UCA products significantly improved the mechanical resistance and prevented water penetration into the stone, and consequently the stone degradation due to salt crystallisation, which is one of the main decay mechanisms for "Pietra di Noto", was avoided. Moreover, we demonstrated a significant reduction in water ingress for the hydrophobic product. Finally, we confirmed the self-cleaning activity of the photoactive product by the degradation of methylene blue.

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Preservation issues in naval museums. The example of two 18th century frigate sterns taken out of the sea 40 years ago

B. Gasca Giménez

Museo Naval de San Fernando, San Fernando, Cádiz, Spain
bgasgim@fn.mde.es

Spain is a country with a huge and diverse naval maritime heritage. The collections kept in our naval museums are so heterogeneous (naval models, oil paintings, engraves, documents of all sorts, uniforms, archaeological items, navigational and scientific instruments, etc.) that complicates in many ways how to set down basic standards in preservation issues. This fact is directly connected to economic problems due to financing procedures. Military museums in Spain are under the entire Defence Department budget. Of course, this is a challenge for museums professionals who are focused in the search of finding the best and most suitable technics in conservation matter at lower expense. There is also a big naval heritage which is not preserved in a cultural institution but scattered all over military quarters. This is the example of two 18th century frigates sterns which were taken out of the sea water many years ago, in a naïve way, with no archaeological standards. This kind of heritage needs a special effort in order to be rescued, to be properly restored, to be detailed and thorough studied, and finally converted into museum-status items to exhibit them and giving out all the breakthroughs. The Naval Museum of San Fernando is now fully engaged in this particular project.

The preservation issues in naval museums are also determining by the location of the museum itself. Naval Museum in Madrid doesn't have the same problems as the one in Cádiz, or in Cartagena or Ferrol; the three of them placed right next to the ocean. With this reflection here, I will try to give an idea of how the role of the curator in naval museums has been developing in the past twenty years, working together with military personal who are now a days deeply involved in the very important task of preserving their heritage and holding it in trust for public benefit, and how these institutions of naval culture are turning from 19th century's standards into 21st century new museology.

Underwater photogrammetric monitoring techniques applied to deep shipwrecks

E. Aragon[1], S. Munar [2], J. Rodríguez[2], K. Yamafune[3]

[1] Flinders University, Adelaide, Australia
[2]Institut Balear d'Estudis en Arqueologia Maritima, Palma, Spain
[3]Texas A&M University, College Station, Texas, USA
enrique.aragon@flinders.edu.au

The Cabrera archipelago, off the east coast of Spain, near the island of Mallorca, has a proliferation of maritime cultural heritage sites. While there have been studies on numerous underwater sites, the Spanish archipelago still surprising us with new discoveries in deeper waters.

Near Cabrera's maritime sanctuary, lies a ´tumulus´ of amphora cargo associated to a 3rd-4th century AD shipwreck. Exceptionally well preserved, this archaeological assemblage was totally unknown, resting in barely 70 metres of water. The cargo, without evidence of looting activities, is a magnificent "in situ" context showing the intact dispersion of the artefacts.

Over the last few years technical diving has become more accessible, making it possible to access this deep water where the underwater archaeological remains were considered "untouchables". This new context has to be interpreted as a potential risk by anthropic factors. Is necessary in consequence, at this point, that new approaches of monitoring techniques are developed to ensure the protection of this exposed ¨mid-deep¨ Underwater Cultural Heritage.

From this view, the discovered shipwreck was considered as a priority with local authorities, making a necessary action plan. The project was managed by the "Institut Balear d'Estudis en Arqueologia Marítima (IBEAM)". IBEAM was established in 2012 with the aim of researching, protecting, preserving and disseminating the richness of the area's underwater/maritime culture heritage in line with the 2001 UNESCO Convention on the protection of Underwater Heritage.

In this paper we will present an approach for monitoring techniques apply to the so called ¨mid-deep¨ shipwreck survey, based on photogrammetry combined with technical divers. This technique offers an immediate resource to cover the essential first stage in the protection and record of an underwater archaeological site at this depth. The process gives us short term results, ensuring a total coverage of the site, as well as recording high-definition images making available a site computer model with millimetres of accuracy.

Archaeometric study of waterlogged wood from the Roman cryptoporticus of Lisbon

G. Coradeschi[1], A. Manhita[1], N. Mota[2], A. Caessa[2], C. Nozes[2], L. Sadori[3], F. Branco[4], L. Gonçalves[5], C. Barrocas Dias[1]

[1]Laboratório HERCULES, Universidade de Évora, Évora, Portugal
[2]Centro de Arqueologia de Lisboa, Departamento de Património Cultural, Direcção Municipal de Cultura, Câmara Municipal de Lisboa, Portugal
[3] Università La Sapienza', Roma, Italy
[4]CIDEHUS, Universidade de Évora, Évora, Portugal
[5]Faculdade de Belas-Artes, Universidade de Lisboa, Lisboa, Portugal
ginevrac@uevora.pt

The Roman cryptoporticus of Lisbon was first discovered in 1773, during the reconstruction of the city after the big earthquake of 1755, and is located in the heart of the Baixa Pombalina.

The flooded underground vaulted complex was constructed in the middle of the first century, and everything seems to indicate that it was already flooded during that century. The cryptoporticus probably served as an artificial platform, or foundation for other constructions, in the old port front of the Roman city (*Felicitas Iulia Olisipo*).

Since 2015, the *Centro de Arqueologia de Lisboa* has been excavating the site and recovered several artefacts of waterlogged wood from a *cloaca*. This sewer structure seems to have been added to the original project, and was built externally in one of the internal galleries of the cryptoporticus. Although the cryptoporticus continued to be used, cessation or deactivation of this *cloaca* occurred in the third century, when the rise of the average level of water prevented an effective drainage, leaving the wood preserved in the muddy sediments which accumulated inside it. The wood materials recovered nowadays include structural elements (i.e., parts of window frames), utilitarian items (i.e., spoon) and also several unidentified fragments.

In this study, wood taxa identification was done based on the anatomical features of the three diagnostic sections of the wood samples observed under optical microscope with transmitted light (LEICA DM2500M equipped with a camera). Small-scale anatomical features were observed on a selection of wood fragment using a scanning electron microscope (Hitachi 3700N VP-SEM-EDS with Bruker XFLASH 5010 SDD detector). Specialized bibliography (Crivellaro and Schweingruber, 2013; Schweingruber and Schweingruber, 1990) was used as comparative tools for wood identification.

Anaerobic erosion bacteria can slowly degrade cellulose, hemicellulose and lignin materials, resulting in a porous and fragile structure, poor in polysaccharides and mainly composed of residual lignin, which can easily collapse during drying. The expected future musealization of the recovered archaeological artefacts required a full chemical characterization of the wood structure in order to choose an appropriate consolidation procedure for the waterlogged wood. In this study, Pyr-GC-MS (Tamburini *et al*., 2014) was used to evaluate the content of cellulose and lignin based components of the waterlogged artefacts studied.

A general method to recover and stabilize superfragile materials from underwater archaeological sites

L.C. Zambrano[1], M.L.A. Gil[2], M. Bethencourt[3]

[1]Department of Conservation and Restoration, Museum of Cadiz, Spain
[2]Department of Chemistry and Physics, Faculty of Sciences, University of Cadiz, Spain
[3]Department of Materials Science and Metallurgical Engineering and Inorganic Chemistry, University of Cadiz, Marine Science and Technological Center of Andalusia, International Campus of Excellence of the Sea (CEI・MAR), Spain
luisc.zambrano@juntadeandalucia.es almoraima.gil@uca.es manuel.bethencourt@uca.es

A variety of materials made with plant fibres are included in ancient ships such as: cordage, sails, baskets and cloths. Consequently all are candidates to be found during underwater excavations. The probability that they could be reported is the result of an equation with several factors: the object fabric and nature, the object-ambient conditions, the length of burial and the success of excavation.

Scientific knowledge predicts a low percentage of survival for cellulosic materials as a consequence of their particular fabric which consists of small fibres. Evidences of the use of ropes and relatives materials in archaeological sites from prehistory are valuable documents that can only be reported when exceptional circumstances of conservation occur. A very significant is the underwater location where these materials may appear in unreal good conditions hiding a very fragile object with a poor level of physical resistance. We call these superfragile materials and the experience shows that they invariably disappear during archaeological excavations. This work is aimed for the scientific interest and the principles of conservation.

Our premise is that the manufacture of moulds with elastomer avoids collapse during excavation. In addition to serving as a support during extraction, the moulding should not hinder the future conservation of the object.

To test the effectiveness of this method has been experienced an underwater moulding technique with silicone elastomers followed by infiltration of reactive polysiloxanes using the technique called "plastination". These tests were performed under laboratory conditions on samples of artificially aged rope. Experimentation has pursued to test the incidence of the viscosity and the moulding pressure in relation to the level of degradation of the object as key factors in this process. Also, the interaction was investigated of the three factors (viscosity, pressure and degradation) to establish a general method adapted to each level of degradation.

Experimentation includes the physical characterization of the object (rope) and the product (silicone). The molds and copies obtained in the laboratory have been analyzed with graphic analysis software, optical metrology - 3D profilometer - and stereoscopic microscopy. Subsequently, in response to the necessary consolidation of the recovered material, the impregnation of the material inside the mold has been experienced. The consolidation procedure has achieved the physical consistency necessary to make a scientific and museological use of recovered material. In this process, the physical-chemical stability and the aesthetic qualities of the object have been preserved. As a conclusion to the research process, a general model is obtained for recover and stabilize superfragile objects in underwater archaeological sites.

A Disaster Risk Management Plan for Suasa Archeological Park (Italy)

L. Nobile

Dept. DICAM,University of Bologna,Campus of Cesena, Via Cavalcavia 61, 47521 Cesena,Italy
lucio.nobile@unibo.it

The Suasa archaeological park is an archaeological area in Castelleone di Suasa (Italy) including the remains of the ancient town of Suasa. Since 1987 the University of Bologna, in collaboration with the "Soprintendenza Archeologica per le Marche", has launched a research program in the area where the ruins of the Roman amphitheatre were visible. The excavations have thus gradually allowed identifying the trade forum, some sepulchral areas, the theatre, the old paved road on which was based the whole settlement of the city of Suasa and, above all, the *Coiedii Domus*.

The trade forum, named *Suasa Foro*, consisted of a large square, around which were arranged the big porch, commercial and representation spaces. In the first period the *Domus* porch was the fourth side of the *Foro*, establishing a single system. In a later period, on the front towards the *Decumanus*, a septum closed the *Foro* view of the road and had three main entrances. The remains of the theatre have not yet been excavated, and at present the theatre's profile is visible only at certain times of the year, when the vegetation takes on a different colour.

The amphitheatre is an oversized archaeology, when you consider the size of the urban reality of Suasa. This means that it had to work on a larger scale, it probably represented the attraction pole for the people of the valley. Currently the amphitheatre, as well as being a beautiful ruin, is used for some exhibitions and events during the summer season. The *Coiedii Domus* is the most important Roman house found out in Castelleone di Suasa archaeological site, founded after the battle of Sentinum (295 B.C.). The insula with the *Coiedii Domus* has an incredible history of stratification during its long life, from the 2nd c. B.C. to the 5th c. A.D. Archaeologists have some more precise references of a building of the following period known as the Republican *Domus*, which is located in the north-western position of the insula, and the so-called *Domus* of the First Style for its wall-painting and decoration belonging to this Roman style. This *Domus* is located in the southern part of the insula. In the 2nd c. A.D. the Republican *Domus* expanded itself, damaging the other houses of the insula, and the First-Style House was destroyed. The Republican *Domus* became soon a 3000 m^2 house, called the *Coiedii Dom*us. In fact, the finding of an inscription dedicated to L. Coiedius Candidus, let the archaeologists guess the ownership of the house. The dwelling was very big related to the dimension of the urban area, and had a beautiful *perystilum*, a guest sector and a thermal area. After this flourishing period, the *Domus* started to fall from its condition and was partially used until its decline. The progressive loss of Heritage properties as a result of hazards such floods, mudslides, fire, earthquakes, call for a development of proper disaster risk reduction plans in order to prevent the disasters, or at least considerably reduce their effects. The main objective of this paper is to develop a Disaster Risk Management Plan for Suasa Archeological Park (Italy) based on the Manual "Managing Disaster Risks for World Heritage" by ICCROM, ICOMS, IUCN and UNESCO and on Italian Guidelines.

Preparing cultural heritage for a natural disaster

K. Bennett[1], K. McLeod[2]

[1]Department of Archaeology, Flinders University, GPO BOX 2100, Adelaide, SA 5001, Australia
[2]Edwin Fox Maritime Museum, Marlborough Heritage Trust, Dunbar Wharf, Picton 7281, New Zealand
kurt.bennett@flinders.edu.au

Natural disasters, particularly earthquakes, are experienced by many countries around the world, and subsequently threaten our cultural heritage. Due to the unpredictable nature of these natural phenomena, how can we as heritage practitioner's best prepare for such events to decrease the levels of deterioration or destruction of significant cultural heritage? In light of recent earthquake activity experienced in New Zealand and using a local case study, this presentation discusses museum management and archaeological recording methods and how together these contribute to minimising the loss of cultural heritage during a natural disaster.

New Zealand is located on the boundary of the Pacific and Australian tectonic plates, making the island nation prone to earthquakes. Situated in Picton, at the top of the South Island, is the Edwin Fox Maritime Museum. This museum administers the Edwin Fox collection, including a preserved ship's hull, which the museum is named after. *Edwin Fox*, measures 48 metres in length by 9 metres in beam making it the largest item in the museum's collection and by far the most challenging to manage. The ship's significance can be measured both by its longevity and its service. Constructed in India in 1853, the ship served as an English troop transport in the Crimean war, transported convicts to Australia, immigrants to New Zealand and at present, is the last surviving example of a nineteenth century English East Indiaman. The hull currently serves as the main exhibit for museum patrons. The ship's significance is recognised by Heritage New Zealand, the government body that legislates for the protection of cultural heritage in New Zealand, designating the vessel Category 1—its highest protection.

This paper will be presented in two parts. The first highlights the natural disaster risk and the curatorial responsibilities and management plan implemented by the museum. The second part explores different archaeological recording methods such as photogrammetry and traditional ship recording techniques used to accurately record *Edwin Fox*. In conclusion, by drawing together both parts of the presentation, the authors contribute to the discussion on how we can best prepare for the deterioration and loss of heritage during natural disasters.

Towards Zero Emission Refurbishment in Historic Urban Districts

A. Loli, C. Bertolin

Department of Architectural Design, History and Technology, Norwegian University of Science and Technology (NTNU), 7491 Trondheim, Norway
arian.loli@ntnu.no

The built environment consists, in large part, of residential and public buildings built over the last 70 years and of a more restricted group of historical buildings. The last group, among the built environment, has a significant cultural value in identifying cities shapes and plays a social role in providing sense of identity to the community. However, the historic buildings are nowadays posed at risk due to both natural weathering, (e.g. ageing, climate changes effects, extreme events) and anthropic effects as urban pollution and common practise to rebuild instead of maintaining and restoring.

In Norway, studies from Heritage at Risk [1], have shown that up to 1% of the historic buildings from before 1900, are lost every year. At this rate of losing, the country's cultural heritage over the next future will be at high risk of threats. Therefore, it is of critical importance, to plan sustainable refurbishment interventions at district level as well as to propose conservative management strategies for this specific group of buildings. Moreover, the refurbishment of historic buildings will act as a driving factor to improve the living comfort of inhabitants and to generate economic development with investments for tourism and leisure.

Enhancing the importance of historic buildings and broadening solutions for their sustainable preservation is possible by addressing both conservative needs and achievements of required greenhouse gas emissions targets during refurbishment and maintenance interventions. In the construction sector, while an existing building can reach the target of near Zero Emission Building (nZEB) during its operation phase, an historic building, due to additional challenges required to maintain original aesthetic and historic appearance and materials, can eventually reach only Zero Emission target in the Refurbishment stage (ZER). Strategies to reach ZER for historic buildings need to optimize the re-use of existing material taking advantage of "embodied energy" already available in the building, preserve as much as possible the original materials, increase the building lifetime by recognizing areas of the building envelope more vulnerable to climate-induced degradation and minimize waste production during restoration interventions.

This paper reviews the current policies and methodologies used in the refurbishment strategies of historic buildings, and identifies research needs to enhance sustainable interventions at European level to reach the Zero Emission Refurbishment target.

[1] ICOMOS (2003). *Heritage at Risk – ICOMOS World Report 2002/2003 on monuments and sites in danger*. The international Council on monuments and sites (ICOMOS).

The Nerja Cave as a model of conservation of the subterranean Cultural Heritage

L.E. Fernandez[1], C. Liñán[1,2], Y. del Rosal[1],

[1]Nerja Cave Research Institute, Nerja Cave Foundation, Nerja, Málaga, Spain
[2]Ecology and Geology Department, Faculty of Science, University of Málaga, Malaga, Spain
yolanda@cuevadenerja.es

The Nerja Cave is one of the main tourist and cultural resources of the province where it is located. The cave, declared as Good of Cultural Interest with the category of Archaeological Zone, houses one of the most important archaeological sites of the Iberian Peninsula with rock art that could be the most abundant and oldest of southern Europe. In addition, the Nerja Cave has an exceptional natural heritage with large halls and spectacular speleothems with great scientific interest and where, moreover, is developed a unique ecosystem that hosts endemic species. The preservation of the cave and its heritage for future generations requires interdisciplinary researches. At the beginning, a few months after the discovery, the research projects were focused on the archaeological excavations but soon the geology and biology take part in the cave research. Since 1999, the Research Institute of the Nerja Cave is in charge research, preservation and dissemination of the cave heritage. Thus, in the last years it has carried out, together with numerous external researchers, an Interdisciplinary Research Project aiming to: (1) determine the pressures in the cave, especially the anthropic impact and its relationship with microclimate changes and biodeterioration factors (2) characterize the cultural heritage of the cave and surroundings with the specific preservation of the rock art, (3) lay the groundwork for the design a management model according with and adequate conservation of the heritage and with the tourist nature of the cave. The results of this project, which are described in this article, have provided to the Nerja Cave Foundation mechanisms, tools and valuable information indispensable for the development of a rational management plan of this Good of Cultural Interest, based on conservation, research and dissemination of its heritage.

Public Institutions as deposits for lean-intensive-care Cultural Heritage objects

J.M. Gallardo[1], E. Díaz-Gutiérrez [2], R. Sepúlveda[1]

[1]Departmento de Ingeniería y Ciencia de los Materiales y el Transporte, Universidad de Sevilla, Sevilla, Spain
[2]Asociación de Investigación y Cooperación Industrial de Andalucía, Camino Descubrimientos s/n, 41092 Sevilla, Spain
josemar@us.es

Museums frequently cannot house all the collections they have. It also occurs that private objects with cultural heritage value are not presented in an adequate way because lack of appropriate expositive volume. It is then possible that Public Institutions may borrow those items to provide a proper scenario for public displaying the object. Indeed, it is very common that buildings like City Halls, Ancient Universities, Houses of Parliament, etc. portraits enough free space with big dimensions that allow accommodating for such pieces. Unfortunately, those Institutions have scarcely any kind of curator. For that reason, items that could be shown in this way should require no or only slight care, having low probability to be damaged.

One such case occurred after the statue of *El Giraldillo* restoration. The vane iron axle is a remarkable example of big iron part forging, produced in different parts dating back from 16th to 19th centuries. With no artistic value the axle and auxiliary mechanical parts was forgotten in a warehouse; this paper deals with the treatment and process of their installation at the hall of the Escuela Técnica Superior de Ingeniería de Sevilla.

Conservation Policy for Urban Heritage in Darmo, Surabaya, Indonesia

E. Yuni Astuti

URBANgrad, Faculty of Architecture - Technische Universität Darmstadt El-Lissitzky-Straße 1, Darmstadt, Germany, and School of Architecture, Planning and Policy Development, Institut Teknologi Bandung Jl. Ganesha 10, Bandung, Indonesia
astuti@stadtforschung.tu-darmstadt.de

Tangible cultural and natural heritage are key components of the European identity. This research builds and contributes to work in built heritage conservation. Although studies in built heritage conservation have examined urban heritage there has not been much research on residential areas. As such, this study provides additional insight into the conservations of residential heritage areas. The analytic focus on inhabitants enables other contributions to urban heritage policy. This study analyses inhabitant's attitudes in a residential heritage area in Surabaya.

On the one hand, architects' and urban planners' ideas in conservation, supported by their standpoint, are based on theory linked to aesthetic, uniqueness, authenticity and some other parameters. Urban heritage areas as part of cultural values have often been appreciated by those qualities. On the other hand, it is important to investigate inhabitant's opinions which in many times have been seen as a part of to the conservation issue. This different point of view can be a path to integrate urban planners' concept with what inhabitants need to sustain the development of the city. Mostly, the heritage areas in Indonesian cities consist of private buildings and supported infrastructures, so the willingness to maintain the old buildings depends on the owner. Due to its large scale, urban heritage conservation requires huge resources in terms of funding for technical support in infrastructure and building maintenance. This study conducted in Indonesian city with large and expanding population growth, control over development of the city is driven by the private sector. The research was conducted in Surabaya, the second largest city in Indonesia in 2014. Investors aiming to improve economic activities through Surabaya are competing for land. The research gives insight into understanding conservation of residential areas in Indonesian cities.

The research explores inhabitants' main interests in the area of conservation, to find their motivation to keep these buildings and vice versa, in addition to find a better understanding of inhabitants' opinions. The research found that inhabitants have an interest in architectural aspects, for example, aesthetics, rarity and the thermal insulation system of their heritage buildings. The inhabitant's awareness found in this research is shown by their willingness to keep their buildings. In the context of Indonesian cities, the heritage project will need a different approach because the owners can make their own decisions about their buildings. To conserve this large area will be much easier through the acceptance and support from its inhabitants. This work has broader implications of heritage conservation in South-east Asia as different with Europe. In short, to conserve urban heritage area in Asia, it needs to be based on inhabitants' social values, not only material or economic value.

Archaeological predictive modelling using the weights of evidence: Canton Zurich as a case study

M.E. Castiello[1], C. Satchwell[2], F. Veronesi[3], A. Hafner[1]

[1]Institute for Archaeological Science, University of Bern, Bern, Switzerland
[2]ESRI Schweiz, Zurich,Switzerland
[3]Institute of Cartography and Geoinformation, ETH, Zurich, Switzerland
maria.castiello@students.unibe.ch

The preservation of archaeological remains in Switzerland is a striking problem, especially because of the ongoing massive expansion of urban settlement areas and the development of transport infrastructures. At the date, GIS and archaeological cartography are not commonly used, neither for preservation purposes.

In this paper, we propose for the first time to develop "Archaeological Potential Maps" as a predictive model to simulate the optimal location of ancient settlements on the Swiss landscape to a certain degree of probability.

Taking advantage of Geographical Information Systems (GIS) we approached the question with a mathematical and statistical method, such as Weights of Evidence technique. This method, already tested in other Countries, has never been tested in Switzerland before.

The result is an interesting overview on the environmental parameters which affect the human location preferences in the Roman period. The model was tested and then validate in the Canton of Zurich by using the database of the roman settlements provided by the Cantonal Archaeological Service.

The final output is a first attempt on the way to create a powerful tool for the long-term preservation of archaeological remains in Switzerland that could be used by the local authorities in the decision-making process related to urban planning.

The current built environment of the medieval forts on Arwad Island in Syria based on summer microclimate measurements

M. Hassan [1,2,3], H. Xie [1,2], T. Rahmoun [1,3]

[1] Faculty of Architecture and Urban Planning, Chongqing University, Chongqing, China
[2] Key Laboratory of New Technology for Construction of Cities in Mountain Area, Ministry of Education, Chongqing University, Chongqing, China
[3] Faculty of Architecture, Tishreen University, Lattakia, Syria
eng.mayahassan@gmail.com

The defensive forts of Arwad Island in Syria, the citadel and the tower, are national heritage buildings still in use until now, they used for defensive purposes in the period of construction, then they reused through the following successive historical periods for military and defence functions down to be used as a museum today. This paper discusses a study of their microclimate based on data collections and analysis, and field measurement in summer; to gather the facts and evaluate the indoor thermal environment and the adaptive reuse of these two historic buildings as museums, in order to determine problems and define where we are now, and find out the outlines for future and control strategies for the preservation of the buildings and their collections. By analysing the results obtained in the buildings, the most values of the temperature and relative humidity exceeded the standard for sedentary activity during summer conditions that can damage the building structure and materials, cause a human discomfort, and promote mould growth. In both case studies, the first floor rooms have a higher temperature than the ground floor rooms, and no matter the courtyard is small or big in these two buildings, the ventilation still has slight values, due to the closure of the massive walls outward and inward openness in the design of origin, and the semi-closed windows during the operating. Both buildings need an increase of ventilation ranging between 0.06-0.1 ms^{-1}, taking into account the consideration of conservation collections. The reduction the relative humidity and securing passive ventilation were primarily recommended for these buildings to improve the thermal environment. The recommendations and actions be taken during the hot period are discussed.

Analysis and structure of the water distribution system in the distribution depot of the Carmona Gate as a way of supplying water to the Royal Alcazar of Seville

C. Bandrés[1], M.D. Robador[2], A. Albardonero[3],

[1] Student thesis, Architecture Faculty, University of Seville, Seville, Spain
[2] Technical Architecture Faculty, University of Seville, Seville, Spain
[3] Art History Faculty, University of Seville, Seville, Spain
mbandres@us.es

It is of great importance for the cultural heritage to know the water supply from the *Caños de Carmona* aqueduct has been, for many centuries, an essential resource to supply the Royal Alcazar and the city of Seville. This research tries to analyze the system used in the distribution of water that went to palaces and gardens of the palatine complex in the Modern Age. This study focuses mainly on the water deposit located in the Carmona Gate, the last section of the Sevillian aqueduct.

To analyze this hydraulic construction, the following main objectives have been set: to propose a hypothesis and verification of the location, distribution and operation of the Carmona Gate Water Reservoir. Second, interpret, draw and weigh the measures of the plant and the elevation of the Depot from plans of the seventeenth century, in order to grasp the structure and calculate the theoretical flow of water that supplied the Royal Alcazar. Likewise, a third objective has been to carry out a hydraulic study of the theoretical loss of water load produced in the supply Reservoir. And finally, considering the different water distribution of the Reservoir to other customers, taking into account that it is distributed by gravity and that the construction is located in one of the highest points of the city wall.

In the study, the state of the matter has been approached to know the different hypotheses published so far on the distribution of water in the Carmona Gate Deposit. Through the search of graphic, documentary and literary sources, scaled blueprints of the studied object have been made. At the same time, a topographic work has been carried out analyzing the remains of the aqueduct, which has served to establish the geographical coordinates of reference with the Geographic Information System (GIS), the exact location of the sections of the aqueduct still standing and to take the hydraulic height over sea level, since it is an invariable measure over time, and essential for the distribution of the flow by gravity. With all this, the planimetric survey of the longitudinal profiles has been carried out to determine: the level with which the water of the *Caños de Carmona* reached the Reservoir, the theoretical sheet of water inside and the minimum height that the depot needed to fulfill its mission.

Figure 1. Engraving Puerta de Carmona, Genaro Pérez Villamil (1845)

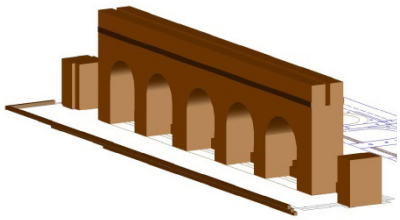


Figure 2. Planimetric study of the aqueduct of Seville.

Humane considerations in Architecture and the outstanding universal significance of 20th Century Cultural Heritage: The case of Paimio Hospital in Finland

A.G.A. Tawab

Department of Architectural Engineering, Faculty of Engineering, Tanta University, Tanta, Egypt, 23 Alphrid Liean Street, Roushdi, Alexandria, Egypt
a_g_a_abdeltawab@yahoo.co.uk

20th century heritage represents a significant pattern of cultural heritage that has been found under-represented on the World Heritage List. Because of the previous fact, many States Parties to the World Heritage Convention have nominated sites representing 20th century heritage for listing on the World Heritage List. One of these sites is Paimio Hospital in Finland designed by Alvar Aalto. One of the major themes that have been adopted to justify the hospital's Outstanding Universal Value is the humane considerations in Alvar Aalto's design. On the other hand, none of the projects designed by Hassan Fathy in Egypt, which represent the under-represented patterns of 20th century and vernacular heritage, has been inscribed as a World Heritage Site. The main aim of this study was to analyse the common themes and criteria that have been frequently adopted to justify the outstanding universal significance of 20th century heritage properties listed on the World Heritage List or on Tentative Lists. The study also aimed at discussing the humane considerations in Alvar Aalto's design of Paimio Hospital and the relevance of these considerations to the justifications of the outstanding significance of the heritage of Hassan Fathy in Egypt. To achieve the previous aims, seven case studies representing 20th century heritage were adopted for the analysis of the common themes and criteria adopted to justify the outstanding universal significance of this pattern of cultural heritage. One of the previous case studies, which is Paimio Hospital, was adopted for a further detailed analysis of the humane considerations in its design. The findings revealed the diverse humane considerations in Alvar Aalto's design of Paimio Hospital. The findings also revealed that amongst the most frequently adopted criteria to justify the outstanding significance of 20th century heritage is criterion (i), which was adopted to justify the outstanding significance of Paimio Hospital based on the humane considerations in its design. Criterion (i) is concerned with the cultural properties representing a masterpiece of human creative genius. The study suggests that humane considerations in architecture can also be adopted to justify the outstanding universal significance of the heritage of Hassan Fathy in Egypt.

Decision making processes in the conservation of stone built heritage. Laboratory and field perspectives

J. Delgado Rodrigues

National Laboratory of Civil Engineering, 1700-066 Lisbon, Portugal
delgado@lnec.pt

A conservation intervention is a sequence of multiple steps, involves multiple actors and spans through large domains of uncertainty. It involves the material components of the object and the scientific contributions and perspectives of experts, but it integrates a lot of immaterial aspects that start by influencing the onset of the intervention process and its development path, ending as a crucial component of the quality of the end results.

The entire process is full of cross roads, not always with a clear best option, which constitute moments of uncertainty that introduce a certain degree of risk to the decisions to be taken. When is the process to start? Who starts? What experts to convene? What diagnostic steps to follow? What treatment to apply? Is this treatment effective? Is that one compatible? How do I know? How will the contractor be selected? Is cost or quality to be prioritized? Etc.

Scientific literature provides an inexhaustible source of information of indisputable interest to prepare conservation interventions, but very rarely we can find well-structured methods to transform the scientific information into workable instruments to help decision-makers to take their options.

This presentation will address this difficult question, both from the laboratory and field perspectives, supported in the past experience as a laboratory researcher and incorporating the lessons learnt from the interaction with the real world and from the difficult situations of having to take decisions even when insufficient data or scarce resources are available.

Monitoring and modelling, a proposed method to assess the refurbishment projects in historic buildings

C.M. Muñoz González, A. León Rodríguez, I. Acosta García, M.A. Campano Laborda, J. Navarro Casas

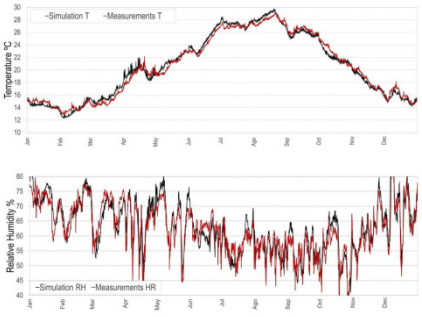
Instituto Universitario de Arquitectura y Ciencias de la Construcción, Universidad de Sevilla, Escuela Técnica Superior de Arquitectura, Av. de Reina Mercedes, 2, Sevilla, Spain
carmenmgonzalez@us.es

Churches are an important part of Southern European cultural heritage; the society agrees need to be preserved for present for future generations. The indoor climate is an important factor in preserving the fabric of these building and their artworks; although there may be several European Standards which were motived by the need to reflect the special characteristics of these places. These strategies were usually defined for heating and specific climates of Northern Europe with low temperature during the winter, so that their application may not be as positive when extrapolated to other locations like Spain. The main characteristics of churches are their construction; beside they were not designed as living or working spaces; their intermittent use of environmental systems, and the vulnerability of their surface decoration or movable heritage.

The use of simulation software to calculate environmental conditions and energy consumption in buildings before carrying out interventions is a very useful tool which enables us to predict the behaviour of the different climate conditioning systems and installations. However, the results obtained for this specific type of building do not always provide accurate approximations since this type of software is designed to evaluate other more modern buildings. Therefore, it is necessary to use monitoring and real measurements as elements for validating and contrasting the results obtained with the simulations. The use of onsite measurements makes possible to generate simulation models with behaviour close to reality.

In this research project, experimental research carried out on historic buildings in a temperate climate (Seville, Spain). Measurement on thermal properties, and hygrothermal indoor were carried out to validate the numerical code provided by Design Builder version 3.4.0.041, EnergyPlus 8.1. Three groups of techniques - passive, active and combined - were evaluated. Passive techniques consist of actions on the constructive elements of the thermal envelope of the church: openings, roof, façade walls and floor. Active techniques consist in installing cold-heat HVAC systems in the building, with and without damp control, using different systems and technology and the third group is a simultaneous combination of passive and active hypotheses

Finally, it was concluded that detailed knowledge about the hygrothermal response of each historic building and a risk-based analysis with a validated simulation model before the refurbishment project could lead to energy savings and the improvement of conservation and thermal comfort.



Fuzzy logic applied to the analysis of the heritage buildings' performance

A.J. Prieto[1], J.M. Macías-Bernal[1], M.J. Chávez[2], F.J. Alejandre[1], A. Silva[3]

[1]Departamento Construcciones Arquitectónicas II, ETSIE - Universidad de Sevilla, Avda. Reina Mercedes, 4A, Sevilla, Spain
[2]Departamento Matemática Aplicada I, ETSIE - Universidad de Sevilla, Avda. Reina Mercedes, 4A, Sevilla, Spain
[3]Departamento Engenharia Civil, IST - Universidade de Lisboa, Avda. Rovisco Pais, 1049-001, Lisboa, Portugal
ajpi@me.com

Maintenance strategies are essential to control the progressive degradation of constructions over time. Therefore, preventive activities, either maintenance or conservation actions, allow avoiding potential failures in buildings and their elements. These actions are thus fundamental to enhance the buildings' functional service life.

In this sense, the search, compilation and analysis of documentation on cultural heritage assets is an indispensable task in the protection and conservation of historic buildings. A sustainable management of the buildings during their life cycle requires a systematic collection and recording of data that identifies the history of the monument, its architectural attributes, conservation, and the possible interventions it has undergone throughout its service life. Therefore, preventive maintenance of historic buildings is a complex task since usually the stakeholders are faced with several difficulties, especially when it is intended to define the most appropriate time for their intervention.

In this study, the application of a fuzzy expert system, capable of establishing the level of functionality of the buildings analysed, is implemented. This research intends to identify historic events that had a significant impact on the level of functionality of the constructions analysed, evaluating their influence on the maintenance and conservation actions performed in these buildings.

The methodology considers a total of 17 variables directly related to vulnerability and risk characteristics. The output of the model generates a ranking regarding the priority of intervention from among the constructions analysed. These constructions are in the same social, cultural, economic and environmental background. It is intended to guarantee acceptable levels of functionality of the buildings analysed, with special concern to those who have the greatest preventive maintenance needs. In this work, a total of 20 religious buildings located in south Spain were considered. Nearly 400 historical records were analysed, covering information collected from the 15th to 16th centuries and up to the present.

This study provides behaviour patterns for the functionality of religious buildings over time. In addition, the main events that have influenced the functionality of the buildings during their life cycle were identified, allowing a more exhaustive and detailed design of future conservation and preventive maintenance strategies in buildings with similar risk conditions.

This information is extremely relevant to aid decision-making processes based on expert knowledge, which lead to the establishment of priorities of action in terms of protection of the cultural heritage, using the available historical records, thus learning from lessons of the past.

Working methodology for the development of a Master Plan of Action on the Historical Immovable Heritage

J.M. Aragon[1], M.L.A. Gil[2], J.A. Ruiz[1], D. Zorrilla[2]

[1]Departamento de Historia, Geografía y Filosofía, Facultad de Filosofía y Letras, Universidad de Cádiz, Avenida Doctor Gómez Ulla, 3, 11003, Cádiz Spain
[2]Departamento de Química Física, Facultad de Ciencias, Universidad de Cádiz, Polígono del Río San Pedro, S/N, 11510, Puerto Real, Cádiz, Spain
jantonio.ruiz@uca.es

A large part of our historical heritage involves immovable properties which in most cases are badly deteriorating. However, not all factors responsible for the damages have been identified yet. This leads us to implement a range of solutions –usually palliative solutions– which may help to foster historical studies at all levels as well as to highlight and to exhibit our heritage for our own use and enjoyment. Under these circumstances, it becomes a priority to redefine future historical research from a broader perspective in order to address other important issues related to the preservation and survival of our heritage in the best possible conditions by developing a master plan of actions which complements those taken on the immovable heritage in the field of Archaeology. For this, we need to resort a combined system consisting of three different kinds of actions: (a) going through the relevant written sources and archaeological actions on the site where the study is being conducted; (b) analysing and characterising the building materials; (c) studying the local environmental conditions.

Pre-project and diagnosis for restoration of modern architecture

F. Fernandez

IEMEST, Euro-Mediterranean Institute of Science and Technology, Via Michele Miraglia, 20 - 90139 Palermo (Italy)
federicafernandez@iemest.eu

Talking about *restoration of modern architecture* could be actually considered incoherent, because it doesn't really exist a different approach from that one applied to the cultural heritage and the same methodology should be used: even considering the design, there is a conceptual unity starting from the survey, the historical study, the analysis of materials. The differences mainly involve the building techniques, the competences of the specialized craftsmen working in the process. The use of innovative construction techniques and the presence of more modern materials, such as stoneware, aluminum or composite materials, in fact requires skilled workers able to intervene properly and with specific expertise.

In this direction, the restoration of buildings of modern architecture, today has acquired the consciousness that a correct diagnosis allows an intervention matching the real needs and, at the same time, is cost-effective and is respectful of the architectures. Preliminary activities in drafting the executive project are different and complex, and are identical to those that are routinely adopted for the historic buildings.

The first step of the process is the recognition and comprehension of the formal and aesthetic values represented by the building, followed by the knowledge of its physics and its material consistency, and then the study of the conservation problems can take place. The sequence of these phases is very important because a correct diagnosis is the prerequisite for a successful intervention. This paper presents a case study in which all the identifiable activities of the pre-project have allowed an adequate choice of interventions to be implemented.

This paper shows a method for the recording of the data collected in the pre-design phase with the creation of data sheets carrying pictures and detailed descriptions of the decay phenomena and the possible interventions to be carried out: this method can be replicated with the dual purpose of being a fundamental tool for the restoration process, as well as for the creation of an important documentation of the building's history.

Thanks to this new approach, even in the case of modern architecture, the restoration will be the moment of recognition, and not only a technical act, but a critical and culturally oriented activity, adjusted to the real needs of the building.

Green biocides for Cultural Heritage: Biotechnological Approach

M. Silva [1,2], M. Gonzalez-Pérez[2], R. Vieira[2], D. Teixeira [1,2], A. Candeias [1,2], A.T. Caldeira [1,2]

[1]Chemistry Department, School of Sciences and Technology, Évora University, Rua Romão Ramalho 59, 7000-671, Évora, Portugal
[2]HERCULES Laboratory, Évora University, Largo Marquês de Marialva 8, 7000-809 Évora, Portugal
Marasilva50@hotmail.com

The damaging of buildings and monuments by biological contamination is a cause of serious concern. Biocides based on chemical toxic compounds have been used to mitigate this problem. However, in the past decade many of the most effective biocides have been banned due to their environmental and health hazards. Proper remediation actions for microbiologically contaminated historic materials based on environmentally safe solution are a key point in artworks safeguard.

Lipopeptides (LPP) produced by some *Bacillus* strains, including surfactin, fengycin and iturin are particularly relevant as antifungal agents. Its production seems to be correlated with a starvation process that naturally occurs in *Bacillus* species. The knowledge about the factors that trigger the production of antifungal LPP compounds by *Bacillus* strains and the factors underneath their production are vital in the search of alternative biological means to act against biodeteriogenic fungi that promote biodeterioration of built culture heritage.

Therefore, this study constitutes a breakthrough research which can lead to be considered on scale-up of the production process for future applications as a new natural biocide. This work intends to clarify the physiological behaviour associated to the LPP bioactive compounds production by *Bacillus* sp. CCMI 1053, a strain previously isolated from *Quercus suber* and selected due to their high capacity to produce bioactive LPP with potent antifungal activity against heritage biodeteriogenic fungi.

Flow cytometry coupled with fluorescent dyes (Annexin V and 7-aminoactinomycin D, 7-AAD) allowed the detection of different physiological stages of *Bacillus* sp. CCMI 1053 sporulation inside a culture. The correlation between the growth profile and the production of bioactive compounds were study in order to characterise, interpret and understand the LPP production and the relation with cell viability and sporulation.

The results of *Bacillus* sp. CCMI 1053 cell dynamic pointed out a possible correlation between sporulation, the begging of apoptosis and the increase of bioactive compounds production. This approach has significant potentiality for further application in view of the production improvement of natural metabolites for use in the development of novel green biocides for Cultural Heritage.

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In situ assessment of biocides action on epilithic lichens colonising dolostone

J. Wierzchos[1], S. Pérez-Ortega[2], A. de los Ríos[1], V. Souza-Egipsy[3], R. Fort[4], C. Ascaso[1]

[1]Museo Nacional de Ciencias Naturales, CSIC, 28006 Madrid, Spain
[2]Real Jardín Botánico, Plaza de Murillo 2, 28014 Madrid, Spain
[3]Instituto de Estructura de la Materia, Serrano 113 bis. 28006 Madrid, Spain
[4]Instituto de Geociencias (CSIC, UCM), José Antonio Nováis 12, 28040 Madrid, Spain
j.wierzchos@ccma.csic.es

To address the microbial biodeterioration of stone monuments, treatments inhibiting biological growth are needed. In prior works the efficacy of different biocides has been tested on monument stones. However, determination of biocide treatments effectiveness over particular microbial communities colonizing certain lithic substrate should be considered as a first step in cultural heritage restauration process.

This study examines the impacts of two biocides, Koretrel (Tokai Concrete Co., Japan) and a mixture of biocides provided by Thor Especialidades S.A. (Barcelona, Spain), used to treat *Verrucaria nigrescen*s and *Protoparmeliopsis* sp., respectively. Both lichens species colonize dolostone rocks in an ancient quarry 50 km north of Madrid (Spain). The dolostone from this quarry appears in numerous historic monuments in the Madrid province. We assessed the damage produced by each biocide to the thallus structure in two different types of crustose thalli. Biocide actions on the ultrastructure of the photo- and mycobionts were also examined. As Koretrel is of limited use, *Protoparmeliopsis,* which shows a very robust thallus structure, was treated with Thor biocide. Our SEM-BSE and TEM observations clearly revealed fissures inside the thallus of *V. nigrescens* and dramatic changes in its cell ultrastructure in response to treatment with both agents. In *Protoparmeliopsis*, Thor caused caking of the thallus layers and total destruction of the photobiont cells through intense plasmolysis.

The method (SEM-BSE and TEM) used here to determine the efficacy of biocide treatments is among the best investigation strategies available to observe biocide actions even at the intracellular level. However, it is very time consuming. Recently we developed a new application of the VisiSens system (PreSens GmbH, Germany) to assess lichen thallus viability based on visualizing the quantity of oxygen present in the microenvironment of the healthy or biocide-damaged lichen thallus. In response to both biocides, signs of damage were coupled with observable variations in the amount of oxygen produced by the thalli. Such damage will impair the normal functioning of the symbionts and would contribute to eradicate the lichen from the rock. This approach offers a rapid “in situ” and “in vivo” indication of the efficacy of a biocide and also allows for direct analysis of the health state of a small quantity of biological material on the facade of a historical monument or building.

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Multifunctional inorganic nanomaterials based on magnesium and calcium hydroxides for heritage conservation

A. Sierra-Fernandez[1, 2], S. De la Rosa-García[3], S. Gómez-Cornelio[3], L.S. Gomez-Villalba[1], M.E. Rabanal[2], P. Quintana[4], R. Fort[1]

[1] Instituto de Geociencias (CSIC, UCM), Madrid, Spain
[2] Carlos III University of Madrid, Department of Materials Science and Chemical Engineering, Madrid, Spain
[3] Universidad Juárez Autónoma de Tabasco (UJAT), División de Ciencias Biológicas, Tabasco, México
[4]CINVESTAV-IPN, Departamento de Física Aplicada, A.P.73, Cordemex, Mérida, Yucatán, México
arsierra@ucm.es

The effects of aggressive microclimate variations and biological decay on the historic monuments lead to decay forms that threaten our cultural heritage. Accordingly, the development of effective consolidant products with antimicrobial properties is necessary in order to return the lost cohesion of the stone substrates and face their deterioration phenomena. The application of new nanomaterials for the conservation and restoration is undergoing an important attention due to the advantages of these materials (high surface to volume ratio and small particle size).

The physical-chemical compatibility of the consolidants and protective products with the stone material is one of the most important requirements for its use in heritage preservation. This is why the main challenge of this research has been the design and development of highly compatible nanomaterials for the conservation of carbonate stone substrates (dolostone [$CaMg(CO_3)_2$] and limestone [$CaCO_3$]). These products are based on magnesium hydroxide ($Mg(OH)_2$) and calcium hydroxide ($Ca(OH)_2$) nanoparticles (NPs) with different $Mg(OH)_2$ / $Ca(OH)_2$ weight ratio (50:50, 90:10, and 10:90 wt%) synthesized via sol-gel method. The nanoparticles were firstly characterized by Field Emission Scanning Electron Microscopy (FESEM), Transmission Electron Microscopy (TEM), and X-rays Diffraction (XRD). In addition, the antifungal activity by the diffusion agar method at different concentrations (to 10 from 0.07 mg/mL) and by the microdilution method to determine the minimum inhibitory concentration (MIC) of the different nanoparticle formulations has been studied. The study has been carried out using *Aspergillus niger* and *Penicilium oxalicum* as model organisms. Both types of fungus were isolated from stones with a black biogenic surface, and are particularly interesting because they have shown to be potentially active in the deterioration of stone. Also, in order to assess the antifungal activity of the NPs on the stone, the developed NPs were applied on dolostone (Laspra, Spanish dolostone), and limestone (Conchuela, Mexican limestone), widely used in the heritage of Spain and Mexico, respectively. Their protection efficiencies were then evaluated in terms of antifungal activity, surface properties, and appearance.

The synthesized inorganic nanoparticles showed a wide spectrum of antifungal activity against *A. niger* and *P. oxalicum* fungi, being detected the most efficient activity on the $Mg(OH)_2$/$Ca(OH)_2$ NPs (50:50 wt%). Related to the effectiveness of the hydroxide NPs on the stone substrates, the nanoparticles increased the surface microhardness of the treated stones; had a limited impact on surface colour of the stones and decreased the fungal growth of the microorganisms evaluated.

Investigations of the wood decay by Fungi in the hunting lodge of "La Muette", Saint-Germain-en-Laye, France

A. Slimen[1,2], R. Barboux[1,2], A. Mihajlovski[1], S. Moularat[3], F. Bousta[2], P. Di Martino[1]

[1]Laboratoire ERRMECe, Université de Cergy Pontoise, Cergy Pontoise, France
[2]LRMH-CRC-USR3224, Sorbonne-Universités, Champs sur Marne, France
[3]Division Agents Biologiques et Aérocontaminants, CSTB, Champs sur Marne, France
patrick.di-martino@u-cergy.fr

"La Muette" is a hunting lodge built under the reigns of Louis XV and Louis XVI in the forest of Saint-Germainen-Laye in France. The pavilion is currently unoccupied, and subjected to water infiltrates due to leakage at the roof. For these reasons, the woods inside the pavilion are contaminated by different types of fungi at the level of the paneling, floors, stairs, and beams. This study consisted in the implementation of multidisciplinary analytical tools allowing the analysis of the fungal biocontamination of the monument. The first step in the diagnosis of wood biodeterioration was the mapping of biocolonization by macroscopic visual observation of all the parts of the monument. At the same time, air sampling was carried out in order to analyze the Volatile Organic Compounds (VOCs) specific to the activity of the fungal agents by gas chromatography. Wood samples were collected from areas with visible fungal colonization and subjected to culturing, extraction of DNA and analysis of the ITS sequences after PCR amplification. By visual observation, the species of fungi *Coniophora puteana*, *Phellinus megaloporus*, and *Serpula lacrymans*, and Moulds were highlighted. Biocontaminated areas were located on the staircase leading to the first floor (moulds), the first floor (*S. lacrymans*, *P. megaloporus*, *C. puteana*) and the second floor (*S. lacrymans*, *P. megaloporus*, *C. puteana*, and moulds). Of the 59 isolates obtained by culturing, microscopic observation enabled the identification of 6 fungal genera: *Penicillium* sp, *Cladosporium* sp, *Acremonium* sp, *Humicola* sp, *Rhizopus* sp and *Mucor* sp. Isolates not identified by this approach were identified by analyzing ITS sequences: *Trichoderma viride*, *Trichoderma atroviride*, Uncultured Ascomycota, and *Umbellina isabellina*. Samples from these areas were also directly subjected to DNA extraction, amplification and analysis of the ITS sequences. Additional fungal species were identified: *Penicillium citreonigrum*, *Chaetomium elatum*, uncultured *Aspergillus*, and *Coprinellus aff. radians*. The calculation of the fungal indexes ICM and ICF based on the VOCs detected at the different sampling points confirmed the presence of active developments of moulds and *Serpula lacrymans* in the pavilion. In conclusion, a strong fungal diversity comprising lignivorous fungi and moulds was highlighted in the zones of the biodeteriorated wood in the lodge of "La Muette". The different technical approaches used in the study proved complementary to enrich the knowledge of the fungal biodiversity associated with wood decay.

CNR-CISC, jointly activities, not only a scientific collaboration

P. Tiano

Istituto per la Conservazione e la Valorizzazione dei Beni Culturali, CNR- ICVBC, Via Madonna del Piano 10, 050019 Sesto Fiorentino (FI), Italy
p.tiano@icvbc.cnr.it

The first collaboration with Cesareo started with the project "COALITION" (Contract No EVK4-CT-1999-2001). A concerted action on "Molecular microbiology as an innovative conservation strategy for indoor and outdoor cultural assets", coordinated by. Dr. C. Saiz-Jimenez and whose partners were: Dr. Sabina Rölleke, Prof.Dr. Werner Lubitz, Prof. Dr. Jean Swings, Prof. Dr. Mirja Salkinoja-Salonen, Prof. Dr. Wolfgang E. Krumbein, Dr. Piero Tiano, Dr. Clara Urzi, Dr. Nieves Valentin.

The purposes of COALITION were to provide, firstly, a review of current knowledge on molecular biology and biotechnology techniques suitable for the diagnosis of biodeterioration problems and, secondly, to provide the European scientists, conservators, restorers and other end-users with better access to data at EU and at national levels. After the successful closing of the project the deliverable electronic newsletter COALITION is still published on line (last issue January 2014 at http://www.technoheritage.es/coalition.html.). This action was the starting point of a new biotechnological approach for studying biodeterioration processes in the cultural heritage field.

The second opportunity to work together was due to the approval of a bilateral agreement CNR-CISC (2009-2010) on "Technology and biotechnology for the conservation of hypogean cultural heritage".

The project included the study of hypogean environments located both in Spain and in Italy, represented by some Roman tombs in the necropolis of Carmona and some Etruscan tombs in the Chiusi -Tarquinia district respectively. In the selected environments were monitored the micro-climatic parameters, which may influence the development of biodeteriogens, and investigated the biodiversity of such particular environments.

Some micro samples have been collected for the characterization of mortar and pigments. An innovative methodology using the microwave system, for the bio contamination control, has been tested. The surface pattern (roughness and color) of sample areas was investigated by the use of the micro photogrammetry system, used as diagnostic tool (x,y,z parameters). The study of biodiversity was concentrated on bacterial and actinobacterial identification by applying biotechnology methods (PCR, DGGE).

The common scientific background, the numerous occasions to meet both in Spain and in Italy, together with the sincerity of the personal relation have created a relationship that was and is beyond a simple scientific collaboration.

Coniophora marmorata as responsible of a fungal outbreak in the Catacombs of SS. Marcellino and Pietro

F. De Leo[1*], I. Dominguez-Moñino[2*], V. Jurado[2], L. Bruno[3], C. Saiz-Jimenez[2], C. Urzì[1]

[1]Dept. of ChiBioFarAm, University of Messina, Italy
[2]Institute for Natural Resources and Agrobiology, Spanish National Research Council (IRNAS-CSIC), Sevilla, Spain
[3]Dept. of Biology, University of Rome 'Tor Vergata', Italy
urzicl@unime.it

Cave and catacombs microbiota and especially fungi are sensitive to organic input changes in their close environment. New input of organic sources (soil, dead animals and microorganisms, etc.) associated to favorable microclimatic parameters often lead to the overgrowth of fungi that may cover (colonize) a wide extension of available surfaces. The present research reports of a sudden fungal outbreak occurred in the corridor near the entrance of the Catacombs of SS. Marcellino and Pietro in Rome.

A heavy fungal growth was observed one year after a restoration treatment that interested the walls of the entrance of the Catacombs and some artifacts placed *in situ*. Some marble slabs in fact, were restored and placed back into the walls. The colonization was observed only on the left side of the corridor around the marble slabs and on the vault. No growth was observed in the right side were similarly treated marbles slabs were placed. However, a high circulation of airborne fungal spores was observed.

Mycological analysis were done on samples taken on the catacombs vault and side, as well as from soil and tree roots coming from upper ground above the catacombs. The combined use of microscopical, cultural and molecular tools showed that the vault and the left side of the corridor entrance were colonized by the brown Basydiomycetes *Coniophora marmorata*, that was able to form colonies with a diameter up to 57 cm, while secondary colonizations were due to different microfungi belonging to the genera *Hypomyces chlorinigenus, Purpureocillium lilacinum, Acremonium persicinum, Penicillium* spp. and *Alternaria* sp. The comparative analysis of roots and soils showed that fungi were present in all samples but a different distribution and diversity was observed. Due to the fast rate of growth of the fungi on the walls, a three steps emergency treatment was done with intervention on the environment, on the biodeteriogens and further by a close monitoring on monthly basis.

Despite the successful intervention, it was clear that several causes could have created this fungal outbreak and for this reason, a continuous monitoring of the catacomb's surfaces was planned.

***** Both Authors contributed equally in the isolation and characterization of fungal isolates.

A multi-analytical approach to study Limestone Biodeterioration and Biological colonization in the Old Cathedral (Sé Velha) of the UNESCO World Heritage site 'University of Coimbra - Alta and Sofia'

J. Trovão[1], F.Soares[1], N. Mesquita[1], C. Coelho[1], I. Tiago[1], F. Gil[2], L. Catarino[3], G. Piñar[4], A.C. Pinheiro[1], A. Portugal[1]

[1]Centre for Functional Ecology, University of Coimbra, Coimbra, Portugal
[2]CFisUC - Center for Physics of the University of Coimbra, Portugal
[3]Geosciences Center, University of Coimbra, Coimbra, Portugal
[4]University of Natural Resources and Life Sciences (BOKU), Vienna, Austria
jtrovaosb@gmail.com

In 2013, UNESCO classified the 'University of Coimbra – Alta and Sofia' as a World Heritage site. Within this area, several limestone monuments (with different physicochemical characteristics and mineral composition) exhibit clear signs of biodeterioration. These structures are highly prone to degradation by weather, atmospheric conditions and other abiotic factors, while providing sustainable, protected and widely available colonization niches for distinct biodeteriorative microbial populations.

Fungi, Bacteria, Archaea and Algae are powerful stone biodeteriogens. They colonize the surface and interior of soft and porous limestone, contributing physically and biochemically (acids and osmolytes) to their structural deterioration, leading to cultural loss; they form surface biofilms and produce pigments that stain the substrata, causing aesthetic damage; they are also able to produce salt efflorescences, resulting in adverse physical and chemical alterations.

The construction of the old cathedral (Sé Velha) lasted from the 12th to the early 13th Century, with the erection of the cloister. The Romanesque church, built in yellow limestone, is located on a hillside and is composed of three naves, prominent transept and tripartite head. The single-floored cloister is arranged laterally to the south of the church and exhibits severe signs of biodeterioration.

The aim of this work is to apply a multi-analytical approach combining biological, physical, geological, and architectural sciences to characterize limestone biodeterioration and biological colonization in the cloister of the Old Cathedral (Sé Velha) of the UNESCO World Heritage site 'University of Coimbra - Alta and Sofia'.

Limestone degradation was assessed by characterization of decay products, mineral modifications and aesthetic alterations (e.g. pigmentation) using microscopy techniques (SEM/OM/XRD/FTIR/RAMAN) and complemented with identification of microbial communities using morphological and molecular methods (DNA extraction/PCR/Sequencing).

Preliminary results encompass: a characterization of the microbial communities colonizing limestone (Fungi, Bacteria, Archaea and Algae); a detailed inventory of the biodeterioration issues affecting the cloister of the old cathedral (biofilm, salting, pigmentation, physical and chemical alterations), and the putative linkage between the observed phenomena and the responsible microorganisms.

The knowledge obtained from this work provides a better understanding of the problematic of limestone biodeterioration, and a deeper insight on the relationships between specific biodeteriorating organisms, substrata types and deterioration phenomena. Hence, this information will allow more adequate and better-informed control/decision-making regarding future stone restoration and conservation procedures in this UNESCO World Heritage site.

New discovery of rosy discoloration in Vesuvian Areas: the study case of "Casa del Bicentenario" (Herculaneum, Italy)

M. Tescari[1], F. Bartoli[1], E. Frangipani[1], P. Visca[1], L. Rainer[2], G. Caneva[1]

[1]*Department of Science, University Roma Tre, Viale G. Marconi, 446, (00146), Rome, Italy*
[2]*The J. Paul Getty Trust, 1200 Getty Center Drive, (CA 90049-1679), Los Angeles, USA*
giulia.caneva@uniroma3.it

The growth of bacteria, algae and fungi on mural paintings can implicate not only corrosion, dissolution and solubilisation of materials, but also staining phenomena and biofilm formation on the surfaces, producing aesthetical damages. The discoloration of mural paintings, giving rise to blackening, whitening, and also their changing into rosy colorations, are often attributed to chemical processes, such as to pollution or saline effects, and rarely and the biological origin of some of these alterations is understood. Indeed, often pink coloured patinas and rosy discolorations on masonry are referable to biological phenomena, whose geographical spread is increasing due to the larger cases where they are described in literature.

In this work we report, for the first time, the presence of rosy discoloration of biological origin in the Vesuvian area, and in particular in the archaeological site of Herculaneum. In fact, during the restoration activity carried out in the "Casa del Bicentenario", in occasion of Herculaneum project, we observed a wide diffusion of rosy discoloration, on masonry and on Roman frescoes. A sampling campaign was then, performed with non-invasive methods, in order to isolate and identify the biological agents. Simultaneously, observations on the distribution of patinas, and measurements on physical parameters (illuminance, RH and temperature), were performed during different seasons, in order to characterize the ecological factors, which can favour their development. Cultural approach, with complete and selective medium, was used to isolate pink-red pigmented microorganisms. The isolation trough a selective medium resulted in 8 isolated colonies of bacteria, which were also observed trough SEM analysis. Bacterial identification was performed with 16S rRNA gene sequences resulting in 6 different species (*Gordonia rubripertincta Rhodococcus* sp., *Brevibacterium* sp., *Methylobacterium extorquens, Dietzia maris,* and especially *Arhtrobacter agilis*) among which only two were recognized, in literature, as associated to pink patinas.

Our work highlighted that the patina morphology is similar to some previously studied pink patinas, and our taxonomical characterization increases the number of pink producing bacteria associated to this phenomenon. Furthermore environmental observations on the distribution of pink patinas suggest their relationships with low light conditions and salt efflorescence in the walls, confirming their ecological preferences for semi shadowing conditions and for high osmotic values.

Patinas on stones, metals, glasses and ceramics: a protection strategy?

M.A. Villegas

Instituto de Historia, CCHS-CSIC. Calle Albasanz, 26-28. 28037 Madrid, Spain

The interaction of the environment with materials leads to the formation of surface layers known as patinas. Heritage building materials and also the objects conserved in museums are subjected to such weathering interaction and the result is the appearing of patinas of different characteristics and properties: some of them are well adhered and resistant and could be considered as protective coatings, while others are thick, stratified and chemically reactive, thereby enhancing the base material degradation. Some classifications refer to natural patinas depending on their origin as ageing, soiling, washing, discolouring, or biogenic patinas. Moreover, patinas can be induced artificially both on Heritage materials and objects to repair the whole appearance of the weathered item, or to add a kind of finishing layer more or less harmonic with the historic/artistic ensemble, or to endow a protective interface able to isolate the Heritage item from an aggressive environment. Obviously, the formation of patinas on materials and their further response against the environment depends on the nature and former degradation history of the material to be considered, as well as on the patina origin, natural or artificially induced. Thus, even taking into account that patinas are no more than a kind of degradation or corrosion layer, their adherence level upon the substrate and their thickness play a noteworthy role that is different for each material. In general thin and well adhered patinas generated as a natural weathering or by artificial treatment should be maintained upon the base material since, at least, they isolate the materials surface from further contact with the ageing or corrosive agents. However, thick poorly adhered layers able to react with the base material generate reactive compounds that cause the base material degradation. In addition, such a low adhered layers are easily detached and leave unprotected the material surface, which is weathered again and again in a reiterative process that endangers the material integrity. This kind of layers could not been considered patinas but alteration/corrosion layers and should be released during cleaning or restoration works. Patinas on stone substrates are usually protective and contribute to the study of the stone degradation processes as well as to point out data on constructive techniques and the weathering history of the building. They should not be released nor cleaned with synthetic products. Even so, too thick stone patinas could be reduced by cleaning the most external layer or soiling crust and preserving always the first layer directly in contact with the stone substrate. The formation of patinas on metals and alloys depends, on the one hand, on the chemical composition, homogeneity level and production technology of the substrate and, on the other hand, on the environmental parameters (temperature, humidity, pollutants, etc.). Iron and steel patinas are poorly adherent and stratified and commonly formed by iron oxides, hydroxides, carbonates and sulphates. *Corten* steel is a weathering resistant material with a rusty appearance and well adhered dense patina formed after several years of atmospheric interaction. Copper and bronze patinas are protective layers showing nice colours and texture and composed by copper oxides, hidroxycarbonates and sulphates. Lead and lead alloys patinas also have a protective role as passivation layers frequently composed by lead hydroxides, oxides, carbonates, etc. The presence of chlorine ions in the metals surface layers usually destroys the potential protective character of the patina. Glasses are sensitive to humidity in all the pH range and thus they are subjected to acid, neutral and basic attack. The result is the formation of a surface silica gel layer that behaves as a patina. In restoration works the preservation of such natural patina, once the soiling and degradation crusts are carefully released, is essential. The formation of patinas on ceramic materials depends on their chemical composition, firing temperature and residual porosity. In general ceramics are good resistant against weathering, even though porosity enhances water penetration and subsequent reaction of some ceramic components with pollutants dissolved in water causing potential swelling.

Fungal stains on paper: What you see is what you get?

S.O. Sequeira[1,2], H. Paiva de Carvalho[3], N. Mesquita[3], A. Portugal[3], M.F. Macedo[1,2]

[1]Departamento de Conservação e Restauro, Faculdade de Ciências e Tecnologia, Universidade NOVA de Lisboa, 2829-516 Monte de Caparica, Portugal
[2]VICARTE, Faculdade de Ciências e Tecnologia, Universidade NOVA de Lisboa, 2829-516 Monte de Caparica, Portugal
[3]Centre for Functional Ecology, Department of Life Sciences, University of Coimbra,Calçada Martim de Freitas, 3000-456 Coimbra, Portugal
s.o.sequeira@gmail.com

Biodeterioration caused by moulds is a major problem that affects paper based collections in museums, archives and libraries all over the world. Fungi have the ability to decompose paper materials, namely by the production of a variety of metabolites and enzymes. These excreted substances and the fungal structures themselves are often coloured and interfere with the readability of the artefacts, diminishing their artistic and monetary value.

Even when the fungi are already dead and the paper has been mechanically cleaned, most stains still remain on the paper and the deposited metabolites continue their degrading action. Consequently, the successful removal of fungal stains from paper is an important conservation task, being considered a research priority by paper conservators. In order to better target cleaning methods, the mechanisms and colorants responsible for the stains need to be assessed.

In the present work, different stains were studied in terms of colour and causative fungal species from three paper documents (two books and one print). Fungal identification was performed by *in situ* observation of fungal structures with stereoscopic and optical microscopy and compared with identification of collected samples by culture and molecular biology methods. Twenty-eight stains were sampled and most of them were black or dark brown coloured, with a few yellow/orange or purple. Positive correlations between the observed fungal structures *in situ* and the identified fungal species were achieved for several samples. Black and dark brown stains were mostly caused by *Chaetomium globosum*, *Chaetomium murorum*, *Myxotrichum deflexum* and *Stachybotrys chartarum*. *Eurotium rubrum* was identified in a foxing stain. *Penicillium citrinum* was identified on yellow stains with *Penicillium* type conidiophores. Other species that did not correspond to the fungal structures observed in the documents were also identified, being most probably aerial contaminants. Most stains developing on paper that had been formerly mechanically cleaned did not result in a positive fungal identification by molecular methods probably due to a lack of sampling material. Other collection methods are currently being tested for that kind of stains.

From Plant to Cultural Assets

F. Palla

University of Palermo, Laboratory of Biology and Biotechnology for Cultural Heritage - Department STEBICEF - Sec. of Botany and Environmental Biology, Via Archirafi 38, 90123 Palermo, Italy
franco.palla@unipa.it

The biodeterioration of historic-artistic manufacts is related to several biological systems, including fungi and bacteria, whose metabolic activities and vegetative development have a direct consequence on the conservation of cultural assets. Generally, different chemical compounds are utilized as biocides to control the colonization of artworks surfaces by macro-micro biological systems. In order to develop alternative methods, under the point of view of the *green conservatio*n, natural biocides have been tested to control fungal and bacterial colonization. Recently, bioactive molecules have been isolated from invertebrate marine organisms and applied to control bacterial (*Bacillus*, *Micrococcus*) or fungal (*Aspergillus*, *Penicillium*) growth.

Particularly, these microorganisms were isolated from colonized canvas artifacts and characterized by an integrated approach based on *in vitro* culture, microscopy observation and molecular investigation.

In our laboratory we are testing the antimicrobial activity of different concentrations of three plant products, such as Tea tree essential oil, *Calamintha nepeta* and *Allium sativum L*. extracts, against *Bacillus subtilis*, *Micrococcus luteus*, *Penicillium chrysogenum* and *Aspergillus spp*., performing three different *in vitro* antimicrobial assays (micro-dilution in microtiter plates, well plates diffusion and agar disc diffusion methods). The bioassays show a different microbial susceptibility to the plant products, establishing for each bacteria and fungi the Minimum Inhibitory Concentration (MIC) and defining the diameter of the growth inhibition area. These result supports the data reported in literature and shows an important potential suggestion for the possible use in the control of microbial deterioration of cultural heritage, safe both for human and environment.

Moreover the control of the antimicrobial activity by other plant extracts (Citrus) is in progress.

Functionalized SiO_2-Ag nanoparticles for the production of multifunctional biocide and superhydrophobic coatings for preserving stone

R. Zarzuela[1], M.Carbú[2], M.L.A. Gil[1], M.J. Mosquera[1]

[1]TEP243 Nanomaterials group, Departamento de Química Física, Universidad de Cádiz
[2] Dpto. de Biomedicina, Biotecnología y Salud pública, Universidad de Cádiz. Facultad de Ciencias
Campus Universitario Río San Pedro s/n. 11510 Puerto Real, Cádiz, Spain
rafael.zarzuela@uca.es

The preservation of the building materials that conform both modern and historical buildings is one of the challenges present in our society. In any environment, the building materials are usually exposed to a combination of physical, chemical and biological agents, which promote their decay and cause remarkable aesthetical and structural damage over time. Furthermore, it is common for the aforementioned agents to show synergistic effects (i.e. water acting as a vehicle for microorganisms or biofilms modifying water absorption capabilities).

Nanotechnology has arisen as a promising approach to solve the mentioned problems. Specifically, metallic nanoparticles have been widely used for the control of microbial growth on different materials, including metal surfaces, plastics, ceramics and stone. On the other hand, the creation of hierarchical structures, combining micro- and nano- roughness, leads to the formation of superhydrophobic materials, which show high water repellence. A simple way of obtaining this kind of roughness is the addition of SiO_2 nanoparticles to a product synthetized via sol-gel route.

In the present research work, we propose a method for the preparation of silica nanoparticles (NPs) loaded with AgNPs for their use on the preparation of superhydrophobic and biocide treatments for building materials. The addition of the prepared particles can simultaneously create the nano-roughness required for superhydrophobicity and give rise biocide properties. The modification of the SiO_2 nanoparticles was carried out by functionalization with an aminoalkyl-alkoxysilane. The aminoalkyl moiety binds to the Ag nanoparticles, whereas the akoxysilane groups hydrolyze to form covalent bonds with the SiO_2 surface. The measurements of surface Z-potential and FTIR confirmed the modification.

The functionalized particles were incorporated to a sol prepared from ESTEL1100 (CTS), polydimethylsiloxane in order to improve the hydrophobic and mechanical properties, and n-octylamine as a catalyst to accelerate the sol-gel process and to prevent cracking during the drying process.

The biocide effectiveness was tested in the produced xerogesl against two reference microorganisms: a bacterium (*E. coli*) and a yeast (*S. cerevisiae*). We observed an increase in growth inhibition as Ag content is raised. The products were applied on different stones and their superhydrophobic properties were confirmed by measuring dynamic contact angles. The biocide effectiveness on the treated stones was evaluated against a bacterium, a yeast and a fungus (*Aspergillus spp.*). The results confirmed the biocide effectiveness of the product under study.

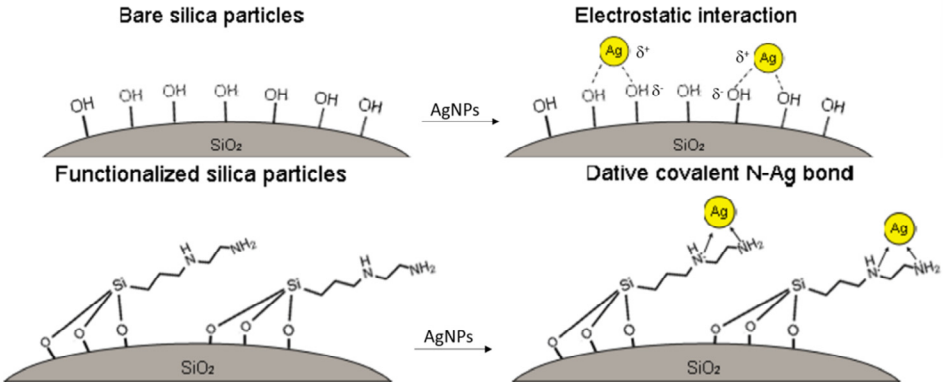

Figure1. Schematic representation of the SiO_2NPs functionalization.

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The Roman Necropolis of Carmona, Spain: 10 years of research

S. Sanchez-Moral[1], A. Fernandez-Cortes[2], S. Cuezva[1], J.C. Cañaveras[3], D. Benavente[3], J. Elez[4], M. Hernandez-Marine[5], J.L. Santos[6], E. Alonso[6], J.A. Gonzalez-Perez[7], L. Laiz[7], M. Diaz-Herraiz[7], I. Dominguez-Moñino[7], M.A. Rogerio-Candelera[7], A.Z. Miller[7], V. Jurado[7], B. Hermosin[7], C. Saiz-Jimenez[7]

[1]Museo Nacional de Ciencias Naturales, MNCN-CSIC, Madrid
[2]Departamento de Biologia y Geologia, Universidad de Almeria, Almeria
[3]Departamento de Ciencias de la Tierra y del Medio Ambiente, Universidad de Alicante Alicante [4]Departamento de Paleontologia, Universidad Complutense, Madrid
[5]Facultad de Farmacia, Universidad de Barcelona, Barcelona
[6]Escuela Politecnica Superior, Universidad de Sevilla, Sevilla
[7]Instituto de Recursos Naturales y Agrobiologia, IRNAS-CSIC, Sevilla, Spain
saiz@irnase.csic.es

The first tomb of a Roman Necropolis in the area of Carmona (Seville, Spain) was accidentally discovered in 1830. Few more tombs were exhumed between 1868 and 1869. These tombs were plundered until the beginning of the archaeological excavations in 1882. This necropolis, located in the town of Carmona, represents one of the most significant Roman burial sites in Southern Spain, and was in use during the 1st and 2nd centuries AD.

Initially, the necropolis was used as quarry from which stone blocks were extracted and used for building construction. The quarry was then abandoned and reused as necropolis due to the workability of the rock. The Necropolis has suffered numerous and extensive interventions since its discovery. The first one was the adaptation of the necropolis for visits in 1885, including the construction of a trail, design of gardens around the tombs and plantation of trees. Nowadays, the gardens are considered one of the most deteriorating factors affecting the conservation of the tombs due to irrigation and consequent percolation of water inside the tombs, in addition to the damage caused by roots.

Taking into account the cultural, artistic and religious importance of the Necropolis of Carmona, its preservation and conservation are a major issue, both from cultural and economic points of view. This importance emphasizes the need to define accurate and sustainable intervention protocols based on a deep understanding of the environmental and/or anthropogenic-induced deterioration processes. The design of effective preservation and/or conservation strategies should be based on exhaustive *in situ* surveys and laboratory investigations. Here we review 10 years of research in the Necropolis and we focus on the Circular Mausoleum, as a case study, including an assessment of its conservation state, and the identification of the main deteriorating agents. In addition, an intervention proposal for the preservation of the Circular Mausoleum was presented.

Desalination of granites using poultices made with different components: influence of the properties of the rocks and of the salt system on the effectiveness

J. Feijoo, I. de Rosario, T. Rivas, J. Taboada

Dpt. Ingeniería de los Recursos Naturales y Medio Ambiente (University of Vigo) Lagoas-Marcosende s/n, 36310 Vigo, Spain
jfeijoo@uvigo.es

The historic and artistic heritage is subject to several alteration processes that get their future preservation in risk. Among these processes, the crystallization-dissolution of soluble salts generates several pathologies which in many cases get in risk the integrity of the materials [1]. One of the main direct interventions aimed at minimized the harmful effects related with soluble salts consist in the desalination of the materials. The desalination can be performed using different methods, being the application of hydrophilic materials (poultices) the most applied. These compounds allow reducing the salt content present into the rocks by ionic mobilization through diffusion and advection processes [2]. The effectiveness of poultices of different composition in the desalination of sedimentary and carbonate rocks is well documented in the literature [3, and references therein] but not so for the case of the granitic rocks, scarcely studied from this point of view [4].

In this work, the evaluation of the effectiveness of different poultices made on pure materials (cellulose or sepiolite) or made with mixtures (cellulose-sepiolite, kaolin-sepiolite and kaolin-cellulose-sepiolite) on the salt removal on granite is evaluated. Two different granites widely used in NW of Spain, contaminated with NaCl and sea-water, were used. So, the influence of the composition of the poultice, the properties of the stones (mainly pore system) and the saline system contaminating the rock in the effectiveness of the desalination tests has been analyzed.

The results showed that the porosimetric distribution of the granites and the poultices is the main parameter influencing the extraction effectiveness; specifically, the differences on the pore volume corresponding to the capillary range (0.1-100 μm), between the rocks and the poultices determine the process through which desalation takes paces, i.e. diffusion or advection. Therefore, previous knowledge of the porosimetric distribution of granite is essential for the correct choice of the poultice in order to achieve a greater efficiency in desalination. Also, an influence of the type of salt on the effectiveness of the treatment has been found; in the case of the extraction of less mobile ions, such as sulfate, it is necessary to apply poultices that favor the ion mobilization by capillary suction.

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Cleaning tests. Elimination of carbonates in the wall paintings of *Castulo*

T. López Martínez, A. García Bueno, V.J. Medina Flórez

Dpt. of Painting (Faculty of Fine Arts, University of Granada) Granada, Spain
terelm@ono.com

Before addressing a conservation and restoration intervention, it is essential to review the possible treatments to be taken into consideration and assess the treatment-artwork interactions that may arise.

Cleaning is one of the most delicate processes to undertake as it clearly highlights the reversibility criterion that any intervention must meet, therefore requiring to be carried out by an art restorer with special training and sensibility. Moreover, the artwork area is a factor to be taken into account in wall paintings, as it makes it difficult to obtain a homogeneous result throughout the whole surface due to the usually heterogeneous state of conversation of the pictorial layer. Since this type of interventions may cause changes in the pictorial layer which depend on several factors, it is necessary that the conditions in which the different test treatments take pace simulate as much as possible the original characteristics.

The project FORVM MMX discovered in 2012 the *Sala del Mosaico de los Amores* in the archaeological site of *Castulo*, dating back to the 2nd century BC. That room had very rich mosaic and wall decorations, and part of those wall coverings was moved to the University of Granada for restoration.

For all these reasons, and as study prior to the intervention of the aforementioned paintings, several cleaning tests have been conducted on decontextualized fragments of the wall covering, so that it is possible to assess the interaction of the treatments with the artwork, without interfering neither with its understanding nor its legibility.

Regarding the cleaning processes, those aiming at the elimination of the carbonated layers have been chosen, analyzing both the reactive to be used as the application procedure. In this way, the six cleaning treatments chosen have been applied with two different procedures. This has led to the assessment of both the efficacy of each product as the ideal application procedure, and at the same time it has proven the advantages of the use of rigid gels in the face of cellulose pulp (Fig.1).

Figure 1. Cleaning tests with EDTA, applied with cellulose pulp in the left image and with a gel in the right image.

A study of the effect of 1064 nm Nd-YAG laser cleaning of gilding wood support

A. Gómez-Morón[1], A. Lara Luque[2], P. Ortiz-Calderón[2]

[1]Instituto Andaluz de Patrimonio Histórico, C. Descubrimientos, s.n., 41092, Seville, Spain
[2]Pablo Olavide University, Department of Phisycal, Chemical and Natural Systems, Ctra. Utrera,1, 41013 Seville, Spain
mariaa.gomez.moron@juntadeandalucia.es

The results of a study on the efficiency and feasibility of 1064 nm pulsed laser cleaning of gilding on wood support are reported. The conditions for the optimization of this technique have also been analyzed.

Ninety 4 x 4 cm test samples of gilding on wood have been made for this study. A half of the samples are of pure gold and another half of brass leaf. Three types of adhesives have been used to bond gold leaves to substrate: water based mixtion, oil based mixtion and fish glue. Four types of protecting coatings and one patina have been applied on these samples: Titan satin varnish, shellac, microcrystalline wax – Paraloid B-72®, Paraloid B-72® and bitumen. Repainting with purpurin has been applied to a half of the samples. Several types of dirt have been deposited on these samples: virgin wax candle smoke, paraffin wax candle smoke, virgin wax deposit and paraffin wax and dust deposit.

Starting from some initial parameters, the effect of laser cleaning on the samples has been assessed. Optimal results have been found for 75mJ-20Hz, 50mJ-20Hz y 35mJ-20Hz.

To assess the cleaning and to characterize the materials the following techniques have been applied: colorimetry, optical microscopy, stereomicroscopy, scanning electron microscopy and FTIR spectroscopy. Additionally, the temperature and heat diffusion on the gilding caused by laser pulses have been analyzed by means of a thermal imaging camera.

Finally and basing on the results for the test samples a study on real artwork has been performed.

As a conclusion, for both kinds of tested smoke dirt, virgin and paraffin, laser cleaning has been effective although with nonuniform results. It is not even sure that the optimal values on one region of the sample work properly on other region of the same sample. Nd-YAG laser cleaning has not been effective neither for the removal of waxes, both virgin and paraffin, on gilding nor for the dust dirt simulated in this project.

For the real artwork the results are similar to those previously observed on test samples. Very heterogeneous results are found, finding both cleaned regions and damaged regions (gilding loss, whitening and bulging).

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Scientific evaluation of restoration tratament in polychrome stone

L. Ferrazza, G.M. Contreras Zamorano, M.T. Pastor Valls, D. Juanes Barber

Subdirección General del Instituto Valenciano de Conservación y Restauración IVC+R (Culturarts Generalitat) Pintor Genaro Lahuerta 25, 3º, Valencia, Spain
livio.ferrazza@gmail.com

This abstract proposes a research project focused on the scientific evaluation of the risk and effectiveness of different restoration treatments such as the cleaning and stabilization of the pictorial layers in the 14th Century Portal of the Apostles of the Arciprestal Basilica of Santa María La Mayor of Morella (Castellón, Spain).

The gothic portal is one of the most important polychrome stone in the Valencian Community, where it is necessary to study the decorative techniques analyzed the pictorial materials (pigments, binders, metallic sheets, etc.) and chemical, physical and biological deterioration processes factors that have affected them as a phase prior to the application of restorative treatments.

The evaluation of the effectiveness of the work and of the risk will focus on the determination of the action of the restoration systems used (cleaning with gels, laser, adhesives and consolidation stability), permanence of residues and possible changes of colour, texture and compactness that can be produced on the treated surfaces. In this way, a comprehensive, objective and scientific evaluation of the risk that each proposed restoration treatment can represent in a specific way for the conservation conditions of the set, allowing proposing in an objective and reliable way optimal systems of intervention.

The study is carried out in the laboratory whit sample extraction and preparation of test specimens, such as in situ on pilot areas, by EDXRF energy dispersion X-ray fluorescence, optical microscopy, scanning electron microscopy (SEM), microanalysis by dispersion of X-ray energies (EDX) and compositional organic analysis by gas chromatography - mass spectrometry (GC-MS) and infrared spectrometry (FT-IR).

The results obtained will be evaluated, determining the advantages and disadvantages of each of the applications, identifying those critical parameters that will serve to define the most appropriate methodologies based on the chemical-physical characteristics and conservation status of the treated surfaces.

The results will allow establishing which are the methodologies and products of restoration more in accordance with the conservation conditions as well as the thermohygrometric conditions to which the work is exposed, and the possible changes to introduce in the methodology and in the materials with the aim to optimize applications and their effectiveness.

A comparative evaluation between Nano-lime and Nano-silica consolidants on fossils

A. Rodríguez Rueda [1], J. Becerra Luna[2], J.M. Martín Ramírez[2], A.P. Zaderenko Partida[2], M.P. Ortiz Calderón[2]

[1]*Institute of Human Palaeoecology and Social Evolution (IPHES), (Campus Sescelades), 43007 Tarragona, Spain*
[2]*Department of Physical, Chemical and Natural Systems (University Pablo de Olavide, Carretera de Utrera Km 1, ES-41013, Seville, Spain*
ainoarueda@gmail.com

This study draws a comparison between two consolidants based on nanoparticles of different nature: calcium hydroxide dispersed in isopropyl and aqueous colloidal dispersion of silica. The goal is to determine by scientific tests their suitability for the substrata they have been used.

Tests have been conducted on fossil materials found at the palaeontological site Baza 1, located at the Baza basin in Granada. Based on the discovered fauna, chronologically framed within the Pliocene period and its Ruscinian age (4.0- 4.5 Myr).

The samples consist of damaged fragments from fractured and non-classifiable bones belonging to ungulates of average/big size, which does not provide any taxonomic information or any information to researchers. The fossils show damages such as a lack of cohesion and/or mechanical resistance, fractures/fissures, and disintegration due to changes of temperature, relative humidity, weathering, sediment compression and vegetation. Thus, their proper treatment is their consolidation.

To evaluate the efficiency of the consolidants, the materials have been characterized before and after their application of nanoparticles, determining this way several variables such as their aspect, degree of consolidation, penetration and compatibility.

Scanning electron microscope (SEM), magnifying glass, and photography with natural light were used to identify morphometric changes.

Physical-mechanical properties were analysed by absorption of water under atmospheric pressure, colorimetry, conductivity, and ultrasound propagation velocity.

It can be concluded that the results show how both products produce a porosity decrease from 46%±2 to 38%±3. Nevertheless, there are differences between the Nano-silica and the Nano-lime relevant for their applicability in cultural heritage:

Applying nano-silica results in an increase in surface brightness levels and therefore luminosity, although since that increase is less than 10, it cannot be noticed by the human eye. The Nano-silica does penetrate but creates layers that overlap each other and craze, thus exposing areas of the fossil.
When using calcium hydroxide nanoparticles, the colour of the samples turns cloudy, whereas compact bones turn yellow, and spongy bones turn red. This treatment produces a heterogenous increase in calcite reticule that leaves areas exposed and appears to be more compatible with the substrata.
A further study is required to establish the best method to apply nanoparticles on fossil consolidations.

Micro- and nanoparticles based on alkali-earth metal hydroxides for cultural heritage conservation

P.I. Girginova[1,2], C. Galacho[1,3], J. Mirão[1,3], R. Veiga[2], A.S. Silva[2], A. Candeias[1,3]

[1]HERCULES Laboratory (University of Évora) Évora, Portugal
[2]National Laboratory for Civil Engineering (LNEC) Lisbon, Portugal
[3]School of Sciences and Technology (University of Évora) Évora, Portugal
penka@uevora.pt

Wall renders are subject of constant aging and deterioration and they therefore need repair and treatment. The polymers used in the past for consolidation show many drawbacks and often accelerate the deterioration. This implies the need of new non-toxic materials, preferably of the same composition as the original art work, compatible, with long-term efficiency, without side effect, easy for application. Different inorganic materials have been proposed. The lime-based materials are convenient but not efficient enough, so that different approaches to enhance their efficiency must be found. Nanomaterials exhibit distinct properties when compared to their bulk analogues and have been seen as a good alternative of compatible materials for long term preservation [1].

In this context our research intends to study and optimize successful preparative strategies of micro- and nanolimes, and to improve their efficiency in the inhibition of the degradation process and in the consolidation of wall renders and stone [2,3]. The work is focused on the innovation of the tradition lime materials towards long-term efficiency and compatibility with the surfaces of original works, taking into account environmental and human risk factors.

In this communication we report the synthesis and characterization of micro- and nanoparticles based on alkali-earth metal hydroxides for cultural heritage conservation. We discuss synthetic strategies applied and optimum preparative conditions, such as temperature, synthesis duration, addition of surfactant and others, in order to obtain well defined functional magnesium and calcium hydroxides nanoparticles. The composition, morphology and crystallinity are analysed mainly by microscopical techniques and by X-ray powder diffraction. Additional structural and chemical data are collected with other common techniques: Energy Dispersive X-Ray Spectrometry, micro-FTIR, micro-Raman, simultaneous thermal analysis (TGA/DTA) among others, when needed. We also discuss the laboratory tests conducted to assess the efficiency of the nanolimes on mortar specimens (porosity, dynamic elastic modulus, compressive and flexural mechanical behaviour) and the feasibility of their application.

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Ammonium Methyloxalate as an alternative precursor of Calcium Oxalate for the protection and consolidation of carbonatic decayed materials in cultural heritage

A. Murru[1], R. Fort[2], P. Meloni[3], L. Maiore[4], M. Arca[5]

[1] Dipartimento di Ingegneria Civile, Ambientale e Architettura, Dipartimento di Ingegneria Meccanica, Chimica e dei Materiali, Università degli Studi di Cagliari, Via Marengo 2, 09123 Cagliari, Italy
[2] Instituto de Geociencias (CSIC, UCM), C/ José Antonio Novais, 12, 28040 Madrid, Spain
[3] Dipartimento di Ingegneria Meccanica, Chimica e dei Materiali, Via Marengo 2, Università degli Studi di Cagliari, 09123 Cagliari, Italy
[4] Dipartimento di Chimica e Farmacia, Università degli Studi di Sassari, Via Vienna 2, 07100 Sassari, Italy
[5] Dipartimento di Scienze Chimiche e Geologiche, Università degli Studi di Cagliari, S.S. 554 bivio per Sestu, 09042, Monserrato (Cagliari), Italy
ariannamurru@unica.it

This study consists in the evaluation of the novel inorganic salt ammonium methyloxalate (AmMeox) [1] for the reinforcement and consolidation of decayed carbonate materials of cultural heritage. In particular, AmMeox was tested as an alternative precursor of calcium oxalate (CaOx), in place of the ammonium oxalate (AmOx) widely used [2].

As previously observed with AmOx, the reaction of a solution of AmMeox with calcium carbonate substrates induces the deposition of mono- or di-hydrated CaOx, one of the mineral phases contained in the historical patinas, able to passivate and protect the surfaces of a great number of monuments and manufacts of historical interest [3]. However, the treatment with AmOx aqueous solutions afforded the formation of the CaOx phase only on the surface of the treated stone samples, and the consolidating ability of this salt resulted not yet been completely satisfactory. [4] In contrast, the solubility of AmMeox in aqueous media is more than double than that of AmOx, so that a larger amount of the precursor of CaOx can be available in solution for the metathesis reaction. Two carbonatic lythotypes, representative for their use in sculptural and architectural context and for their high vulnerability to weathering agents, where chosen for this study. In particular, a biomicritic limestone from Santa Caterina di Pittinuri (Sardinia, Italy) and a type of Carrara marble (Marmo Statuario Michelangelo) were employed. All the samples were previously subjected to artificial aging by thermal stress and then treated with a poultice of a saturated aqueous solution of AmMeox during a period of 24 hours at room temperature.

Results of the treatment with an aqueous solution of AmMeox on these decayed rocks showed some variations in the porous microstructure of the material, due to the presence of the new mineralogical phases. The physical properties of the treated material (total porosity, pore size distribution, size of the new crystals, surface hardness, speed of the propagation of ultrasounds, water absorption behaviour) revealed improvements testifying for a reinforcement induced by newly formed phases. Experimental details and results of this study will be presented.

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Previous assays to the consolidation of pictorial layers in plasterwork using a twelve-month cycle of natural aging. Courtyard of the Maidens, Alcazar of Seville

A. Calero-Castillo, A. García Bueno, V.J. Medina Flórez

Departamento de Pintura (Universidad de Granada), Avd. Andalucía, s.n.
Granada, Spain
anacalerocastillo@hotmail.com

The Courtyard of the Maidens is one of the constructions made by Pedro I (1356- 1366) within the monumental complex Alcazar of Seville. The importance of the palatial city determined its inclusion in the World Heritage List of UNESCO in 1987, along with the Cathedral and the India's Archive. His status as permanent residence of the Spanish monarchs has allowed its preservation over the time. However, it has been intervened several times since its construction.

This sequence of interventions is especially noticeable in the Courtyard of the Maidens plasterwork, where successive pictorial layers and lime layers hide the carving delicacy and the remaining of the original polychrome. In addition, these historical interventions, which were often made with resins and oils, have contributed to the disintegration of materials creating a layer that prevents the permeability of internal materials. Along with the aforementioned, a preliminary study carried out on the plasterwork showed the need of addressing in depth research on candidate materials to be used for the consolidation of its colours, in order to avoid its definitive loss.

This work presents the methodology used to assess consolidating treatments (acrylic resin, ethyl silicate, polyvinyl butyral, barium hydroxide and bacterial biomineralization of calcium carbonate) applied on test specimens made from the materials identified in plasterwork of the Courtyard of the Maidens. The study was performed using a twelve month cycle of natural aging, monitorized by a meteorological station consisted of pyranometer, anemometer, radiation / UV radiation sensor, anti-radiation bell and temperature and relative humidity sensor. Different methods subject to the applicable regulations have been used for the evaluation of the results (e.g. colorimetry study, assessment of the capacity of water absorption, resistance to adhesion or solubility test) (Figs.1, 2).

The results showed the behaviour of the tested consolidating treatments informing the selection of the most appropriate treatment for the consolidation intervention of plasterwork polychrome. Therefore they provided valuable information before facing the intervention of restauration of the Courtyard of the Maidens plasterwork. These results are also applicable to address the restoration of works with similar chronology and conservation problems.

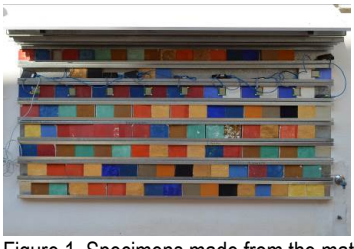

Figure 1. Specimens made from the materials identified in plasterwork.

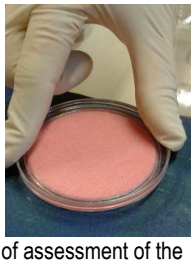

Figure 2. Method of assessment of the capacity of water absorption.

Evaluating the performance of Calcium Tartrate as a Consolidant for soft Limestone

C. Cardona, D. Vella

Department of Metallurgy and Materials Engineering (Faculty of Engineering, University of Malta) Msida, MSD 2080, Malta
christina.cardona.12@um.edu.mt

In this study calcium tartrate was evaluated as a potential consolidant material for a soft Maltese Globigerina Limestone (GL). A 2-molar aqueous solution of di-ammonium tartrate precursor was applied by capillary uptake method. The precursor solution works in a similar way to a conversion coating: upon contact with stone, calcium tartrate forms by dissolution of calcite followed by precipitation of the calcium tartrate consolidant material.

In this laboratory study, the consolidant was tested on three different surfaces using the same stone type: (i) a desalinated stone; (ii) a desalinated and artificially weathered stone; (iii) a desalinated, artificially weathered and salt-loaded stone.

Dried control and consolidated stone test specimens were characterised by different techniques including X-ray diffraction (XRD), scanning electron microscopy coupled with energy dispersive spectrometry (SEM-EDS), infra-red spectroscopy, mercury intrusion porosimetry, contact angle, colour measurements and profilometry. Resistance to salt crystallization and resistance to drilling tests were carried out to evaluate improvements in respectively, the physical durability and mechanical properties of the stone. Water transport properties were assessed by a water absorption by capillarity test.

Results showed that the consolidant was successfully precipitated on all GL test blocks types evaluated. Electron micrographs showed that the consolidant material calcium tartrate favourably deposited over the within stone pores presenting itself as a crystalline layer with distinct crystallographic orientations. The formation of a crystalline form of calcium tartrate was confirmed by XRD. Additionally, mechanical properties and resistance to salt weathering were markedly improved at the expense of the stone's ability to absorb water. This fact was not expected given that calcium tartrate has hydroxyl (-OH) groups that theoretically should improve the stone pore's affinity to water through hydrogen bonding. A reduction in stone water transport properties is indeed not desirable. Electron microscopy and mercury intrusion porosimetry appear to suggest that an over-deposition of consolidant material might have occurred at the stone surface, leading to partial or full surface pore blocking. Remedial action is being proposed to limit this effect.

Preparation and characterization of cellulose nanocrystals for decayed old wood consolidation

R. Basile[1], L. Bergamonti[2], F. Fernandez[1], C. Graiff[2], A. Haghighi[3], C. Isca[2], P.P. Lottici[4], B. Pizzo[5], G. Predieri[2]

[1]Master for "Researcher Experts on Nanotechnology and Nanomaterials for Cultural Heritage" (University of Palermo), Italy
[2]Dip. di Chimica (Università di Parma), Parma, Italy
[3]Dept. of Wood Science and Technology (University of Tehran), Karaj, Iran
[4]Dip. di Fisica e Sci. della Terra (Università di Parma), Parma, Italy
[5] CNR IVALSA, Via Madonna del Piano 10, Sesto Fiorentino, Italy
giovanni.predieri@unipr.it

Wood is one of the oldest materials used in a large variety of human artifacts thanks to its particular aesthetic characteristics and mechanical properties. Wood is an organic, hygroscopic and anisotropic material and for its nature is subjected to physical, chemical and biological degradation. Current treatments adopted for historical wood conservation often have undesirable side-effects which can have an impact on the aesthetical and mechanical characteristics of the wooden artifacts. This work is an attempt to obtain new consolidants inspired by nature, completely compatible with organic substrates such as wood and paper.

Cellulose nanocrystals are new class of cellulose materials that find wide applications in various research areas over the past two decades. Cellulose can be extracted by different materials i.e. wood, cotton, hemp and nanocrystalline cellulose can be obtained by acid hydrolysis of cellulose [1]. The potential applications of cellulose nanocrystal in the area of paper and paperboard manufacture is evident. Cellulose nanocrystals are expected to enhance the fiber-fiber bond strength and, hence, have a strong reinforcement effect on paper materials. The main aim of this study is to test the consolidant efficacy of the CNC on rotted wood samples to improve their mechanical properties. Suspensions of cellulose nanocrystals (CNC) were prepared by sulfuric acid hydrolysis starting from α-cellulose. The crystalline nature of nanocellulose was confirmed by XRD analysis (Fig.1). The CNC sol was applied on wood sample by total impregnation, under vacuum. The products tested were CNC and CNC mixed with lignin and/or PDMS. The mechanical tests were carried out on a Dynamic mechanical analyzer (DMA) in three-point bending. The best results in consolidation efficiency (% improvement of elastic modulus, Fig. 2) have been obtained with CNC alone. Actually, CNC appreciably improves the stiffness properties of the decayed wood, in particular in the case of the maximum decay class (A). Minor results have been obtained in the case lower decay classes (B, C).

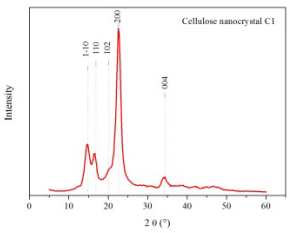

Figure 1. XRD diffraction pattern of synthesized CNC

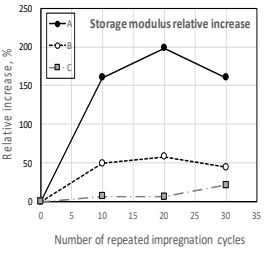

Figure 2. DMA test on decayed wood treated with CNC

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Evaluation of the effectiveness of a surfactant-synthesized PDMS/Silica nanomaterial in granitic rocks

I. de Rosario[1], T. Rivas[1], J. Feijoo[1], M.J. Mosquera[2]

[1]Dpt. Ingeniería de los Recursos Naturales y Medio Ambiente (E.T.S.I. Minas. Universidad de Vigo), Campus Lagoas Marcosende, Vigo, Spain
[2]TEP-243 Nanomaterials (Dpt. de Química-Física, Facultad de Ciencias, Universidad de Cádiz) Campus Universitario Rio San Pedro. Puerto Real, Cádiz, Spain
irosario@uvigo.es

One of the main problems presented by most conventional commercial water repellents is that they are usually applied dissolved in organic solvents, fact that could imply the migration of the polymers towards the evaporation surface previously to the gel formation. In addition, because the polysiloxanes are partially or totally polymerized, the penetration depth achieved is poor and the fine film formed on the surface of the stone is insufficient to increase the mechanical strength. Organically modified silicate (ORMOSIL) has been synthesized by the co-condensation of tetraethoxysilane (TEOS) and poly(dimethylsiloxane) (PDMS) with a neutral catalyst in the presence of a surfactant in order to obtain an only mesoporous nanomaterial organic-inorganic hybrid of double effect (consolidating and water repellent) with a uniform pore size and crack-free. The hydrophobic effectiveness of this nanomaterials in sedimentary and carbonate rocks has been evaluated [1-3], but its effectiveness in granites, the main construction material in NW Spain has not been sufficiently addressed. So, this study has the aim to characterise the efficacy of a new surfactant-synthesized PDMS/Silica nanomaterial as protective treatment on two granites, in comparison with two commercial water-repellents based in silanes-siloxanes products (Tegosivin HE 328 and Tegosivin HL 100).

Whit this purpose, two granites widely used in building construction and restoration in Galicia (NW Spain) with different texture, porosity and mineralogy were used. The application of the products was carried out under different moisture conditions of the rocks and the efficacies of the treatments were evaluated by comparing uptake and dry matter content, static and dynamic contact angles, contact angle hysteresis, distribution and morphology of the coatings on the rock surfaces by SEM, mercury accessible and porosimetric distribution porosity (MIP) and depth of penetration. In addition, the durability of these treatments by means the evaluation of the changes on the hydrophobic behaviour after a salt crystallization acceleration test and after the exposure to UV radiation. The effects of the treatments on the colour and permeability to water vapour of the rocks were also determined.

The results indicate that, despite of the low penetration obtained, the commercial water-repellents showed a higher level of hydrophobicity than the nano water repellent. However, TEOS / PDMS hybrid material allowed better results in terms of durability and depth of penetration; these improvements are related to the modification of the porosimetric distribution of the rocks produced by the product, to the role played by n-octylamine in its basic catalyst action of polycondensation reactions and to the absence of COV's, which allows to reach a percentage of dry matter on the rock higher than that obtained with the rest of products evaluated.

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Synthesis and characterizations of polyacrylate/silica hybrid films for coating applications in Cultural Heritage

F. Sbardella[1,2], M.P. Bracciale[1], M.L. Santarelli[1], J.M. Asua[2]

[1]Department Chemical Engineering Materials Environment (DICMA), (University of Rome "La Sapienza"), Via Eudossiana 18, 00184, Rome, Italy
[2]Department of Applied Chemistry (University of the Basque Country, (UPV/EHU), Centro Joxe Mari Korta), Avenida de Tolosa 72, 20018, Donostia-San Sebastián, Spain
francesca.sbardella@uniroma1.it

In the last years, new inorganic-organic hybrid polymers were used in a wide range of applications as adhesion, biomaterials, protective coatings, composites, microelectronics, thin-films, etc.

In this study, great attention has been paid to optimize the multi-component formulations of the MMA-BA latexes with the addition of two different types of silica: a non-modified commercial one and a laboratory-modified one. Different percentages of the silica in the formulation (2-5-10%) with the combination of different amount of anionic surfactant was studied.

The aim was to combine the high thermal stability and high mechanical properties of the nanosilica with the elasticity and the capability to form coatings of the acrylates, to produce a good protective film that can be applied on building materials (ancient and modern).

The functionalization of the silica improves the compatibility between organic and inorganic phases, but also enhance the interaction between the components at the interface level. In order to have a silica with high affinity with the organic phase, the modification with methacryloxy(propyl)trimethoxysilane (MPS) was performed, with two different solvents.

In order to characterize the final products, we followed an integrated approach based on different analytical techniques (contact angle, DLS, solid-state NMR, tensile test, scrub test, water uptake and TEM analyses) to acquire a deeper knowledge of the characteristics of the latexs and the relative films. Their properties will be useful to define their interaction with different types of stone support, especially bricks, sandstones and limestones.

The results obtained showed that the nature of the functionalization of the silica affected directly the morphology of the latexes.

The addition of different percentages of anionic surfactant improved the stability of the latexes, but the results of the scrub test showed that the high level of surfactant affected the resistence of the film, probably due to the migration of the surfactant on the surface of the film.

The presence of the silica in the polymer matrix showed an interesting improvement in the mechanical properties and in the scrubbing characteristics in comparison with the neat polymer. The properties of the obtained hybrid films can be considered significant as protective coating to improve the durability and the conservation of stone monuments.

Colloidal nanocrystalline semiconductor materials as photocatalysts for environmental protection of architectural stone

F. Petronella[1], A. Pagliarulo[1], M. Striccoli[1], A.Calia[2], M. Lettieri[2], D. Colangiuli[2], M.L. Curri[1], R. Comparelli[1]

[1]CNR-IPCF, Istituto per i Processi Chimici e Fisici, U.O.S. Bari; Bari, Italy
[2]CNR-IBAM, Istituto per i Beni Archeologici e Monumentali; Lecce, Italy
r.comparelli@ba.ipcf.cnr.it

Preventive conservation of historical building and monuments is a crucial challenge. Coating used to protect monument surfaces should provide: i) hydrophobic properties to prevent water infiltration; ii) they should be compatible with the substrate and reversible, iii) resistant to weathering and to UV light; iv) able to preserve the aesthetics of the monuments. So far, protection of stone materials was mainly achieved by means of polymeric coatings, such as acrylic, fluorinated and alkoxysilane. Despite their widespread use, they have shown several drawbacks including loss of adhesion, photo-oxidative irreversible modifications, chemical aging, yellowing and lack of self-cleaning ability. Such properties can be achieved by integrating photocatalytic nanomaterials as TiO_2 in polymer-based coatings [1]. In the present work a preliminary investigation has been carried out, by coating the surface of porous calcarenite called *Pietra Leccese* (PL) with rod-shaped anatase TiO_2 nanocrystals (TiO_2 NRs) capped by oleic acid molecules (OLEA) synthesized by colloidal chemistry routes. TiO_2 NRs were directly applied to treat the PL stone surface. Such an approach has been selected because it allows a prompt evaluation of the nanomaterial properties avoiding the drop of performances that can occur when nanoparticles are embedded in polymeric matrices that are prone to undergo degradation phenomena. Two different deposition techniques, namely casting and dipping, were tested. Colour, wettability, water transfer properties of the stones and stability of the coatings were monitored as a function of time and of the application method. The photocatalytic activity of TiO_2 NRs was tested at solid/air interface, both under irradiation with a solar light simulator and outdoor under real sunlight and weather exposure, by using the azo dye Methyl Red as target compound. The ensemble of results pointed out the high efficiency of TiO_2 NRs that can be recognised as a promising candidate for protection of building materials in the context of the cultural heritage [2].

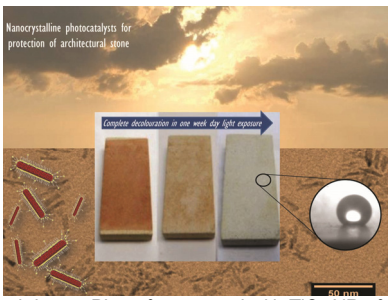

Figure 1: Bleaching of Methyl Red dye on PL surface treated with TiO_2 NR after 1 week exposure to day light. Inset: Water contact angle highlight the hydrophobicity of the treated surface.

Acknowledgments: This work was supported by the Apulia Region Funded Projects NanoApulia (MDI6SR).

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Chromatic reintegration in marbles of historical heritage. Evaluation of its effectiveness and durability outdoors

M.P. Sáez-Pérez[1], J.A. Durán-Suárez[2], J. Rodríguez-Gordillo[3]

[1]Department of Architectural Constructions. Advanced Technical School of Building Engineering, University of Granada, Granada, Spain
[2]Department of Sculpture. Faculty of Fine Arts, University of Granada, Granada, Spain
[3]Department of Petrology and Mineralogy. Faculty of Science, University of Granada, Granada, Spain
mpsaez@ugr.es giorgio@ugr.es gordillo@ugr.es

The conservation of material heritage represents a complex field of multidisciplinary research. Current restoration actions in sculpture and architectonic elements of marble, with or without polychromy, exposed to the elements, determine the choice of pigments and agglutinants for their chromatic reintegration, both regarding tone matching in relation to the original altered and unaltered support as well as the time course of the degrading environmental agents that the paints used could encounter in these restoration efforts.

Different studies corroborate that knowledge of the material composition of the pigments, as well as the technique and agglutinant used are essential to define the degradation processes that they might undergo after being applied on the corresponding supports to be restored. Given the breadth of materials currently used in the chromatic-reintegration phase of the supports, the use of classical materials as well as the new incorporation proves indispensable for precise experimentation and solution of the problem.

The present study concerns the white synthetic inorganic pigments (zinc and titanium) in different natural and artificial agglutinant media to be applied in corrections of colour loss on marble supports exposed to the elements. For this, the impact of 11 agglutinants used in this study were analysed with respect to the whitening capacity of zinc and titanium oxides, with the aim of choosing the pictorial mixture most appropriate for the reintegration of the historical Macael marble supports. Also, a study was made of the colour gamut of the Macael marbles most commonly used in historical and artistic heritage from 150 samples of this type of material. In parallel, to evaluate their resistance to environmental exposure, both the white colour mixtures as well as the marble samples were subjected to accelerated ageing cycles (UV, infrareds, and saturated atmospheric humidity). All this was undertaken to specify as accurately as possible the reintegration materials most suitable for this type of restoration. The composition of the pigments, agglutinants, and marble supports were studied by DRX, mass spectrometry, scanning electronic microscopy, and colour measurement by quantitative spectrophotometry, before and after the induced ageing.

The main results have indicated a substantial colour variation in the reintegration materials, basically a loss of luminosity and subsaturation, as well as a slight tonal skew towards yellow. Similarly, in the marble supports, noteworthy shifts were observed, such as darkening and yellowing.

Hemp concrete for the sustainable retrofit of the vernacular architectural heritage in the region of Senhaja Srair (Morocco)

M.P. Sáez-Pérez[1], J.A. Durán-Suárez[2], M. Brümmer[3]

[1]Department of Architectural Constructions. Advanced Technical School of Building Engineering, University of Granada, Granada, Spain
[2]Department of Sculpture. Faculty of Fine Arts, University of Granada, Granada, Spain
[3]PhD Program in History and Arts (Territory, Heritage and Environment), University of Granada, Spain
mpsaez@ugr.es giorgio@ugr.es mbrummer@correo.ugr.es

The protection and restoration of rural anthropological architectonic heritage requires adequate knowledge of the pertinent construction techniques and typologies. The structural layout of such architecture, as well as the exclusive use of local materials, specific to the geographic context where it developed emphasize the conservational value both in the maintenance of the this heritage as well as the use of restoration materials linked to the vernacular tradition.

The present work, conducted in Senhaja Srair, an ethnic Berber group of the central Rif area of Morocco, is based on an integral approach to restoration that starts with the most exclusive qualities of its architectonic heritage, its formal composition, organized in houses of one or two floors around a central patio, as well as its building composition based on the use of naturally existing resources in the local surroundings, primarily earthen (clays, slates, and quartzites), wooden (cedar from endemic forests), and cultivated (different species, notably hemp from ancestral cultivation) with the main aim of applying emerging conservation and restoration trends that have a positive impact on the environmental and socioeconomic aspects of the area.

The abundance of mortar and concrete in different locations of this vernacular architecture (e.g. walls, roofs, foundation, and plastering) focuses attention on these as being damaged and highly deteriorated and thus as the main elements to be reinforced and restored. Most of the native mortars characterized are made with materials based on clays present in the sediments of the area and fragments of feldspar and quartzite, which have high compactability and plasticity. This served as the basis to propose new mortars for repairs and restoration, starting with the above-mentioned natural agglomerants together with the incorporation of dry vegetable fibres from local hemp plants, which improve the durability, thermal and acoustic insulation, and the habitability of the architectural structures restored.

The materials studied are two types of restoration mortar: MN1, based on a natural agglomerant from local clayey sediments, straw, and hemp fibre. The physical trials made for these new mortars indicate improvements for construction, adhesion, and durability, as well as thermal and acoustic conductivity values, as well as hygrothermal performance.

Virtual exhibitions and educational methodology research: an Americanist case of study

R. López Guzmán, A. Contreras-Guerrero

Department of History Art, University of Granada.
Faculty of Philosophy and Letters, Campus of Cartuja, 18071-Granada, Spain
rlopez@ugr.es contreras@ugr.es

The possibilities offered by Internet as a decentralized and global network allows the creation from anywhere on the planet. Thanks to it we are able to create visual virtual structures with artistic, aesthetical or educational purposes in which the user can adopt different roles: from simple observation to proactive participation, even taking part in the content creation.

In this regard, museums and cultural institutions offer a large amount of audiovisual resources that allow the exhibitions that had took place in their facilities to continue in time; furthermore, there are virtual exhibitions that don't exist physically. The options between these two choices are numerous.

In this cyberspace of infinite and variable options, our research group proposes a museographic project that is based on the digital modeling of real objects and an architectural space that combined to create virtual exhibitions; our aim is to put forward an educational research model supported by a previous scientific work and results.

Under these criteria, we had created the exhibition "From South America: Viceroyalty Art in Andalusia". It brings together the aforementioned characteristics of research and knowledge transfer as an integral part of our interests. It is divided in three exhibition halls that create an immersive tour experience. This tour has not a single or obligatory route; it has two information options, a minimum and a complementary one, depending on the needs of the visitor. We also have created traditional characteristic of real exhibitions such as the catalog or text panels, which following the accessibility character that we aim, can also be downloaded from the web.

In addition, the pieces shown were chosen following heritage criteria, which are based on identity and historic concepts. This type of selection is absent in more generic and linear models. The value of these pieces, generally treated as secondary, will force us to consider their state of conservation and the need to consider them in a more democratic and multi-pluralistic historiography.

Producing Hydrophobic Concretes

J. Gonzàlez Coneo, F. Elhaddad, M.J. Mosquera

TEP-243 Nanomaterials Group, Physical-Chemistry Department, University of Cadiz, Campus Universitario Rio San Pedro 11510 Puerto Real (Cádiz), Spain
jorge.gonzalezconeo@alum.uca.es

Water is the main vehicle of pollutants and other agents (chlorides and sulfates) producing concrete decay. Thus, the production of hydrophobic concretes is a relevant challenge. In this study we evaluated the effectiveness of a hydrophobic nanomaterial developed and patented by the University of Cadiz to produce hydrophobic concretes. The nanomaterial was synthetized by mixing silica oligomers (TES40) and organosiloxane (PDMS) in the presence of the surfactant. The effectiveness of the hydrophobic product admixture on concrete was characterized by contact angle measuring. In order to confirm the hydrophobic behaviour of the concrete, the samples were subjected to a test of water absorption by capillarity (WAC) as recommended in UNE-EN 192514. Changes in the properties of the samples, porosimetric distribution, vapour diffusivity, FTIR and colour were also evaluated. We have also observed the changes of morphology of the stone after treatments by SEM and AFM.

The results of this study showed that concretes with nanostructured and hydrophobic surface were obtained. Specifically, static contact angles around 130º and 85% reduction in water absorption were obtained.

This work has been supported by the Spanish Government/ FEDER-EU (MAT2013-42934-R).

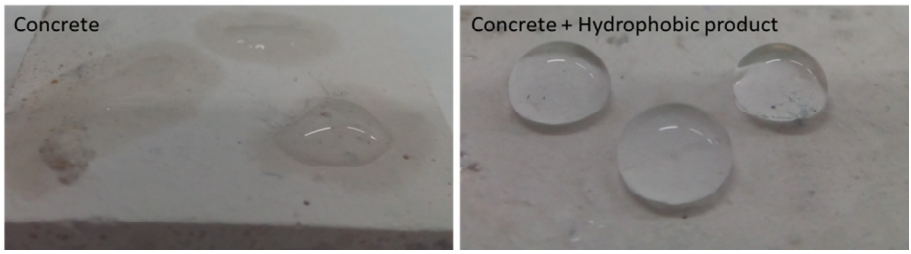

Figure1. Images of water drops in concrete surfaces.

Contemporary paints: materials identification and fabrication techniques

C. Garcia,[1] M. Gomez,[1] T. Lopez-Morán,[2] M. Lazzari,[1] D. Reggio[1]

[1]Center for Research in Biological Chemistry and Molecular Materials (CIQUS)
University of Santiago de Compostela, 15782 Santiago de Compostela, Spain
[2]Centro Galego de Arte Contemporanea (CGAC) 15703 Santiago de Compostela, Spain

The long-lasting collaboration between the University of Santiago de Compostela and the CGAC conservation laboratory [1] is giving the chance to investigate two twin paintings by the artist Manuel Eirìs, titled *Aún te vas a enfermar de saturnismo (2013, 2015)*. Our primary research question concerns the essential role of materials in differentiating these two artworks. The artist intended to replicate the same concept by using the materials available to him in the very moment of creation, repeating the same fabrication process (e.g. horizontal painting). The second research question explores to what extent the effects of such differences will affect the future behaviour of the materials, therefore their conservation; and how chemical analyses can provide useful information to predicting such behaviours.

A close collaboration between the artist, the conservator and the scientists allowed to initiate an interview-based contemporary art documentation program. Documenting the fabrication technique and asking to the artist his reasoning behind conservation issues revealed to be a key factor of this research. For both artworks, linen fabrics were adopted as substrates of the painted layers applied on various polymeric preparatory materials. The identification of the materials comprised FTIR-ATR and UV-Vis spectroscopy, and spectrophotocolorimetry, whereas the long term stability was investigated under accelerated ageing conditions [2].

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Some insights on the photoinduced degradation of cellulose nitrate

S. Kunz[1], E. Gómez-Sánchez[2], J. Pesch[1]

[1]Faculty for Organic Chemistry, University of Applied Science Nuremberg
Prinzregentenstrasse 47, 90491 Nürnberg, Germany
[2]Materialkundelabor, Deutsches Bergbau-Museum Bochum
Hernerstrasse 45, Bochum, Germany
simon_kunz@gmx.de

Cellulose nitrate (CN), one of the first synthetic polymers, had an impact on the life of societies over many generations like few other polymers. First commercialised as a surrogate for ivory or tortoiseshell and later as a product for itself, notably enabling the film industry, or as lacquers for wooden furniture, the latter still in production, CN can be found in many museums, such as those collecting technical heritage.

CN is well known for its intrinsic instability. Due to its military use as smokeless-gunpowder or rocket propellant (degree of substitution 12.2 – 14.1 %N), both the thermal and hydrolytic degradation of CN are well studied processes in higher substituted CN (12.2 – 14.1 %N). On the contrary, photoinduced degradation processes, especially on lower substituted CN such as those used in lacquers (10.7 – 12.2 %N), have been thus far less studied. It is indeed known that CN yellows over time after having been exposed to certain wavelengths during relatively short periods of time, time after which the degradation can further proceed in the absence of light. Without such ‚triggering', CN can remain colourless and stable over decades when stored in the dark. The mechanisms and species responsible for the colour change, however, have not yet been identified. Knowledge about these mechanisms, the wavelengths involved in this degradation and the role of the additives could help establish preventive conservation measures for this material.

The present work presents preliminary results on the photoinduced ageing of CN. In the frame of the study, pure CN and a CN-lacquer were chemically characterised using various spectroscopic techniques such as ATR-FTIR, UV-Vis and ^{1}H- and ^{13}C-NMR. Furthermore, the CN was artificially aged for several days (1, 2, 4 and 8 days) with a UV-Vis light source and compared with the unaged counterpart. After a second ageing period in darkness at room temperature for 6 months (ONGOING) the aged samples will be reinvestigated. So far, infrared spectroscopy allowed to follow the increase of the carbonyl band upon ageing, while UV-Vis and NMR should allow to follow the appearance of absorbing species and identify their key structural features, respectively (ONGOING ANALYSES). The additives of the CN-lacquer were identified using GC-MS, allowing to identify a range of plasticisers; the reaction of the additives with NO_2 as described in the literature will be monitorised with ageing time. The results of the evaluation of the triggered samples at different times will be presented at the conference.

A non-destructive approach to the study of 20th century gelatine negatives

M. Nunes[1], S. Costa[1], C. Miguel[1], A. T. Caldeira[1,2], T. Ferreira[1,2]

[1]HERCULES Laboratory, University of Évora, Évora, Portugal
[2]Chemistry Department at the Science and Technology School, University of Évora, Évora, Portugal

In the mid-19th century photography enthusiasts witnessed a remarkable series of technological innovations. One of these was introduced in 1871 by Maddox who presented a process based on the use of a gelatine emulsion which was named the gelatine dry plate negative [1]. The replacement of collodion by gelatine was a major and far-reaching technical innovation in the history of photography [2]. Compared to their predecessors, the gelatine dry plate not only allowed shorter exposure times as its production was much faster and freed photographers from the need to carry a portable darkroom into the field. Gelatine dry plates are in fact gelatine emulsion plates where gelatine is used as the binder for the photosensitive silver halides. The silver halides were slowly precipitated and stayed in a suspended form in the matrix by adding bromide or iodide of different metals to the gelatine followed by a silver nitrate solution. The emulsion was then poured onto glass support and dried before use. The image obtained this way had an exquisite clarity and detail [1, 2]. These photographic negatives have complex physical and chemical structures whose preservation presents special challenges. Gelatine negatives are prone to different types of degradation phenomena, namely physical, chemical and microbiological, that can occur in the binding media and in the glass support. As to the physical damages, they usually result of improper handling and housing while chemical damages are due to the interaction between the different constituents and the environmental conditions, namely temperature and humidity, and the decomposition of the gelatine itself [3].

In this work, two gelatine negatives dated from the 20th century, of Eduardo Nogueira's (1898-1969) authorship and belonging to the Photographic Archive of Évora, were studied. The present work aims to evaluate the materials used in the negatives production and to show some mechanical and chemical degradation patterns. An approach of non-destructive in-situ analytical techniques were used for the plates' characterization and degradation patterns. Technical photography under different illuminations and optical microscopy (MO) were used as a primary tool for morphological evaluation. Scanning electron microscopy, in the variable pressure mode, coupled with energy dispersive X-ray spectroscopy (VP-SEM/EDS) was also used for more detailed morphological aspects and for the study of the inorganic materials used in the plates' preparation and the degradation compounds formed. Micro-Fourier transform infrared spectroscopy (μ-FTIR) was particular important for the binder analysis.

Acknowledgements: The authors acknowledge the Photographic Archive of Évora for the negatives supply.

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TiO_2/SiO_2 photocatalysts for application as self-cleaning coatings on historic concrete

S. Khannyra[1,2], M. Luna[1], R. Zarzuela[1], M. Addou[2], M.J. Mosquera[1]

[1] TEP243 Nanomaterials group, Departamento de Química Física, Universidad de Cádiz, Facultad de Ciencias Campus Universitario Río San Pedro s/n. 11510 Puerto Real, Cádiz, Spain
[2]Optoelectronic and Physical Chemistry of Materials and Environmental Laboratory, Faculty of Science, Kenitra, Morocco
khannyra.souad@gmail.com

Recently, the preservation of building materials has increasingly gained attention from many research fields due the rise in atmospheric contamination, especially on urban areas. Historic concrete buildings are habitually exposed to a wide range of contaminants, including particulate matter and other components like organic and elemental carbon, and nitrogen oxides. These contaminants tend to deposit extensively on the surface of concrete buildings, which promotes their decay in the form of aesthetical and structural damages over time.

The development of self-cleaning surface treatments could be a very promising approach in order to preserve the original aesthetic aspect of surfaces and decrease the deposition of pollutants, reducing soiling and the onset of degradation processes on concrete surfaces. Since TiO_2 nanoparticles (TiO_2NPs) photoactivity was discovered, it has become the most popular photocatalyst for several reasons: stability, availability, low cost, lack of toxicity and excellent photocatalytic properties. A layer of titanium dioxide applied on the concrete can contribute to air-purifying and self-cleaning properties due to photocatalytic processes activated by sunlight.

In the present work we investigate the photocatalytic performance under visible light of coatings containing TiO_2 modified by gold nanoparticles on concrete samples. This self-cleaning ability is further improved by the photo-induced hydrophilicity on the treated surfaces. The self-cleaning effect was evaluated for two different staining agents: (1) methylene blue, as a model agent. (2) Soot, as an agent found in real urban and industrial settings. The degradation of both methylene blue and soot on the treated concrete samples is evaluated by means of colorimetric measurements.

Concrete facade conservation of the Peru Pavilion of Seville (1927). Analysis of decay and evaluation of protection treatments

V. Flores-Alés[1], F.J. Alejandre[1], R. Villegas[2], F.J. Blasco[1], J.R. Baeza[1]

[1]Architectural Constructions II Dpt., University of Seville
Av.Reina Mercedes nº4, 41012 Seville, Spain
[2] Chemical and Environmental Engeneering Dpt., University of Seville
Camino Descubrimientos, s/n. Isla Cartuja, 41092 Seville, Spain

The Peru Pavilion of the Iberoamerican Exposition 1929 (IE) was projected in 1927 by the architect Manuel Piqueras Cotolí (1886-1937). Aging and weathering with high humidity conditions and little sunlight, because it is placed surrounded by great size trees, have developed a constant decay. Its proximity to Maria Luisa Park and the lack of maintenance of drainage system of rainwater favours mentioned moisture conditions. The building is included in the IE and Maria Luisa Park Cultural Interest Catalogue.

The aim of this work is to analyze and determine the origin of the observed pathologies in the original concrete forming the ornamental elements integrated into the brick facade of the Pavilion and later evaluate the conservation treatments effects. Three cores were drilled in order to analyse the main chemical, mineralogical, physical, structural and mechanical properties to establish their conservation status. XRF, XRD, soluble salts content, carbonation depth, porosity accessible to water and compressive strength were the techniques and test used.

In order to evaluate the conservation treatments selected and their effects, compatibility with the original concrete, products efficacy and performance against existing aggressive agents was studied determining the velocity of ultrasound transmission, colour, vapour permeability and water absorption by capillarity. The same properties have been measured before and after subjecting the samples to an accelerated thermohygrometic alteration test.

Chemical analysis results do not confirm enough amount of soluble salts presence to develop a degradative process by crystallisation and efflorescence formation, nor to accelerate oxidation processes of steel elements that assemble the structure of concrete. There has been a significant advance of carbonation front causing steel depassivation and the consequent loss of protection against atmospheric agents with oxidant capacity.

With respect to treatments, the most decisive property observed in concrete conservation is the permeability to liquid water, being essential to protect the concrete with water- repellent products to mitigate/decelerate the oxidant reaction that is favoured by concrete carbonation and accelerated by the rain water availability.

Isotopic composition of Lead used in the El Giraldillo Casting

J.M. Gallardo[1], M. Hunt[2], E. Díaz-Gutiérrez[3]

[1]Departmento de Ingeniería y Ciencia de los Materiales y el Transporte, University of Seville, Camino Descubrimientos s/n, 41092 Sevilla, Spain
[2]Facultad de Geografía e Historia, University of Seville, Doña María de Padilla, s/n, 41004 Sevilla, Spain
[3]Asociación de Investigación y Cooperación Industrial de Andalucía, Camino Descubrimientos s/n, 41092 Sevilla, Spain

The foundry tale related to Benvenuto Cellini Perseus depicts a shop got in fire, an unattended dropping furnace temperature and the household tin cutlery and dishes thrown into the melt to decrease frizzing temperature. A parallel, but not so complete history is known about the casting of El Giraldillo by Bartolome Morel, some five years later after the previous history. Nevertheless, in this case Tin content is relatively low and Lead content is above the usual values for Renaissance bronze statues. A characterization of Lead isotopic composition may reveal whether it comes from a single source, i.e., Lead was bought and added intentionally to the melt or there were used every lead object at hand in a hurry to decrease frizzing temperature. In addition, some other lead objects retrieved during the 2001-2005 restoration of El Giraldillo have also been analyzed.

Reneration Project Room D. Manuel – National Tile Museum (Lisbon – Portugal)

F. Barbosa Araújo, C.J. Abreu da Silva Costa

Atelier Samthiago – Conservation and restoration
Rua de Ourense, 121 – r/c – 4900-374 Viana do Castelo, Portugal

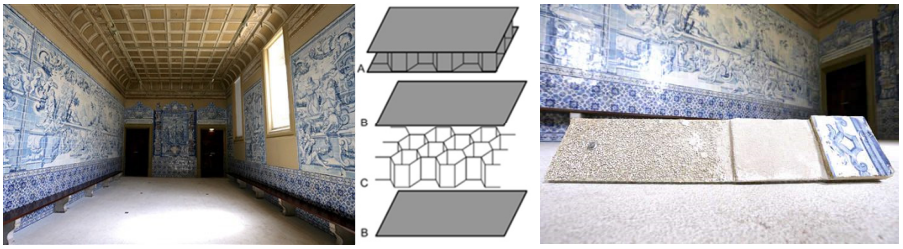
National Tile Museum, in Lisbon (Portugal), is the main focus of interest and study for the Portuguese tiles; this kind of art is considered nowadays as one of the main icons of Portuguese Heritage, lying ongoing UNESCO candidacy of the Portuguese Tile to Heritage of the Humanity.

In this context, and input into the current practice of preservation and conservation of the Portuguese tile heritage, one of the main rooms of this important National Museum - D. Manuel Room – was recently intervened.

This intervention, promoted by the General Directorate of Cultural Heritage of the Portuguese Ministry of Culture and held under the patronage of Millennium BCP Bank Foundation, is revealed as crucial, not only from the iconographic and typological point of view, but also from the museological perspective. It actually allowed, for the first time in history, the D. Manuel room was open to the public and framed on regular circuit of the Museum visit. In addition, it made possible to know the important work of Manuel dos Santos, one of the most significant names of the "Cycle of the Masters", the golden period of Portuguese tiles.

Nevertheless, the greatest value of the work lies in the technical aspect: an innovative solution which seeks to cancel permanent causes and consequential pathologies associated to the presence of moisture and circulation of soluble salts, one of the main causes of tile degradation.

The solution passed through the creation of a box-to-air, on which the tiles were applied in *Aerolam*® plates - material used in the aerospace industry. It was the first time this procedure was used in Portugal in tiles. It has numerous practical advantages: allows the panels to be applied in its original location and the use of a traditional method of settlement of the tiles on the boards; still, it allows that the flows, transportation and crystallization of salts remain girded the-box-to-air, not interfering with the health and good conservation of the tile panels.



As described, this is a very important intervention, not only individually analyzed, but also and above all as a precedent in the technical future of conservation and tile restoration, thus it contributes to the recognition and appreciation of the Portuguese tile heritage and its safeguarding, safety, conservation, restoration, and enjoyment disclosure.

3D techniques for the reconstruction and analysis of high sensitive archaeological sites: the Galerías de las Huellas (Ojo Guareña, Burgos, Spain)

A. Benito-Calvo[1,2], A. Martínez-Fernández[1], A.I. Ortega Martínez[1,2,3], T. Karampaglidis[1,2], F. Ruiz García[2], M.A. Martín Merino[2], I. Campaña[1], E. Bruner[1]

[1]*Centro Nacional de Investigación sobre la Evolución Humana (CENIEH), Paseo Sierra de Atapuerca 3, 09002, Burgos, Spain*
[2]*Grupo Espeleológico Edelweiss. Excma. Diputación Provincial, 09071, Burgos, Spain*
[3]*Fundación Atapuerca, Carretera de Logroño 44, 09198 Ibeas de Juarros, Burgos, Spain*

The Galería de las Huellas site (Burgos, Spain) is located at the third level of the Ojo Guareña multilevel karstic system, in two passages whose floors preserve several tracks of Palaeolithic human footprints. They are preserved on unconsolidated and wet loam sediments, very sensitive to any physical approach to document and study their geometry and spatial distribution. In this work, we show the work carried out at this site focused on the accurate three-dimensional identification and mapping of the footprints, applying non-destructive and non-invasive methods to prevent potential damages. In order to identify and map the footprints, first a topographical survey was carried out using 3D laser scanner techniques. This technique allowed capturing high resolution 3D point clouds, without walking on the sensitive areas. From 3D data we applied several morphometric indices to enhance the floor morphological features and recognize footprints. Footprint mapping was subsequently carried out using automatic methods, such as GIS and 3D morphometric classification techniques, and then compared with results derived from manual digitalization. This method has allowed us to obtain a spatial distribution model for the Palaeolithic human itinerary, without causing any interference at the site and reducing time-consuming processes, such as manual digitalization of archaeological geometries. These techniques can be applied to recognize and analyze other archaeological items or features.

Single set-up for pulsed laser excitation of Raman-LIF-LIBS signals: analysis of heritage stone and mural paint samples

M. Oujja[1], M. Sanz[1], E. Carrasco[1], V. Detalle[2], M. Castillejo[1]

[1]*Instituto de Química Física Rocasolano (CSIC), Serrano 119, 28006 Madrid, Spain*
[2]*Centre de Recherche et de Restauration des Musées de France, 14 quai F. Mitterrand 75001 Paris, France*

Hybrid instruments, where a single pulsed laser source serves for excitation of Raman, laser induced fluorescence (LIF) and laser induced breakdown spectroscopy (LIBS) signals, provide detailed, complementary molecular and elemental analytical information that allows the identification of materials of cultural heritage substrates and for studying the state of conservation. The selection of excitation wavelength is crucial in order to provide meaningful spectral information in the three signal modalities and strongly depends on the type of sample under study; however ultraviolet excitation wavelengths allow collecting LIF spectra for a wider range of materials.

In this work, we present the analysis of heritage stone and model mural paint samples using a laboratory–based Raman-LIF-LIBS system using as exciting source a Q-switched Nd:YAG laser operating at its fundamental wavelength of 1064 nm or its harmonics of 532, 355 and 266 nm (pulses of 17 ns, repetition rate of 10 Hz). The system includes the appropriate optics for beam delivery and signal collection, including Notch and cut-off filters to reject the laser Rayleigh scattered light, and a spectrograph (Oriel MS257™ 1/4 m, 300 or 1200 lines/mm gratings) coupled to a time-gated intensified charge coupled device (iStar CCD 334T, Andor Technologies) for spectral analysis and detection with temporal resolution.

Heritage stone samples of limestone, marble, alabaster and gypsum were examined upon excitation at 355 nm. Raman spectra display the characteristic vibration modes of free CO_3^{2-} (at 1085 cm^{-1}) of calcium carbonate in limestone and marble and of SO_4^{2-} (at 1008 cm^{-1}) of calcium sulphate in alabaster and gypsum. LIF spectra reveal a characteristic band centred at 382 nm in alabaster and a broader band at longer wavelengths for the other three samples. LIB spectra revealed the elemental stone composition, displaying line emissions of Mg, Si, Ca, Al, Mn, K, Sr, Na, C_2 and CaO, with different intensities according to the stone sample.

Model mural paint samples, based on traditional blue, black, yellow and red pigments, prepared as fresco or mixed with egg yolk and linseed oil binders, were also studied with excitation at 355 nm. The complementary information provided by the Raman, LIF and LIBS signals allowed the identification of the pigments used in the samples preparation, i.e. blue azurite, manganese black, nickel titanium yellow and red vermillion.

A discussion on gamma radiation hazards related to granitic materials and its implication on historical buildings use

J. Sanjurjo-Sánchez[1], C. Alves[2]

[1]*Instituto Universitario de Xeoloxía "Isidro Parga Pondal", University of A Coruña, A Coruña, Spain*
[2]*Lab2PT (FCT UID/AUR/04509/2013; FEDER COMPETE POCI-01-0145-FEDER-007528) and Earth Sciences Department, School of Sciences, University of Minho, Braga, Portugal*

Among ionizing radiation exposure sources for people, building materials may contribute to radiological hazards by external dose (gamma radiation). The Council of the European Union, in Article 75 of Directive 2013/59 / EURATOM of 5 December 2013, presents in Annex XIII an "Indicative list of the types of building materials to be taken into account due to their emission of gamma rays ", highlighting some natural materials, namely granites, that deserve special attention and for which activity analyses are indicated. Granites constitute the main geologic material in historical constructions of NW Portugal and Spain (they might have variable importance according to different building typology). In the present work we lay out our research regarding radiological hazards related to granites used as building materials in the perspective of its implications for the use of historical buildings where granite is the main material. It is proposed that this issue is relevant for the management of historical buildings with granitic materials for two reasons:

- To assess possible limitations to the use of spaces, particularly in relation to employees working on them (since they are exposed for longer periods), as well as the need to adopt monitoring and intervention measures;

- To prepare responses (with clear explanations) for any outbursts of alarmism associated with these issues, such as those which have been observed in relation to other applications of granitic materials with lesser amounts (e.g. kitchen tops).

In this work will be discussed several scenarios for the conservative assessment of gamma radiation hazards in historical buildings considering published values of radioisotopes in granitic rocks which will be compared with the criteria of Directive 2013/59/EURATOM but also with assessments based on the application conditions of the materials, particularly in terms of area extension (related to diverse building typologies) and time of exposition (assessing the impact of the different modelling scenarios on the maximum number of hours per year that should be allowed for a given reference value for external dose). These results will be compared with published gamma radiation measurements performed in situ (in historical buildings with granites) by portable gamma-ray spectrometry to assess the characteristics of the spaces with increased likelihood to gamma radiation exposure.

Spectroscopic and optical techniques applied to the characterization of an anonymous painting of a *Virgin with Child*

M.J. Nuevo[1], M.A. Ojeda[2], A. Martín Sánchez[1]

[1]Departamento de Física. Universidad de Extremadura. Badajoz, Spain
[2]Centro de Conservación y Restauración de Bienes Culturales, Dirección Gral.de Patrimonio Cultural, Consejería de Educación y Cultura, Gobierno de Extremadura, Mérida, Spain
maria@unex.es

Several techniques have been applied to the study of the materials used in the composition of an anonymous easel painting whose topic is a Virgin with the little Jesus on her lap (Fig. 1), exhibited at the Secondary School "Barbara de Braganza" in Badajoz, Spain. This non-named painting seems to be a copy of the famous *Virgin with Child* by Adrian Isembrandt. Because of its deterioration conditions, some cleaning and restoration works were required to this artwork, in order to prevent further damages. Throughout these processes, various studies were carried out focused on finding out about the approximate date or even the possible pictorial school which this painting could belong.

Figure 1

Figure 2

A first step was the application of the X-ray fluorescence technique [1] (EDXRF), carried out in the restoration-centre laboratory. In spite of the elementary information of this method, it has the advantage of being a non-aggressive and a non-destructive spectroscopic technique that can be easily ported to practically any place [2, 3]. This basic method provided some hints about the possible date of this painting, suggesting a date not earlier than the XIX century. In order to confirm this hypothesis and others about the elaboration of this artwork, small pieces of samples were removed and embed in resin, and other deeper and more powerful technique, such as scanning electron microscopy (SEM-EDX), was carried out at the facilities of the research-support services of the University of Extremadura (SAIUEX). Moreover, on the other hand, the optical technique of illuminating with infrared light has also been applied to the study of the composition of several pigments used in this artwork (Fig. 2). Although no definitive conclusion about the date can be affirmed, the results from these two last techniques suggest that this painting could be older than initially assumed.

[1] M.J. Nuevo et al., *Appl. Radiat. Isot.* 69 (2011) 574-579.
[2]M.J. Nuevo et al., *X-Ray Spectrom.* 41 (2011) 1-5.
[3]M.J. Nuevo et al., *Microchemical J.* 124 (2016) 675-681.

RAMAN/LIF non-invasive microanalysis of frescoes from St. Alexander catacombs in Rome (Italy)

S. Almaviva[1], R. Fantoni[1], F.Colao[1], A. Puiu[1], F. Bisconti[2], V. Fiocchi Nicolai[2], S. Cascioli[3], S. Bellagamba[4]

[1]ENEA, Italian national agency for new technologies, energy and sustainable economic development, via Enrico Fermi, 45, 00044, Frascati (Rome), Italy
[2]Pontificia Commissione di Archeologia Sacra, Via Napoleone III, 1, Rome, Italy
[3]Restauro e Conservazione di Opere d'Arte, Fiumicino (Rome), Italy
[4]Bellagamba Sonia, Restauratrice, Rome, Italy
pcas@arcsacra.va stella.cascioli@tin.it

The complex of the early Christian catacombs of St. Alexander was discovered in 1854, when the Sacred Congregation of Propaganda Fide led a campaign of excavations in locality Coazzo, near Rome. The remains of a basilica adjacent to a graveyard full of inscriptions and paintings were discovered.

The basilica was probably built by a local clergy, who provided the Government of the inhabitants of rural communities of Ficulea and Nomentum. The small burial center was recognized as the graveyard of St. Alexander pope (106-115 AD), for the discovery of a dedicatory inscription that indicated the graves of Alexander and his fellow martyrs Evenzio and Theodule, probably victims of the persecution of the Emperor Traiano (3 May 115 AD).

The catacomb consists of two separate cores developed on one floor with a network of interconnecting tunnels.

In the framework of the COBRA project (ENEA technologies for cultural heritage, availability and perspectives for technology transfer) two frescoes (named G6 and G15) of the catacombs were non-destructively analysed by micro-Raman spectroscopy, in order to determine the identities of the pigments and materials thereon.

Pigments like red ochre, yellow ochre and minium were detected after scanning the coloured areas for few tenths of seconds (Fig.1), whereas calcite was detected as pictorial background material. Further information on any surface contamination by organic residues, salt deposits, or the presence of consolidating substances (Primal, Paraloid) were obtained with the synergistic use of LIF (laser-induced fluorescence) spectroscopy, another non-destructive, contactless, laser-based technique that allowed to clearly identify large areas subjected to conservation treatment and localize the presence of any contaminant.

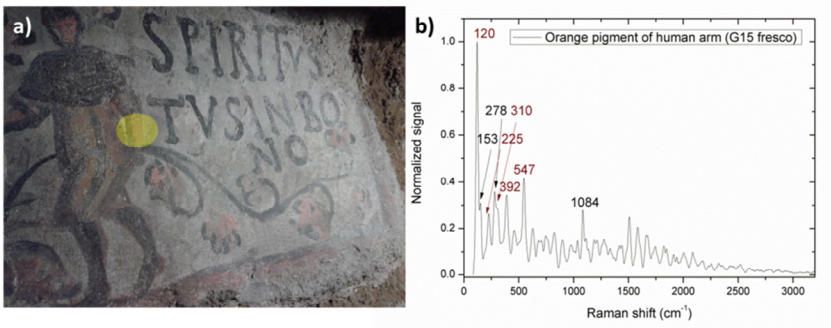


Figure 1. a) Portion of the G15 fresco inside the catacomb with one of the scanned area (in yellow). b) Raman spectrum of the analysed pigment (minium + calcite).

Analytical investigation of Mudéjar polychrome on the carpentry in Mudéjar Palace of Alcázar of Seville using non-invasive analytical techniques

M.D. Robador [1], L. de Viguerie[2], M.A. Garrote[1], J. Castaing[2], J.L. Perez-Rodriguez[3]

[1]Technical Architecture Faculty, University of Seville, Seville, Spain
[2] Laboratoire d'archéologie moléculaire et structurale, Sorbonne Universités, UPMC Univ Paris Paris, France
[3] Materials Science Institute of Seville (CSIC-Seville University), Seville, Spain

The King Pedro I built the Mudéjar palace between 1364 and 1366 in Seville (Spain) which is an example of the Andalusian Mudejar style. Wood was frequently used to performed important artefacts of the Mudéjar monuments. This work deals with the use of non-invasive techniques, XRF, XRD and Raman spectroscopy, for the characterization of polychrome used on the carpentry of Mudéjar Palace of Seville Alcázar. The study was carried out in the carpentry of *Cuarto Real Alto* and *Patio de las Doncellas* (Fig. 1 shows photos of some zones of the carpentry studied in this work). We have investigated in-situ the polychrome doors by means of portables XRF and Raman spectroscopy. XRD and Raman spectroscopy have also been used complementary on tiny samples. The main objective of this work was to elucidate if the materials used and if the pigments are original or were modified during the different restorations realized in the Mudéjar Palace.

The study of the polychromy from *Cuarto Real Alto* revealed yellow ochre, vermilion and azurite respectively for yellow, red and blue colours. Bone and carbon black have also been used as well as gypsum and lead white for white and/or ground. The analysis made on the metallic sheet showed high amount both iron and gold, which suggested that, this sheet was made with gold leaf on bole (above a gypsum ground).

In the doors of *Patio de las Doncellas*, in addition to those pigments, green colour was obtained with a copper pigment. More interestingly XRF analysis on the blue colour showed the presence of Si, Al, Na, S and K characteristic of artificial ultramarine blue. XRF analysis performed in situ showed that the leaf adhered to the surface is composed of gold, copper, silver and zinc. Besides, the presence of lead chromate showed that the actual gilding was realized after the year 1818. The presence of such pigments that was discovered and applied in 19th century confirmed that the paints were not original and had been changed during the restoration performed in 19th century in the Alcázar. This pigment (lead chromate, yellow chrome) was used either as the mordant, under the gold layer or as false gold. The data stressed important differences between the two studied carpentry attributed to the application time.

Figure 1. Photos of some zones of the carpentry studied in this work.

Characterization of granite columns of 2nd Century from Écija (Spain)

I. Turbay[1], J.M. Martín[2], I. Carrasco[3], A. Fernandez-Ugalde[4], R. Ortiz[2], P. Ortiz[2]

[1]Universidad Antonio Nariño Palmira, Colombia
[2]Department of Physical, Chemical and Natural Systems, University Pablo de Olavide, Carretera de Utrera Km 1, ES41013 Seville, Spain
[3]Department of Geography, History and Philosophy, University Pablo de Olavide, Carretera de Utrera Km 1, ES41013 Seville, Spain
[4]Museo Municipal de Écija, Écija, Spain

Many of the cities of Hispania Baetica constituted an important part in the functioning of the Roman Empire, and Astigi certainly was one of them. Because of their economic position as a commercial center of olive oil, and its transformation of evergetism behavior of the high society, in the second century B.C. Astigi presents a growing construction activity, Roman architectural models and sophisticated construction materials imported from distant parts of the Empire, are used in the development and beautification of this Roman city. Granite columns of different sizes are the reminiscence of this period.

The shafts of granite columns that made up buildings of Écija and whose fragments today are part of the streets or deposited in the museum are the subject of this study.

An architectonic analysis of sizes and shapes was carried out and lithotypes were characterized by different techniques. The weathering forms present in the columns were studied by means of visual inspection, in accordance with ICOMOS-ISCS glossary. Sampling followed the recommendations of the CNR-ICR NORMAL 3/80 technical commission. The texture of the granites was studied using a petrographic microscope and a scanning electron microscope model JEOL JSM-5400, fitted with energy dispersive x-ray analyzer.

The combination of techniques allow us to know the provenance of the columns, the shafts may come from Troade, the most common type of granite imported for the Roman constructions of the provinces; the quarries of Gerena (Spain) or Elba (Italia). In summary, most of the granite shafts conserved on the urban site of Écija - Astigi, may correspond to the reforms and monumentalization of public spaces carried out by Hadrian during the first quarter of the second century A.D., when building materials were imported mainly from Eastern Mediterranean quarries that reached the city through the river Genil (Singilis), works of magnitude probably financed through the evergetism or thanks to the imperial house.

Etruscan render mortars from *Domus dei Dolia* (Vetulónia, Italy)

S. Rafanelli[1], P. Moita[2], C. Galacho[3], M. Beltrane[4-6], G. Coradeschi[4], A. Carvalho[5], P. Braga[5], R. Vicente[6], C. Dias[3], A. Candeias[3], J. Mirão[2]

[1]Museum of Isidoro Falchi, Vetulonia, Italy
[2]Laboratory Hercules, Dpt. of Geosciences, Univ. of Évora, Portugal
[3]Laboratory Hercules, Dpt. of Chemistry, Univ. of Évora, Portugal
[4]Laboratory Hercules, Univ. of Évora, Portugal
[5]Dpt. of Geosciences, Univ. of Évora, Portugal
[6]Cátedra Unesco em Património Imaterial e Saber-Fazer Tradicional
simrafanelli@gmail.com pmoita@uevora.pt pcg@uevora.pt ginevrac@uevora.pt masimo@uevora.pt

Destroyed as a result of a fire, the ruins of the *Domus dei Dolia* remained hidden until 2009, the year of the beginning of the archaeological work. The *Domus dei Dolia* is located in the Hellenistic quarter of the old town of Vetulonia, now Poggio Renzetti. Basing on the classification of the archaeological materials recovered the *Domus, and the whole city,* was probably destroyed around the first century BC. The city was destroyed due to the reprisals made by Lucio Cornelio Silla after the victory over Gaio Mario in the bitter dispute that saw the Etrurian cities take party in favour of the latter during the Roman civil war. The different materials used and the artifacts found reveal the richness of the building and its inhabitants.

In the context of the collaboration between the HERCULES laboratory, the Isidoro Falchi de Vetulónia Museum and the Town Hall of Castiglione della Pescaia, eight render mortar samples were collected for their compositional and textural characterization. All the samples come from the same division of the house, the *triclinum*, and display red, blue, yellow and black mural painting. Most of the samples exhibit a clear stratigraphy: a chromatic layer over a white/grey mortar render, which in turn rests on a beige/yellowish mortar. The data acquisition techniques consisted of X-ray diffraction (XRD), thermogravimetric analysis (TGA), scanning electron microscopy coupled to X-ray dispersive energy detector (SEM-EDS) and thin-section optical microscopy.

The integration of the various techniques indicates that render mortars consist of a preparatory layer (*intonaco*) with calcitic aggregates displaying very angular contours which suggest the use of in situ brittled recrystallized limestone/marble. Quartz aggregates are rare and very small in size. The binder is an aerial calcite lime. Due to the presence of calcitic aggregates in this layer, the determination of the trace (binder:aggregate) of 1:1 was made by point counting on thin section.

The underlying beige/yellowish mortar is clearly contrasting from the compositional and textural point of view. The aggregates are mainly silicates prevailing the quartz over the feldspars and lithics (sandstones, slates, cherts), being still observed nodules of lime. The shape of the aggregates is rolled to well rolled suggesting a significant transport, probably corresponding to a river sand. The binder is identical to the intonaco that is an aerial lime of calcitic composition. For the arricio the trace was determined using the TGA; in these layers values of 9 to 11% were obtained for mass loss in the range 500-900°C corresponding to a calcite amount of 21 to 39% attributed to the binder. That is a trace of 1: 1.5 to 1:4 for the masonry mortars. The dispersion obtained may be related to the small sample size.

The results obtained for the different samples show a strong coherence with each other, corroborating the fact that it is a single division coating. On the other hand they reveal clear criteria in the choice of the raw materials as well as the specific techniques of application for each layer.

Georeferencing of historical iconography for the knowledge of the built heritage

S. Acacia[1], M. Casanova[2]

[1] DSA, University of Genoa - stradone S. Agostino 37, 16123 Genoa, Italy
[2] DAStU, Politecnico di Milano - via Bonardi 3, 20133 Milan, Italy

Starting from practical examples, the paper aims at showing how a deeper knowledge can be favoured by georeferencing in GIS environment.

This tool works on a large range of images, such as historical maps, aerial shots, project, paintings and old photos.

In this way it is possible to detect changes not only in the building volume but also in the evolutions of its connections with the neighbourhood, to draw useful information to understand the origin of some decay phenomena. For example, the comparison between painting or georeferenced historical photos and current orthophotos may highlight changes to fronts, as works on windows or the existence drawings not clear any more.

Besides, the reading of the graphical records can support the structural condition assessment of the building; for example, laying historical maps over the current land survey can reveal important ground movements or changes in the flow of rivers, which let the cracking map on the surface of the building, be understood.

Therefore, the suggested approach seems a non-destructive test method of the historical building, a cheap one if you choose to use free and/or open-source software as much as possible.

Besides, this work technique has the advantage to provide even non experienced people with easily readable results because learnt through a visual language.

It is certainly compulsory to have a sufficient starting documentation to be found thanks to a precise historical both bibliographical and archival research.

Technological characterization of polychromies on a Balearic medieval stone Altarpiece of 15th Century

L. Bosch Rubio[1], M.A. Gomez-Moron[1], P. Ortiz[2]

[1] Instituto Andaluz de Patrimonio Histórico, C. Descubrimientos, s.n., 41092, Seville, Spain
[2] Pablo Olavide University, Department of Phisycal, Chemical and Natural Systems, Ctra. Utrera 1, 41013 Seville, Spain

There are many examples of Gothic art introducing polychrome finishes on stone sculpture, both in the religious and civil spheres in the Iberian Peninsula. In the Balearics, with the Christian conquest, this practice was also extended. The *Passio Imaginis* Altarpiece, at San Salvador Sanctuary in Felanitx (Mallorca) has been studied. The sculptor Huguet Barxa carved the relief along 1448-1453 on a sedimentary stone and Joan Marsol made the polychromy.

The characterization of the polychromies began with an organoleptic examination and photograph of general visible light and flush, assessed by digital image analysis (DIA). DIA allowed revealing traces of polychromies that had not been detected by naked eye in order to carry out the proper sampling. The samples were analyzed by optical microscopy; scan electron microscopy (SEM-EDX), and the study of organic binders.

Detail of the *Pasio Imaginis* Altarpiece.

The results obtained in the stratigraphic studies revealed the application of a sequence of layers of calcite and/or albayalde preparation. The pigments identified were vermilion, azurite or lapis lazuli; these pigments do not provide data on the chronology but coincide with medieval symbolism of colour and pigments employed in Iberian Peninsula. Binders detected are egg or animal glue. Data indicates that it is most likely an original finish.

Colour, as part of stone sculpture, is the logical consequence of different aesthetic-functional criteria that serve the concept of medieval beauty and symbolism, the protection of stone, the ordering of reading and its ornamentation. Colour study contributes through the knowledge of the *Passio Imaginis* altarpiece and the awareness of its remains, to avoid the misinterpretation and / or destruction of the pictorial strata present in stone carvings.

Characterization of mural paintings from the archaeological site of Cercadilla (Cordoba, Spain)

A. Gil-Torrano[1], J.M. Martín[1], R. Ortiz[1], M.C. Fuertes-Santos[2], A. Gómez-Morón[3], P.Ortiz[1]

[1]Department of Physical, Chemical and Natural Systems, University Pablo de Olavide, Carretera de Utrera Km 1, ES41013 Seville, Spain
[2] Andalusian Council. Ministry of Culture. Andalusian Agency of Cultural Institutions, Spain
[3] Andalusian Historical Heritage Institute, Seville, Spain

There are many reasons why the study of the archaeological site of Cercadilla (Cordoba, Spain) is of special interest. The archaeological site includes a complete chronological sequence since 1st century AD. The most relevant period correspond to 3rd century, moment in which the Roman monument was built, and has been considered, by numerous studies, to be the headquarters of the emperor Maximiano Herculeo; until the eleventh century, Caliphal period in which the suburb was possibly abandoned.

This study has been focusing on the analysis of pigments and preparation layers of the two different periods: one of the bathtub, located in the thermal baths from the Roman palace complex, which preserves white mural paintings with vertical and horizontal edges decorations and red bands, and the mural paintings found in two houses of the Caliphal period.

Nineteen samples were collected: eight Arabic and eleven Roman. Multiple techniques were used to study the mural paint of the archaeological site, such as colorimetry, macrophotography, optical microscopy, scanning electron microscopy, micro X-ray diffraction, X-ray powder diffraction and X-ray fluorescence. The results obtained have made it possible to determine the composition of materials used in both Roman and Arabic eras, and to establish the differences between them. Likewise, it was possible to know the conservation condition of the mural paintings of the site and the many alterations that was affecting the archaeological ensemble.

With respect to the pictorial layers, in the case of the Roman ones it was deduced that red ochre was used as the red pigment and calcite, and a small quantity of calcined bones, as the white pigment. Whereas in the case of the Arabic paints, hematite was found as the principal pigment used, beside a little amount of red ochre as a secondary pigment; and the white pigment was compound of calcium carbonate (calcite). The Roman mural paintings presented more preparatory layers than the Arabic mural paintings, which concur with the literature consulted; however, it was observed that the Arabic paints presented two pictorial layers, probably due to a repaint at some point in the past.

3D imaging and analysis of the inner structure of the "Tufo Giallo Napoletano": a contribution to the study of the architectural decay of Castel Nuovo

G. Mele, L. Gargiulo, B. Di Matteo

National Council of Research – CNR ISAFOM, Via Patacca 85, 80056 Ercolano NA, Italy
giacomo.mele@cnr.it

Façades of Castel Nuovo, a medieval castle located in front of the city hall in central Naples, Italy, are made with bricks of "Tufo Giallo Napoletano" (TGN), a widespread yellow tuff of that area. Castel Nuovo is one of the main architectural landmarks of the city, and shows, among other types of stone decay, a certain extent of black crusts. Such a kind of degradation, independently from its origin is affected by the typical porous structure of that rock material.

Multiscale scanning of samples of TGN from the south-western façade of the castle has been carried out by means of the X-ray microCT technique in order to reconstruct images of its natural and degraded inner structure. The 3D image analysis algorithm of "successive opening" has then been applied to determine the size distribution and the connectivity of the outer connected pores of the TGN. The crust thickness distribution and its development inside the pores under the surface of the rock material have also been evaluated.

In the not degraded material the open macroporosity was 27.6% with size ranging between 20 and 660 microns and a percolation threshold of 96 microns. Closed porosity was about 10% of the open one and porosity inside the black crusts reduced to 8.2% with an increase in the layer just below the crusts to 36.1%. Black crusts exhibited an average thickness of 39.3 microns with propagation below the surface of the stones of about 1.2 millimetres. Analyses in thin sections of the crusted layers by transmitted light microscopy allowed to identify as gypsum as main composition of the black crusts.

Overall results allowed recognizing the X-ray microCT as a useful technique of investigation of stone decay in the framework of a multidisciplinary approach aiming at addressing the restoration treatments of porous construction materials.

The global positioning (GPS) and geographic information systems (GIS) applied to old maps georeferencing to obtain information for temporary studies

B. Jigena[1,3], A. Fernández-Ros[1], C. Torrecillas[1,2], K. Mukanovic[3], M. Berrocoso[1]

[1]Laboratorio de Astronomía, Geodesia y Cartografía, Facultad de Ciencias
Campus de Puerto Real, 11510 Puerto Real,Cádiz. Spain
[2] Escuela Técnica Superior de Ingeniería. Universidad de Sevilla, Sevilla, Spain
[3]Escuela de Ingenierías Marina, Náutica y Radioelectrónica, CASEM,
Campus de Puerto Real, 11510 Puerto Real,Cádiz. Spain
bismarck.jigena@uca.es

The positioning systems combined with geographic information systems are fundamental tools for the georeferencing of cartography from diverse origins and periods of time that allows us to link thematic information of maps or images with the real position in the field.

With this paper we seek to define a methodology for the use of old cartography in obtaining georeferenced geographic information for use in spatial and multi-temporal studies.

For this paper, several points have been positioned all around the bay, which were identified on the map and positioned with GPS techniques and they have been used as control points, so they can be inserted in an ArcGIS layer for the georeferencing and adjustment of the 1789 map. The points were referred to the ETRS89 Geographic Reference System and for the positioning were used Leica Geodetic GPS receivers, model 1200, Leica Geomatic Office GPS geo-processing software and ArcGis Software for GIS and remote sensing.

By applying these combined techniques we have detected the urban changes in the area, but the most important are the changes in the coastline and in the configuration of the littoral zone. The most important conclusions of the study are that the use of the combined technique of GNSS systems, geographic information systems and remote sensing is an excellent tool for spatial and multi-temporal analysis and provides us with a satisfying result in the detection of the changes produced in the urban and coastal area which are owed to urban growth and changes in sea level due to local and global environmental changes.

Near infrared applied for forecasting of pathologies in Alamillo Bridge (Seville, Spain)

D. Seda[1], C. Torrecillas[1], B. Jigena[2], I. Barbero[2]

[1] Escuela Técnica Superior de Ingeniería, Universidad de Sevilla, Sevilla, Spain
[2]Laboratorio de Astronomía, Geodesia y Cartografía, Facultad de Ciencias, Universidad de Cádiz, Puerto real, Cádiz
torrecillas@us.es

Infrastructures need constant inspection and maintenance for monitoring of deterioration. Therefore, the vast number of consequences that would have a possible collapse can be avoided. Non-destructive testing techniques are increasingly used in the inspection tasks. In this way, the inspection does not interfere with the structure and the infrastructure service itself. This text provides a case study of near-infrared application for bridge inspection, concretely Alamillo Bridge in Seville (Spain), a special construction built in 1992.

With more than 200 multispectral frames, various pathologies in the material of the lower part of the bridge board were detected such as rust, cracks or smashed paint using image classification methodologies.

The most important conclusions that can be drawn from the study are that the methodologies used in remote sensing, applying the combination of near-infrared bands and image classification, provide fine results for detecting diseases in infrastructure. But to achieve a good outcome is essential to process the pictures, considering that the classification is very sensitive to factors such as shadows. Thereby multispectral images are used, mixing spectral bands from images obtained with the different filters, allowing us to mitigate the effect of the shadows, obtaining satisfactory results, with a high kappa index correlation value.

Two types of band combinations were used. A first one mixing the NIR-G-B bands, obtaining images in false colour or CIR, and a second one, with 12 band pictures, 3 of the visible, 3 of W + B 093, 3 of W + B 092 and 3 of W + B 099, in this order, choosing the band combination 4-7-12 in the case study because their results are a little better than the CIR colour.

Finally, structure-for-motion software was used to create a 3D model of the infrastructure and in addition, the development of this model allows us to create an orthophoto of the infrastructure to carry out measurements.

Ways to make history and archaeology with non-invasive techniques. The application of GIS, RPA and GPR in *Hasta Regia* roman city

P. Trapero

IVAGRO, University of Cadiz, Campus de Puerto Real, Spain
Pedro.trapero@uca.es

To advance knowledge of the ancient land of Hasta Regia Roman colony, located in Mesas de Asta in Jerez de la Frontera. We need to use non-invasive techniques in a space where there only information were some excavations conducted between the year 1942 and 1956, in very specific and peripheral areas of a huge archaeological site. This space could be put in value, because it is one of the most important settlements of the Roman Baetica province. Now with the unit of georadar and the service of drones of the University of Cadiz, we could advance the knowledge of this city, using some new non-invasive archaeological research techniques, which involve the data colection, without the need to alter the archaeological vestiges. These techniques are the geographical information systems (GIS), the drone remote pilot aircrafts (RPA) and the georradar ground penetrating radar (GPR), all in order to model the natural and historical environment of the place, as well as to detect possible structures without the need for excavations.

X-ray and ion irradiation effects on pictorial samples

E. Carrasco, M. Oujja, M. Sanz, J.F. Marco, M. Castillejo

Instituto de Química Física Rocasolano, Spanish National Research Council (CSIC) Serrano 119, 28006 Madrid, Spain

Intense radiation sources (synchrotron radiation, ion and laser beams) are increasingly used for the analysis of cultural heritage samples. This motivates the study of radiation damage mechanisms and the necessity of developing mitigation strategies [1]. In this regard, painting materials analysis with synchrotron X-ray photons [2] and PIXE [3] is considered challenging. X-ray photoelectron spectroscopy (XPS) is a surface-sensitive technique, which has also been employed to analyse both environmental ageing effects and X-ray induced damage in pigments [4].

In this work, XPS was employed to identify the surface chemical changes on model pictorial samples induced by X-ray and ion irradiations. In the first case, X-ray effects on the samples were evaluated by periodically acquired XPS spectra. In the second case, the model samples were irradiated with Ar^+ at low energy (1 KeV) for consecutive short intervals. After each ion treatment, XPS spectra were acquired.

The study was carried out on pellets of azurite, malachite and alizarin pure pigments and on azurite and alizarin tempera paint mock-ups, where the pigments were mixed with egg yolk.

Under X-ray irradiation, a progressive chemical reduction of azurite and malachite (copper-based pigments) and the formation of cuprite are observed. Alizarin does not experience chemical modifications by X-ray exposure in the same conditions as the copper pigments. On the contrary, alizarin tempera is modified in a shorter time scale than the analysed pure pigments and the spectra display alterations in the egg yolk binding medium. A similar rate of degradation of the organic constituent is observed in azurite tempera. In addition, the analysis indicates that azurite is partially reduced in the tempera paint at the beginning of the experiment. Further reduction is induced by X-ray exposure.

Ion bombardment produces significant surface modifications in few minutes in contrast to several hours for X-ray exposure. However, the spectra present similar characteristics after both types of treatment. Further details about the involved chemistry will be discussed with the objective of addressing and mitigating radiation damage of these materials.

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Relation of the presence of iron, copper and zinc in the iron gall inks of the Valencian manuscripts from the 13th to the 17th centuries

G.M. Contreras

Institut Valencià de conservació, restauració e investigació. IVC Generalitat Valenciana
C/ Pintor Genaro Lahuerta 25, 3ª. Valencia, España
contreras_gem@gva.es

The significant artistic and documentary contribution of the manuscripts makes them unique instruments of knowledge that we must guard and know. Most of the manuscripts of Europe and America are written with iron gall inks, documented from 4th century to 19th century; and already since the 17th century we have news of the problems of conservation that generated because the same scribes echoed the convenience or not of its use.

The Valencian archives conserved numerous documentary collection from the period after the Conquest, but those of the stage between 1450 and 1600 stand out by the deficient state of conservation.

For this reason it has been tried to go in depth into the characterization of the components of these inks in relation to their preservation. Given the high iron content of these inks and in the majority there are impurities of copper and zinc, a systematic study of 989 microsamples has been carried out. The iron/cupper/zinc concentration ratio results obtained have been evaluated - since the samples are not homogeneous and the proportion of ink in the paper could modify and the filament current values could also be different - depending on the dates and the archives which to the microsamples belong, with the semiquantitative results offered by SEM / EDX analysis.

A statistical study has been carried out using an ANOVA analysis of iron/cupper/zinc concentration as a function of the archive. On the other hand, the concentration of iron/cupper/zinc is analyzed according to the date in which there is an increasing trend of the means between the thirteenth and seventeenth centuries. These values can be related to the incorporation in the preparation of recipes for new organic and inorganic ingredients, as well as the difference in preparation and concentration of iron/copper sulphate according to the solvent used.

The integrated study of historical sources and elementary analyzes help to recognize both the materials and the state of conservation of the same, which facilitates the process of conservation and restoration.

Determination of the presence of wine in the medieval Valencian inks of the Municipal Archive of Cocentaina by HPLC-MS/MS

G. Fernández Martínez

Dept. Conservación y Restauración UPV – Máster, Dr. Vila Barberá 12, 7ª, Valencia, Spain
gonzalofermar@hotmail.com

The union of tannins with metallic salts to produce black dyes has been known since antiquity. Since then and until they came into disuse in the early twentieth century, there have been numerous components used in obtaining black ink suitable for writing as it is collected in treatises and chemistry books. Galls, copper or iron sulphate and gum arabic were mixed to form, with the use of a solvent, the inks known as iron gall ink and whose inherently acidic character poses a challenge for its conservation.

The progressive incorporation of analytical techniques into the study of cultural heritage, allows us to characterize the materials present in works of art, to understand their behavior and deterioration, and to design conservation strategies necessary for the safeguarding and preservation of our collections. However, the study and analysis of the handwritten inks only interested the inorganic compounds to be responsible for the oxidation process that the inks experience, with the consequent deterioration of the type page.

This article presents the research developed to identify the presence of wine in manuscript inks from the 13th to the 16th centuries. For this, a series of samples extracted from the books of Cort of Justice from the Municipal File of Cocentaina and samples of standard ink elaborated from ancient recipes by High Performance Liquid Chromatography coupled to Tandem Mass Spectrometry (HPLC / MS-MS).

From the known acids of the wine (Fig. 1) it has been possible to establish a method for its determination in iron gall ink inks present in the studied manuscripts. Based on the value of the written sources and the knowledge of the ingredients as well as the way of making the inks (with temporal and geographical characteristics), the present research opens a new line of study not only of solvents, but also the organic components of these inks and their involvement in the degradation process. Initial results from the samples studied indicate the use of white wine as the most common solvent in Valencia area between XIII to XVI centuries (Fig. 2).

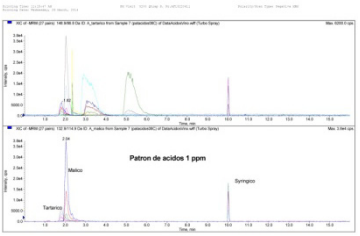

Figure 1. HPLC-MS/MS chromatogram of organic acid pattern.

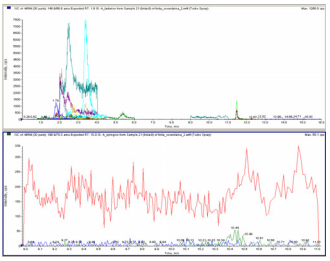

Figure 2. Chromatogram of the sample no 9 of the Court of Justice of Cocentaina of 1356-1357. The presence of white wine is detected.

Stone alteration and tourism

J. Sanjurjo-Sánchez[1], C. Alves[2]

[1]*Instituto Universitario de Xeoloxía "Isidro Parga Pondal", Universidade da Coruña, A Coruña, Spain*
[2]*Lab2PT (FCT UID/AUR/04509/2013; FEDER COMPETE POCI-01-0145-FEDER-007528) and Earth Sciences Department, School of Sciences, University of Minho, Braga, Portugal*
jsanjurjo@udc.es

After its emplacement in the built environment, natural stones can undergo several modifications resulting from interaction with external agents, modifications frequently seen as aesthetically negative and can imply non-recoverable losses (namely by erosion). The study of alteration processes can contribute to identify conditions that promote these processes, which may be avoided in future works or be considered in interventions in existing ones. Regarding intervention measures, it is first necessary to assess their need and benefit. The question of necessity relates to avoiding the continuation of degradation processes or restoring to an earlier situation. Certain changes, such as black crusts or biological colonization, may have an essentially visual effect but generally have no significant negative effects on the physical consistency of the material. Other changes might promote erosion of the material but it will be necessary to try to assess the temporal evolution, in particular whether the processes will continue or certain stabilization has been achieved. In terms of visual effect, and considering also the assessment of the benefits of the intervention, alteration products might contribute to conceal objects characteristics but they might be seen as a time stamp (and their removal might not be appreciated by the public). It may also be considered that the alteration products themselves may be interesting for other tourism perspective such as those based on education activities, from basic levels to university ones (as well as participants in scientific meetings), and with a multidisciplinary potential, including Sciences (namely Biology and Geology), Engineering, Architecture and, of course, Heritage (including heritage conservation). Additionally, sometimes there are no guarantees about the beneficial effects of interventions and there might be risks associated with them. Another line of analysis, especially for responsible tourism, concerns the sustainability implications of interventions, since these interventions will involve the consumption of resources (rocks for stone replacement, sands and lime or cement for mortars, water and other substances for cleaning, energy for all this), as well as the possible emission of pollutants and production of waste. It may also be necessary to evaluate the choice between high frequency and low intensity procedures and others with longer longevity but with greater implications in terms of risk and sustainability. Biological colonization might illustrate this discussion, as it begins with poor adhesion patches (usually removable with a gentle cleansing) and it might evolve towards coatings that are more difficult to clean.

Vulnerability study of three monumental gates from 12th century (Marchena, Spain)

J. Benítez, R. Ortiz, P. Ortiz

Department of Physical, Chemical and Natural Systems, University Pablo de Olavide, Carretera de Utrera Km 1, Seville, Spain
benitezjimenezjulia@gmail.com

The objective of the present work is to study the vulnerability of three monumental gates belonging to the walls of Marchena according to the methodologies developed [1].

Marchena (Seville) is located in the right margin of the Valley of the Guadalquivir. It was founded in 169 B.C. In the Muslim period, the urban nucleus was composed of the Alcazaba and the hamlet, with irregular blocks and streets that departed from the different gates in the wall. The village passed to hands of Christians in 1240. In the 14th and 15th centuries the village suffers significant changes, the walls are reconstructed, the Alcazaba is transformed in a stately castle and the hamlet is renewed. The monumental gates of the wall have a great importance as they communicated the main exit routes, and in the course of the 16th and 17th centuries, the expansion outside the walls of the village, depart from them. During the following centuries, the village continues growing, and the tree gates studied (*Puerta del Tiro*, *Puerta de Sevilla* and *Puerta de Morón*) became a cultural image of citizen heritage.

The gates are built with stonework, tapial, brick and masonry. The evaluation of the current state of the buildings is made using cataloguing cards where is collected the damages that presents the building and their extension, for what is necessary to perform in-situ observations of each building.

The extension of the damages is established according to the frequency of appearance of the indicators of alteration. This frequency is classified in three levels: 1, when the indicator is scarce and it is difficult to see; 2, when it can be observed easily; and 3, when the indicator is abundant.

The three monumental gates belonging to the walls of Marchena presented a good state of conservation. *Puerta del Tiro* presents the greatest damages, being the environmental factors, like wind and rain, and the action of the man the main causes of them. *Puerta de Morón* pathologies are mainly due to the climatic conditions. *Puerta de Sevilla* presents the best state of conservation because although presents damages, the frequency with which it appear is lower than in the rest.

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Social Media like point of artists' international connection

M.L. Cueva Ramírez

Departamento de Didáctica de la Expresión Musical, Plástica y Corporal, University of Jaén, Jaén, Spain
lorenacue14@gmail.com

Nowadays the social media is a fundamental tool for everyone who wants to support an international relation.

In the artistic relationships have the similar situation, for that with this communication I want to highlight that social media has become in a big meeting point between artists, helping us in our artistic investigations.

We can show our artworks through an artistic web page, which let other people interested in the artistic production, to know what is happening in other parts of the world.

Moreover, it is interesting because links are created and professional international relationships too, which gives rise to being able to carry out in different parts of the world and in a simultaneous way artistic projects, being able to share the process and the results in a real time.

As a tool for working artistic projects in the schools from different countries this is very enriching, because we do not only get to create a relationship between artists if not that we can create relationships between artists and students from different origins.

This type of approach also helps to educate students for the use of social media, which in this case as well as an entertainment they are also used as tools for working and learning.

Finally the projects carried out in common are exposed in these social media, which allows a global dissemination of them, and anyone on the planet can have access with a simple click. Showing once again how art has no limits.

Surveying buildings as an essential tool for conservation tasks: the case of Royal Hospital in Granada

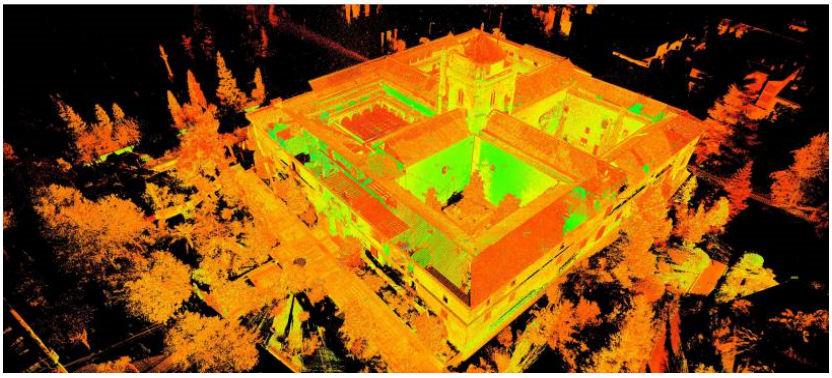
J.F. Reinoso-Gordo[1], C. León-Robles[2], J.L. Ramírez-Macías[2], F.J. Ariza-López[1]

[1]Cartographic, Geodesic and Photogrammetry Engineering, University of Jaén, Jaén, Spain
[2]Architectural and Engineering Graphic Expression, University of Granada, Granada, Spain
jreinoso@ugr.es fjariza@ujaen.es cleon@ugr.es jlramac@correo.ugr.es

Architectural survey is not only getting the geometric shape and size of a building, it should facilitate the interpretation of transformations occurred from its built to the present day. Heritage buildings traditionally have been tackled from several points of view: architectonic features, architectural style, archaeology, history, structural engineering, chemistry, conservation guidelines, etc. And finally all documents derived from those studies were classified and put together to form the documentation for consultation, taking decisions about its conservation, restauration and functional dedication. If the survey task is performed in a suitable way it will be an invaluable witness from the relation between the building and the society inhabited it.

Nowadays there are technologies facilitate registration in a so precise way that when possible they should be used; among those technologies photogrammetry and scanner laser are the most versatile in surveying buildings. Both techniques are complementary, although a comparative study about the accuracy obtained by each one would be necessary. In our case we have use a more precise technique (structured light) in order to compare both photogrammetry and scanner laser. This comparison was necessary because we were surveying the Royal Hospital in Granada, Spain (1511-1526) and there were inaccessible areas for the scanner where photogrammetry was carried out. The conclusions obtained from the experiment pointed that photogrammetry and scanner laser could be used as complementary techniques because their similar accuracy.

On the other hand the main objective was to get a complete an accurate survey for the Royal Hospital because of its historical importance and the necessity of conservation for such an invaluable cultural heritage building. The survey will be used to model the structural and architectural elements in order to create an HBIM (Heritage Building Information Model). A HBIM will facilitate the building management and the making decision in conservation tasks such as roof intervention or columns, ceilings and stones protection. One of the main achievements has been getting the complete survey of an exceptional cultural heritage building which includes several architectonic styles going from Gothic, to Renaissance, including some Mudéjar arms. The next figure shows a perspective view for the complete point cloud.



Non-destructive study of the degradation processes in underwater metallic materials

E. Estalayo[1], J. Aramendia[1], L. Garcia[2], K.Castro[1], I. Garcia-Camino[2], J.M. Madariaga[1]

[1]Department of Analytical Chemistry, University of the Basque Country (UPV/EHU), Bilbao, Spain
[2]Arkeologi Museoa/Archaeological Museum of Bizkaia, Bilbao, Spain
Kepa.castro@ehu.eus

Sub-aquatic archeology is the branch of science responsible for the study of the documentation, the analysis and the study of the conservation of the traces of human existence having a cultural, historical or archaeological character which have been underwater, partially or totally in periodic or continuous form, according to Unesco. This area of study, which must be developed in a multidisciplinary way, is nowadays acquiring more importance due to the large number of underwater pieces that are stored in museums experimenting degradation processes without any solution, losing their heritage or cultural value.

One of the most important problems that affect these pieces is sulphur accumulation. This accumulation is very common for marine archaeological wood preserved under anoxic conditions in seawater and finally could affect to other materials which are in contact with that wood (metal, textile, etc.). When the reduced sulphur compounds present in the recovered material brought into contact with oxygen after extraction from the water media, sulfuric acid is produced by a natural oxidation process, which causes serious degradations problems in the recovered pieces. Due to the importance of the Underwater Cultural Heritage and due to the few number of studies carried out, a research program has been focused on materials extracted from a shipwreck located in Bakio (Bay of Biscay, Basque Country). For this work, one of the two muskets extracted from Bakio's Shipwreck was analyzed, which is currently preserved in the Archaeological Museum of Bilbao. The conservation state of the piece is acceptable because it was treated by tannic acid; however, several pieces have been released from the main structure (Fig. 1).

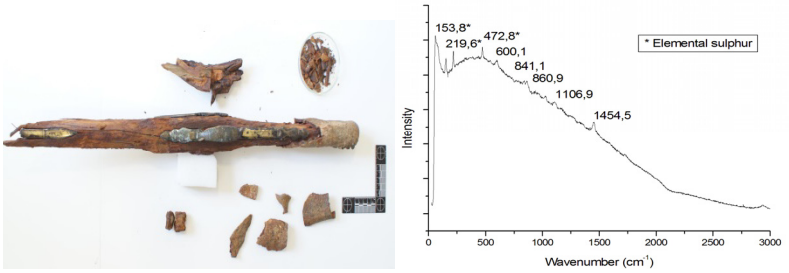


Figure 1. (left) the musket extracted in 1999 from Bakio's Shipwreck; (right) Raman spectrum of elemental sulphur.

To study the raw composition of underwater materials, the degradation processes and in order to find the better conservation procedure, non-destructive analytical techniques were used. By means of X-Ray Fluorescence, elemental characterization was performed and for the molecular characterization Raman Spectroscopy was used. The results obtained, showed the presence of iron oxides such as goethite and lepidocrocite, elemental sulphur and lead carbonate in the bullet analyzed. In conclusion, the presence of iron oxides in the piece corroborates the degradation processes that the musket suffered since it was extracted until now. Furthermore, finding elemental sulphur in both wood and metal areas, confirms the theory that the possible presence of sulfur compounds in wood has been able to affect the metal areas on the musket.

Deterioration of cinnabar and azurite tempera mock-ups under marine and industrial outdoor exposition

T. Rivas[1], D. Barral[1], C. Cardell[2]

[1]Dept. Ingeniería de los Recursos Naturales y Medio Ambiente. E.T.S.I. Minas. Universidad de Vigo. Campus Lagoas Marcosende, Vigo 36310, Spain
[2]Dept. of Mineralogy and Petrology, Faculty of Science, University of Granada, Campus Fuentenueva s/n, 18071 Granada, Spain

The stability under different exposure conditions of cinnabar and azurite, used in tempera paintings mixed with protein binders, is well documented. Nevertheless, the literature on the effects of marine aerosol and industrial and urban emissions (mainly SO_2 and NO_x) remains insufficient. Moreover, it is undoubted that the stability of tempera depends on the interaction of pigments and binders, an aspect that are also scarcely addressed.

In this work, the results of the monitoring of the changes suffered by tempera mock-ups made with cinnabar and azurite on two different protein binding media during one year of outdoor exposure in Vigo (NW Spain) are presented. Different pigment grain sizes and two different binders -rabbit glue and egg yolk- were used; thus, the influence of both, the binder-pigment interaction and the pigment grain size were evaluated.

The exposure site is characterized by high levels of sea spray and atmospheric pollutants derived from traffic and industrial activity, being the main inorganic contaminants chloride, SO_2 and, to a lesser extent, nitrates. Before and after the outdoor exposure, tempera mock-ups were characterized: colour following CIEL*a*b* standards, texture by means of stereomicroscopy and optical microscopy, mineralogical composition by X-ray Diffraction, chemical composition by means of Fourier transformed infrared spectroscopy-FTIR, and texture and chemical composition by means of SEM-EDS.

Changes suffered by the tempera mock-ups were different depending on both the pigment (nature and crystal size) and the binder. Azurite-based tempera made with egg yolk suffered more extensive damage than those made with rabbit glue. Conversely, cinnabar-based tempera made with rabbit blue showed more significant colour changes than their counterpart made with egg yolk. Colour changes occurred faster in azurite-based tempera and slower and progressive on cinnabar tempera samples. Also, results suggest that fine grained azurite and cinnabar based tempera were less stable than coarse grained ones. Hence, in the case of cinnabar-based samples, blackening occurred more intensely in samples of extra-fine grain. After the exposure, no neoformed minerals were detected in any case, although several x-ray diffraction reflections disappeared, which suggest changes in the crystallinity of the pigments. This effect is more evident in tempera made with rabbit glue and in paint mock-ups made with cinnabar. FTIR results showed conformational changes of the binder, especially in the case of rabbit glue, which confirms the contribution of the pigment-binder interaction on the paint weathering process under natural urban exposure.

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Influence of cinnabar particle size on pigment-binder interactions during photo-chemical aging

K. Elert[1], A. Herrera[1], A. Garrido[1], I. Guerra[2], C. Cardell[1]

[1]Dept. of Mineralogy and Petrology, Faculty of Science, University of Granada, Campus Fuentenueva s/n, 18071 Granada, Spain
[2]Scientific Instrumentation Centre, University of Granada, Campus Fuentenueva s/n, E 18071 Granada, Spain

Cinnabar has been used as a pigment since ancient times. As a result of its resistance to acids and alkalis, it was traditionally used with various binding media including oil, lime, and tempera. Historical sources mention the limited photo stability of this pigment and numerous studies have been dedicated to light-induced changes of cinnabar [1]. However, very limited data are available on the interaction of cinnabar with protein-binders upon photo-chemical aging [2]. These interactions influence the durability of the paint film, possibly inducing binder degradation and subsequent pigment loss. Previous research indicated that pigment particle size might be crucial, affecting the degree of binder-pigment interaction.

This work investigates the effect of cinnabar on optical, physical and chemical properties of protein binder-based paints. To this end paint dosimeters were prepared following traditional recipes using cinnabar pigments of different grading and rabbit glue or egg yolk. Then dosimeters were exposed to accelerate and natural aging tests including 1-month relative humidity cycling and UV-B exposure, and 2-year outdoor exposure with or without direct sunlight exposure under urban air contamination conditions.

Chromatic features, morphology and spectroscopic characteristics of paint dosimeters were determined using spectrophotometry, Field emission scanning electron microscopy, and attenuated total reflection – Fourier transform infrared spectroscopy ATR-FTIR. The mineralogical composition, impurities, and contamination of cinnabar pigments and exposed dosimeters were determined using X-ray diffraction. The comparison of data obtained before and after exposure showed an important influence of cinnabar on conformational changes of rabbit glue and egg yolk. These changes were more pronounced in the case of paints prepared with fine grained pigments. Pigment grain size also controls binder distribution and, thus, affects crack formation in paint films upon climate change. The obtained experimental results contribute to a better understanding of binder pigment interactions and will hopefully help conservation specialists in the selection of adequate paint materials for restoration treatments.

Acknowledgements: Financial support was provided by Andalusian Research Group RNM-179 and Research Projects CGL-2012-30729 and P12-FQM-1889. Analyses were performed at the Scientific Instrumentation Centre of the University of Granada, Spain.

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Natural stone: artificial ageing test versus natural weathering

R. Bellopede[1], N.M. Luodes [2], P. Marini[1], L. Zichella[1]

[1]Department of Environment, Land and Infrastructure Engineering, Politecnico di Torino, Corso Duca degli Abruzzi, 24, Torino, Italy
[2]Geologian Tutkimuskeskus, Neulaniementie 5, FI-70211 Kuopio Finland

Natural stone has always been one of the main materials used in architecture for its singular beauty and durability. However, ornamental and structural stone elements might show decay essentially induced by climate factors such as atmospheric pollution, freezing–thaw action, thermal shock or acid rains.

The deterioration of natural stone doesn't concern only a worsening of its aesthetical properties, but mostly a decreasing in mechanical strength. To detect and to analyse the dominant destructive factors for stone durability is important to forecast the trend of the deterioration in the long term. For this reason, the comparison of the natural weathering with the results of artificially ageing tests on the same kind of stone is useful.

This research compare the decay artificially induced in laboratory (according with the test method foreseen by European standard to evaluate the durability) with the one caused by natural ageing (with the action of the different climatic agents).

In laboratory, six different kinds of stone and in particular marble, sandstone, limestone, gneiss, granite and tephra, have been tested by means of two different artificial ageing tests: determination of resistance to ageing by means of thermal shock and freeze and thaw cycles. In order to assess the variation of mechanical resistance, flexural strength tests under concentrate load and ultrasonic test have been performed before and after the artificially ageing cycles. The tested stone gave different variations in mechanical strength for the two different artificial ageing tests. This different behaviour has been explained by means the analysis of petrographic characteristics of the stone tested.

Finally, a comparison of three case studies of natural weathering of stones in historical buildings in different climatic zones of Europe, have been made. For the evaluation of in situ decay, the study has been focused on marble, granite and gneiss, recognising their main weathering forms and comparing them with those obtained with the artificially ageing tests.

New approaches to assess building stone decay

J. Dassow[1], A. Leslie[2], S. Hild[3], P. Harkness[4], L. Naylor[1], M. Lee[1]

[1]University of Glasgow (School of Geographical and Earth Sciences)University Avenue, Glasgow, Scotland
[2]Historic Environment Scotland
[3]University of Glasgow (School of Physics and Astronomy)
[4]University of Glasgow (School of Engineering)

When evaluating the deterioration of building stone, consistent methods of measurement and empirical data analysis need to be defined in order to substantiate the classification of such decay. Analysing and understanding the amount and timescale of stone weathering can help to determine the best preservation methods and / or replacement strategies. Our project uses non-/minimally invasive tools to examine weathering processes in sandstone. The equipment includes a laser interferometer and an ultrasonic assisted drilling tool to investigate decay below the surface of the stone.

The laser interferometer analyses dilation of the stone caused by water saturation or salt crystallisation at a nanometre scale. The range and the frequency of those dilation events can provide insight into the state of decay of the building material. The condition of the stone below the surface is analysed with an ultrasonic drilling device. This technique creates a 3 mm diameter hole to depths up to 4 cm. During drilling the power consumption is monitored and variation in the power allows determination of the sample's structural properties such as porosity. The force exerted on the sample is very low compared to other drilling techniques, allowing penetration with less associated damage to the stone. Ultrasonic drilling is also able to analyse stones with high compressive strengths.

These techniques allow for better prediction of the weathering behaviour of building stones, and can be scaled up from the lab to the building site. Potentially the devices can be used in situ on historical buildings under site conditions to enable a precise characterisation of their state of decay.

A multi-analytical study on 19th century ambrotypes

M. Nunes[1], S. Costa[1], C. Miguel[1], A.T. Caldeira[1,2], T. Ferreira[1,2]

[1] HERCULES Laboratory, University of Évora, Largo Marquês de Marialva, 8, 7002-554 Évora, Portugal [2]Chemistry Department at the Science and Technology School, University of Évora, Rua Romão Ramalho, 59, 7000-671 Évora, Portugal

The adoption of glass as a negative support in the mid-nineteenth century marked the beginning of a new era in negative technology [1]. However, glass support did not become dominant until 1851 when Archer presented the much faster wet-plate collodion process. Collodion (cellulose nitrate, alcohol and ether) solution containing cadmium or potassium iodide and bromide were deposited on a transparent or coloured glass and the plate was then immersed on a silver nitrate solution, with the formation of the light-sensitive deposit [1, 2]. The ambrotype is a thin or underexposed collodion negative that when backed with a black varnish, paper or cloth turned into a positive. Ambrotype is, in fact, a generic term for all direct positives made on glass by the wet collodion method. These photographic items are subjected to various types of degradation, being the most frequent mechanical and chemical damages of the support and binder, namely, fracture, abrasion, loss of transparency, surface roughening and collodion reticulation which usually occur on the emulsion side, leading to detachment from the support. Silver mirroring is also a common form of degradation of the silver image forming particles and appears as a bluish iridescent metallic deposit on the binder's surface, with a mirror-like effect [2, 3]. To sum up, ambrotypes are multi-layered items, composed of organic and inorganic compounds and the degradation phenomena are strictly related to the layers' composition; hence the importance of the analysis of this kind of objects.

This work is part of an ongoing study, focused on the material characterization of two 19th century cased ambrotypes which belong to a private collection. Visual observation complemented with technical photography under different illuminations and optical microscopy were essential for degradation patterns evaluation. The study was complemented by micro-Fourier transform infrared spectroscopy (μ-FT-IR) and micro-Raman (μ-Raman). μ-FT-IR confirmed the use of collodion (cellulose nitrate) as the binder material and suggested that denitrification (the inversion process of collodion formation) is taking place. A triterpenic resin as also identified in one of the items in the area underneath the brassmat used in the cased ambrotype. Scanning electron microscopy with energy dispersive X-ray spectroscopy coupled (SEM-EDS) allowed to register different degradation patterns and confirmed the used of gold to enhance jewellery. Microbiological colonization was also studied. Isolation and characterization of the contaminating microorganisms as well as evaluation of cellulolytic activity of fungal isolates were done.

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Carbonation of pigments present in paint dosimeters exposed to polluted urban air

A. Herrera[1], A. Burgos-Cara[1], K. Elert[1], N. Navas[2], C. Cardell[1]

[1] Dept. of Mineralogy and Petrology, Faculty of Science, University of Granada, Campus Fuentenueva s/n, 18071 Granada, Spain
[2] Dept. Analytical Chemistry, and Biomedical Research Institute of Granada (IBIG), University of Granada, Faculty of Science, Campus Fuentenueva s/n, 18071 Granada, Spain

In the last two decades an increase in environmental CO_2 levels has been recorded in urban areas due to climate change and air pollution. Effects on building materials are of major concern and thus numerous investigations have tackled this issue [1]. However fewer studies have addressed the damage of outdoor exposed painted artworks [2]. This work investigates the risk impact of the CO_2-rich urban air of the city of Granada (South Spain) on paint dosimeters exposed long-term in pilot open-air monuments. The dosimeters are paint binary mixtures prepared blending a combination of calcite and portlandite with either egg yolk or rabbit glue as binders. The obtained paint was extended over glass slides which were placed in eight strategic semi-open monuments in Granada during 30 months. The goal was to assess different trend effects of urban air on dosimeters according to location in the city. An array of complementary analytical techniques was applied to characterize them, e.g. spectrophotometry, micro-Raman, XRD, ATR-FTIR and FESEM. Our study showed that paints containing minium (Pb_3O_4), calcite ($CaCO_3$) and portlandite ($Ca(OH)_2$) were the most affected by air pollution. Results revealed that minium started to carbonate into white lead ($2PbCO_3 \cdot Pb(OH)_2$) within eighteen months of exposure to the CO_2-rich atmosphere of Granada. Instead calcite and portlandite changed their morphological features around six months of natural aging. In these paintings the FESEM images displayed dogtooth spar crystals of calcite over the portlandite crystals on twelve months aged dosimeters. Moreover the micro-Raman analysis indicated that portlandite gradually changed its composition towards calcite through carbonation during outdoor exposure. Fig. 1 shows the steady reduction of the portlandite band at ca.357cm^{-1}, distinctive of the υ Ca-O bonds in $Ca(OH)_2$, which is lacking in spectra of twelve months naturally aged paint dosimeters.

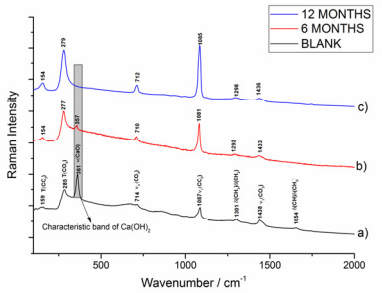

Figure 1. Raman spectra of calcite/portlandite during twelve months of exposure to urban air.

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Study of Vulnerability in the historical center of Popayan (Colombia)

I. Turbay[1], R. Ortiz[2], P. Ortiz[2]

[1]Universidad Antonio Nariño Palmira, Colombia
[2]Dept. of Physical, Chemical and Natural Systems, University Pablo de Olavide, Seville, Spain
[3]Museo Municipal de Ecija

In this study, the methodologies developed for vulnerability analysis [1] have been employed to assess the conservation degree of different monuments of the historical center of Popayan (Colombia). The goal is to provide a tool for decision-makers to prioritize strategies for cultural heritage preservation that could be applied to similar cities in Colombia. The vulnerability analysis is based on matrix and the relationship of damage with static and structural factors, climatic conditions, air quality, urban planning and social agents for preventive conservation of cultural heritage in urban centers. To determine the first vulnerability approach of each monument, vulnerability indexes (VI %) were calculated, based on a Leopold matrix depending on intrinsic variables and the life of the monuments. The influence of deterioration agents has been balanced with a Delphi forecast based on architects' opinions. Popayán is a city located to the southwest of Colombia between the central and western cordillera, founded in 1537 on the Valley of Pubenza by S. de Belalcazar after the Spanish conquest. Today it has the largest historic center of Colombia, maintaining today its image of colonial city. Popayan's urban layout evolved according to the ordinances of Spanish laws, a grid model base with streets, blocks a main square as main components, to which were added the *ejidos* and meadows for the distribution of land. In the rural areas it was fundamental in the installation of economic activities such as mining, agriculture and livestock, which through the *encomiendas* regime gave rise to a consolidated city of great importance in its time.

The heritage buildings surviving today in Popayan are of a modest Hispano-Arab influence, several would date of this time of boom, but few are conserved in intact conditions due to the geographic and geological conditions, besides having undergone several reconstructions not so fortunate. In this work several buildings of civil and religious architecture have been taken mainly, e.g. the church of San Francisco built in 1775 in neogranadino baroque style, with its cloister today turned into hotel, in addition to survive to several earthquakes and interventions daily undergone to the somewhat inclement conditions of the current use. The church of Santo Domingo (18th century) with its cloister that today is a university seat, opens with a large portal stone quarry in American baroque and a square with a fountain, suffering an average rainfall per year of c. 2250 mm and a relative humidity of 78%. The church of San Agustín, rebuilt after the earthquake of 1735 which opens to a square in stone of river, by one of the many vehicular streets of the center, and where they parked uncontrollably vehicles daily. The degradation of building materials and structures is mainly due to deterioration caused by static-structural damage during the last earthquake in 1983, as well as lack of planning and little knowledge about conservation. Both some monuments and the urban image of the center are used as trademarks, so the social conscience of the preservation of cultural heritage

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Intensive damage due to salt crystallization by rising damp in the Colegio Santo Domingo of Orihuela (Alicante, Spain)

D. Benavente[1], J.M. Elena-Carbonell[1], Y. Spairani[2], C. Pla[3], C.M. Grossi[4]

[1] Dpto. CC. de la Tierra y del Medio Ambiente. Universidad de Alicante, 03080, Alicante, Spain
[2] Dpto. Construcciones Arquitectonicas, Universidad de Alicante, 03080, Alicante, Spain
[3] Dpto. Ingeniería Civil, Universidad de Alicante, 03080, Alicante, Spain
[4] School of Health Sciences, University of East Anglia, Norwich NR4 7TJ, UK

The Colegio Santo Domingo of Orihuela (Alicante, Spain) was built from 16 to 18th centuries with a biocalcarenite and a micritic dolostone in baroque style. Several historic buildings of the city, including the Colegio Santo Domingo, suffer a rapid and severe damage due to salt crystallization by rising damp. Samples were collected from the exterior and interior of the building. Salts were analysed using X-ray diffraction (XRD) and scanning electron microscopy coupled with energy dispersive spectroscopy (SEM/EDS).

The exterior walls and columns of the building show loss of material (scaling, granular disintegration and alveolization) and surface modifications (efflorescences, crusts and deposits). The main salts are gypsum and halite.

Granular disintegration is the main deterioration process and efflorescences are widely spread in the interior of the building. The mineralogy of salts shows both a strong vertical and horizontal variability. Different precipitation sequences are observed in the vertical profile, where the more soluble salts are located at higher heights of walls and columns. SEM images reveal different conditions in the saturation degrees of minerals, ranging from isometric shapes to needle-like crystals. Single salts are halite, silvite, gypsum, thenardite, epsomite and hexahydrite, whereas double salts are humberstonite and aphthitalite. Double salts, which precipitate via incongruent reactions, show a near equilibrium crystal shape, which may be conditioned by water level variations in the building foundation.

The Mosaic of Baco (Puente Melchor, Cádiz), an archaeometric approach

A. Durante Macías[1], S. Domínguez-Bella[2], D. Bernal[3]

[1]IES Pablo Ruiz Picasso, Avda. de la Diputación, S/N. Chiclana de la Frontera, Cádiz, Spain
[2]UGEA-PHAM. Dpto. de Ciencias de la Tierra, Facultad de Ciencias, Universidad de Cádiz, Cádiz, Spain
[3]Dpto. de Historia, Geografia y Filosofía, Facultad de Filosofía y Letras, Universidad de Cádiz, Cádiz, Spain
anamaridurante@gmail.com

In the year 2004 a Roman villa was discovered in the construction of the N- IV motorway new course, section Puerto Real – Tres Caminos, between K.P. 666,8 to K.P. 678,8. One of the rooms of this villa contained a mosaic of large dimensions, presenting an inverted T shape and polychrome busts of Baco and his procession inserted in compartments of black and white geometric designs. After the extraction, the mosaic was taken to the Museum of Cádiz. The aim of this paper is to study from an archaeometric point of view the different stone *tesselae* used in the elaboration of the mosaic and to determine the possible provenance of the rocks used. The macroscopic study took place in the Museum of Cádiz. The optical microscopy, X-Ray diffraction and the X-Ray fluorescence of the samples were carried out in the UGEA-PHAM archaeometric laboratories of the Faculty of Sciences of the University of Cádiz. Ten analytical data sheets (including X-Ray diffraction and fluorescence analysis results, macroscopic observations and optical microscopy photographs of the thin sections of the rocks) with the characteristics of each type of lithology were elaborated after studying the different rocks of the *tesselae*.

Three main groups of lithologies were found: limestones, sandstone and volcanic rocks. Limestones and sandstones are common rocks in the Mediterranean area, so its origin is not clear. However, the igneous rocks of volcanic type, does not exist in the province of Cádiz or in the southwest of the Iberian Peninsula. This may allow us to think that they were brought by the mosaic artisans from other places where this type of rock could have existed. Therefore, we may consider that this mosaic is a good example of *tesserae* trade in the Mediterranean area.

Ship ballasts in the Bay of Cadiz: their use as pavements in the Cadiz Old City quarters during XVII-XIX centuries. Petrological and Archaeometric approach

S. Domínguez-Bella, L. Criach, J. Martínez López

UGEA-PHAM. Departamento de Ciencias de la Tierra, Facultad de Ciencias, Universidad de Cádiz
salvador.dominguez@uca.es

In this project we are studying the constructive materials used as pavements in many streets and squares of the Cadiz old city centre as well as in other localities of its bay. These rounded, variable-sized boulders present a wide variety of lithologies, which are mostly exotic respect to local or regional geological materials.

An interdisciplinary methodology that has combined archaeometric studies based on the petrological, mineralogical and geochemical analysis of these rocks, together with the historical investigation in the local archives, allows establishing their nature and dates of use in the construction of the pavements. In this way, we also hope to provide information on the provenance of the ships that discarded their stone ballasts after making trips through the American continent, the Canary Islands, the ports of the European Atlantic or the Mediterranean coasts. Nowadays it is relatively frequent even to find these anthropic accumulations of boulders in some points of the Cadiz Bay, where these *saburrae* were shed, often illegally, in the salt marshes.The macroscopic study of the ballast was carried out in the UGEA-PHAM archaeometric unit at the Earth Sciences Department of the Cadiz University and the optical microscopy of the thin sections of the rocks, X-Ray diffraction and the X-Ray fluorescence analysis of the samples in the laboratories of the SCCYT, UCA.

Different groups of lithologies like sedimentary (limestones, flint, sandstones or conglomerates), igneous (basalts, granites) and metamorphic (quarzites, serpentinites, gneiss) were found. Preliminary results show that a great number of lithologies are present in the ballast, many of them have been identified up to now; for instance, flint nodules that possibly come from the English Channel area. Limestones and sandstones are common rocks in the province of Cádiz but lithologies as the igneous rocks (plutonic or volcanic) and practically all the metamorphic types are clearly allochthonous to the area and their origin is clearly exotic.

The huge number of ships that came to Cadiz over these centuries and the great number of existing routes makes very large the variety and possible geographical origins of these materials, no doubt an exciting challenge for the present and future study of these historical materials.

Identification of fungi present in the paneled ceiling of the Maidens' courtyard

A.C. Coba Peña[1], I. Martín Sánchez[2], A. García Bueno[1]

[1]Departamento de Pintura, Facultad de Bellas Artes, Universidad de Granada Av. de Andalucía, s/n, C.P. 18071, Granada, Spain
[2]Departamento de Microbiología, Facultad de Ciencias, Universidad de Granada, Av. de Fuente Nueva, s/n, 18071, Granada, Spain
anacristinacoba@hotmail.com

The *Real Alcazar* is one of the most emblematic architectural ensembles which are preserved in the city of Seville, being declared as UNESCO World Heritage in 1987 because of its great density and complexity in relation to the chronological evolution and all the functions carried out in it.

Among the most important and representative areas as a whole, we spot the palace of *Pedro I* -also known as Mudejar Palace- which was built between 1356 and 1636. Our team is attached to the *Grupo del Plan Andaluz de Investigación, "Laboratorio de Arqueología y Arquitectura de la ciudad" (HUM-104)*, from where many research works about the study of the architectural decoration of one of the most important courtyards of the palace - the courtyard of the Maidens - are being carried out. It´s a wide part of this research the study of the paneled ceiling, which is located in the South-East area of the low galleries.

Its location in an open area, like it is in the courtyard of the Maidens, makes it to be constantly exposed to a variety of intrinsic and extrinsic factors that in combination with the action of microorganisms like bacteria and fungi end up being the main responsible agents of the biodegradation of this architectural area.

It is necessary to pay special attention to the fungi. As a result of their saprobiontic and eukaryotic nature, they play an essential role in the biodegradation as they affect to the growing conditions of the hyphae and mycelium as well as their enzymatic process. Regardless of the way, both cases generate mechanical, chemical and aesthetic variations.

That's why, the principal aim of this work is to show the complex research done in order to discover the phenotypic identification of the involved fungi in the biodegradation of the courtyard of the Maidens. The methodology is divided in two different phases: one is focused on a fieldwork based in photographic documentation and sample collection. The second one is about laboratory work, where the study of sample, cultivations and identification are carried out.

The results show the presence of ascomycetes from the genus *Alternaria*, *Cladosporium*, *Trichoderma* and *Penicillium* among other non-identified ones. From these results, it will be possible to develop a specific conservation and restoration proposal to fight against all the variations produced by these species not only in the paneled ceiling, which is the target of this research, but in other similar problematical works.

Biodiversity and cleaning of phototrophic biofilms in Cueva del Tesoro, Rincón de la Victoria, Málaga, Spain

V. Jurado[1], M. Hernandez-Marine[2], C. Saiz-Jimenez[1]

[1]*Instituto de Recursos Naturales y Agrobiología, IRNAS-CSIC, Avenida Reina Mercedes 10, 41012 Sevilla, Spain*
[2]*Facultad de Farmacia, Universidad de Barcelona, Spain*
vjurado@irnase.csic.es

Caves are considered experimental locations of remarkable geological, ecological and microbiological interest, with diverse compartments that differ in physical, chemical and microbial composition. The study of the microbial diversity is important for many different reasons, but perhaps one of the most important is that caves may be potential sources of novel microorganisms producing bioactive compounds of medical interest.

In the last few years Cueva del Tesoro has been investigated regarding the need to control phototrophic biofilms colonizing cave speleothems. Cleaning of caves and speleothems should be preceded by an inventory of species and testing of treatment protocols due to the fact that cleaning with biocides revealed important negative effects in some caves.

We observed that the green phototrophic biofilms in this cave were uncommon and presented some characteristics worthy of study. These communities were triggered by the artificial lighting which is located in selected places along the visitor´s trail. The assemblages were mainly composed of Cyanobacteria (*Friedmannia* sp., *Nostoc* sp., *Phormidium* sp., *Gleocapsa*-like members, etc.) Chlorophyta (*Friedmannia* sp., *Chlorella* sp, *Choricystis* sp.), Rhodophyta (*Cyanidium* sp.), Bacillariophyta (*Diadesmis contenta*). Some locations develop abundant populations of the bryophyte *Eucladium verticillatum*. Some of the Chlorophyta and Rhodophyta are parasitized by unknown virus-like structures located on the cell walls, a topic of potential scientific interest.

Regarding the bacteria, three novel species are being studied and will be described: *Acinetobacter thesauricus*, *Bacillus thesauricus* and *Paracoccus speluncae*. In addition, two new species of the fungal genus *Aspergillus* were described: *Aspergillus thesauricus* and *Aspergillus baeticus*. The species name *thesauricus* refers to the place where the bacterial and fungal species were first isolated and described.

We tested three cleaning methods: i) Mechanical cleaning with liquid nitrogen, ii) Cleaning with sodium hypochlorite and iii) Cleaning with hydrogen peroxide. The most effective method was the use of hydrogen peroxide which was used by the restoration company carrying out the works. In addition, a remodelling of the lighting system and installation of new LED lamps in more appropriate places were suggested.

Cueva del Tesoro revealed to harbour a rich bacterial, fungal and algal diversity. The removal and cleaning of the biofilms was focused on biodeteriorated walls and speleothems. However, the analysis of the microbial communities revealed that this cave seems to be an important reservoir of microbial diversity, which suggests that in addition to cleaning and control of the biofilms, some actions are needed to preserve this cave and its microbial diversity. In fact, it was proposed and accepted by the managing cave authority to leave some reservoirs of biofilms in the cave, distant from the rock art galleries, that does not represent a threat for the cultural heritage, in order to preserve biodiversity.

Stone biodegradation and mitigation – the case of Convent of Christ, Portugal

T. Rosado[1], M. Silva[1,2], A. Galvão[3], J. Mirão[1,4], A. Candeias[1,2], A.T. Caldeira[1,2]

[1]HERCULES Laboratory, Évora University, Évora, Portugal
[2]Chemistry Department, School of Sciences and Technology, Évora University, Évora, Portugal
[3]Convento de Cristo, Direção Geral do Património Cultural, 2300-000 Tomar, Portugal
[4]Geosciences Department, School of Sciences and Technology, Évora University, Évora, Portugal
tania.s.rosado@gmail.com

The preservation of our built heritage has a determinant role in society, due to its architectural, historical and cultural value. Stone is a durable and long-lasting material; nevertheless, stoned monuments are constantly at risk due to inherent composition of the materials and the environmental conditions as well as to deterioration/degradation by microorganisms, which increases in urban environments, where deposition of pollutants enhances the deterioration rate. There are many factors that influence the growth and survival of the microorganisms like humidity, light, temperature, nutrients source and the nature of the materials. In favourable circumstances, the biological growth can compromise the artistic and historical values of stone monuments and contribute to its physical and chemical decay.

The Convent of Christ (UNESCO's World Heritage Monument, Tomar-Portugal) is one of the most expressive testimonies of Portuguese architecture, whose huge structure include seven cloisters, different monastic constructions and the emblematic Chapter Window (or Manueline Window). Unfortunately, over the years the stone materials have been suffering structural and aesthetic damages, which have modified the appearance of the surfaces and their integrity and conservation.

To answer key questions involving the dichotomic problem alteration-conservation of cultural heritage materials, multidisciplinary analytical methodologies together with microbiological and biomolecular approaches were applied to signalise the presence of microbial proliferation and characterise in detail the coloniser microbiota. Culture dependent-techniques allowed the identification of the cultivable microbiota which is very useful for simulations assays while the metagenomic approach based on Next Generation DNA Sequencing offered the possibility of profiling either the cultivable and uncultivable members of the microbial community, which provided a complete view of the total population that colonise this monument.

The study revealed that the stone materials of the Convent of Christ are strongly altered by stains, biofilms, cracks and detachment of some fragments and that these altered areas present high biocontamination levels, whose main players are bacteria, microalgae, cyanobacteria and filamentous fungi. Attending to the negative effects of the microbial population on the rock surfaces, our research is actively pursuing the microorganisms responsible for biodeterioration/biodegradation and attempting to quantify their effects and signalise the biodeteriogenic agents. Furthermore, simulation assays and the development of mitigation strategies, based on alternative green solutions, have been successfully tested and applied, promoting the safeguard of these stone materials.

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Assessing the effect of different coloured lighting in controlling biological colonization

P. Sanmartín[1], D.Vázquez-Nion[1], J. Arines[2], B. Silva[1], B. Prieto[1]

[1]Universidade de Santiago de Compostela. Departamento de Edafoloxía e Química Agrícola. Facultade de Farmacia. 15782 - Santiago de Compostela, Spain
[2]Universidade de Santiago de Compostela. Departamento de Física Aplicada. Facultade de Física. 15782 - Santiago de Compostela, Spain
patricia.sanmartin@usc.es

Growth of phototrophic microorganisms (algae and cyanobacteria) depends on the quantity (duration and intensity) and quality (colour or wavelength) of light. Microorganisms only use the spectral energy corresponding to peak absorption of pigments. Monochromatic LED lamps have a narrow spectral bandwidth and therefore may be useful for controlling the growth of phototrophs. In order to address this topic, we measured the specific emission spectra of green, blue and red LED lamps (which vary from 490-550 nm, 440-480 nm and 620-660 nm, respectively) with a BlueWave spectrometer (StellarNet). We also extracted the photosynthetic pigments from five cultures derived from natural subaerial biofilms developed on historical granite buildings and measured their specific absorption spectra with a UV-Vis spectrophotometer (Varian Cary 100). Two of these were monospecific cultures formed by green algae *Bracteacoccus minor* (C2) and cyanobacterium *Nostoc* sp. The other three cultures (C3, C4 and C5) contained common and widespread taxa of green algae (chlorophyta) and cyanobacteria. The emission band of the red and green LEDs occupied an area where there was no absorption peak of any of the five cultures (except *Nostoc* and C3 for the green light), which suggests that these lights did not favour growth of the microorganisms in any of the five cultures. The light emitted from the blue LED appeared to favour growth of all microorganisms studied, except *Nostoc* sp. In order to confirm the study findings, culture C5 was exposed to light from the three LED lamps: the biofilm thrived under blue LEDs, whereas red and especially green LEDs had a weak biostatic effect. These findings are consistent with the hypotheses proposed in the present study, and we believe that the method described here could be used with other phototrophic cultures.

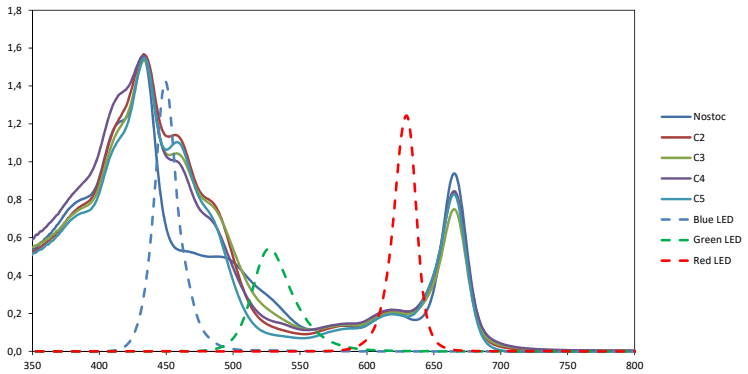

Figure. Absorption spectra of pigments and emission spectra of LED lamps in the range 350-800 nm.

Effect of multiple interactions between fungal species on the colonization of two limestone lithotypes

S. Gómez-Cornelio [1], A. Morón-Ríos [1], A. Sierra-Fernández [2,3], S. González-Gómez [4], S. De la Rosa-García [5], S. Cappello-García [5], P. Quintana [4]

[1]El Colegio de la Frontera Sur, Av. Rancho polígono 2A, Ciudad Industrial Lerma, 24500, Campeche, México
[2]Instituto de Geociencias (CSIC, UCM), Madrid, Spain
[3]Carlos III University of Madrid, Dept. of Materials Science and Engineering, Madrid, Spain
[4]Departamento de Física Aplicada, CINVESTAV-IPN, A.P. 73, Cordemex, 97310, Mérida, México
[5]División Académica de Ciencias Biológicas, Universidad Juárez Autónoma de Tabasco, Carr. Villahermosa-Cárdenas Km. 0.5, 86150, Villahermosa, México
arsierra@ucm.es

The growth of organisms, or biofilms, on the surface of cultural patrimony sites is often considered to lead to aesthetic and visual deterioration. In these biofilms, a large variety of microorganisms coexist, including fungal communities. These communities vary as a result of multiple factors, such as substrate bioreceptivity, environmental conditions, and the time of exposure of the substrate to the environment. However, the role of multiple species in the protection or the deterioration of substrates, as well as in the colonization and establishment of the dominant fungi on lithotypes of calcareous rock, has not been investigated. Of the total fungal community growing on rock walls, two species of high frequency were selected from biofilms with 1, 5 and 10 years of exposure to a tropical environment. *Phoma eupyrena* (9%) and *Paraconiothyrium* sp. (7.4%) were selected from the 1-year biofilm, *Curvularia lunata* (32%) and *Fusarium redolens* (12.7%) from the 5-year biofilm, and *Myrothecium roridum* (6%) and *Pestalotiopsis maculans* (4%) from the 10-year biofilm. To evaluate the colonization of these fungi, 120,000 spores were inoculated in either compact or porous lithotype blocks (2x2x1 cm). The treatments included: as controls each fungal species inoculated alone, and also evaluated the interactions between the two species of each biofilm, among 4 species (two species from each biofilm in all possible combinations), and, lastly, among all 6 species. The blocks were incubated at room temperature for one year, and moisture was applied each week. We found homogeneous colonization of fungal species on both rock lithotypes. However, in treatments with hyaline species, a preference was observed for colonizing rock pores, while species with melanized structures colonized the whole area of both lithotypes. Fungi *P. eupyrena* and *C. lunata* had the highest frequency of growing in isolation and being melanized, and these fungi exhibited the best capacity to establish on and colonize rocks of both lithotypes. Only *Paraconiothyrium* sp. and *P. maculans* produced calcium oxalate crystals in the controls, while the crystal production of interacting fungi was variable and a function of the interacting species. In interactions with fewer numbers of species, melanized fungi covered a larger area, while in those with greater numbers of species, melanized structures showed less coverage. Fungi protected the blocks by inhibiting the growth of species with biodeteriorating potential. Species with higher colonization rates could cause an esthetical deterioration of walls yet also have a protective function, which would be relevant for the conservation of cultural heritage sites.

Environmental-like colonization of granitic rocks in laboratory for bioreceptivity studies

D. Vázquez-Nion, B. Silva-Hermo, B. Prieto-Lamas

Universidade de Santiago de Compostela. Departamento de Edafoloxía e Química Agrícola, Facultade de Farmacia, 15782 Santiago de Compostela, Spain
benita.silva@usc.es

In most bioreceptivity experiments, single species or a mixture of isolated strains have been used to inoculate the stone under study. These simplified laboratory models can be very useful owing to their simplicity, genetic tractability and high degree of experimental control. However, microorganisms develop naturally on stone in complex microbial communities forming subaerial biofilms. Therefore, tests carried out with a single type of organism may not enable the complex processes involving an environmental community structure, such as the competition and/or synergy between colonising microorganisms, to be taken into account. The use of cultures that resemble the microbial communities of natural subaerial biofilms, especially if they include pioneer colonizers such as green algae and cyanobacteria, could lead to a better simulation of environmental biofilm development in these types of studies.

The present research focuses on the development and evaluation of a phototrophic multispecies culture in order to be used as standard inoculum in experiments directed to the study of the bioreceptivity of granitic rocks. For this purpose, a subaerial biofilm naturally grown on a granitic historic building (Monastery of San Martín Pinario, Santiago de Compostela, NW Spain) was cultured in BG11 liquid medium until establishment of stable microbial communities. The culture comprised several taxa, including Bryophyta (*Syntrichia ruralis* protonemata), Charophyta (*Klebsormidium* sp.), Chlorophyta (*Bracteacoccus* sp., *Chlamydomonas* sp., *Chlorella* sp. and *Stichococcus bacillaris*) and Cyanobacteria (*Aphanocapsa* sp. and *Leptolyngbya cebennensis*), which can be considered as common pioneer colonisers of building stone surfaces, including granite. Subaerial biofilms were successfully developed in laboratory by inoculating this culture on granite blocks, which were subjected to stationary conditions of temperature (23 ºC), light (~20 µmol photon m^{-2} s^{-1}, 12h light/dark photoperiod) and moisture (95% relative humidity and permanent access to water by capillarity). Biofilm growth was assessed by PAM fluorometry, reflectance spectroscopy and confocal laser scanning microscopy (CLSM). Chlorophyll fluorescence and colour measurements enabled biofilm formation to be reliably and non-destructively monitored, while CLSM enabled observation of biofilm composition and spatial organization. An environmental-like colonization of granite in laboratory was achieved, showing sigmoidal growth curves that resemble natural biological successions and chl*a* values up to 6.86 µg cm^{-2} in the phototrophic biofilms formed. The phototrophic multispecies culture proved thus suitable for bioreceptivity studies, mainly due to its microbial richness, rapid adaptability to the substratum and high capacity for colonization.

Antimicrobial activity of essential oils: a green alternative to treat cultural heritage

N. Macro[1], C. Sbrana[2], S. Legnaioli[3], E. Galli[1]

[1]IBAF-CNR, Research Area of Rome1-Montelibretti,Via Salaria km 29,300, Rome, Italy
[2] IBBA-CNR, Via del Borghetto 80, 56124 Pisa, Italy
[3]ICCOM-CNR, Via G. Moruzzi, 1 - 56124 Pisa
emanuela.galli@ibaf.cnr.it

Fungi are ubiquitous organisms able to colonize organic substrates such as paper, paintings, stone or even synthetic polymers giving rise to phenomena of biodeterioration or biofouling. The best approach to the conservation remains the prevention, controlling temperature and relative humidity and keeping the museums free of dust and dirt. However, sometimes these measures are not sufficient and biocidal products must be used to disinfect the contaminated object or environment. Unfortunately, often these products are toxic for the operator and/or pollutant for the environment.

Essential oils (EOs) are the odorous, volatile products of the secondary metabolism of aromatic plants. The recent interest in researching for natural solutions is leading to these substances, which can be used as a fumigant, as an alternative to conventional chemicals. Several studies have shown that some EOs have a strong antifungal, antiviral, insecticidal and anti-oxidant effect, while showing little harm to humans and warm-blooded animals.

The inhibitory activities of vapour phase of essential oils of *Eugenia caryophyllata*, *Cinnamomum cassia* and *Cinnamomum camphora* were tested against fungi that usually attack and colonize library and archival materials. The oils have been chosen on the basis of the main functional groups: alcohol for *C.camphora* oil, phenol for *E. caryophyllata* oil and aldehyde for *C.cassia* oil. GC-MS analysis showed that the main component concentration was superior to 75%.

Aspergillus flavus, *Aspergillus niger*, *Stachybotrys chartarum* and *Chaetomium globosum* were grown in Petri dishes containing optimal grow medium. Different amounts of EOs (1, 5, 10, 20, 30, 40 or 50 µl) were spread on paper or cotton discs, placed in the centre of the Petri plate lids. The fungi diameter was measured after 7 and 14 days.

Antifungal activity was documented for all the tested EOs and their action was more or less significant depending on the substance and the quantity used. *A. flavus* showed the smaller sensitivity to all the EOs tested, still growing in the presence of 30 µl of *C.cassia* and *C.camphora* oil at 14th day.

EOs from *E. caryophyllata* and *C. Cassia* showed the strongest antifungal activity by growth inhibition of *C.globosum* and *S.chartarum* already at low quantities.

Cave microorganisms and their role in the conservation and effective management of wild and show caves

S. Cuezva[1,2], J.C. Cañaveras[3], V. Jurado[4], A. Fernandez-Cortes[5], D. Benavente[3], S. Sanchez-Moral[2], C. Saiz-Jimenez[4]

[1]Geomnia Natural Resources SLNE, Madrid, Spain
[2]Museo Nacional de Ciencias Naturales, MNCN-CSIC, Madrid, Spain
[3]Dpto.de Ciencias de la Tierra y del Medio Ambiente, Universidad de Alicante, Alicante, Spain
[4]Instituto de Recursos Naturales y Agrobiologia, IRNAS-CSIC, Sevilla, Spain
[5]Dpto. de Biología y Geología, Universidad de Almería, Almería, Spain
scuezva@geomnia.es

Microbial colonization of different substrata is one of the greatest threats for cultural heritage conservation. This problem constitutes a major challenge in subterranean environments (caves, catacombs, etc.), especially in those touristic sites. Walls, ceiling and sediments are usually coated with microbial communities in the form of colored spots (yellow, white, grey, rosy, etc.). For this reason in an hypogea conservation survey, identifying the microbial assemblages is one of the main aspect to be considered. Assessing their interactions with the diverse substrata (paintings, rocks, speleothems, etc.) is another main one.

The microbial growth curves show that once installed on a substratum, the bacteria undergo a first lag phase or adaptation of their metabolism to the environmental conditions and substratum characteristics. This phase is characterized by a low rate of reproduction and growth of the microbial community, "they are but are not seen".

The duration of this phase depends mainly on the nature and availability of nutrients. The main challenge is to find out the environmental and ecological conditions that make possible the persistence and development of a specie until the exponential growth phase is achieved. Knowing this, perhaps the future studies of conservation could be focused to avoid irreversible deterioration problems. Our previous researches show that microorganisms forming biofilms on rock surfaces interact with rock, water and underground air and have the ability to control their own micro-environment and to trigger large scale changes in cave environment. For this reason, it is necessary to develop environmental studies with the aim of characterizing each sub-environment in the studied underground ecosystem.

In this study, we present some examples of biodeterioration by bacterial activity in different caves and underground archaeological sites. Different methods have been used: Electron microscopy observations revealed that a dense network of microorganisms composes these spots, which are coated with overlying bioinduced $CaCO_3$ crystals. Molecular analysis indicated that these spots are mainly formed by complex assemblages of microorganisms, mainly undescribed species of the phylum Actinobacteria. On the other hand, CO_2 efflux measurements in areas heavily colonized by bacteria indicated that some groups of bacteria have the ability to promote the uptake of this gas, usually very abundant in the caves. This leads to dissolution of the rock substratum and the precipitation of $CaCO_3$ crystals during periods of lower humidity and/or CO_2.

Effect of calcium zincate dihydrate purity synthesized via sol-gel, on its antimicrobial activity

S.C De la Rosa-García[1], M. Soria-Castro[2], Y. Sánchez-Román[1], U. Zagada-Dominguez[2], S. Gómez-Cornelio[1], A. Sierra-Fernández [3,4], P. Quintana[2],

[1]División de Ciencias Biológica Universidad Juárez Autónoma de Tabasco, México
[2]Departamento de Física Aplicada CINVESTAV-IPN, AP. 73, Cordemex, Mérida, Yucatán, México
[3]Instituto de Geociencias (CSIC, UCM), Madrid, Spain
[4]Carlos III University of Madrid, Dept. of Materials Science and Engineering, Madrid, Spain
arsierra@ucm.es

Nowadays, one of the main problems for the conservation of historical monuments constructed with limestone in the Yucatan Peninsula (humid tropical climate) of Mexico is their biodeterioration due to the metabolic activity of several microorganisms growing on them. Thus, the development of an effective nanomaterial with antimicrobial properties is necessary, in order to minimize the deterioration process. Previously, we reported the antifungal activity of calcium zinc hydroxide dihydrate, $Ca[Zn(OH)_3]_2 \cdot 2H_2O$ (CZ) [1]. The main objective of this study was to determine the antimicrobial efficiency of CZ nanoparticles synthesized by the sol-gel method with different grades of purity and crystallinity (94, 82 and 76%). The CZ nanoparticles were characterized by X-ray diffraction (XRD) and their antimicrobial activity to different concentrations (10 at 0.078 mg/mL) was detected by the diffusion agar method, and by the microdilution method to obtain the minimum inhibitory concentration (MIC), using international reference strains of *Staphylococcus aureus*, *Escherichia coli*, *Candida albicans* and two filamentous fungus (*Penicillium oxalicum* and *Aspergillus niger*) isolated from a black biofilm consolidated in a calcareous rock . Results by XRD of the synthesized CZ showed development of different compounds, mainly calcium zinc hydroxide dihydrate ($Ca[Zn(OH)_3]_2 \cdot 2H_2O$, CZ), and in minor proportions portlandite ($Ca(OH)_2$) and Calcite ($CaCO_3$). The phase ratio for different percentages is: for the higher concentration at CZ94%+$CaCO_3$6%; then CZ82%+$CaCO_3$18%; and for the lower at CZ76%+$CaCO_3$18%+$Ca(OH)_2$ 6%. The antimicrobial assay showed that all CZ nanoparticles have broad-spectrum antimicrobial activity, although, the higher efficiency activity was detected for CZ (76%), where the antimicrobial activity of CZ nanoparticles is combined with calcite and portlandite. Results obtained by the diffusion agar method of CZ (76%), showed inhibition zone of 11 at 23 mm at a concentration of 0.625 mg/mL. In general, Gram-negative bacteria and yeast are more resistant than Gram-positive bacteria and filamentous fungi. With respect to MIC, we determined that 0.078 and 1.25 mg/mL of CZ (76%) are necessary to inhibit *S. aureus* and *E. coli*, respectively; while the minimum concentration of CZ (76%) which inhibited the growth of yeast and filamentous fungus was 0.156 mg/mL for *A. niger* and 0.312 mg/mL for *P. oxalicum* and *C. albicans*. Based on the results of antimicrobial tests, CZ (76%) showed a higher potential as a novel material for the protection of limestone against the biodeterioration, based on the idea to combine the compatibility of these phases and their synergic effect with CZ.

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Coupling air and surface samples: input on the study of biodeteriorated limestone and public health analyses

A.C. Pinheiro[1], N. Mesquita[1], C. Coelho[1], F. Soares[1], H. Paiva de Carvalho[1], F. Gil[2], L. Catarino[3], G. Piñar[4], J. Trovão[1], I. Tiago[1], A. Portugal[1]

[1]Centre for Functional Ecology, University of Coimbra, Coimbra, Portugal
[2]Centre for Studies of X-Ray Diffraction Material, University of Coimbra, Coimbra, Portugal
[3]Geosciences Center, University of Coimbra, Coimbra, Portugal
[4]University of Natural Resources and Life Sciences (BOKU), Vienna, Austria
aportuga@bot.uc.pt

In 2013, UNESCO classified the 'University of Coimbra – Alta and Sofia' as a World Heritage site which elevates the level of commitment society must devote to its preservation.

Built between the XII and the XIII century, the Old Cathedral (Sé Velha) is one of the Monuments included in this site but the soft and porous limestone with which it was built is prone to a series of deteriorating agents: weather, pollution and microorganisms are some of them. Bacteria and Fungi are two major groups of these microorganisms and they can both induce chemical and physical changes in petrous materials.

Mycostone – a project developed to better understand the agents and mechanisms responsible for the actual state of conservation of this World Heritage site – encompasses extensive sampling of both surfaces and the air surrounding them. Fungi and bacteria are especially under scope since these are powerful biodeteriogens and are normally encountered - due to their intrinsic features – in both types of samples.

Because their presence is seldom investigated at the same time and location, the study on the correlation between air and surfaces is one of the outputs of this project. As happens in other settings, settlement of fungal spores and bacteria is expected and similarities between communities will arise. However, given the unique opportunity to deeply analyze the relationship between endolithic and epilithic damage and the fungal/bacterial agents present it will be possible to confirm if otherwise considered as common airborne microorganisms do play a pivotal role in the biodeterioration of limestone.

Another important aspect also focused in Mycostone is public health and human exposure to potential toxinogenic fungi. Air samples are used to assess this important parameter for which data are very scarce in Portuguese Monuments.

Overall, this work allows not only a better understanding of the problematic of limestone biodeterioration, but also a deeper insight of the relationship between air and surface samples, specific biodeteriorating organisms and phenomena, and air fungal and bacterial load, as seen by a conservation and a public health point of view.

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