HEROMAT
Protection of Cultural Heritage Objects with Multifunctional Advanced Materials

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"Protection of cultural heritage objects with multifunctional advanced materials"
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FINAL REPORT

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Project website: www.heromat.com

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I. EXECUTIVE SUMMARY

The multidisciplinary research project HEROMAT was focused on the development of innovative environmental friendly materials with value added functions aimed to the protection of immovable cultural heritage assets. The project cross-linked a Pan-European team from the UK, Italy, Slovenia, Serbia and Russia, including experienced researchers, young researchers, conservation scientists, restorers and industrial SME partners. The project investigation involved chain of activities from the synthesis, establishment of the methodology for characterization and testing of novel protective materials through their pilot production and, finally, to the in situ application and monitoring on the selected historical buildings, giving also their life cycle assessment. The final results embrace a set of novel materials applicable for the protection of different inorganic mineral substrates providing multiple added functions: consolidation, self-cleaning and anti-microbial effects. New materials are applied onto two case study historical objects: Bač Fortress in Serbia located in urban and Dornava Manor in Slovenia, placed in rural environment, both having continental climate.

Three final HEROMAT products, two consolidants (carbonate based and silicate based) and one photocatalytic protective material are providing sustainable solution for the preservation of the physical state and the resistance to degradation of the immovable cultural monuments, sustaining the functionality and the aesthetic appearance through a long period of time. The carbonate consolidant was protected as the patent under the number PCT/SI2014/000028, while the photocatalytic coating is protected by the means of business secret. During the project lifetime HEROMAT products application went beyond the planned project scope. The carbonate consolidant was applied on frescos in two cultural heritage monuments, whereas protective coating was used on walls of the Petrovaradin Fortress on the Danube River.

The project brought new research results to the market. New eco-friendly materials could help heritage managers to ensure that cleaning and protection works become less frequent and less costly. The products are ready for industrial production, and once available on the market, they will have wide application potential, both in terms of cultural heritage protection and even in modern civil engineering.

The project also developed a methodology for assessing the adhesion characteristics of the photocatalytic suspension on porous mineral substrates, and for evaluating the antifungal characteristics of porous mineral substrates. Project results have been published in reviewed scientific papers, while HEROMAT also featured during Europe Heritage Days, a locally-led EU initiative that provides access to thousands of rarely opened sites to over 20 million people every year. By participating, HEROMAT hopes to have helped reconnect citizens with local cultural landmarks. On the occasion of the Europe Heritage Days 2013 a short documentary on HEROMAT was broadcasted on Euro News in the award-winning program Futuris. The HEROMAT also contributed to networking and acted as one of the founders of the cluster “Nano and Advanced materials for Cultural Heritage” – NANOMECH which provides a powerful mechanism for sharing knowledge and experience within a network of different stakeholders active in the cultural heritage sector.

II. SUMMARY DESCRIPTION OF THE PROJECT CONTEXT AND THE MAIN OBJECTIVES

HEROMAT PROJECT CONTEXT

The cultural heritage (CH) protection, conservation and preservation are a team work, placed in the middle ground between science and technology. In recent years a lot has been done to develop new treatments for the conservation of CH objects (immovable, movable) and to respond effectively to the degradation and its various causes. Significant efforts are being devoted to achieve compatible eco-friendly materials and new techniques for more durable treatments and healing of the damages of CH. In addition to an efficient conservation-restoration, the purpose is also to maintain the object "healthy" over time. In that sense, there is an increasing need for non-invasive investigation of CH materials. The preservation of the material testimony, by the use of new conservation materials and techniques, gives the cultural assets a chance to last longer in order to be preserved for future generations, but also opens up a path towards future conservation. There is emerging need to promote awareness of the CH as non-renewable resource and foster synergies amongst stakeholders in decision making, promotion of CH research and education on a national and international level.

The idea behind the HEROMAT project was to put in use the most advanced inter- and multidisciplinary knowledge existing within the Consortium in the field of materials science, technology, architecture, arts as well as SMEs expertise for design and application of new materials for consolidation and protection of immovable cultural heritage objects. Two case study sites were selected for in-situ characterization of historic materials, application of HEROMAT developed materials and in-situ monitoring of their effects, including environmental monitoring. Those two sites are both placed in European continental climate: Bač Fortress in Serbia in urban area and Dornava Manor in Slovenia located in rural setting. The HEROMAT project involved Pan-European team from Serbia, Slovenia, Italy, United Kingdom and Russia, which complement each other and provide research outcomes based on the most advanced knowledge and skills in the specific areas of their expertise.

The research started with selection and characterization of historic materials from the case study immovable CH objects, continued with preparation of model substrates and their ageing, synthesis and laboratory production of advanced materials, their laboratory application onto the model substrates and characterization of these systems. It included establishment of new methodologies for characterization and improved the existing ones, launched pilot production of the novel materials, performed in-situ application and in-situ monitoring, life cycle assessment of the HEROMAT materials and finally designed multidecision tool for heritage managers and professionals to facilitate future market placement of HEROMAT materials and support choosing them over the competing ones.

The HEROMAT project joined the first cluster in cultural heritage organized among FP7 funded projects www.nanomech.eu launched in November 2012. It acts as platform for sharing knowledge and experience within a network of different stakeholders active in the cultural heritage sector such as research institutions working on materials and technologies for heritage applications, policymakers, manufacturing SMEs and other industrial companies, conservators, galleries, museums, representatives from heritage sites, etc. The mission of the cluster is to disseminate the results of the projects, contribute in maximizing exploitation opportunities by SMEs and help improving European cultural heritage sector. It also serves as staring ground for new project applications dealing with protection and conservation of immovable and movable cultural assets.

PROJECT CONSORTIUM

No	Name	Short name	Country
1	TEHNOLOSKI FAKULTET NOVI SAD	TFUNS	Serbia
2	ZAVOD ZA GRADBENISTVO SLOVENIJE	ZAG	Slovenia
3	CONSIGLIO NAZIONALE DELLE RICERCHE	CNR – ISTM	Italy
4	UNIVERSITY OF THE WEST OF SCOTLAND	UWS	United Kingdom
5	FEDERAL STATE AUTONOMOUS EDUCATIONAL INSTITUTION OF HIGHER PROFESSIONAL EDUCATION NOTHERN (ARCTIC) FEDERAL UNIVERSITY	NArFU	Russian Federation
6	POKRAJINSKI ZAVOD ZA ZASTITU SPOMENIKA KULTURE NOVI SAD	PZZSK	Serbia
7	JAVNI ZAVOD REPUBLIKE SLOVENIJE ZA VARSTVO KULTURNE DEDISCINE	ZVKDS/IPCHS	Slovenia
8	GRADEVINSKO PREDUZECE HGP DRUSTVO SA OGRANICENOM ODGOVORNOSCU	GP HGP	Serbia
9	SANING INTERNATIONAL PODJETJE ZA SANACIJE OBJEKTOV DOO KRANJ	SANING	Slovenia
10	Eura Conservation Ltd	EURA	United Kingdom

OVERVIEW OF THE PROJECT WORK PACKAGES ORGANIZATION AND OBJECTIVES

The project was organized in 10 work packages (WP) listed below with their activity types (RTD, MGT, DEM, OTHER), star and end months, lead partner and specific objectives.

MANAGEMENT OF THE PROJECT CONSORTIUM			Work package: WP1
Type of activity: MGT	Start month: 1	End month: 48	Lead: TFUNS

- ensure effective communication and good work relationships among the partners; financial monitoring and manage financial reporting; facilitate exchange of information within the Consortium; ensure effective communication with the EU Commission and services.

RTD COORDINATION			Work package: WP2
Type of activity: RTD	Start month: 1	End month: 48	Lead: TFUNS

- ensure effective lead, coordination organization, monitoring and reporting on RTD activities; guarantee deliverables are reported and milestones achieved on time; assure quality of the project (technical and scientific level of the activities, reports, demonstration parts, and deliverables); support and facilitate implementation of the project tasks, communication and dissemination of research results; develop alternative plans, if necessary or desired, and manage risks, contingency plans/responsibilities.

SELECTION, PREPARATION AND CHARACTERIZATION OF MINERAL SUBSTRATES			Work package: WP3
Type of activity: RTD	Start month: 1	End month: 18	Lead: ZVKDS/IPCHS

- design model substrates (stone, clay brick, mortar, render, colour finishing layer) on the basis of the results of investigation of materials from specific historical sites; simulate aging and degradation processes of the selected model substrates; characterize model substrates before and after aging and degradation processes; create substrates for testing newly developed materials prior to their application onto the selected historical objects.

DEVELOPMENT OF PROTECTIVE AND CONSOLIDATIVE MATERIALS WITH ADDED FUNCTION			Work package: WP4
Type of activity: RTD	Start month: 1	End month: 24	Lead: TFUNS

- define targeted performances of protective systems, consolidated systems and protective-consolidated systems to be developed; synthesize powdered photocatalytic active inorganic-inorganic nanocomposites using LDHs and photocatalytic active semiconductors; develop photocatalytic active suspension as coating precursor; develop consolidant formulations for carbonate and silicate substrates as part of the multifunctional systems.

ESTABLISHMENT OF METHODOLOGY FOR MATERIAL CHARACTERIZATION AND TESTING			Work package: WP5
Type of activity: RTD	Start month: 7	End month: 24	Lead: ZAG

- characterize and examine in detail the promising formulations of the coating precursors and consolidants selected in WP4 according to the adopted method; determine methods for characterization of physico-mechanical properties of protective, consolidated and protective-consolidated systems; determine the appropriate methods for investigation of photocatalytic efficiency of protective and protective-consolidated systems; determine the appropriate method for investigation of antimicrobial efficiency of protective and protective-consolidated systems; determine the appropriate method for investigation of hydrophobic effect (surface tension) of consolidated systems; determine the appropriate methods for investigation of consolidant efficiency on the selected model substrates; systemize methodology for complete evaluation of protective, consolidated and protective-consolidated systems performances.

LABORATORY APPLICATION OF OPTIMAL FORMULATIONS ON MODEL SUBSTRATES AND TESTING			Work package: WP6
Type of activity: RTD	Start month: 13	End month: 34	Lead: SANING

- determine the most efficient techniques for the application of coating precursors and consolidant formulations on model substrates (MSUB) and on broad range model substrates (BRMSUB) prepared in WP3; apply (with the most efficient techniques) coating precursors and consolidant formulations on MSUB and optimal coating precursors and consolidant formulations on BRMSUB; investigate durability of protective system, consolidated system and consolidated-protective system.

PILOT PRODUCTION			Work package: WP7
Type of activity: DEM	Start month: 19	End month: 30	Lead: GP HGP

- establish pilot production of developed coating precursors; establish pilot production of developed consolidants; implement novel equipment based on the results of the laboratory research (WP4 and WP5); estimate the manufacturing cost; train the SMEs work force.

In situ APPLICATION AND MONITORING			Work package: WP8
Type of activity: RTD	Start month: 12	End month: 42	Lead: CNR-ISTM

- select specific areas at case study heritage objects for the application of newly developed materials, previously prepared in pilot production (WP7); define the most appropriate surface pretreatment for the application in real conditions on the site of specified objects (Bač Fortress and Dornava Manor); apply newly developed materials on the selected areas of cultural heritage objects; in situ monitoring of the treated surfaces on Bač Fortress and Dornava Manor with a non-invasive multi-technique method.

LCA OF ADVANCED PROTECTIVE MATERIALS			Work package: WP9
Type of activity: RTD	Start month: 7	End month: 42	Lead: ZAG

- support development of new innovative materials for protection of cultural heritage in regard to low impact on the environment; ensure push towards new materials with low or zero adverse environmental impacts.

DISSEMINATION OF RESEARCH RESULTS			Work package: WP10
Type of activity: OTHER	Start month: 1	End month: 48	Lead: PZZSK

- disseminate project results with academic and professional community; disseminate project results and raise awareness about the project aims among broader audience (scientists, industry and local communities of case study cultural heritage sites); enhance the reputation of participants at local, national and international level; enhance the international visibility of the developed products; generate market demand for the developed product or services.

TWO CASE STUDY CULTURAL HERITAGE OBJECTS

Bač Fortress is of a special value as the cultural heritage, a unique example of a "water town" built on the marshy left bank of the Danube. Although its physical integrity is substantially lost, the preserved elements indicate a sophisticated fortification school of High Gothic style, with the elements of early Italian Renaissance.

Bearing in mind that the Bač Fortress is in ruins (architectural and archaeological remains of a fortress after it was mined at the beginning of the 18^{th} century), much is expected from the new material implementation, both in terms of mitigating the harmful effects and the consolidation of the already existing damages.

Dornava Manor - After several decades of accelerated degradation, exposed to various environmental factors and inappropriate restoration actions, the exterior elements (façade, statues and other ornaments) today show only a faint picture of the past splendour of the manor. Therefore, it was selected to be the subject of an in-depth research giving indicators that would stop further deterioration of the manor.

III. DESCRIPTION OF THE MAIN SCIENTIFIC & TECHNOLOGICAL RESULTS/FOREGROUNDS

Two historical sites were selected as case study objects for the application of newly developed materials, one in Serbia (Bač Fortress) and one in Slovenia (Dornava Manor). The study on the constituents and conservation state of the case study buildings was done at the beginning of the project in order to facilitate proper selection of model substrates and aging conditions during laboratory research. Selection of materials, sampling and characterisation was the first step which included all substrate materials (stone, clay brick, mortar, render and colour finishing layer).

On the basis of the results of analytical work on the samples collected from two historical sites (WP3) model substrates (MSUB) and broad range model substrates (BRMSUB) were prepared. The selected MSUB and BRMSUB were laboratory aged, involving several procedures: outdoor exposure (accelerated UV exposure, temperature cycling under the controlled humidity conditions), freeze-thaw cycling, SO_2 polluted atmosphere, exposure to the salt crystallization, and microorganism contamination. Before the application of newly developed HEROMAT materials, the model substrates were divided into two groups. First group of substrates was artificially aged, while the second group of substrates was used as the control samples.

For the development of new consolidative and protective materials (WP4) their targeted performances were set: compatibility with the selected historical materials, increased durability, reversibility, and adaptability to different application techniques and different level of material physical damage. Three types of new materials were designed and synthetized in laboratory conditions:

- consolidant for carbonate based substrates
- consolidant for silicate based substrates
- photocatalytic coating as self-cleaning protective material.

Methodology for characterization (diagnostic tool) of newly developed multifunctional systems was established to serve for evaluation (WP5) of promising formulations of coating precursors and consolidants developed and selected in WP4. It included physico-chemical characterization, photocatalytic activity and antimicrobical efficiency, consolidation efficiency and penetration depth. The characterization of promising coating formulations revealed no significant difference of textural properties of the model substrates after applying coating formulations, appropriate durability, photocatalytic and antimicrobial activity, no significant reduction of water vapour permeability and very good transparency. Consolidants for carbonate based substrates exhibited high consolidation efficiency, deep penetration depth and negligible colour change of substrates after application, high water vapour permeability with unchanged water absorption, uniform drilling force through entire profile and non-toxic character. The promising formulation for silicate based substrates showed deep penetration depth into model substrates, high consolidant efficiency, negligible decrease of water vapour permeability, small colour change after application. Based on the results obtained, three optimal formulations of new materials were selected for pilot production in WP7 and for the application on the broad range model substrates in WP6.

In order to assess the newly developed materials and application techniques in real environmental conditions, the experimental panels were designed (WP6). For example, wooden panel with bamboo background with a layer of mortar of similar characteristics with the old mortar built in the walls of the Bač Fortress was divided into four equal, smaller parts. In the upper two parts, the mineral substrates such as bricks, renders and the pieces of old brick were embedded. The lower parts of the panel contained mineral substrates such as renders and mortars. The protective coating was applied on all kinds of the mineral substrates. After the application, the panel was placed on the wall of the Bač Fortress in order to be exposed to the same environmental conditions. After one year of exposure the visual inspection of the experimental panel showed no changes considering the surface appearance. Similar experiment was set up in the Dornava Manor.

The pilot productions (WP7) of the newly developed coating and consolidant precursors were set in the third project year. The optimization of the production parameters was chosen to improve the most important functional properties of the newly designed materials and to optimize the cost of the production itself. The pilot production was set up in premises of SME partners: GP HGP, Serbia (photocatalytic suspension) and Saning, Slovenia (consolidants).

After an educated selection of the testing areas, the newly developed multifunctional systems were applied on different types of historical surfaces (WP8). The chemical, physical and mechanical properties of the treated surfaces were assessed over one year using a multi-technique approach based on different non-invasive spectroscopic, optical and mechanical methods. All the analytical data were digitally organized using a documentation tool, thus being available for future monitoring activities. Newly designed HEROMAT systems resulted highly compatible with the aesthetic properties of originals substrate determining negligible or temporary colour variations. The good durability of the photocatalytic coating was proved on all treated areas, while the treatments with carbonate and silicate base consolidants improved durability.

The environmental footprints (WP9) of novel materials were found to be relatively low and products can be considered as environmentally friendly using the Life-cycle assessment methodology (LCA). This was also the first reported work with LCA applied to restoration materials in cultural heritage sector. To support cultural heritage managers and professional to opt for HEROMAT materials a multi-decision tool was designed taking into consideration the main characteristics of any consolidative and protective materials gathered from their data and safety sheets. Comparing performance characteristics and health and safety data a preliminary decision was made, as to which of the available materials are the most suitable for treatment of a given piece of cultural heritage.

The promotion of research results expanded mixing dissemination activities in many different ways. Most of the targeted groups were approached including academic, industry, local communities, stakeholders and decision makers, students and even school children. As result, ideas and project outcomes started to spread among people outside the Consortium countries. Outstanding contribution to project visibility was brought by website and social networking. Putting the project on the social networks, Facebook and Twitter attracted much more people, mostly young generations and made the results and activities more visible for the public.

The highlight of the media promotion was definitely the unique TV documentary *A new "skin" for old stones*, the leading European information networks Euro News in collaboration with award-winning program Futuris recorded in a form of short documentary about the project HEROMAT. It was broadcasted in the framework of the week of European cultural heritage in September 2013 to 130 countries in thirteen languages.

MAIN SCIENTIFIC AND TECHNOLOGICAL FOREGROUNDS

Main scientific and technological foregrounds, including developed HEROMAT products, new methodologies and generated knowledge, are all listed in the Exploitation Agreement signed by all partners before the end of the project.

Foreground ownership and access rights

No.	Description of Foreground	Related WP	Owner(s)	Partners to which access rights will be granted and conditions
1	Methodology for characterization of mineral historical materials (stone, render, mortar, brick, concrete, finishing coating)	WP3	ZVKDS/IPCHS UWS TFUNS CNR-ISTM NArFU PZZSK ZAG	Free user rights for all project partners for educational and research purposes.
2	Preparation of model substrates	WP3	TFUNS ZAG ZVKDS/IPCHS Saning	Free user rights for all project partners for educational and research purposes.

No.	Description of Foreground	Related WP	Owner(s)	Partners to which access rights will be granted and conditions
3	Artificial ageing	WP3	TFUNS ZAG ZVKDS/IPCHS	Free user rights for all project partners for educational and research purposes.
4	Development of new photocatalytic coating – IP protected by means of business secret	WP4	GP HGP TFUNS	License / Commercialisation rights to GP HGP for commercial exploitation (production). Conditions for exploitation will be defined in separate contract between TFUNS and GP HGP.
5	*Patent PCT/SI2014/000028* - Development of new consolidants	WP4	ZAG Saning	Preferential rights / License / Commercialisation rights to Saning for commercial exploitation (production). Conditions for exploitation will be defined in separate contract between ZAG and Saning.
6	Methods and techniques for examination of photocatalytic and antimicrobial efficiency	WP5	TFUNS ZAG ZVKDS/IPCHS	Free user rights for all project partners for educational and research purposes.
7	Methodology for examination of the depth of penetration and rate of consolidation	WP5	ZAG CNR-ISTM ZVKDS/IPCHS	Free user rights for all project partners for educational and research purposes.
8	Data on the performance characteristics of the photocatalytic and consolidant HEROMAT formulations on substrates	WP5, WP6, WP7, WP8	all	Free user rights for all project partners for educational, research and commercial purposes.
9	Non-invasive and invasive techniques for evaluation of protected historical objects in field	WP8	ZVKDS/IPCHS UWS TFUNS CNR-ISTM PZZSK ZAG	Free user rights for all project partners for educational and research purposes.
10	Methodology for environmental assessment (LCA) of protective and consolidative systems in the field of cultural heritage	WP9	ZAG TFUNS GP HGP Saning CNR-ISTM UWS NArFU PZZSK EURA	Free user rights for all project partners for educational and research purposes.
11	Multidecision tool for decision makers regarding cultural heritage management	WP9	all	Free user rights for all project partners for educational and research purposes. Commercialisation rights to ZAG for preparation of environmental product declarations (EPDs). Discount (30%) for consortium partners for EPDs for HEROMAT products (valid only 5 years after HEROMAT project ends).

HISTORICAL MATERIALS AND MODELS

METHODOLOGY FOR CHARACTERIZATION OF MINERAL HISTORICAL MATERIALS

- **stone, render, mortar, brick, concrete, finishing coating**

Due to the priceless value of CH objects the methodology for characterisation of selected materials was set and tested to intervene with the selected objects as little as possible. To minimize micro-sampling as much as possible, the analyses of the original materials were done first non-invasively using portable equipment (X-ray fluorescence spectroscopy (XRF), Fourier Transform infrared spectroscopy in reflection mode (FT-IR), fiber optic Raman spectroscopy, unilateral Nuclear Magnetic Resonance (NMR-MOUSE)).

To gain further important information on the samples composition micro-destructive methods were applied by using laboratory instrumentations (petrographic/mineralogical characterisation, SEM/EDS, morphology, XRD, FT-IR and Raman microscopy, measuring of surface energy, surface roughness and micro-hardness, mercury intrusion porosimetry, gas sorption, X-ray microtomography and biodeterioration study). The generated foreground can be transferred to any other material characterisation with minimal adjustments.

		Sample size					
	techniques	CNR-ISTM	TFUNS	ZAG	UWS	NarFU	IPCHS
Non-invasive	XRF	2 cm³					
	Fibre FTIR (MID and NIR)	*					
	Fibre Raman	*					
	NMR Mouse	*					
Invasive and/or destructive	petrography				2 cm³		
	SEM/EDS				*		
	µ-FTIR	*					
	µ-Raman	*					
	XRD		powder 2 cm³			powder 2 cm³	
	Hg-porosimetry			2 pieces of 2 cm³			
	gas-sorption			*			
	µ-tomography			2 pieces of 2 cm³			
	contact angle		3 pieces of 4x5 cm*				
	biodeterioration						organic 0,5 cm³
	µ - hardness		*				

Table 1: Analytical methods applied for the characterization of historical materials

Selection of materials from historical objects - the study on the constituents, materials (stone, clay brick, concrete, mortar, render and colour finishing layer) and conservation state of the case study buildings, one in Serbia (Fortress of Bač) and one in Slovenia (Manor in Dornava) was done in order to properly select model substrates and aging conditions during the laboratory research.

The following areas were selected for characterisation of historic materials: Area I / North–eastern rampart; Area II / Round tower with Gothic chapel on the upper floor – buttress; North-eastern rampart – outside surface of the wall; Area IV / Gothic chapel built on a round tower and Area V / Dungeon tower – south western façade (Fig. 1).

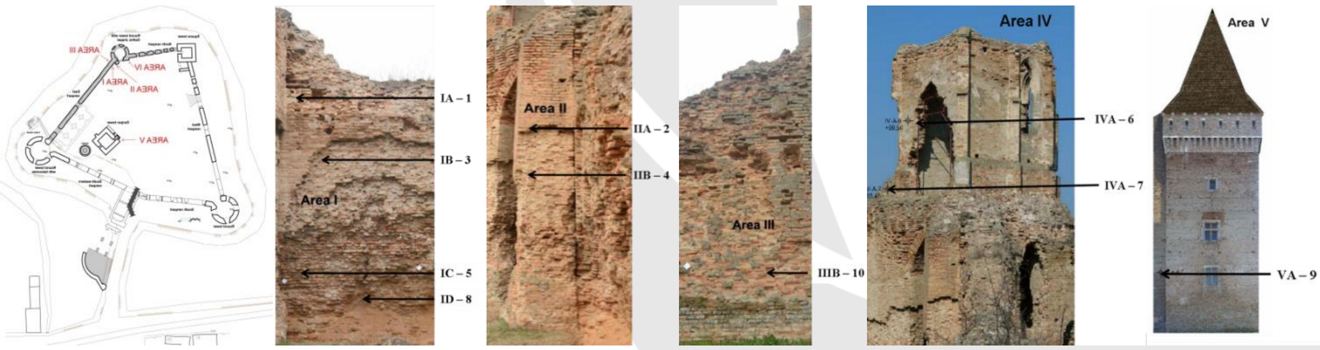

Fig. 1. Plan of the Bač Fortress and scheme of the sampling areas

The sampling at the Dornava Manor was focused on the stone elements and the facade surfaces with the render and color finishing layers, Fig. 2. According to their composition and the expected step of degradation, 7 areas were selected. The value of the stone statues was taken into consideration, and the sampling was done as less as possible.

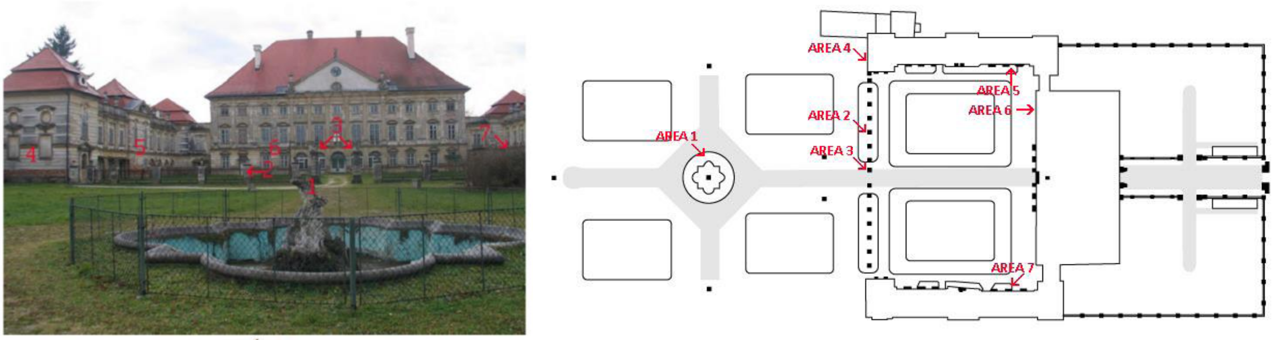

Fig. 2 Dornava Manor with the selected sampling areas

Characterization of mineral historical materials (stone, render, mortar, brick, concrete, finishing coating)

The results obtained by the non-invasive methods compared with those gained by the laboratory bench top with micro-destructive and non-destructive techniques showed that a considerable level of information was reached by the non-invasive approach identifying most of the compounds constituting the analysed samples.

BAČ FORTRESS - the bricks are calcareous, but somewhat variable in texture, possibly related to their firing conditions. Temper is quartz rich probably of metamorphic rock origin, up to medium grained and sub angular, set in a groundmass of hematite bonded sheet silicates. It is not easy to distinguish feldspar in thin section (analyzed by the SEM analysis). The carbonate inclusions are plastic and sometimes indistinct- the boundaries margining with the fully mixed binder. Macro-porosity is commonly deformed and several millimetres in size. Temper can sometimes be concentrated in certain zones, suggesting poor working (mixing) of the clay before firing. The porosity values for clay brick samples ranged from 36.99 to 42.96%, while BET (Brunauer–Emmet–Teller method) surface area is ranged from 5.99 to 22.92 m^2/g.

The mortars and renders are lime-based with abundant lime inclusions mostly of a featureless nature (giving little away about lime source). These mortars contain mostly a quartz-rich lithic aggregate with a lithic content of fine grained metamorphic rock types. The carbonate grains are present in the aggregate, appearing distinct from the lime inclusion content. The lime inclusion content points to the mortars having been hot-mixed. Exterior weathering crusts on the mortars appear low density, around 100-500um thick and often have a final exterior carbonate encrustation. The contact between mortar and brick can be fractured parallel to the boundary, and in one sample the brick is reacted with the mortar, the brick material expanding into the mortar. The porosity value of the mortar samples ranged from 39.67 to 45.18 %, while the BET surface area varied from 3.03 to 6.57 m^2/g.

The stone specimen, Biosparite, from Bač is a highly porous coarse grained calcitic. The external weathering layer shows evidence of biological colonization and the formation of a fine grained but low density mineral crust, composed of very fine grained silicates and carbonates, but also the structures suggest the possible presence of algae and fungi. The algae penetrate the calcite grains at the surface of the samples. The microbiological examination of the fungi was performed by using a non-destructive method (wet swab). The identified microbiological contaminants, Penicillium sp and Cladosporium sp., are common for the region of the Bač Fortress and its climate. The porosity value of the stone samples was 33.37 %, while the BET surface area was 0.40 m^2/g.

DORNAVA MANOR - the bricks are silicate, with a groundmass of fine grained silicates (quartz, clays, sheet silicates) with interstitial fine iron oxides, tempered with mainly fine quartz grains of metamorphic source. They have deformed macro-pores, and plastic inclusions of darker red Fe oxide enriched groundmass. Concentric layered inclusions suggest textural remnants from the original clay, and dark opaque organic inclusions. Porosity for clay brick samples ranged from 35.42 to 45.98 %, while BET surface area is ranged from 0.43 to 1.03 m^2/g.

The sedimentary rocks are fine to medium grained, very well compacted, and very rich in carbonate. They can be classified as calc-arenites (>50% carbonate) with a high content of muscovite mica. Detrital silicate grains are metamorphic poly-quartz and schist with feldspars and exotics such as zircon, rutile, pyrite, apatite. The carbonates are calcitic and high Mg Calcite. The external weathering crusts are thin (100µm) and carbonate rich, and can also exhibit sub surface staining by Fe-oxides near the surface in thicker crust formation. The limestone samples are fine to medium grained bioclastic, some micritic, particularly from micritic intraclasts, exhibiting a thin carbonate weathering crust. The other samples are with spar cement, porous, and with high calcium in nature, with very occasional fine silicate grains. Porosity of the stone samples ranges varies between 9.08 and 33.07 %, while the BET surface area is ranged from 0.6819 to 12.02 m^2/g.

The mortars and renders from Dornava are variable: some are hydraulic, exhibiting belite in thin section, suggesting a possible early Portland cement or Roman Cement. The most are lime mortars, with a slight suggestion from the binder chemistry, including the analysis of lime inclusions, of being hydraulic (with the content of SiO_2, 6 mas. % at most). The lime mortars and renders are binders, rich with a binder-aggregate ratio of approximately 1:2 and mostly rich in lime inclusions suggesting a hot mix method of preparation. Carbonate aggregate is common in the mortars, both the hydraulic type and lime mortars, mixed with the silicate sands to at most 30% of the aggregate. This aggregate is a full dolomite; though the binder is never dolomitic, it does sometimes contain a small amount of Mg (<5%). The aggregates often contain small amounts of garnet (Fe-Mg-Ca varieties), ilmenite, biotite, muscovite and monazite. Very occasionally in the lime mortars a small fragment of an older, recycled mortar can be seen. The silicate sands are mostly quartz rich, poly crystalline with metamorphic rock fragments (schists and phyllites). Occasional brick fragments are seen, but the quantity is small and probably not added deliberately as a pozzolan. The lowest values of the microhardness compared to the all other types of samples (brick, concrete and stone) were measured. Porosity of mortar/render samples ranged from 25.5 to 39.34 %, while the BET surface area showed high variability and ranged between 1.04 and 10.61 m^2/g.

Five major types of lichen were discovered in the investigated specimens: Candelariella sp. (C. medians, C. aurella); Lecanora sp. (L. albescens, L. dispersa); Caloplaca sp. (C. citrina). They are well adapted to sunlight (from scarce direct solar irradiation to sites with very high direct solar irradiation) and can tolerate low water accessibility. In some of the lichens parietin, an orange organic pigment was found, indicating the sun exposed areas. Additionally, carotenoids and pulvinic acid derivatives were identified, from which the metabolic pathway of lichens can be determined. These products can also represent biomarkers that can be linked to the survival strategies of lichen communities in stressed environmental habitats.

Therefore, the main differences in the chosen areas of the two buildings are related to their orientation with respect to sun irradiation, since all the areas are generally exposed to rain and wind. These different exposures are particularly important for the monitoring of the efficiency of photocatalytic materials as the function of the type and amount of the presence of light.

PREPARATION OF MODEL SUBSTRATES

The model substrates were prepared according to the composition of materials found at the two historical sites. The model substrates (MSUB) - limestone, brick, mortar and render with finishing layer were prepared in order to mimic the structure and assure similarity with the existing "selected case studies" materials. These model substrates, prepared from the local materials and based on traditional technologies, are used during development of new materials - promising formulations (consolidants and photocatalytic material). The second group of substrates denoted as broad range model substrates (BRMSUB) was also prepared. These are carefully selected substrates of the project targeted historical materials (stone, clay brick, mortar, render, colour finishing layer) covering different mineralogy and microstructure (porosity). In total 1664 pieces of models were prepared.

Fig. 3 Preparing models substrates

ARTIFICIAL AGEING OF PREPARED MODEL SUBSTRATES

In order to mimic the substrates obtained on the cultural heritage objects which were partially deteriorated due to the different actions (climate, microorganisms, salts), model substrate were exposed to artificial accelerated AGING to get structures similar to the original substrates. Aging procedures were selected according to experience of scientists involved in restoration projects and according to the findings on original substrates, and they include:

- aging on SO_2 before application to verify the influence of SO_2 ,
- frost damage to mechanically weaken the material,
- salts contamination (nitrate, sulphate, oxalate, NaCl): salts are often present in outdoors materials and can influence the efficiency and durability of newly developed materials,
- exposure to microorganisms to see whether their presence will anyhow influence the efficiency and durability of newly developed materials,
- wetting of materials before application to see the influence of dampness.

SO_2 exposure - samples were exposed in SO_2 chamber for 20 cycles according to EN ISO 6988:1999 (ISO 6988:1985). One cycle means: 8 hours at 40°C and 100% of relative humidity, and a blow of 0,2L SO_2, then samples are left at room conditions for 16 hours at 22°C, and relative humidity of 30%. Remark: According to the criteria for anticorrosion coating systems (EN ISO 12944-Part 6:1998) the exposure to 10 cycles represents up to 5 years in real conditions, and the exposure to 20 cycles represents between 5 and 15 years in real conditions.

Freezing – thawing exposure was performed according to the EN 12371:2010. All samples were exposed to the 50 cycles of freezing – thawing where one cycle consists of 5.5h at 15°C in water, then water was sucked out of the chamber and the temperature reached -4°C within 2h. In next 4h the samples were cooled to -10°C; after that water again was poured into the chamber.

Salt contamination - $NaSO_4$, KNO_3, NaCl - standard test procedure EN 12370:2000 was followed. Firstly, samples were dried for 100 hours at a temperature of 40°C. Then samples were introduced into a container and covered with the solution at a temperature of 20°C for 3 days. Samples were exposed to each solutions; 14% w/w Na_2SO_4 solution and KNO_3. Then samples were taken out of the container and introduced into the heating chamber at 60°C for 3 days. For contamination with NaCl samples were exposed to saturation solution of NaCl for 24 hours. After that samples were taken out of the container and introduced into the heating chamber at 60°C for 3 days. Oxalate application was done by introducing the samples into a container and covering them with the 5% solution of the ammonium oxalate for 5h. All the samples were then dried in an oven at the temperature 60°C for 3 days.

Microorganism aging - microorganisms Asperigillus niger ATCC 6275 were deposited on the surface of the selected substrates in order to induce their products of metabolic activities onto the surface and into porous interior of substrates. The samples were left in the chamber for 6 months.

Wetting (exposure to high humidity) - samples were immersed into water for 24 hours. After that, they were put into the climatic chamber at 95% of humidity and stay there till the application of the consolidants.

By the applied methodology the project team succeeded to mimic the material structures taken from the cultural heritage objects and these samples then served as substrates for the application of newly developed products. With the preparation and ageing of broad range model substrates (BRMSUB) there was achieved a wide diversity of samples considering their mineralogical composition, as well as a wide range of porosity (from 1.6% for stone up to 45% for bricks and mortar) and BET specific surface (from 0.07 for stone to 13.9 m^2/g for mortar).That opened real possibility for HEROMAT project to perform testing beyond the materials found at the selected historical sites. It enables testing a wider use of developed consolidants and protective coatings providing very important information to the conservation communities for any future use of HEROMAT materials.

The model substrates (MSUB - one stone - limestone, one brick, one mortar and one render with finishing layer) as well as broad range model substrates (BRMSUB - limestone with low porosity, limestone with high porosity, silicate sandstone, carbonate sandstone, two different bricks (with and without carbonates), two different lime mortars (with silicate and carbonate aggregates), two different renders (stucco marble and render on gypsum base), one finishing coating, and one concrete) were characterised before and after simulation of degradation procedures for identification of material composition and their degradation using SEM/EDS, FTIR, Raman, XRD, XRF analysis, as well as for characterisation of their physical – mechanical properties utilising NMR-MOUSE, Hg porosimetry, gas-sorption, free surface energy (contact angle measurements), and micro hardness.

Comparative characterization of model substrates - the main significant result at this stage laid in the fact that the prepared and aged model substrates have almost the same mineralogical composition as the samples removed and selected from the Bač Fortress and the Dornava Manor. In particular brick and render samples have almost identical mineralogical composition as the old historical materials. Furthermore, the porosity and BET specific surface of the aged substrates do match the characteristics of the selected historical materials. The aged model substrates contaminated with microorganisms, brick and stone models, have the same contact angle values as the old materials sampled from the Bač Fortress. The aged model substrate and the old brick have almost identical micro hardness values.

Characterised model substrates (MSUB) after simulation of degradation treatments

STONE 1 - the stone mainly comprises quartz, dolomite, feldspar, muscovite and unusual minerals such as zircon and apatite. It also contains a fine grained pore filling matrix/cement of a high Fe content, of uncertain mineralogy, that occasionally forms porous matted and fibrous concentrations. Secondary interstitial calcite cement is also present. The sample after freezing thawing shows loss of cement in the most affected areas, surface-parallel cracking and loss of bond between grains. In the sample exposed to microorganisms investigation revealed also the presence of a carotenoid and polysaccharides, which can be attributed to the presence of microorganisms, still remaining at the substrate surface after the aging was completed. It was also shown that the carbonate-based compounds (calcite and dolomite) signals decrease in intensity or are not detected in areas where micro-organisms grow. After exposure to the freeze-thaw cycling and microorganism contamination a slight increase of porosity of the Stone 1 was observed. On the other hand, average pore diameter increased significantly, while the BET surface area values increased. Besides aesthetic changes, significant differences in contact angle values between the control sample and sample contaminated with microorganisms (aged stone samples) were identified. Evidently, after the microorganisms' adhesion, the surface of the contaminated sample becomes rougher with lower surface energy. However, there is no significant change in micro-hardness value before and after the microbiological contamination of the stone.

BRICK 1 - the main mineralogical composition of Brick 1 is quartz, dolomite, mica, calcite, hematite, feldspar, and chlorite. It contains Ca in discrete coarse carbonate grains that form part of the temper, and in finer grains that form part of the groundmass of the brick, short grains of sheet silicates, in between angular quartz and feldspar temper grains, ilmenite and rutile. It can be concluded that the model substrate Brick 1 and the old brick from the Bac fortress have almost identical mineralogical composition. The degradation effect of freeze thaw exposure is obvious; large scale cracking through the brick groundmass and around the edges of larger inclusions. The calcite crust surrounding the sample is more surprising, but could be due to the mobilisation of calcium from the constituents of the brick during immersion in water during the test, particularly during the thaw cycle. Physical degradation due to reaction of sulphur dioxide with the sample is not observed, however alteration of Ca bearing phases to gypsum has certainly taken place, though this has not yet resulted in an observable or measured reduction in performance. Molecular characterisation of the SO2 aged sample showed the presence of gypsum at the surface and no signals from calcite. Taking in account that gypsum was not detected on the fresh sample, it seems plausible to admit that its formation as decaying compound is related to the occurrence of substrate sulphatation process. Similarly as for the Stone 1 substrate, carotenoids, polyamides and carbohydrates were identified; originating from the microorganisms remains after the ageing was completed. Compared with the original substrate composition, differently from what observed in the sample Stone 1, the area subjected by the micro-organism contamination underline higher signals from the carbonate-based compounds. When comparing the Brick 1 samples, it is possible to observe that values of porosity are reduced after the ageing of samples. This is especially evident in the case of SO_2 exposure test. In addition, average pore diameter is also diminished. Pore size distribution of Brick 1 samples is unimodal. The overall porosity of bricks slightly decreased after the freeze-thaw cycling, but there is a certain increase in the area of bigger pores, representing whether pores or cracks. That could mean that brick is susceptible to freezing action. The values of BET surface area are significantly increased after ageing for all samples, and it is the highest after the microorganism contamination. Furthermore, the aged samples had increased values of the contact angle values in comparison with the control samples, while there is a significant reduction of the micro hardness values after the performed aging procedure. This can be explained by the fact that the bricks thermally treated at lower firing temperatures are less durable materials than stones, and their aging leads to rapid weakening of the mechanical properties.

MORTAR 1 is composed of a Ca-rich lime based binder, with a well sorted sub angular medium grained aggregate composed of quartz, feldspar, biotite mica and combinations of these in metamorphic rock fragments. For the sample subjected to freeze thaw weathering, there is very little observable change. There is possibly evidence of some interaction with the water used in the test, as there is some surface densification at the edge of the sample and in some pores, suggesting mobilisation and recrystallization of carbonate material in the binder phase, but it is on a small scale. Values of porosity and average pore diameter are reduced after freeze-thaw cycling, most probably due to the dissolution-reprecipitation processes in pores. The pore size distribution of the control sample is bimodal, while values of BET surface area significantly increased after freeze-thaw cycling indicating a deleterious effect of the freezing on mortar.

RENDER 1 - the binder of the render 1 is dolomitic. It also contains some fine grained silicate minerals, either dust from the aggregate and/or hydraulic phases. Furthermore, a grain of C3S-bearing cement clinker was observed. The surfaces (edges) of the sample show irregular indetations on the sawn surface, the cast surface has a thin layer of fine grained micritic carbonate, possibly crystallised from a surface latience layer confined in the mould. Compared to the control sample, the Render 1 exposed to freezing - thawing shows increased cracking subparallel to the exterior, and a surface encrustation of calcite, possibly related to dissolution of calcite portions of the binder during the freeze thaw test. Porosity of the sample is reduced significantly after the freeze-thaw cycling, while the change in average pore size is not significant. There is also a significant increase in BET surface area of Render 1 after the freeze-thaw cycling.

RENDER 1 WITH COLOUR LAYER - the composition of the render is the same as described for Render 1 above, while the dolomitic binder phase appears denser, perhaps more coarsely crystallised (carbonated) in a layer near the surface (the colour layer), containing the red pigment hematite. After the exposure of the substrate polyamides and carbohydrates were identified originating from the microorganisms deposition. The porosity of Render 1 with colour layer is significantly reduced after the microorganism contamination, but increased after the UV exposure. Average pore diameter is reduced after the microorganism contamination, while after the UV exposure no change is observed. BET surface area of the Render 1 with colour layer is significantly increased after the microorganism contamination, whereas no change is observed after UV exposure. There were also no significant changes in micro-hardness before and after the microorganism contamination of the Render 1 with colour layer.

BROAD RANGE MODEL SUBSTRATES (BRMSUB) - similarly as MSUB samples, also BRMSUB samples (Lipica unito - limestone with low porosity, quarzitic-calcareous sandstone Strtenica - limestone with high porosity and carbonate sandstone, tuff Peračica - silicate sandstone, concrete, brick 2 – non carbonate, mortar 3 (carbonate), stucco marble, gypsum render, colour layer on gypsum render, render) were exposed to the same environmental influences and characterised. These results, as well as prepared and aged BRMSUB were important for further experimentation, to test the developed HEROMAT materials on a wider range of substrates, not only the ones found at the two selected historical sites. With the preparation and ageing of broad range model substrates (BRMSUB) the project accomplished a wide enough diversity of samples considering their mineralogical composition, as well as a wide range of porosity (from 1,6% for stone up to 45% for brick and mortar), and with BET specific surface (from 0.07 for stone to 13.9 m^2/g for mortar). That way the new developed consolidants and protective coatings can be tested to a wide range of materials, not just the ones that are found at the selected historical sites, and a wider use of developed consolidants and protective coatings can be predicted.

HEROMAT PRODUCTS

The development of the HEROMAT products was accomplished considering the compatibility with the historical materials and the substrates selected and characterized. Three groups of new innovative materials were developed: one photocatalytic coating precursor and two consolidant formulations - one for carbonate and one for silicate based substrates. The targeted performances of the developed protective materials were defined as the following:

- compatibility to the selected substrates for protective systems, consolidated systems and protective-consolidated systems;
- increased durability towards the action of pollutants – self-cleaning properties (photocatalytic and antimicrobial activity, hydrophilic surface properties) for protective and protective-consolidated systems;
- reversibility of all developed systems;
- protection of the selected substrates surface for protective and protective-consolidated systems;
- consolidation of the selected substrates for consolidated systems and protective consolidated systems;
- appropriate water vapour permeability value;
- application method to suit technological requirements of the protective system precursors;
- adaptability to different application techniques and different level of material physical damage.

PHOTOCATALYTIC COATING

Business secret

The following Parties jointly decided to use business secret as protection mechanism regarding the "Development of new photocatalytic coatings":

- Partner Građevinsko preduzeće HGP društvo sa ograničenom odgovornošću, Novi Sad (short name GP HGP)
- Partner Tehnoloski fakultet Novi Sad (short name TFUNS)

These partners are collectively responsible for any additional preparation, filing and prosecution of any protection mechanism to the business secret related Foreground and maintenance and extension of any and all protection mechanisms and protection rights. These partners (GP HGP and TFUNS) also bear all costs related to such actions.

HEROMAT Exploitation Agreement

The research team from TFUNS was responsible for the laboratory synthesis of the photocatalytic active nanomaterials and their characterization. These materials, based on layered double hydroxides – LDH (anionic clays) and photocatalytic active semiconductors (TiO_2) were synthesized by the co-precipitation method. In order to satisfy the targeted performances many variations of the process parameters and compositions were done. The synthesis of LDH structure started with non-nitrate based precursors in order to produce adequate quantity of the desired ions. By varying the pH values ranges during the synthesis process it was optimized to the range of 9-9.5 to satisfy the mineralogy (examined by XRD analysis) and particle size distribution (there were no particles above 1 µm, controled by zeta sizer analysis). For obtaining a TiO_2-LDH nanocomposite structure, the TiO_2 suspension, was added to the reaction batch at the beginning of the synthesis. It prevents nanoparticle aggregation, provides adequate surface porosity and improves compatibility with the porous building materials due to simmilarity regarding the LDH structure with porous building materials. Optimization of the TiO_2 quantity added during synthesis (lower and higher content were added) was done regarding the mineralogy (examined by XRD analysis), particle size distribution (controled by zeta sizer analysis), and the photocatalytic activity assessment (measured by UV/VIS spectrophotometry and FTIR) and self-claning efficiency (contact angle measurement). It was concluded that higher quantity of TiO_2 which was used during synthesis led to better functional properties since the appropriate mineral structure, particle size (all particles were below 850 nm, in the nano range) and exsistance of sufficient photocatalytic activity and self-cleaning efficiency were very good. The appropriate particle size distribution properties of the synthesized TiO_2-LDH nanocomposite material was the result of the suitable dispersant usage, which was added prior to the newly chosen precursors and TiO_2 suspension during synthesis procedure. Optimization regarding curring time (1-28 days) of TiO_2-LDH nanocomposite before stabilization shown that 1-7 days of curing leads to optimal functional properties regarding the mineralogy, particle size distribution, photocatalytic activity and self-claning efficiency. The synthesis was performed at room temperature (T=20-25^{o}C) and atmospheric pressure (p=1atm), for the reson of energy consumption and economical costs of the future production line.

The morphology, structure and texture of the synthesized TiO_2-LDH nanocomposite were characterized. Considering the nature and the properties of the substrates on which the protective material was applied, the most promising coating precursors were developed and preliminary tested on the chosen model substrates (bricks, renders, renders with colour layer, mortars and stones) regarding the photocatalytic activity, antimicrobial efficiency, self-cleaning effect, hydrophilicity etc. The GP HGP, in cooperation with TFUNS, established the pilot production of the developed photocatalytic coating precursors.

The production protocol includes the following stages:

- Preparation of the precursors
- Preparation of the reactor and of the synthesis equipment
- Synthesis process and control of the process parameters
- Suspension stabilization
- Packaging of the stable suspension
- Estimation of the manufacturing costs.

Fig. 4. Pilot production in GP HGP

In the course of transfer from laboratory to industrial environment the process parameters were the following: raw material flow rate increased, the pH value range during synthesis was kept the same as in laboratory conditions, and the stirring rate during stabilization was considerably increased in order to decrease the stirring time. Several industrial try-outs were done to test the adopted changes of the process parameters. The laboratory production procedure was optimized in order to satisfy the requirements of the GP HGP logistics and the industrial production capacities in accordance with ISO 9001/2008, ISO 14001/2004, the certificated standards used in the daily production in GP HGP.

Technical characteristics of the photocatalytic suspension

Aggregate state, colour, flavour:	Liquid, whitish, none
pH value:	9-10
Melting point/Freezing point:	No safety significance
Initial boiling point:	100°C
Flash point:	No safety significance
Evaporation rate:	Very low at normal conditions (room temperature)
Upper/lower ignition or explosiveness limit	No safety significance
Pressure of vapour:	Similar to water (approx. 2300Pa/200C)
Density:	Similar to water 1.01 g/cm3
Solubility in water:	Insoluble
Particle size:	Below 800 nm
Polar organic solvent (ethyl alcohol)	No
Total amount of VOC:	No VOC
Temperature of the flammability:	Inflammable
Viscosity:	10^{-3} Pas, similar to water
Consumption:	≈ 0.3 L/m^2

For packaging and storage polypropylene based canisters were used, commonly considered the most suitable due to low moisture vapour transmission, wide usage in the manufacturing of plastic jars, food packaging, laboratory equipment, auto components, and high chemical resistance towards base solutions. The GP HGP has its own production line for the Polypropylene based containers, used in their daily production and packaging. Two varieties of polypropylene containers are chosen for HEROMAT photocatalytic coating: 3.5 litres and 5 litres in volume.

Table 2. Equipment and technical characteristics of the designed pilot production for the photocatalytic suspension

Equipment	Photo	Power consumption per one protocol (MJ)
Pumps		100W – feeding procedure by pumps

Synthesis reactor		2kW – thermal treatment 250W – stirring procedure in reactor 50W – stirring procedure in precursor
Intelligent sensors		50mW - pH unit
Handheld stirrer		450W – stirring procedure in 20 litres reactor
		Total: 19.73 kWh

Estimation of the manufacturing cost

According to the defined stabilization protocol, for one synthesized batch of the concentrated photocatalytic suspension (7 litres) approximately 800 litres of the diluted and application ready suspension is produced. Energy consumption required for the production of the 800 litres of the final product photocatalytic suspension in the total is 19.73 kWh (Table 2), including all four stages of the production. This quantity of power consumption labels the designed pilot production line as a low consumable process. The optimal capacity of the developed pilot production in regard to production parameters in GP HGP premises, with one synthesis protocol, produces 800 litres of final product which is estimated to cover 5000-5500m^2 of a wall surface one layer.

CONSOLIDANTS

<u>Patent PCT/SI2014/000028</u>

The following Parties jointly applied for the world patent priority number: PCT/SI2014/000028, Priority date May 28th, 2013 regarding the "Method for reinforcing porous construction materials and use calcium acetoacetate solution to this aim" (hereafter referred to as "Patent"):

- Partner Zavod za gradbeništvo Slovenije (short name ZAG)
- Partner Saning International, podjetje za sanacije objektov (short name Saning)

These Parties are hereinafter collectively referred to as the "Patent Applicants".

The Patent Applicants are collectively responsible for any additional preparation, filing and prosecution of any protection mechanism to the patent related Foreground and maintenance and extension of any and all protection mechanism and protection rights. The Patent Applicants also bear all costs related to such actions.

HEROMAT Exploitation Agreement

Two types of consolidative material were developed to suite different composition of historical mineral substrates. One final formulation is designed for carbonate based substrates and the other for silicate based substrates. The ZAG team synthetized both consolidant formulations.

For carbonate substrates new consolidant formulations based on soluble calcium compound calcium acetoacetate $Ca(OAcAc)_2$ were developed in three different solvents: methanol (CF1), mixture of ethanol and methanol (CF2) and water (CFW). Modifications and simplifications were made in order to improve and simplify the synthesis process. All promising formulations CF1, CF2 and CFW exhibit high consolidation efficiency, deep penetration depth and negligible colour change of substrates with no whitening after application. Additionally it was found out that CFW has the most suitable properties: good transparency, negligible colour change of substrates' surfaces after application, high water vapour permeability and remained water absorption, the most uniform drilling force through entire profile, the largest depth of penetration and the highest total porosity.

Due to using only water as solvent the CFW formulation does not have any poisonous character. Cross-sections of different substrates (mortar 1, render 2, render 1+color layer and render1) consolidated with CFW and treated with dye indicator sodium nitroprusside in order to evaluate penetration depth of consolidant are shown in fig 5.

The consolidation of porous materials with new consolidant CFW was patent protected – international application No PCT/SI2014/000028 ([1]). In the patent a method for reinforcing porous mineral construction material has been proposed, in which during the first step a solution of calcium acetoacetate in a solvent is prepared, upon which such solution is applied onto each surface of substrate material in order to enable penetration thereof towards the interior of the material, namely into pores therein, by which calcium carbonate is produced and deposited within the pores in the material. The solvent is preferably water, but optionally the solvent can also be alcohol, namely ethanol or methanol, or a mixture thereof.

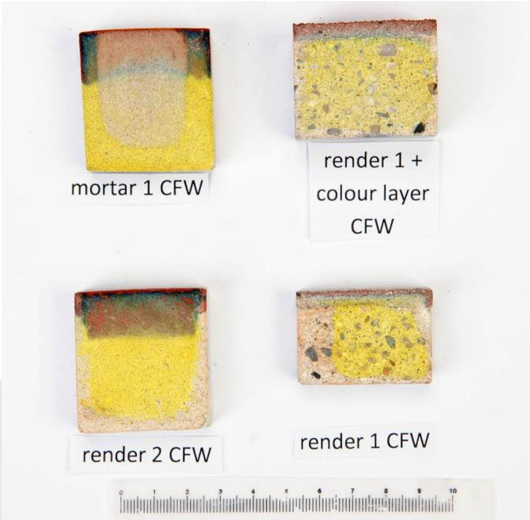

Fig. 5. The crsoss-sections of consolidated model substrate render with CFW and indicated by sodium nitroprusside

Technical characteristics of the carbonate based consolidant

Appearance / colour	Clear, colourless to pale yellow solution.
Packing	1L, 10L, 25L
Expiration date	One year in cold storage below 5°C.
Active component	Calcium salt
Solvent	Water
Density	1.019 kg/l
pH	6.5 – 7.1
Viscosity	1,2 mPas
Resistant against freezing	Yes
Depth of penetration	2 mm – 30 mm; varies on the porosity of the substrate.
Water absorption	Does not change significantly.
Water vapour permeability	Does not change significantly.

Consolidant formulations for silicate substrates were prepared based on TEOS (tetraethoxy silane). Catalysts, solvent and other ingredients were carefully selected and the synthesis parameters were studied and optimized to obtain the promising formulations with high consolidation effectiveness. In order to evaluate the most important properties and find promising formulations, the consolidants were continuously tested in regards to consolidation efficiency, drilling resistance by DRMS method, pore size distribution and total porosity by Hg porosimetry and penetration depth using FT-IR Spectroscopy. The optimal formulation (CF4) with the deepest penetration depth was selected for pilot production.

Technical characteristics of the silicate based consolidant

Appearance / colour	Clear, colourless to pale yellow solution
Packing	1L, 10L, 25L
Storage conditions	Best kept in cool place with low humidity
Active component	TEOS
Solvent	Dioxalane, alkane mixture

[1] L. Škrlep, A. Pondelak, A. Sever Škapin. Method for reinforcing porous construction materials and use calcium acetoacetate solution to this aim: international application no. PCT/SI2014/000028. [S. l.]: European Patent Office (EPO) (ISA/EP), 2014.

Density	0.906 kg/L
pH	Alkaline.
Viscosity	3,222 mPa s
Resistant against freezing	Yes
Depth of penetration	2 mm – 30 mm; varies on the porosity of the substrate.
Drying rate	EN 13579
Water absorption	Does not change significantly.
Water vapour permeability	Does not change significantly.

Both groups of the developed consolidants were produced at SANING on the requirements of the project and prospects to industrial production. Specially equipped chamber with multifunctional reactor was developed and manufactured particularly for the production of newly developed consolidative materials. For the needs of safe mixing of materials an anti-static chamber has been prepared with the following characteristics:

- Anti-static and anti-flammable construction; double-walled panels insulated with non-flammable material;
- Fitted with special filter ventilation systems for the supply of fresh air and for the suction removal of polluted air including dispersed fine powder;
- Water cleaning system for binding and washing of hard particles;
- Anti-static floor with a stainless grid in the mixing area with safety reservoir for spilled materials. Waste materials are then partly cleaned and deposited according to the regulations;
- Heating thermostatic system for maintaining required temperature;
- Special storage area with safety reservoir for storing raw materials.

To simulate laboratory production a special multifunctional reactor was developed with following characteristics:

- Rotating, mixing and milling while maintaining constant negative pressure;
- Rotating and mixing while heating according to the determined protocol;
- Mixing and milling with special milling objects inside the reactor and constant rotating of the reactor;
- Maintaining constant vacuum while reactor is rotating around its axis.

Fig. 6. Specially equipped chamber with multifunctional reactor for the consolidant pilot production

Fig. 7. Carbonate consolidant packaging

Production protocol was defined and optimized using small quantities of input materials in order to minimize the costs of unsuccessful batches. Critical parameters such as temperature, pH and agitation were closely watched and monitored through the process. Production of silicate based consolidant was performed in the developed multifunctional reactor and additional mixers. The production took place under carefully controlled temperature and relative humidity conditions.

Packaging and storage of consolidants

After extensive testing on polypropylene (PP), polyethylene (PE) and different metal containers, polyethylene was chosen as the best material for both consolidants which does not influence their properties. Both consolidants will be commercialized in different containers of 1 l, 10 l and 25 l.

HEROMAT PRODUCTS CHARACTERIZATION

Methodology establishment for characterization - diagnostic tool

The most appropriate methods for the evaluation of all functional (photocatalytic efficiency, antimicrobial activities, consolidant efficiency and hydrophobic effect) and physico-mechanical properties were established. The developed diagnostic tool useful for restorers and researchers for evaluating similar materials (photocatalytic protective coatings and consolidants) is presented below.

PHYSICO-MECHANICAL CHARACTERIZATION OF DEVELOPED MATERIALS		
Material	Selected characterization methods	
Stabilized protective suspensions	Rheology and viscosity Stability Particle size distribution pH value determination Transparency BET	
Protective suspensions applied onto (model) substrate	Textural properties Morphology Durability by rinsing test Water vapour permeability Colour change Surface characterization: a) Microhardness measurements b) Roughness measurements	
Consolidant solutions	Density at 20°C Viscosity Transparency and colour	
Consolidant solutions applied onto (model) substrate	Morphology Surface characterization: a) Micro-hardness measurements b) Roughness measurements Colour change	
DETERMINATION OF FUNCTIONAL PROPERTIES		
(1) Determination of photocatalytic efficiency		
Protective and protective-consolidated systems	a) Determination of photocatalytic efficiency in liquid-solid system by UV/VIS spectrophotometry by monitoring the discoloration of a Rhodamine B (RB) b) Photocatalytic efficiency evaluation by monitoring the degradation of isopropanol in gas phase in sealed reactor system using FTIR	
(2) Determination of antimicrobial efficiency		
Protective and protective-consolidated systems	a) Selection of test microorganisms b) Determination of antimicrobial efficiency	
(3) Determination of consolidation efficiency		
Consolidated systems	Consolidating Value	tensile strength and surface hardness of treated unweathered or weathered mineral substrates ultrasound velocity drilling resistance measurement system (DRMS) flexural strength of consolidated prisms
	Porosity	NMR-MOUSE mercury porosimetry SEM analysis water vapour permeability, water absorption
	Rate of conso-lidation process	Infrared and Raman spectroscopy
	Penetration depth	SEM/EDS mapping, fluorescent and optical microscopy Micro-Raman and micro-FTIR line array measurements on cross-sections DRMS measurements dye indicators
(4) Determination of hydrophobic effect		
Protective, consolidated and protective-consolidated systems	Determination of contact angle and surface tension	

METHODS AND TECHNIQUES FOR EXAMINATION OF PHOTOCATALYTIC AND ANTIMICROBIAL EFFICIENCY

Determination of photocatalytic efficiency

Method 1: The determination of photocatalytic efficiency of newly developed photocatalytic coatings on model substrates in liquid-solid system by UV-VIS spectroscopy

The photocatalytic activity of the coatings was examined by monitoring the discoloration of a Rhodamine B (RB) solution as function of irradiation time. This procedure was adjusted for porous substrates. Namely, the degree of absorption of the dissolved RB molecules was measured by a pre-absorption test. The decomposition rate of the RB under the UVA-VIS light irradiation (photocatalytic activity) was determined by recording its absorption spectrum.

Method 2: Photocatalytic efficiency evaluation by monitoring the degradation of isopropanol in gas phase in sealed reactor system using FTIR

The principle of the method is a quantitative determination of the photocatalytic activity through monitoring the degradation of a model organic compound (isopropanol) in a gas medium utilizing FTIR spectroscopy. Under UV-VIS irradiation isopropanol in a contact with photocatalytic active solid substance oxidizes into acetone and then into several further degradation products. The photocatalytic activity is evaluated as the rate constant of the initial acetone formation.

Determination of antimicrobial efficiency

A broadly accepted procedure for the determination of antimicrobial efficiency is the so called “drop method”, usually exploited for photocatalytic coating applied to non-porous substrates. In the case of the photocatalytic coating applied on porous substrates many difficulties concerning the procedure of antimicrobial activity testing arise due to the characteristics of the surface (roughness, energy charge) and the ability to absorb water within the porous space. Therefore, in the HEROMAT project a specific method for the determination of antimicrobial efficiency has been developed based on several modifications of the above mentioned “drop method”. The first step of the developed method is the pre-absorption of the sterile distilled water by the sterile coated sample while the second one is the surrounding of the sample by sterile distilled water up to ¾ of the sample thickness. The applied suspension of the bacterial cells is retained in the contact with the active surface during the photocatalytic treatment.

The test method for determination of the antifungal activity, ΔR[2], of the photocatalytic materials is based on counting the number of the pre-incubated fungal spores that survive the exposure to UV-A light on the coating.

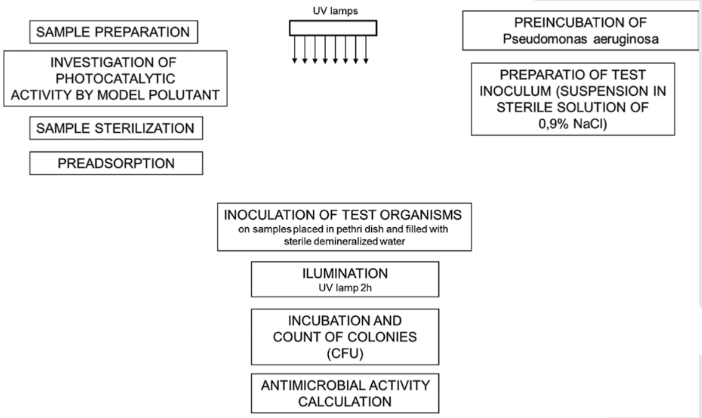

Fig. 8. Scheme of the antibacterial “drop method” procedure modified for porous substrates

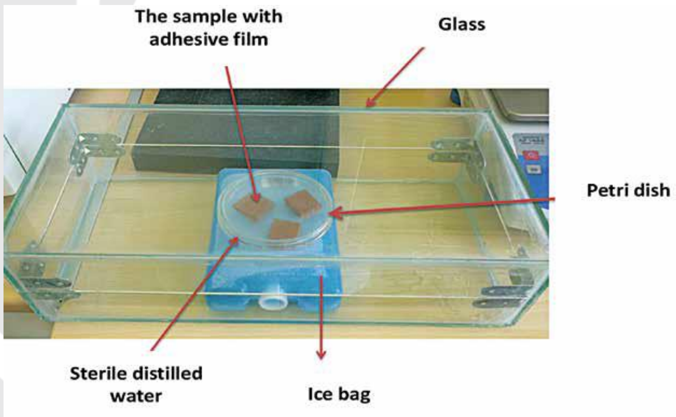

Fig. 9. Sample prepared for the exposure to UV irradiation

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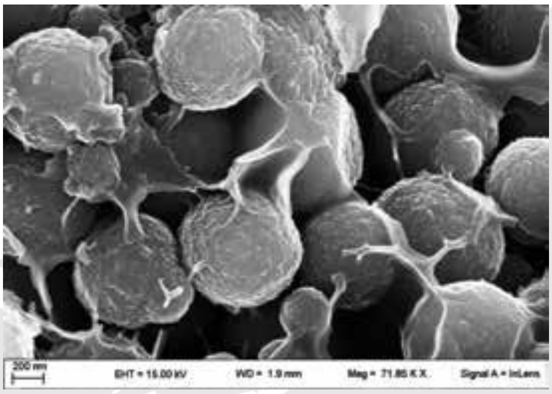
[2] $\Delta R = R_L - \log(\frac{B_D}{C_D})$; $R_L = \left[\log\left(\frac{B_L}{A}\right) - \log(\frac{C_L}{A})\right] = \log(\frac{B_L}{C_L})$,

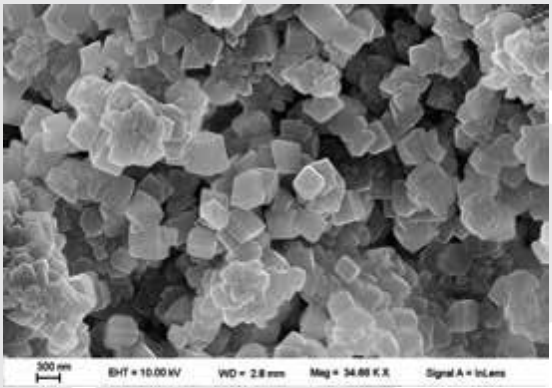
Where: R_L is total antifungal activity value of the coated sample under the UV irradiation conditions; L is UV exposure (mW/cm^2); A is average surviving colony numbers of non-treated substrate following inoculation; B_L is average surviving spore numbers of non-treated substrate at exposure L after 24h; C_L is average surviving spore numbers of treated substrate at exposure L after 24h; ΔR is antifungal activity of treated sample without the influence of UV light; B_D is average surviving spore numbers of non-treated substrate in the dark after 24h; C_D is average surviving spore numbers of treated substrate in the dark after 24h.

METHODOLOGY FOR EXAMINATION OF THE DEPTH OF PENETRATION AND RATE OF CONSOLIDATION

Rate of consolidation process - the preliminary laboratory tests for evaluating the different stages of the consolidation mechanisms (solgel polymerization and crystallization) were performed using Infrared and Raman spectroscopy. These vibrational spectroscopies were applied as a versatile and simple tool to follow tetraethoxy silane based (TEOS-based) consolidation procedures. The reaction rates of commercial products and newly developed consolidants were compared. The influence of the temperature, RH conditions and the effect of salt contamination in the substrate were considered. Similar methodology was also applied to determine the consolidation rate of the carbonate consolidants as affected by temperature, humidity and type of catalyser.

Penetration depth - among the series of methods commonly applied to determine the penetration depth of a consolidant into stone or other inorganic mineral substrate, there are: fluorescent dye indicators, elemental analysis, scanning electron microscopy (SEM) observation, charring in an inert atmosphere, acid etching and iodine vapour, all applied on cross-section samples.





Figs 10,11. FE-SEM images of the carbonate based consolidant formulation CF1 after approximately 10 months of curing: at 40°C and RH = 50% (left), at 40°C and RH = 100% (right)

The depth of consolidation of the promising carbonate consolidants (CF1, CF2, CFW) into model carbonate substrates was successfully investigated by Micro-Raman analysis on cross-sections and dye indicator method. Investigation by Raman spectroscopy is complicated due to the bands overlapping, while the colour change of the indicator can only be followed visually, which sometimes does not precisely identify the penetration depth. Utilisation of both, indicator and Raman spectroscopy, gave the best results, as the shift of Raman modes of CN stretch of the indicator at 2096 and 2122 cm^{-1} to 2101 and 2178 cm^{-1}, respectively, can be followed, when the indicator is in contact with the carbonate based consolidant. Therefore, for the penetration depth investigation Raman spectra were recorded across the depth profile of each substrate previously treated with consolidant and the indicator sodium nitroprusside (5% water solution). The depth of penetration of promising silicate consolidants (CF3 and CF4) was measured on the treated model substrate, prepared as cross section samples, by micro-FTIR spectroscopy in reflection mode. The strongest signal of paraffin (CH stretching at 2925 cm^{-1}) an addictive present in both the promising formulations, was used to spectroscopically map the penetration of the consolidant into the porous structure.

PERFORMANCE CHARACTERISTICS OF THE PHOTOCATALYTIC AND CONSOLIDANT HEROMAT FORMULATIONS ON SUBSTRATES

For the assessment of effectiveness of newly developed photocatalytic coatings and consolidants, 16 different substrates (bricks, stone, renders, mortars, concrete, and gypsum) were prepared. For the assessment of compatibility and durability, the following methods were applied:

- water vapour permeability - EN ISO 12572:2002 (wet conditions),
- mechanical resistance- EN 10545-6:2012
- frost resistance - EN 12371: 2010; visual check,
- resistance to SO2 vapour -EN 13919:2002;
- visual check,
- exposure to UV light; visual check.

For the assessment of functional properties the following properties were tested:

- photocatalytic activity of the coatings was examined by UV/VIS spectrophotometry following the discoloration of a Rhodamine B (RB) solution as function of irradiation time
- effect of consolidation was determined by means of abrasion resistance EN 10545-7 (consolidated system) and by means of Scotch tape (photo-catalytic system).

Fig. 12. Experimental panel for the assessment of the application techniques in the real environmental conditions, Bač Fortress

SIGNIFICANT RESULTS

Water vapour permeability - Application of consolidants and photocatalytic agents did not significantly change water vapour permeability (WVP). Some noticeably changes in the WVP appeared in the case of consolidant application (especially in renders and mortars which are more porous than bricks or stones) but still the values of coated and non-coated samples remained within the same WVP class. Application of the photocatalytic suspension leads to negligible changes of the WVP in comparison with the blank substrate.

Freezing–thawing resistance - some samples were, before application of consolidants and photocatalytic agents, exposed to different environmental factors in order to mimic the structures taken in-situ from the objects. For that purposes samples were contaminated with oxalate, sulphate, nitrate, and inoculated by lichens.

After that these samples together with untreated samples were exposed to freezing-thawing procedures. In the cases with frost resistant substrates no changes due influence of coatings were noticed. On the other hand, Brick 1 and Mortar 1 samples, which are not frost resistant, showed slightly better resistance after application of consolidants compared to blank samples or samples with only photocatalytic agents.

The Brick 1 samples (exposed to the sulphate and nitrates) which are not frost resistant, after application of consolidants were significantly improved in frost resistance and far less damage is observed on them after freezing–thawing test. Similarly, also non-treated samples of Brick 1, Mortar 1 (Fig. 13) and Render 2 have shown improved frost resistance after exposure to the freezing-thawing tests after application of protective materials.

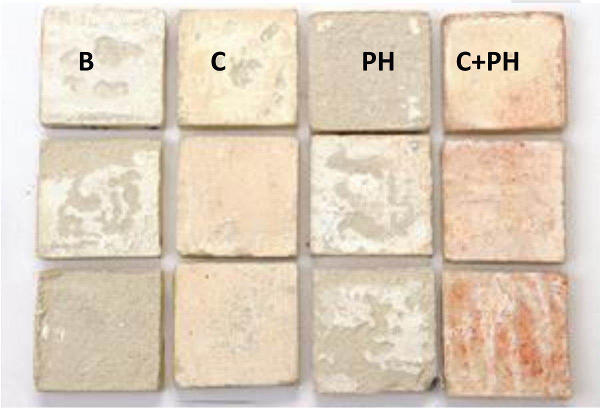


Fig. 13. Visual assessment of aged samples (previously exposed to sulphate) of Mortar 1 after freezing – thawing:
on the left side there are blank samples - B,
next to them samples with consolidants - C,
then samples with photocatalytic agents – PH
and on the right side samples with both coatings – C+PH

Photocatalytic activity of the chosen model substrates (Stone 1, Brick 1, Mortar 1) and broad range model substrates (Limestone low porosity, Limestone high porosity, Sandstone silicate, Brick 2 and Render 2), coated with the photocatalytic suspension, was assessed before and after the freezing–thawing. The photocatalytic activity assessment before and after freezing-thawing ageing procedure suggests an unchanged photocatalytic performance, what gives the confidence that coating was sufficiently durable considering its resistance to freezing-thawing procedure of aging.

Mechanical resistance of consolidated systems - the consolidation effect abrasion resistance was determined by measuring the length of the recess, made by a rotating steel plate and abrasive according to EN ISO 10545-6.

Mechanical resistance of photocatalytic coatings cannot be assessed by the previous method used, since it is too harsh and removes coating completely. Therefore a new technique for the porous samples - scotch tape test - was applied. The obtained results show there was no significant difference in relative mass loss (Δm/A) between the blank and the coated model substrates (Brick 1 and Render 2), what was also confirmed by the photocatalytic activity values measurement before and after the performed scotch tape test (both for blank and for aged samples).

UV and SO_2 exposure (visual assessment) - no visual changes were observed after exposure to UV neither to SO_2. After SO_2 contamination procedure, the assessment of the photocatalytic activity confirmed substrates coated with photocatalytic suspension possess significant photocatalytic performance, both before and after SO_2 aging procedure.

Assessment of the antifungal activity - in order to assess the antifungal efficiency the photocatalytic coating, carbonate and silicate based consolidants and combination of consolidant and photocatalytic suspension were applied to the porous substrates. A modification of ISO-DIS13125 standard was employed. Based on the obtained results, it can be concluded that the photocatalytic coating applied onto the sandstone silicate samples expresses the highest antifungal efficiency, compared to the application of silicate based consolidant only and the application of combination silicate based consolidant and photocatalytic coating.

Conclusion – considering the above results it was concluded that the application of HEROMAT consolidants and photocatalytic agent did not visually change materials. The application of consolidants and photocatalytic agent did not significantly change water vapour permeability (WVP): the most noticeably changes of the WVP were observed after the application of the consolidant formulations; however the values of consolidated and non-consolidated samples remained within the same WVP class; applied photocatalytic suspension leaded to negligible changes of the WVP in comparison with the blank substrate. The consolidant application improved frost resistance of substrates in most cases and improved mechanical resistance notably. After exposure to SO_2 the photocatalytic activity was not significantly changed. Coatings were not sensitive to UV light.

IN SITU APPLICATION AND MONITORING

NON-INVASIVE AND INVASIVE TECHNIQUES FOR EVALUATION OF PROTECTED HISTORICAL OBJECTS ON FIELD

The objective of the research activity was to ensure the final validation of HEROMAT materials through the assessment of their performance on actual historical buildings. Three optimal formulations were applied, namely two consolidants: one (CFW) for carbonate based substrates (mortar, render, calcitic stone, carbonate-rich brick) and the other (CF4) for silicate based substrates (brick, mortar, sandstone, concrete), and one coating precursor. Two immovable cultural properties were selected, both in continental climates - Fortress Bač (14th century) in Serbia, and Dornava Manor (17th century) in Slovenia. Specific areas of the two sites were selected for application and monitoring. For both heritage sites, the selection of areas for application was carried out considering the composition and the alteration state of the original masonry materials as obtained at the beginning of the project.

Substrate pre-treatment and application of consolidants and coating precursors

The newly developed formulations were applied on both cleaned and uncleaned surfaces. A blank surface sector (that received no applications of any treatment) was always left as the control one. Furthermore, on each selected area there was tested the combination of consolidant and coating, as well as more than one application technique. During the application procedures, environmental parameters (temperature and humidity at the surface material and ambience) were monitored. All the treatments were carefully documented to facilitate the analytical performance assessment (fig. 14).

For the Bač Fortress it was decided to physically clean all the chosen surfaces, using brushes of various types and hardness, without water treatments in order to preserve the patina. At the Dornava Manor, the cleaning was made by a mechanical cleaning method – sanding – without preserving any of the natural patina, but removing as much as possible of secondary surface deposits while maintaining the surface design and texture of the on-site materials. Silicate based consolidant was applied on brick and mortar areas at the Bač Fortress, and concrete and sandstone areas at the Dornava Manor. Carbonate based consolidant was applied on render, brick and mortar areas at the Bač Fortress, and concrete, limestone and render areas at the Dornava Manor.

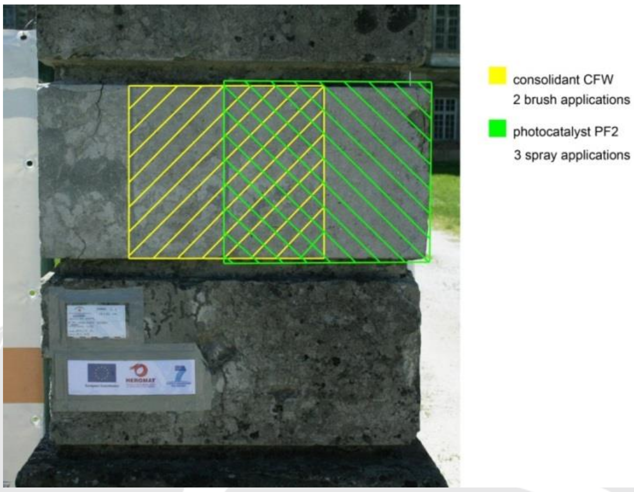


Fig. 14: A systematic digital documentation of the treatments was put in place for both the historical sites

In situ monitoring: the methods

The chemical, physical and mechanical properties of the treated surfaces of the historical materials (stone, brick, render, mortar) at Bač Fortress and the Dornava Manor were assessed immediately after the application (T=0M) and after one year (T=12M) by exploiting a multi-technique approach based on different spectroscopic, optical, and mechanical methods. All the analytical data were organized and archived using a digital documentation tool, thus making them available for future monitoring activities.

Colorimetry - a portable device with an integrating sphere and a vertical alignment was used. Colorimetric CIELAB data were used for monitoring colour changes for aesthetic reasons, but also for understanding weathering, since alterations in colour might indicate chemical/biological changes.

X-ray fluorescence - XRF measurements were performed by a portable spectrometer equipped with an anode Rhodium X-ray tube. The system working in air is able to detect elements with atomic number Z ≥ Al. The XRF elemental profile was used to assess non-invasively the retention of the photocatalytic coating (TiO_2-ZnAl-DLH) over time through the (semi)quantification of fluorescence signals from Ti and or Zn.

FTIR reflection spectroscopy - FTIR spectra in reflection mode were acquired in the range 7000-400 cm^{-1} (near-mid-FTIR). The spectrometer is equipped with a Globar infrared source and a DLaTGS detector. Reflection FTIR measurements were exploited to evaluate: 1. the evolution overtime of consolidant materials; 2. distribution of gypsum, oxalates and other salts; 3. microbiological growths.

NMR relaxometry - a mobile nuclear magnetic resonance (NMR) scanning system was used for transverse relaxation measurements on water-saturated stones and bricks. The NMR analysis was carried out in order to evaluate the change in pore size distribution induced by the different treatments following the relaxation time distributions of water hydrogen proton.

Mechanical tester - Surface hardness measurement was performed using a Proceq Equotip 3 Surface Hardness Tester (C Probe; tungsten carbide spherical indenter of 3mm diameter, and with an impact energy of 3Nmm), and the results expressed as Leeb Hardness (HLC). Moisture content in the substrate was also assessed using a surface contact pinless moisture meter to evaluate whether variable moisture content may have an effect on surface hardness.

Overall around 700 analytical measurements were acquired for each site, while surface hardness tests were carried out on thousand points.

Fig. 15. Monitoring colour changes
for aesthetic reasons, Bač Fortress

Fig. 16. XRF measurements (non-invasive) to assess
the retention of the photocatalytic coating over time, Dornava Manor

In situ monitoring: the results

1. **Silicate based consolidant**

FTIR spectroscopy allowed for the assessment of the consolidant evolution over time. The CF4 consolidant retained *n*-paraffin (C_{11}-C_{13}), for at least 12 months, in the most of the sectors where it was applied. It caused an appreciable but only temporary darkening (decreasing of luminosity) of the surfaces measured by UV-Vis spectroscopy. Specifically, the application of the consolidant determined at T=0M a colour variation around $\Delta E=7$. With time the luminosity tends to recover toward the original values determining a final colour variation at T=12M of about $\Delta E=3$ (below the threshold at which is detectable to the human eye).

As expected the *n*-paraffin retention is dependent on the microclimatic condition, resulting in general much higher at the Bač Fortress walls (in particular for the areas with a northerly exposure) with respect to those of the Dornava Manor. NMR-relaxometry demonstrated in a specific sector at the Bač Fortress that the positive effect of *n*-paraffin is to keep the porosity of the consolidated material rather high. In terms of the surface hardness tests performed as a proxy for mechanical resistance and/or coherence of the surface, in general no statistically significant difference attributable to the consolidant treatment was observable on the majority of treated surfaces.

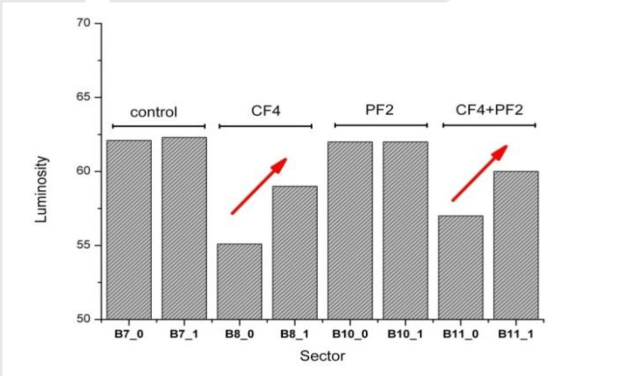


Fig 17: Measurement of the variation of luminosity due to the presence of CF4 alone and in combination with PF2 at T=0 and T=1 year. Arrows indicate the luminosity recovery after one year.

2. **Carbonate based consolidant**

Notably, the carbonate based consolidant CFW resulted highly compatible with calcite/lime-based substrates determining a negligible colour variation. In general for the surface hardness values obtained on consolidated surfaces, there is no evidence of a significant hardening effect, if at all. On the north facing render at the Bač Fortress however, there is an apparent increase, even within variation, though there is still overlap of all the standard deviations of the data sets. Most probably the CF4 mechanical performances are plagued by its slow reaction rate. It was possible to prove by FTIR spectroscopy the formation at T=0M of a new carbonate phase but it seems to decrease at T=12M, probably due to the slow transformation of amorphous calcium carbonate to the more stable vaterite form.

3. **Photocatalytic coating**

As regards the optical properties, the application of the photocatalytic coating to the historical materials of both historical sites represented a zero risk of incompatibility. Indeed, CIELAB data statistically proved that the photocatalytic coating does not have any measurable effect on the appearance of the original materials irrespective of being brick, mortar or render.

Thus, the data acquired in situ confirmed the excellent optical properties of the developed photocatalytic coating reported for its application on models substrate (ΔE ranging from 1.7 to 2.8).

The coating seems not interfere with the consolidant curing, as proved by FTIR spectra. Zinc fluorescence peak (kα at 8.6 keV) can be used as a marker for the photocatalytic coating treatment. Data showed that coating is generally present on the historical surfaces after one year of natural weathering (fig 18).

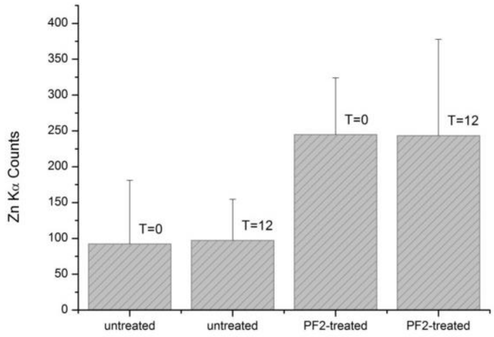


Fig. 18: Average value of Zn fluorescence counts for untreated and PF2-treated areas at T=0 and T=12 months.

The durability of the photocatalytic coating was good albeit a certain leaching of TiO2 has been measured in the case of stone sectors of the Dornava manor after one year from the application, most probably caused not by the instability of the coating itself but rather by weathering and crumbling of the surface. FTIR vibrational data were used to assess the evolution of any biological contamination on sectors treated by the photocatalytic coating (render and stone). Interestingly, some of the untreated sectors are characterized by biological growth (evident through sharp CH and amide signals, e.g. A, Dornava Manor) while the photocatalytic coated counterparts are not (e.g. B, Dornava Manor) as appreciable in fig. 19.

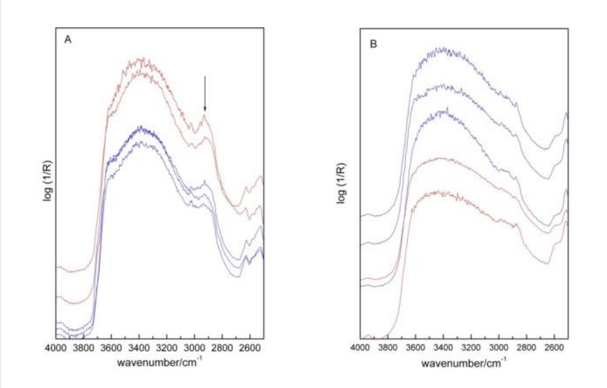


Fig 19: FTIR spectra from Dornava Manor
(red lines T=0, red lines T=1 year). A untreated; B treated

The results of the surface hardness testing strongly suggest that the treatment with the photocatalytic coating has no observable, by these means at least, effect on the mechanical properties of the treated substrates.

Conclusion - After an educated selection of the testing areas, the newly developed multifunctional systems were applied on different types of historical surfaces. The chemical, physical and mechanical properties of the treated surfaces were assessed over one year using a multi-technique approach based on different non-destructive spectroscopic/optical and mechanical methods. All the analytical data were digitally organized using a documentation tool, thus being available for future monitoring activities. Although one year is a very short period for testing durability and performance of both consolidation and protective materials, important information has been obtained.

All newly designed HEROMAT materials, after one year from the application, resulted highly compatible with the aesthetic properties of originals substrate determining negligible or temporary colour variations. The good durability of the photocatalytic coating was proved an all treated areas. Improved durability results from treatment with carbonate and silicate base consolidants, although not necessarily exhibited by increased hardness values. However, the absence of an increased surface hardness on treated areas may be the most compatible outcome in the case of cultural heritage, and may not be related to the improved durability observed.

ENVIRONMENTAL ASSESSMENT AND TOOLKIT FOR DECISION MAKERS

METHODOLOGY FOR ENVIRONMENTAL ASSESSMENT (LCA) OF PROTECTIVE AND CONSOLIDATIVE SYSTEMS IN THE FIELD OF CULTURAL HERITAGE

One of the goals of the project was to develop durable and environmental friendly materials considering their whole life cycle from cradle to cradle. The project performed a study of the environmental footprint of the newly developed protective materials and the evaluation of their environmental friendliness. The study was based on the use of Life Cycle Assessment (LCA) technique.

The project concerned with the identification of existing LCA calculations for similar materials, such as corrosion protective materials, coatings, paint systems and nano-based materials, since previous research had shown that practically no LCA models existed that might be suitable for self-cleaning coatings and consolidants for buildings and other objects of cultural heritage. Data for similar models were analysed by means of existing Environmental Product Declarations, reports and scientific papers. Following an initial study that was performed on existing LCAs, the goals and scope of the HEROMAT LCA study, including the definition of the functional unit and inputs and outputs for the selected systems were set in order to:

- achieve an optimal production for the HEROMAT products (supporting decision-making in the production phase) and consequently developing more sustainable products in comparison with conventional ones;
- improve market penetration for HEROMAT products (data gathered for issuing Environmental Product Declarations at the end of the project);
- support decision making for restorers and owners of the CH objects.

Cradle-to-gate models were developed in order to improve the production phase, while the final goal was to form Cradle-to-grave models for the newly developed HEROMAT materials (carbonate consolidant, silicate consolidant and photocatalytic suspension). These models included the following processes (Fig. 20):

- raw material extraction and processing (module A1);
- transport of raw materials to the manufacturer (module A2);
- manufacturing of the protective materials and manufacturing of packaging material (module A3);
- transportation of packaged protective materials to the construction site (module A4);
- application on the object (module A5);
- recovery or recycling potentials of waste packaging material, expressed as net impacts and benefits (module D).

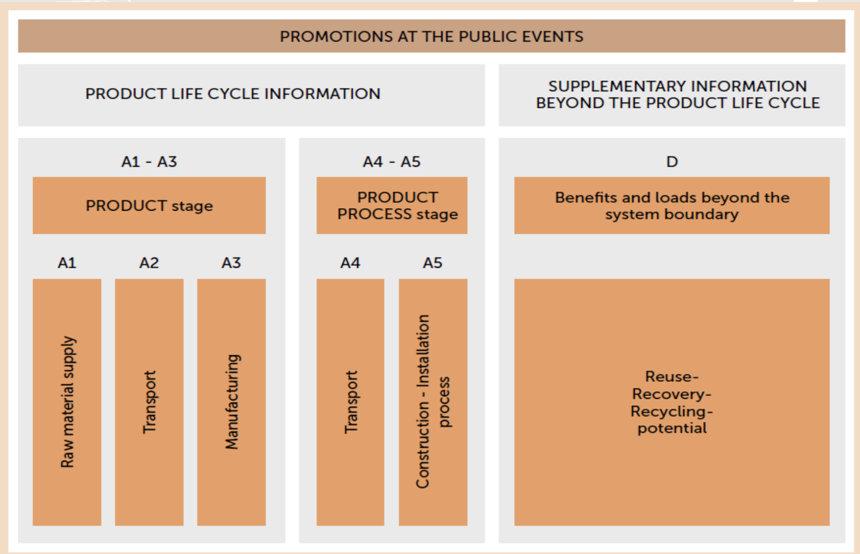


Fig 20: Processes taken into account in cradle-to-grave models of HEROMAT materials

All the above mentioned modules were grouped together into following stages: Modules A1 to A3 correspond to Product stage; Modules A4 to A5 correspond to Construction stage; Module D corresponds to Benefits and loads beyond the system boundary.
However the Use and End-of-life stages were omitted from LCA study because HEROMAT materials do not have a real subsequent Use stage. Moreover, the End-of-life stage is not taken into account because materials are designed for cultural heritage assets. After application, the protective material becomes a part of the cultural heritage objects. End-of-life is not predicted since cultural heritage is to be preserved for as long as possible.

The functional unit of the LCA analysis was defined as the treatment of one square meter of built cultural heritage. Consumption of protective materials varies, as it depends on the type of treated object/substrate (i.e. its porosity). Here the results are based on an average consumption, which is around 0.78 L for consolidants and around 0.30 L for photocatalytic suspension (per square meter).
The environmental burdens of HEROMAT materials were studied in 7 impact categories, which are indicated in ISO standards 15804 and 15978: Global Warming Potential (GWP in kg CO_2 equivalents); Ozone Layer Depletion Potential (ODP in kg R11 equivalents); Acidification Potential (AP in kg SO_2 equivalents); Eutrophication Potential (EP in kg PO_4

equivalents); Photochemical Oxidant Creation Potential (POCP in kg Ethene equivalents); Abiotic Depletion of elements (ADP_e in kg Sb equivalents) and Abiotic Depletion of Fossil Fuels (ADP_f in MJ). In addition, the following were also studied energy consumption (renewable and non-renewable in MJ) and Human Toxicity Potential (HTP in kg DCB equivalents).

The LCA was performed for two types of consolidants (carbonate consolidant and silicate consolidant) and for photocatalytic suspension. Environmental footprint of carbonate consolidant and photocatalytic suspension found to be significantly low, while environmental footprint of silicate consolidant is considered to some extent higher. Manufacturing procedure of all three HEROMAT materials is energy low intensive and thus environmental friendly. It was found that raw materials may show significant contribution to the impact in life cycle of the material. In case of silicate consolidant, use of silane as a raw material was found to be "weak point" from environmental point of view. However, silane is an essential composition material for the production of any silicate based consolidant. The global warming impact of carbonate consolidant amounts up to 0.39 kg carbon dioxide equivalent emissions, in case of silicate consolidant it is up to 30 kg carbon dioxide equivalent emissions, while for photocatalytic suspension it does not exceed 0.22 kg carbon dioxide equivalent emissions.
The HEROMAT project in this way has introduced the LCA in the field of the conservation of built cultural heritage. Till now, only few such examples existed and all of them referred to recent projects. An important step toward development of materials with low environmental impact has been performed. Environmental friendly manufacturing processes have been introduced, however, improvement can be still made with regard to use of raw materials (extraction and processing of some raw materials can show relatively significant environmental footprint).

MULTIDECISION TOOL FOR DECISION MAKERS REGARDING CULTURAL HERITAGE MANAGEMENT

In order to help heritage practitioners to choose the right protective materials among the available ones, a decision tool was developed. It takes into account not only the efficiency of advanced protective materials, but also other factors important for people who directly or indirectly take care for protection of immovable cultural heritage (conservators, scientists, heritage managers, architects, engineers, planners, museum professionals, industry and even visitors). It means that the decision-making tool can help conservators and other stakeholders to make not only efficient, but also sustainable decisions with regard to the selection of consolidative and preservative materials for the treatment of a built cultural heritage.

The decision-making tool in form of tables or decision trees was introduced to heritage practitioners. They had an active role in evaluation of the criteria, which were integrated in the tool. Therefore a simple decision-making tool was prepared based on the results obtained from a survey with international participation. Altogether, 208 respondents took part. Among the target audience, conservators prevailed (76 respondents), followed by scientists (56) and engineers (17). The criteria were scored as indicated above. Relatively more important criteria were listed before relatively less important criteria. However, a score value between 4.5 and 5 meant that the respondents strongly believed that a criterion was important. Two criteria were recognized as strongly important (i.e. performance characteristics and health and safety) among all the target groups, marked with green. The rest of the 7 criteria were evaluated with score values between 3.5 and 4.5, meaning that the respondents mildly believed that the criteria were important.

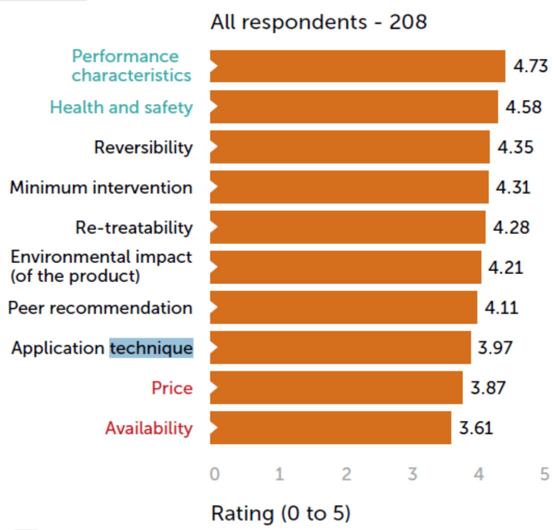


Fig. 21. The criteria for deciding treatment alternatives were evaluated in order to develop a simplified decision making tool

None of the criteria was recognized as "unsure of importance of criterion" (score value between 2.5 and 3.5), "mildly believe criterion is not important" (score value between 1.5 and 2.5)", or "strongly believe criterion is not important" (score value lower than 1.5). Price and Availability are two relatively less important criteria; nevertheless both were scored with relatively high value (above 3.5) and thus still believed to be mildly important.

1. PERFORMANCE CHARACTERISTICS:			
- Photocatalytic activity	Yes/No		
	If Yes, then:		
	Viscosity	Numeric	(mPa s)
	Density	Numeric	(kg/l)
	pH	Numeric	/
	Durability	Numeric	(years)
	Compatibility with substrate	- Color Change	Yes/No
		- Cracking	Yes/No
- Consolidation	Yes/No		
	If Yes, then:		
	Depth of penetration	Numeric	(mm)
	Viscosity	Numeric	(mPa s)
	Density	Numeric	(kg/l)
	pH	Numeric	/
	Durability	Numeric	(years)
	Compatibility with substrate	- Color Change	Yes/No
		- Cracking	Yes/No
	Chemical compatibility	Yes/No	
2. HEALTH AND SAFETY:			
- Toxicity			Yes/No
- Hazardous substance			Yes/No
- Flammability			Yes/No
- Protective equipment			Yes/No
3. REVERSIBILITY			Yes/No
4. MINIMUM INTERVENTION:			Yes/No
5. RE-TREATABILITY:			Yes/No
6. ENVIRONMENTAL FOOTPRINT:			
- Environmental product declaration	Yes/No		
- Energy consumption	Numeric	(MJ/kg of product)	
- Global Warming Potential	Numeric	(kg CO_2 equiv. emissions/kg of product)	
7. PEER RECOMMENDATION:	Yes/No		
	If Yes, what:		
8. APPLICATION TECHNIQUE:			
- Pulp	Yes/No		
	If Yes, what is the consumption	Numeric	(l/m^2)
- Spray	Yes/No		
	If Yes, what is the consumption	Numeric	(l/m^2)
- Brush and roller	Yes/No		
	If Yes, what is the consumption	Numeric	(l/m^2)
- Equipment cleaning with water	Yes/No		
- Equipment cleaning with diluter	Yes/No		
9. PRICE:		Numeric	(EUR/litre)
10. AVAILABILITY:	Yes/No		
	If Yes, what is the delivery time	Numeric	(days)

The decision-making tool is primary aimed for stakeholders and heritage practitioners, but it can stimulate also producers of protective materials to develop sustainable products and to fill the gap with regard to labelling of some important product characteristics. Many products lack several specifications, especially those related with environmental impact. For the users of the material, it is very important that the producers clearly label several characteristics and criteria on the product, including those related with environmental footprint of the material. In such a case, the decision makers can easily compare the most important characteristics of different protective and preservative materials, taking into account discussed tool.

With this multi-decision toll approach the criteria, which are crucial for selection of proper and sustainable protective material, were evaluated with help of international experts in order to provide effective toolkit for decision making.

IV. DESCRIPTION OF THE POTENTIAL IMPACT

SOCIO-ECONOMIC IMPACT AND THE WIDER SOCIETAL IMPLICATIONS OF THE PROJECT

The main project outcomes are new environmental friendly materials for the conservation and protection of immovable cultural heritage assets (such as the upkeep of fortresses, churches and monasteries). However it reached far beyond research activities.

The HEROMAT project investigation and results brought together experts of different professional backgrounds, researchers, heritage managers, restorers and SMEs involved in production of materials and monuments protection. It cross-lined different sectors: universities, research institutes, public institutions, production companies and SMEs. Though joint 4-year work a common language was developed and deeper understating among different disciplines promoted. Project Consortium learned from each other, accelerating knowledge sharing.

In practise the project contributed to promotion of cultural heritage research and education on a national and international level. The project teams engaged young researchers and professionals in all stages of project lifetime. It enhanced their competencies and encouraged them to take lead role in heritage conservation, raising their employability on a local and global market, and teaching them to exploit research results to enhance professional growth and job creation.

Combination of diverse dissemination tools enabled HEROMAT to promote awareness of the cultural heritage as non-renewable resource and foster synergies amongst stakeholders in decision making. Preservation of the material testimony, by the use of new conservation materials and techniques, gives the cultural assets a chance to last longer in order to be preserved for future generations, but also opens up a path towards future conservation. HEROMAT products are all tailored made to suite the background idea of preservation of authenticity, value and aesthetic state of heritage assets. By doing so, HEROMAT has been deeply involved with local communities of the chosen case study objects. That way HEROMAT associated with the preservation of intangible cultural heritage, the identity of local and European societies in the sense of the Framework Convention on the Value of Cultural Heritage for Society.

The project maintained strong links with heritage and conservation professionals who play a key role in applying national and international conservation instruments (including legislative frameworks) in the practical conservation of specific monuments and works of art. They translate key principles and concepts into practice, and consider how material processes and interventions impact on the significance, value and authenticity of cultural heritage. The development, application and promotion of HEROMAT materials and techniques for the conservation therefore involved heritage managers, conservation architects, technicians, restorers, heritage/conservation scientists, traditional building specialists and craftsmen, and where possible those involved in visitor interpretation and presentation.

Newly generated knowledge is already built-in educational process. New research results have entered curriculum on master level of university studies in materials engineering (Faculty of Technology, University of Novi Sad). The results are also presented to research, professional and general public with open access to project publications at the project website.

The economic effects of the project are clear. HEROMAT products which are chosen for industrial production are natural based, produced of inexpensive local raw materials. Once on the market, these new materials: consolidant, photocatalytic coating and combination of those, will directly lead to decrease of ongoing maintenance costs for heritage buildings. They prolong the period between two conservations/restorations, while their relatively low estimated selling prices, and make this kind of works cost-efficient for heritage managers. On the other side, HEROMAT products are designed to be competitive on the market, expending SMEs market share and opening new employment opportunities. When the effects of the global economic crisis had influenced the building industry, materials market and resulted in a decline in the market volume and value, companies that are able to develop new products and new cost effective and long-lasting solutions will gain new pillar for ensuring long-term prosperity.

Significant additional impact also lies in the potential application of these materials in new construction. The developed consolidants and protective coating were tested on a wide range of materials, not just the ones that are found at the selected historical sites. A wider use of developed materials can be predicted. The HEROMAT photocatalytic coating is already recognized to find its placement in modern civil engineering. It greatly extends the lifetime and aesthetic appearance of colour layers of modern buildings, especially in highly polluted environments like cities with heavy traffic.

Finally, grouping of research and production professionals under one project, like done in HEROMAT, brought the most advanced knowledge into product design. It expands application on new materials in cultural heritage protection, besides the well-known and widely used traditional ones. The placement of highly competitive HEROMAT products on the market will start a new innovation cycle at market competitors, opening new employment possibilities for cultural heritage professionals and researches.

MAIN DISSEMINATION ACTIVITIES

The project mixed promotional tools to reach wide targeted public throughout Consortium countries and beyond. Dissemination activities can be summarized in four groups: dissemination of the foregrounds and generated knowledge to academic public, communication of the project results to similar projects, professionals and end-users, and wider project promotion to general public and media. Promotional tools used include project website www.heromat.com, scientific papers published in reviewed journals and posters at scientific conferences, Dissemination Package (available for download under Results section of the project website), various printed materials and roll up banners, printed and electronic media coverage, pages on social media (Facebook, LinkedIn, Tweeter), interviews on TV and Internet, planned visits to fairs and relevant stakeholder events, organization and hosting of workshops, conferences and open sessions for targeted public. Project partners contributed to the coherent, active and heterogeneous project dissemination on all levels. During the project lifetime more has been done than initially planned. Good communication among partners, links strengthened towards the same goals, active discussions and idea sharing contributed to expansion of the activities in many different ways.

PROJECT WEBSITE AND SOCIAL MEDIA PAGES

The HEROMAT website www.heromat.com served as main dissemination tool, ensuring one-stop-shop for all target groups interested in project development and results. Regular updates of the website contents kept targeted publics informed about research, networking activities and project promotion. In order to expand visibility of the project results and activities, and support direct communication with public, especially students and young people, HEROMAT set promo pages on social networks: Facebook in June 2013 and Twitter in December 2013. Facebook and Twitter platforms were used for regular update on dissemination and ongoing activities, and about the field works on both case study historical sites. Official website and social pages of the project are linked to other websites mentioning and promoting the project (e.g. official websites of the project partners, NanomeCH cluster, conferences attended etc.).

DISSEMINATION TO ACADEMIC COMMUNITY

Scientific publications - Sampling, analyses, synthesis, characterization, preparation of model substrates, laboratory and in situ application, monitoring and LCA were all research results covered by scientific papers. The project is still being increasingly promoted through the scientific papers at conferences around the world (list of papers published so far is available on the Participant Portal under Dissemination). Scientific papers are mainly dealing with the characterization of historical materials, synthesis of HEROMAT products, photocatalytic and antimicrobial efficiency (self-cleaning coating precursor).

Workshops and events, student exchanges - Education fostering and foreground sharing were from the very beginning specific aims of the project promotion. Knowledge generated under the project has already been included in guest lectures and curriculum of relevant university courses taught at partner institutions. Students and young researchers have been regularly updated on the project outcomes and take active contribution on the promotion of the HEROMAT results. HEROMAT took part in summer schools and student events. The Summer School of Architecture (August 25th - 30th, 2013) organized in Bač, came as a result of cooperation among the Group of Architects, PZZSK and TFUNS. This was an international summer school, with lectures and workshops for students of architecture and conservation. Since the theme for that year was: the methodology of conservation and restoration of brick walls; lime and mud systems; management of energy consumption, HEROMAT Project experience took significant place. At the Board of European Students of Technology (BEST) conference ,,Meet the POLYMER, explore the power of NANOS" in 2014 in Novi Sad, Serbia, the HEROMAT was presented to international technology students in several session during the event. HEROMAT was also presented in lectures and field work at the DIAnet International School "The role of cultural heritage for the sustainable development of the Danube Region" organized in Gorizia, Italy in March 2015 under the scope of Danube:Future project. Moreover, as a result of international and multidisciplinary character of the project, the professional student exchanges and internships were established. The internship for two master students was organized in cooperation with Raymond Lemaire International Centre for Conservation from Leuven, Belgium.

COMMUNICATION OF THE PROJECT RESULTS TO RELEVANT STAKEHOLDERS

Active collaboration among project partners, constructive discussions and idea sharing over the past months, enabled RTD foreground sharing among professional communities, to end-users, other European projects and EU policy makers. Workshops and other targeted events were organized and attended to make direct links with relevant stakeholders.

HEROMAT workshops - In September 2012 in Bač the workshop and round table "Materials in Conservation" was organized. The first HEROMAT project results were presented to professional and general public, and media representatives. The comparative approach was presented on the examples of three fortresses on Danube: Bač and Petrovaradin Fortress (Republic of Serbia) and Fortress in Ilok (Republic Croatia), with the participation of experts of diverse backgrounds who all act in cultural heritage protection. Presentations and discussions were held in Donjon Tower of the Bač Fortress followed with demonstration of mortar preparation based on the traditional technology approach developed as one of the HEROMAT project results (WP3). A round table "Preservation of Bač Fortress - contributions of the HEROMAT project" was organized in Bač in April 2013. The project was presented to representatives of local community, decision makers and stakeholders from Municipality of Bač and surounding towns, with a special reference to project role and its importance for the local community of Bač. In May 2014 HEROMAT team organized a two-day educational workshop „The use of non-destructive methods for material testing in conservation". This occasion was unique due to presence of mobile laboratories on the field, executing the measurements at the Bač Fortress. Workshop was organized for professionals and conservators to present the results of the project, the methodology and the most advanced equipment for in situ monitoring. It was distinctive opportunity for local professionals and stakeholders to learn from all HEROMAT partners who were present at the site with their specific pieces of equipment. The delegation of European countries' Ambassadors in Serbia leaded by H.E. Michael Davenport, the Head of the EU Delegation to the Republic of Serbia, visited the HEROMAT site at the Bač Fortress and met with HEROMAT partners and workshop attendees on the second day of the event.

ORGANIZATION OF WORKSHOPS						
Workshops organized according to the project plan						
MAIN LEADER	TITLE	DATE	PLACE	TYPE OF AUDIENCE	SIZE OF AUDIENCE	COUNTIES ADDRESSED
TFUNS	Workshop on promising formulations	23th Jan 2013	Novi Sad, SERBIA	Scientific community (Higher education, Research)	100	Serbia, Slovenia, UK, Italy, Russia
CNR-ISTM	New materials for stone conservations: do they work? Assessing the effectiveness of consolidation treatments.	10th May 2013	Perugia, ITALY		100	Serbia, Slovenia, UK, Italy, Russia
SANING	Workshop on developed systems and pilot production protocol definition	20th Sep 2013	Ljubljana, SLOVENIA		100	Serbia, Slovenia, UK, Italy, Russia
Additional events created for different target groups						
PZZSK, TFUNS	Materials in Conservation	21st Sep 2012	Bač, SERBIA	Conservators and Cultural Heritage experts from Serbia and Croatia	50	Serbia, Croatia
PZZSK	Preservation of Bač Fortress - Contributions of the HEROMAT project	19th Apr 2013	Bač, SERBIA	Civil society; Policy makers;	50	Serbia
PZZSK	The use of non-destructive methods for material testing in conservation - EDUCATIONAL WORKSHOP	28th,29th May 2014	Bač, SERBIA	Scientific community (higher education, Research); Policy makers; Media	70	Serbia, Slovenia, UK, Italy, Russia

Table 3. List of HEROMAT workshops for relevant stakeholders, including heritage professionals, decision makers and end-users

Professional fairs – international trade and restoration fairs were excellent opportunity for SME partners to present their results and communicate with potential markets about opportunities for the final HEROMAT products placements.

Clustering - Establishment of links with relevant EC projects, networks and initiatives was of a specific interest of the project. Strengthening links and exchange of foregrounds with other leading European and world projects and institutions involved in protection of cultural heritage driven HEROMAT to join NanomeCH cluster (www.nanomech.eu). The cluster "Nano and advanced materials for Cultural Heritage" was established in October 2012 at EUROMED conference in Cyprus. The European Commission initiated a cluster for projects involved in the FP7 calls ENV-NMP.2011.2.2-5 and ENV-NMP.2011.3.2.1-1 FP7. Established cluster gather five FP7 projects: HEROMAT, IMAT, NANOFORART, NANOMATCH and PANNA around the same goals of sharing knowledge and experience within network and joint market placement of products and devices planned to be developed under scope of those projects. The cluster is jointly coordinated by Dr A. Bernardi, NANOMATCH, and Prof Dr J. Ranogajec, HEROMAT. Several cluster meetings were organized and an important progress was made. One of the meetings was hosted by the HEROMAT in July 2014 in Novi Sad, Serbia, and this occasion was used for cluster members to present their result to regional conservators, restorers and stakeholders. Also, on the final conferences of two cluster members – NANOMATCH, Venice, October 2014 and IMAT, Florence, November 2014, the HEROMAT presented its research results and products. At the HEROMAT Final Conference in November 2015, Dr A. Bernardi, NANOMATCH project coordinator and the Cluster co-coordinator, gave invited lecture on "Innovative materials for consolidation of stone and glass - Past, present and future collaboration between EU projects".

The HEROMAT attended the First Policy Seminar NEW HORIZONS FOR CULTURAL HERITAGE – Recalibrating relationships: bringing cultural heritage and people together in a changing Europe, and the EU projects networking session, both organized on 19 October 2015 in Brussels under RICHES EU project (http://www.riches-project.eu/).

PROMOTIONS AT THE PUBLIC EVENTS					
MAIN LEADER	TITLE	DATE	PLACE	SIZE OF AUDIENCE	COUNTIES ADDRESSED
ZAG	53rd International Fair DOM 2013	12th - 17th March 2013	Ljubljana, SLOVENIA	50000	33 countries
GP HGP	39th International Building Trade Fair 2013	16th - 20th April 2013	Belgrade, SERBIA	51000	18 countries
PZZSK	Salone dell Arte del Restauro e della Conservazione dei Beni Culturali e Ambientali	26th - 29th March 2014	Ferrara, ITALY	26000	20 countries
ZAG	53rd International Fair DOM 2014	11th - 16th March 2014	Ljubljana, SLOVENIA	50000	33 countries
ZAG	BUILDING TEST EXPO	17th - 19th June 2014	Brussels, BELGIUM	50000	Belgium and others

Table 4. List of HEROMAT promotion at professional fairs

Dissemination Package - promotion of RTD work and results was designed to maintain communication with professional public and decision makers ensuring open access to majority of project outcomes. The Consortium decided to present the project results to the wider scientific community in very detailed and research oriented publications. The pattern how to approach WPs and publishing their relevant results was agreed already in May 2014. RTD project results were therefore combined into the Dissemination Package containing six publications presenting work packages in terms of work performed and achieved results. The promotion of the Dissemination Package was organized at the occasion of the HEROMAT Final Conference in November 2015 in Novi Sad, Serbia. Under heading *Results* on the HEROMAT website all publications can be found and downloaded free of charge.

Fig. 22. Dissemination Package of HEROMAT project research results

Application of HEROMAT products beyond project - Awareness spread among professional public about HEROMAT results and final products led to the usage and application of the consolidants and the photocatalytic coating on cultural heritage objects beyond project scope in Serbia, Croatia and Slovenia. Carbonate consolidant was applied on the frescos of church of St. Vincent in Svetvičent, Croatia and of the Franciscan Church of the Annunciation in Ljubljana, Slovenia, while photocatalytic coating was applied on the walls of medieval basilica Arača in Novi Bečej, Serbia and the Petrovaradin Fortress on the Danube River in Novi Sad, Serbia.

WIDER PROJECT PROMOTION TO GENERAL PUBLIC AND MEDIA

Manifestation of European Heritage Days is a regular activity in September in Bač. Since the central place of the event is Bač Fortress, HEROMAT team participated actively during the celebration in 2013, 2014 and 2015. In addition to informative board and panels with substrates placed in front of the sampled walls, in 2014 the project was presented to local and scientific community at the round table Cultural landscape - an opportunity for economic development based on cultural and natural heritage by the project coordinator, while young researchers organized a workshop for children Small World of Heritage in the HEROMAT project Scientific capsule (purchased from the project). Having dealt with attractive topic of cultural heritage protection the HEROMAT also reached children, pupils, high school and university students, involving them in different events like Small world of heritage during the manifestation of European Heritage Days and Summer school of architecture.

HEROMAT on Euro News - the leading European information network Euro News recorded a documentary about the project HEROMAT, in order to follow the latest European developments in the field of cultural preservation. The documentary was created in collaboration between the media network Euro News and the European Commission. It was presented in the award-winning program *Futuris - latest news about the leading scientific and technological research projects in Europe*. Two days of the documentary shooting in August 2013 took place in the TFUNS laboratories, GP HGP production and at the Bač Fortress. The program was broadcast in 340 million households in 130 countries and translated in thirteen languages (English, French, German, Spanish, Italian, Russian, Portuguese, Arabic, Turkish, Persian, Ukrainian, Greek, and Hungarian). Short documentary about HEROMAT titled *A new "skin" for old stones* (www.euronews.com/2013/09/09/a-new-skin-for-old-stones/) was intensively broadcasted (18 times at different times of day) throughout one week (10 - 15 September 2013) on the occasion of the European Heritage Days.

HEROMAT final conference realized by joined forces of all partners as the highlight of the scientific promotion, reached extraordinarily success. Activities organized in addition to the conference attracted great attention of both scientific public and the media. For this purpose in the Central Building of the University of Novi Sad it was hosted the photo exhibition "BEYOND HEROMAT PROJECT" prepared by PZZSK team, dissemination leaders. The exhibition was a great way to remind partners and the wider public of the many activities of the project during the four years of project lifecycle, but also to present the human aspect of us working and growing together for more than four years.

HEROMAT on EU portals - HEROMAT team is especially proud of a new story "A natural, long-lasting solution to preserving Europe's cultural treasures" published right after the Final Conference on the EU portal of HORIZON 2020 programme http://ec.europa.eu/programmes/horizon2020/en/news/natural-long-lasting-solution-preserving-europe's-cultural-treasures.

EXPLOITATION OF RESULTS

It is notoriously difficult to accurately assess the potential market for new materials for use in the cultural heritage arena. The conservative nature of stakeholders and other interested parties, reliance on 'tried and tested' materials and lack of knowledge all contribute to a reluctance to accept something new. 'Word of mouth' communication is a valuable method of overcoming this reluctance and one which the SME partners responsible for the production of the new materials will exploit to the full. The HEROMAT consortium represents a significant network covering large parts of Europe, and beyond, which the SMEs can use to gain a foothold with end-users. Traditional marketing approaches will also be used where appropriate.

The project consortium learnt from the targeted market survey of the opinions of conservation professionals that the most important factors in choosing materials were performance characteristics and health and safety issues. The least important were price and lead-in time for delivery. These attitudes are very positive from a marketing point of view because, once the materials are being considered for use, transport costs and/or delays are less likely to be determining factors.

The main bodies responsible for the maintenance of cultural heritage in the UK for example, spend around €1bn annually. If we assume that 0.2% of that sum is spent on materials, then HEROMAT materials will have a potential market of €2m. If we assume a similar % of GDP across Europe is spent on cultural heritage materials, then we have a potential market of over €10m.

In addition, the materials, particularly the photocatalytic suspension, could be used on new-build projects, where reduced maintenance costs would be important to any developer. In the UK alone, the construction industry turns over in excess of €120bn annually, so the potential market is huge.

In summary, the SME producers have excellent products they can offer and an existing network of heritage professionals to help promote them within a potentially very large and attractive market. Furthermore, the developed HEROMAT materials/systems have proved to have very good properties when applied on wide range of models, as well as in on-site applications, assuring durability, compatibility, no colour change, etc. Application of such materials can fundamentally alleviate necessity for restoration and improve durability of thusly protected outdoor cultural heritage objects. Higher quality of restoration will prolong the time to the next intervention and therefore lower the costs of preservation of cultural heritage and increase its durability.

Producers of the developed materials have defined their production protocols on pilot level into the smallest details. The next step is to enlarge production to full scale level. This step is closely connected with additional investments, research and trials and also with the demand of the market. At the end of the project the demand of the market for developed materials is quite low because materials are not widely recognised. The necessary step before enlarging the production is feasibility assessment, intensive marketing activities including presentations, a lot of different in-situ demonstrations, workshops, seminars and commercial materials as brochures, advertising, promotions etc.

All this activities require new investments in production, product placements and marketing, while having a delayed returning effect of the investment. Due financial crisis and generally poor situation of investing into cultural heritage conservation this represents a great risk to the producers as their marketing investments might not return in a planned returning period. A solution to this obstacle might be in continuation of the activities under the European Commission funding schemes and new projects that provide funding and support for growth and expand of promising - state of the art products and ideas on global markets in order to create an added value to European industry.

Besides innovative products the HEROMAT project has generated new knowledge, methodologies and know-how. New research findings are already presented in the reviewed scientific publications. Generated knowledge is integrated in academic context, including university lectures, bachelor, master and PhD courses, and summer schools taught at the universities which are members of the HEROMAT Consortium. For example, new findings and generated knowledge about characterization of historical materials, preparation of model substrates, their characterization and synthesis of photocatalytic suspension is built-in educational process and has entered curriculum on master level of university studies in materials engineering (Faculty of Technology, University of Novi Sad).

Generated knowledge, established methodologies and know-how will be further exploited for both research and education. Free user rights for all project partners for educational and research purposes is defined previously in the HEROMAT Exploitation Agreement. The public open access to majority of research outcomes is assured with the widely disseminated project foreground in the Dissemination Package, printed and available in e-form at the project website for multiplication. It targets research, professional and general public, media and policy makers, continuing active involvement of the HEROMAT consortium in policy making and raising awareness in cultural heritage.

The HEROMAT research results will be also exploited for advance modifications and optimizations of developed products in order to suit new types of mineral substrates and other climate conditions. New project proposals are being developed and/or planned having HEROMAT products and findings as starting point. For example, SME partners Saning and GP HGP supported by other members of the HEROMAT consortium currently seeks on new funding possibilities to exploit HEROMAT pilot productions and expand them to market ready stage.