

# PROJECT FINAL REPORT

**Grant Agreement number: 213651**

**Project acronym: STONECORE**

**Project title: Stone Conservation for Refurbishment of Buildings**

**Funding Scheme: Collaborative Project**

**Period covered: from 01.09.2008 to 31.8.2011**

**Name of the scientific representative of the project's co-ordinator<sup>1</sup>, Title and Organisation:**

**Prof. Dr. rer. nat. habil. Gerald Ziegenbalg, IBZ-SALZCHEMIE GmbH & Co. KG,  
Gewerbegebiet "Schwarze Kiefern", 09633 Halsbruecke, Germany**

**Tel: +49 (0) 3731 200155**

**Fax: +49 (0)3731 200156**

**E-mail: gerald.ziegenbalg@ibz-freiberg.de**

**Project website address: [www.stonecore-europe.eu](http://www.stonecore-europe.eu)**

---

<sup>1</sup> Usually the contact person of the coordinator as specified in Art. 8.1. of the Grant Agreement.

## Table of Contents

0	<b>Final publishable summary report</b>	3
1	<b>Summary description of project context and objectives</b>	4
1.1	Project context	4
1.2	Project Objectives	5
2	<b>Main S&amp;T results /foreground</b>	7
2.1	Developed materials	7
2.1.1	Calcium hydroxide nano-sols	7
2.1.2.	Other materials	7
2.2	Characteristics of calcium hydroxide nano-sols	8
2.3	Determination of key parameters of materials before and after the application of calcium hydroxide nano-sols	9
2.3.1	Materials used, techniques and methods	9
2.3.2	Properties of materials after the application of calcium hydroxide nano-sols	12
2.3.3	Properties of materials after the combined application of calcium hydroxide nano-sols and silicic acid esters	17
2.4	The use of calcium hydroxide nano-sols to prevent biological growth	21
2.5	Data management system	23
2.6	Non or minor destructive stone assessment methods	24
2.6.1	Peeling test	24
2.6.2	Karsten tube innovation	25
2.6.3	Borehole ultrasonic measurement devices	26
2.6.4	Drilling resistance device	26
2.6.5	Ground Penetrating Radar	27
2.7	Results of trial testing and demonstration	29
3	<b>Conclusions</b>	32
4	<b>Impact</b>	33
4.1	Impact of the STONECORE results on refurbishment of buildings and the conservation of cultural heritage	33
4.2	Dissemination activities and exploitation of results	37
4.3	STONECORE Website + Logo	41
4.4	Partner in STONECORE and contact addresses	42

## 0 Final publishable summary report

Six SME's, four universities, one public research organisation and one public body from seven countries joined together in project STONECORE in order to find a new approach for the refurbishment of stones, mortars and plasters used in the construction of historic monuments. The idea was to develop and test nano-materials compatible to those used during construction, together with new non-destructive methods for the assessment of stone. The development and testing of calcium hydroxide nano-sols was at the centre of interest. In detail, the following was required:

- Fundamental investigations into the synthesis of calcium hydroxide nano-sols and characterisation of their basic properties.
- Determination of the applicability of different nano-materials to natural and artificial stones, mortars and plasters.
- Documentation, sampling and characterisation of the objects foreseen for trial testing and demonstration.
- Demonstration of the efficacy of the developed materials by application on several objects within Europe
- Characterisation of fungal and algal growth on different stones, mortars and plasters as well as development of methodologies to remove biological growth using calcium hydroxide nano-sols.
- Methodology and hardware development for the non-destructive assessment of stone.

STONECORE has led to manifold new approaches for the conservation of stone, mortar and plaster as well as for the overall refurbishment of buildings. Many new consolidants based on calcium hydroxide nano-particles were developed. The nano-particles they contain are characterised by sizes in the range of between 50 and 250 nm. They are stable when dispersed in different alcohols. The small size and electrostatic repulsion forces guarantee that the particles do not sediment. Stable sols are formed. These are able to penetrate deep into deteriorated stones, mortars or plaster. After evaporation of the alcohol, calcium hydroxide particles are present in the treated materials. The alcohols evaporate without leaving any other residues. Conversion into calcium carbonate takes place in a similar way as for conventional lime by reaction with atmospheric carbon dioxide. The achievable strengthening, the distribution of the nano-materials in different stone and mortar samples as well as the development of favourable application techniques were explored through a large number of comprehensive investigations. Within the STONECORE project it could be shown that sols containing stably dispersed nano-lime particles are able to strengthen and disinfect areas affected by algae and fungi and to remove microbiological growth in an eco-friendly way, without chlorine or quaternary ammonium compounds. Safe removal of biological growth is achieved by the dehydrating action of ethanol in combination with the creation of alkaline conditions by the lime particles itself.

The development of new materials for structural consolidation was accompanied by comprehensive research in the field of non-damaging assessment methods. An enhanced peeling test to characterise the surface properties of natural and artificial stone was developed as well as a sophisticated, semi automated device to characterise the water-uptake of porous materials using the for Karsten tube technique. Advanced SEM investigations in combination with digital image analysis have been used to detect calcium hydroxide nano-particle in treated materials. Comprehensive investigations have shown that Ground Penetrating Radar is a useful tool to detect fractures and voids in stones especially when the computer-controlled positioning device developed during the project is employed. A new borehole ultrasonic measurement device and a drilling resistance device were also developed and successfully tested.

The successful use of the developed calcium hydroxide nano-sols was demonstrated on 17 objects. Wall paintings, deteriorated natural stone as well as mortar and plaster was strengthened successfully. STONECORE has achieved fully its objectives and technical goals.

# 1 Summary description of project context and objectives

## 1.1 Project context

In Europe, many buildings are made of either natural or artificial stone. Their normal life exceeds hundreds years and refurbishment is necessary several times. As the age of a building increases, so the importance of conservation increases and questions relating to the protection of cultural heritage become essential. The conservation of the original material becomes the main task. Without any doubt, conservation of historical buildings, sculptures or wall paintings is the most challenging refurbishment task.

The main questions raised during the refurbishment of buildings are:

- Damage assessment and development of treatment strategies.
- Stabilisation, conservation or replacement of damaged artificial or natural stone.
- Selection of materials compatible to those originally used.
- Safe removal of mildew and algae.

In all cases, refurbishment requires materials which are compatible with the components originally used during construction. This is of essential importance for the consolidation of natural stones such as limestone, marble and sandstone as well as for mortar and plaster. However, the materials and components available currently, do not fulfil these demands in all cases. Many examples are well known in which the use of unsuitable materials has caused additional damage. Problems involve mainly; the deep penetration of conservation agents into damaged structures; long term stability and the application of different materials as consolidants such as plastics. In the last years, the demand for reversibility of newly introduced materials has been substituted by the demand for compatibility. This means that the characteristics and behaviour of the original system has to be respected and should not be substantially changed, especially in terms of porosity, stability and retreatability.

Refurbishment as well as conservation requires comprehensive stone characterisation and damage assessment. This should be carried out in a non-destructive manner, for the obvious reason that consolidation is done with the intention of increasing the stone's integrity, which cannot be jeopardised during quality assessment. Up until now, however, non destructive stone assessment methods have not been very well developed.

One large-scale problem in the refurbishment of buildings is the removal of mildew (fungi) and algae. Many fungi grow on the surface of natural and artificial stone as well as on many organic substances. They can present a serious danger for human health as fungal spores are very small and can easily be breathed deeply into the lungs. They cause a number of conditions, from allergies producing cold-like symptoms, short-term respiratory difficulties, nasal and sinus congestion, asthma or sore throat, as well as true infections of the respiratory tract.

The growth of fungi and algae in buildings is often related to problems associated with moisture, including uncontrolled humidity. Apart from drying the affected areas and changing the air circulation, complete removal of mould is often of essential importance. On external surfaces, the growth of microorganisms is obviously strongly influenced by the local environment as well as the orientation of the structure, the presence of vegetation and the condition and nature of the material present in the structure. There are many chemical treatments available that promise the safe removal of such growth. However, many of the agents result in either contamination of the structure by chemicals or cause damage to the substrates. For example, disinfectants and washes based on chlorine, chlorine releasing substances or other biocides need to be reviewed with great care prior to use.

Six SMEs, four universities, one public research organisation and one governmental organisation from seven countries joined together in order to find a new approach for the refurbishment of natural

and artificial stone. The project was based on the combination of applied research performed by the participating SMEs with fundamental investigations realised at universities.

## 1.2 Project Objectives

STONECORE was based on the following three novel approaches:

- Refurbishment by stone conservation with nano-materials leading to natural minerals compatible to stone, plaster and mortar.
- Safe and environmentally compatible removal of fungal and algal growth combined with stone or mortar stabilisation.
- Stone characterisation by non-destructive methods, allowing both damage assessment and evaluation of the conservation at low cost.

This required both development of suitable materials and their testing as well as the field application of the developed non-destructive test methods.

In detail, STONECORE had the following project objectives:

1. Development of  $\text{Ca}(\text{OH})_2$  nano-sols of and their production in volumes sufficient for field testing and demonstration.
2. Development of synthesis possibilities for  $\text{BaCO}_3$ ,  $\text{CaSO}_4$  and  $\text{CaCO}_3$  nano-sols.
3. Comprehensive laboratory testing of all nano-materials on different natural and artificial stones, mortars and plasters
4. Determination of the physico-chemical properties of the nano-sols
5. Determination of key characteristics of selected historic materials before and after consolidation with the developed nano-materials.
6. Development and testing of suitable technologies for the application of nano-materials for refurbishment,
7. Characterisation of fungal and algal growth on different stones and mortars
8. Characterisation of the effectiveness of treating surfaces with ethanolic nano-sols for the prevention of fungal and algal growth.
9. Comprehensive characterisation and documentation of the objects foreseen for trial testing and demonstration
10. Hard- and software development for the use of Ground Penetrating Radar as a tool for non-destructive damage assessment
11. Development of a new drilling resistance device
12. Development of innovative methods for surface degradation assessment
13. Field testing of all non-destructive damage assessment methods.
14. Trial testing of the nano-sols on objects situated in Poland, Czech Republic, Austria, Greece and Germany
15. Demonstration of the successful application of the nano-sols alone or in combination with other consolidants
16. Dissemination of the project results

The main idea behind the developed methods, techniques and devices was to provide conservators and restorers with a collection of tools suitable for the assessment of mechanical properties of mate-

rials non-destructively or with minimum impact and to overcome the limitations of industrial standard tests. Originally, these methods were intended mainly for the evaluation of the mechanical properties of the surfaces treated by nano-limes, but extensive laboratory evaluation and field tests proved their general applicability in other evaluation tasks and, therefore, can be considered another successful outcome of the project.

It was the target of STONECORE to achieve a breakthrough in the application of nano-materials in the conservation and refurbishment business. This required successful demonstration objects as well as comprehensive dissemination of the results in order to gain acceptance for the materials.

The following applications were at the centre of interest:

- Consolidation of limestone, marble and related materials due to the formation of calcium carbonate from calcium hydroxide sols. Use of colloidal calcium carbonate suspensions as an injection agent for the filling of voids and cracks.
- Consolidation of mortar, plaster and sandstone by combining calcium / barium sols with conventional stone strengtheners such as silicic acid esters.
- Destruction of fungal and algal growth using colloidal, alcohol-based calcium hydroxide suspensions combined with consolidation of the treated area due to the formation of calcium carbonate.
- Solidification and conservation of stucco.
- Stabilisation of mortar and plaster as well as wall paintings by the formation of carbonates from calcium hydroxide sols.

All systems were required to be environmentally friendly and free from toxic admixtures.

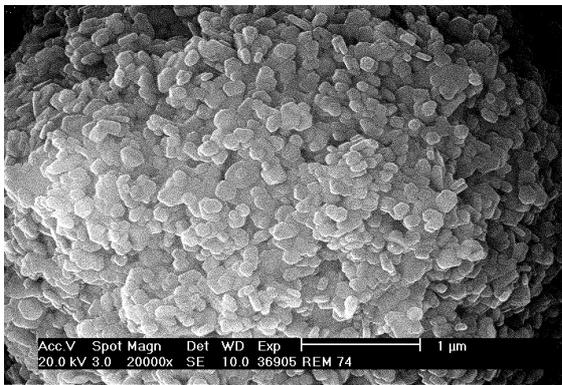
The project objectives were achieved by a combination of research in the fields of applied inorganic chemistry, materials science, microbiology, geophysics and sophisticated materials characterisation along with traditional restoration and conservation work.

## 2 Main S&T results / foregrounds

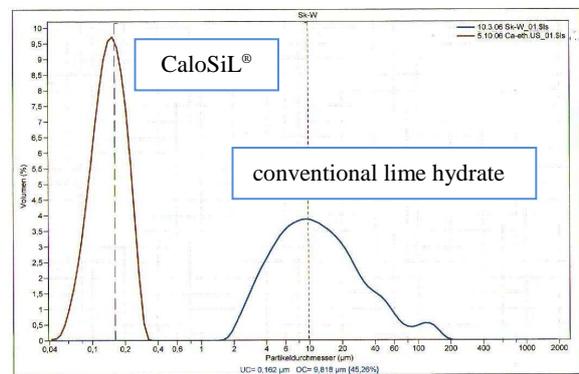
### 2.1 Developed materials

#### 2.1.1 Calcium hydroxide nano-sols

Within STONECORE, calcium hydroxide nano-particles were synthesised with sizes in the range of between 50 and 250 nm. These are stable when dispersed in different alcohols (ethanol, n-propanol, iso-propanol). The small size (Fig. 1,2) and electrostatic repulsion forces guarantee that the particles do not sediment. Stable, alcoholic sols are formed. These are able to penetrate deep into deteriorated stones, mortars or plaster. During the evaporation of the alcohol (which takes place within a few hours), calcium hydroxide particles are precipitated in the treated materials. The alcohols evaporate without leaving any residues. Chemicals or residues deteriorating stone or mortar are thus not formed. These calcium hydroxide nano-particles convert, in the same way as conventional lime hydrate, into calcium carbonate by reaction with atmospheric carbon dioxide. This reaction requires the presence of humidity. The calcium hydroxide nano-sols are offered under the trade name CaLoSiL®.



**Fig. 1** Morphology of  $\text{Ca}(\text{OH})_2$  nano-particles (IBZ-Freiberg)



**Fig. 2** Typical particle size distribution of nano-lime in comparison to traditional lime suspensions (IBZ-Freiberg)

The following CaloSiL types are available:

CaLoSiL®-E: solvent ethanol:

CaLoSiL®-IP: solvent iso-propanol:

CaLoSiL®-NP: solvent n-propanol:

CaLoSiL®-grey: solvent ethanol:

CaLoSiL®-paste like: solvent ethanol:

$\text{Ca}(\text{OH})_2$  concentration between 5 and 50 g/L

$\text{Ca}(\text{OH})_2$  concentration between 5 and 25 g/L

$\text{Ca}(\text{OH})_2$  concentration between 5 and 25 g/L

$\text{Ca}(\text{OH})_2$  concentration between 5 and 25 g/L.

$\text{Ca}(\text{OH})_2$  concentration 300 g/L

CaLoSiL grey is a special product that has, as the name suggests, a grey colour. The other properties are similar to the “standard” materials. The grey colour results from the use of a special raw material for the synthesis. Paste-like CaLoSiL® formulations can be used to adhere loose particles, fill voids and cracks or be used to form the basis of injection grouts and repair mortars.

A special product that was developed is CaLoSiL®-micro. It contains calcium hydroxide particles having sizes between 1 and 3  $\mu\text{m}$ . That means it lies between the CaLoSiL® nano-sols and typical slaked lime (calcium hydroxide slurries obtained by the reaction of calcium oxide with water) and can be used as a bridging material.

#### 2.1.2 Other materials

Using the calcium hydroxide nano-sols it was possible to develop special injection grouts as well as novel repair mortars. The CaLoXiL®-injection grout was formed from fine calcium carbonate fillers in combination with paste-like CaloSiL® formulations which acts as a binder. All components in the

CaLoXiL<sup>®</sup>-injection grout are characterised by particle sizes smaller than 6 µm. The injection grout has free flowing properties and is able to fill also small voids and fissures. The injection grout is characterised by good stability in combination with high flowability. After hardening, porous masses are formed which demonstrate high capillarity. All masses are hydrophilic and are able to act as capillary-active, zone-bridging mortar surfaces, mortar structures and masonry. Another important property is the good adhesion to historic mortar components. The injection grouts are able to adhere single mortar pieces. Pre-treatment with CaLoSiL<sup>®</sup> E-25 or other CaLoSiL<sup>®</sup> types enhances the adhesion of the formed mass to the surrounding surfaces and results in additional structural consolidation.

Typical properties are:

- 36 % porosity
- 4,3 N/mm<sup>2</sup> compressive strength after 30 days
- 1,1 N/mm<sup>2</sup> bending strength
- 23 wt.-% water uptake
- 0,4 % shrinkage
- hydrophilic

The use of paste-like CaLoSiL<sup>®</sup> formulations as a binder has allowed, in combination with special calcium carbonate fillers, the creation of a unique repair mortar that is fully compatible with most historic mortars and plasters. Thus, in combination with the calcium hydroxide nano-sols (CaLoSiL<sup>®</sup>) and the CaLoXiL<sup>®</sup>-injection grout, a set of fully compatible restoration / conservation materials is available.

Characteristic data of the repair mortar are:

Density [g/cm <sup>3</sup> ]:	1,89
Specific surface [m <sup>2</sup> /g]	2,9
Water absorption [wt.-% H <sub>2</sub> O]	16
Porosity [vol.-%]	24-29
Capillary suction up to 5 cm [min.]	20
Coefficient of water absorption in kg/(m <sup>2</sup> h <sup>1/2</sup> )	4,85
Compressive strength [N/mm <sup>2</sup> ] after 21 days	3
Shrinkage [%]	0,2
Hygric expansion [mm]	0,04
Freeze-thaw cyclic test, weight loss [%] after 25 cycles	20

The high capillarity and water suction capacity are typical properties. Water uptake and release takes place rapidly and the mortars can take the role of a protection layer. The mechanical properties of the repair mortar are sufficient to protect the historic materials. The amount of water in the mortar is, due to the use of ethanolic suspensions of nano-lime as binder, low and can be varied on demand.

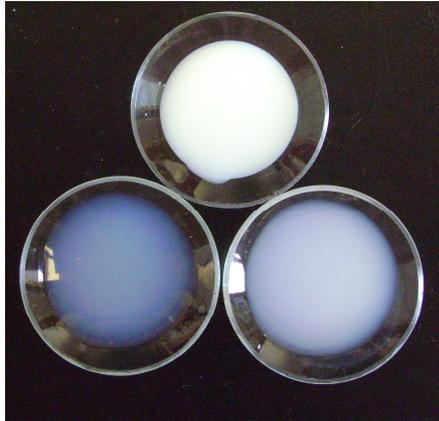
The colour as well as the surface texture of the mortars can be adjusted by the addition of pigments based on the demands of the object and it is possible to imitate weathered and discoloured mortar surfaces.

Within STONCORE, possibilities were also developed to synthesise CaSO<sub>4</sub>-Ca(OH)<sub>2</sub> nano-particles and BaCO<sub>3</sub> nano-sols.

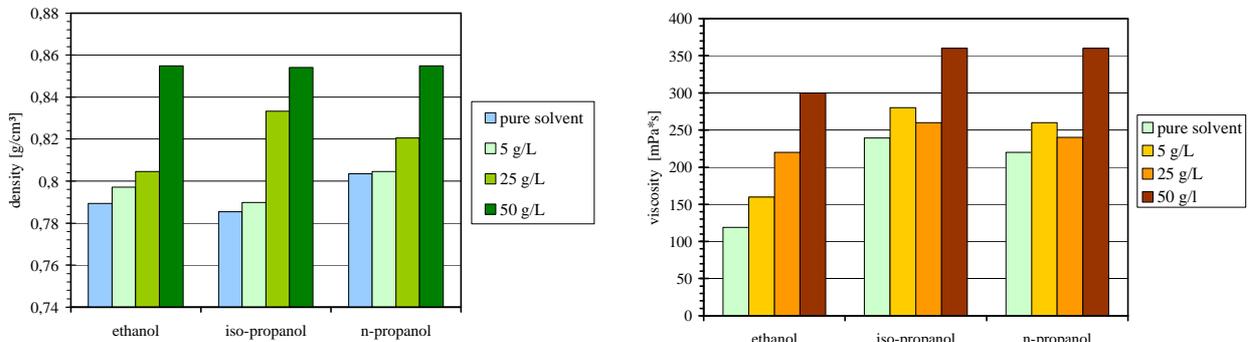
## 2.2 Characteristics of calcium hydroxide nano-sols

Calcium hydroxide nano-sols are opal to white solutions (Fig. 3). Although the particles are in the nano-metre size, they are crystalline showing the typical XRD pattern for portlandite. At low Ca(OH)<sub>2</sub> concentrations, the viscosity of the sols is equivalent to the pure solvents. With increasing concentration, the viscosity increases as one would expect. The largest increase was found with the

ethanol-based systems. The density shows the same tendency as the viscosity. Low concentrations have only a small influence, whereas increasing concentrations result in rising densities. In contrast, sols based on iso-propanol and n-propanol possess, at equivalent calcium hydroxide concentrations, nearly the same density.



**Fig. 3** Different types of calcium hydroxide nano-sols (IBZ-Freiberg)



**Fig. 4, 5** Density and viscosity of different types of CaLoSiL<sup>®</sup> (IBZ-Freiberg)

The solvent used, the content of calcium hydroxide particles as well as temperature and the preparation process influence the shelf-life of the sols. Storage in original, unopened containers is possible for at least four months without any sedimentation. When sedimentation does occur, re-dispersion of the settled particles by, for example, shaking is possible without any negative side-effects.

Tests using an ultracentrifuge have indicated that sols based on iso-propanol have a higher stability than sols based on pure ethanol. Systems formed using n-propanol are characterised by stabilities between them. All nano-sols can be mixed with water free n-propanol, iso-propanol and ethanol in all ratios. Mixing with water is possible but results in the flocculation and sedimentation of the nano-particles.

## 2.3. Determination of key parameters of materials before and after the application of calcium hydroxide nano-sols

### 2.3.1 Materials used, techniques and methods

The tested materials can be divided into the following groups:

- Historic materials sampled from quarries used to supply materials for the original structure,
- Historic materials sampled from sites selected for trial testing and demonstration,
- Model materials (both natural stones and laboratory made mortars).

Tests on materials sampled from historic objects were performed in order to characterise their basic physical and chemical properties before the treatment with CaloSiL<sup>®</sup>, while fundamental investigations concerning the applicability and the limits of CaLoSiL<sup>®</sup> were done on laboratory materials. In the main, the following parameters / methods were used to characterise stone, mortar and plaster:

- Porosity accessible to water, bulk density, real density, saturation coefficient, capillary rise,
- Salt analysis,
- Thermal analysis (DTA, TG),
- Porosity and pore size distribution,
- Ultrasonic velocity measurements,
- Compressive strength, tensile bending strength,
- SEM-BSE/EDX; XRD, polarised light microscopy,
- Drilling resistance measurements,
- Subsurface cohesion by means of peeling tests.

The characterisation of the following properties of the calcium hydroxide nano-sols was at the center of many investigations:

- Film formation, penetration time and depth, distribution of the nano-particles in treated stone, mortar and plaster,
- Time of capillary rise,
- White haze formation,
- Effects of any salts present in the materials to be treated,
- Carbonation time,
- Number of application cycles required to achieve a defined increase in strength,
- Influence of the application method on penetration depth and white haze formation.

The consolidation of loose materials was determined by capillary suction of different CaLoSiL<sup>®</sup> types into O-rings filled with sand, marble and limestone powder with defined particle sizes (Fig. 6-8). Similar tests were realised by applying the nano-sol drop-wise onto the top of the O-rings until full saturation had been achieved (Fig. 9).



**Fig. 6-8** Test kit to characterise the consolidation of loose aggregates by capillary suction (Strotmann & Partner)



**Fig. 9** Drop-wise application of CaLoSiL<sup>®</sup> onto powdered aggregates (Strotmann & Partner)



**Fig. 10, 11** Test kit to characterise the consolidation of loose aggregates between intact stone / mortar (Strotmann & Partner)



**Fig. 12, 13** “Sandwich” samples (Strotmann & Partner)

In many cases, it is necessary to consolidate loose material which lies between zones of intact stone. To simulate this, a test kit was developed which based around two stone plates, between which loose sand, marble or limestone powder was placed (Fig. 10-13). “Sandwich” samples are obtained. CaLoSiL<sup>®</sup> was injected by a syringe directly into this zone.

Other questions that often occur concern the characterisation of the transition zone between consolidated material and intact stone / mortar as well as the characterisation and localisation of the consolidants within the loose material. To address these, holes (diameter 20 mm, depth 10 or 20 mm) were drilled into different stones and then filled with the loose aggregates obtained during drilling (Fig. 14, 15). The loose material was then saturated with either CaLoSiL<sup>®</sup> alone or followed by the treatment with different silicic acid esters. SEM-BSE / EDX analysis was used to characterise the distribution of the consolidants both within the aggregates and the intact stone. The mechanical properties of the consolidated zones were determined by micro-drilling resistance measurements.



**Fig. 14** Drill holes in intact stone after saturation with CaLoSiL<sup>®</sup> (Restauro, Torun)



**Fig. 15** Cross sections of the samples after consolidation (Restauro, Torun)

### 2.3.2 Properties of materials after the treatment with calcium hydroxide nano-sols

The change of the mechanical properties of stone and mortar after the application of CaLoSiL<sup>®</sup> was investigated in detail. In all cases, an increase in both the compressive and bending strength was observed. The results obtained by treating Kutna Hora limestone with CaLoSiL<sup>®</sup>E-25 and IP-25 are given in Table 1. As expected, the effects are much greater when loose material is treated with the nano-sol (Tab. 2).

**Tab. 1** Consolidation Effects on Kutna Hora Lime stone (University Pardubice)

Increase of <b>bending</b> strength (without treatment – 2,99 MPa)	Increase of <b>compressive</b> strength (without treatment – 7,68 MPa)
<b>CaLoSiL<sup>®</sup> IP25</b>	<b>CaLoSiL<sup>®</sup> IP25</b>
after 5 impregnation cycles + 6%	after 5 impregnation cycles + 23%
after 10 impregnation cycles +13%	after 10 impregnation cycles + 38%
<b>CaLoSiL<sup>®</sup> E25</b>	<b>CaLoSiL<sup>®</sup> E25</b>
after 5 impregnation cycles + 23%	after 5 impregnation cycles + 22%
after 10 impregnation cycles + 49%	after 10 impregnation cycles + 75%

**Tab. 2** Consolidation effect on highly corroded lime mortar (University Pardubice)

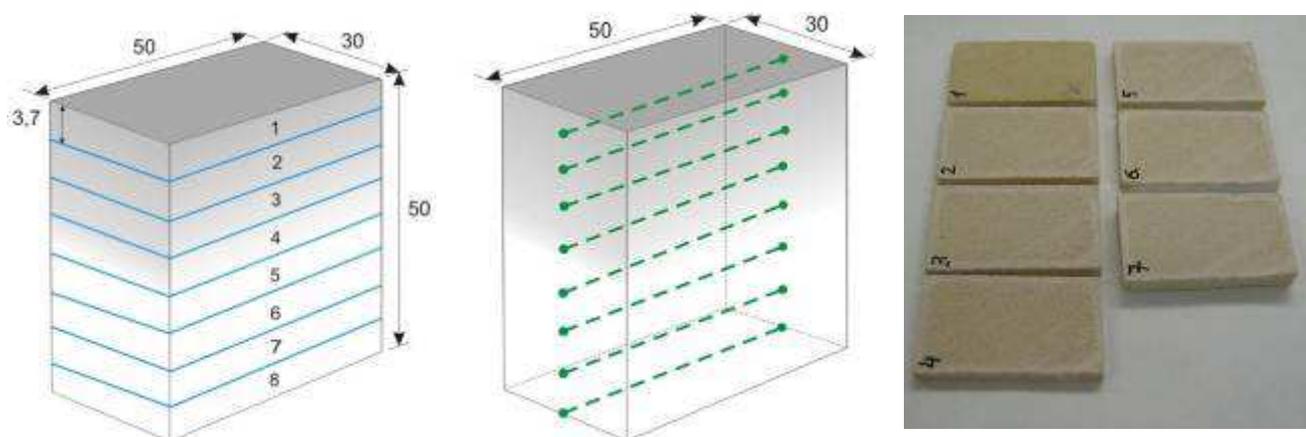
Increase in <b>compressive</b> strength (without treatment: 0,12 MPa)	Increase in <b>bending</b> strength (without treatment: 0,07 Mpa)	Increase in <b>tension</b> strength (without treatment: 0,07 MPa)
<b>CaLoSiL<sup>®</sup> IP25</b>	<b>CaLoSiL<sup>®</sup> IP-25</b>	<b>CaLoSiL<sup>®</sup> IP25</b>
after 5 impregnation cycles + 1717%	after 5 impregnation cycles: + 507%	after 5 impregnation cycles + 1270%
after 10 impregnation cycles + 3994%	after 10 impregnation cycles + 692%	after 10 impregnation cycles + 2782%
<b>CaLoSiL<sup>®</sup> E25</b>	<b>CaLoSiL<sup>®</sup> E25</b>	<b>CaLoSiL<sup>®</sup> E25</b>
after 5 impregnation cycles + 2875%	after 5 impregnation cycles + 635%	after 5 impregnation cycles + 1348%
after 10 impregnation cycles + 4695%	after 10 impregnation cycles + 1041%	after 10 impregnation cycles + 3025%

The penetration into mortar, stone or plaster depends on many factors, however, of special importance are:

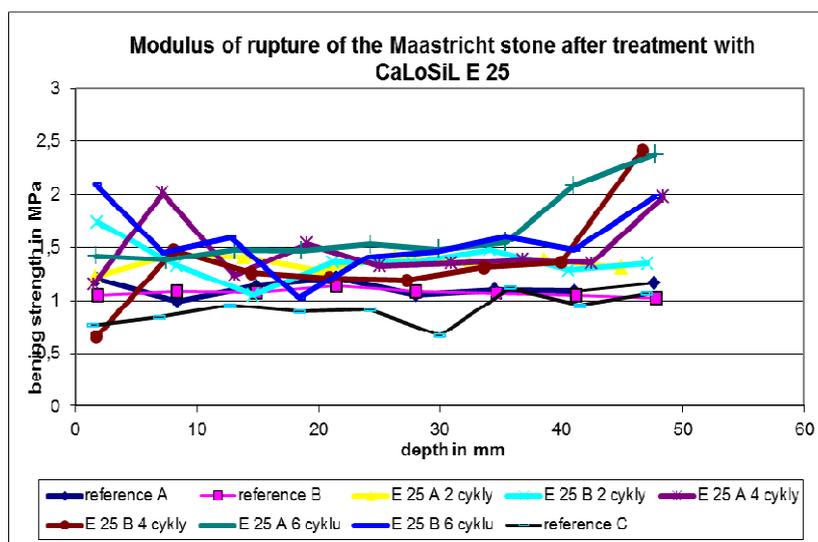
- Characteristics of the calcium hydroxide nano-sol applied,
- Structure and surface characteristics of the materials to be treated,
- Porosity and capillary rise,
- Moisture content of the material,
- Air temperature and air humidity during the application.

When dense materials are treated with highly concentrated nano-sols, the penetration depth is often only low. This is especially the case in the presence of dense surface layers (for examples gypsum crusts on mortars, plasters) where they prevent penetration into deeper zones. The penetration into materials with high moisture contents is generally more difficult than into dry substrates. When necessary, pre-wetting with ethanol may help to reduce the moisture content of the material. After evaporation of the ethanol, it should be possible to apply all CaLoSiL<sup>®</sup> products without any problems.

The bending strength in relation to the penetration depth was investigated using Maastricht limestone, which is a highly porous material. After several treatments with CaLoSiL<sup>®</sup> the samples (50 x 30 x 50 mm) were cut into 8 slices with a high of 3,7 mm (see Fig. 16). As shown in Fig. 17, an increase in the modulus of rupture could be demonstrated with all slices.

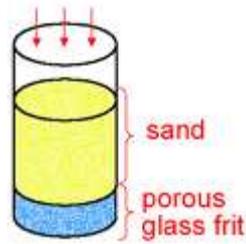


**Fig. 16** Characteristics of the samples used for the determination of the bending strength depending on the penetration depth (ITAM AS CR, v.v.i, Prague)

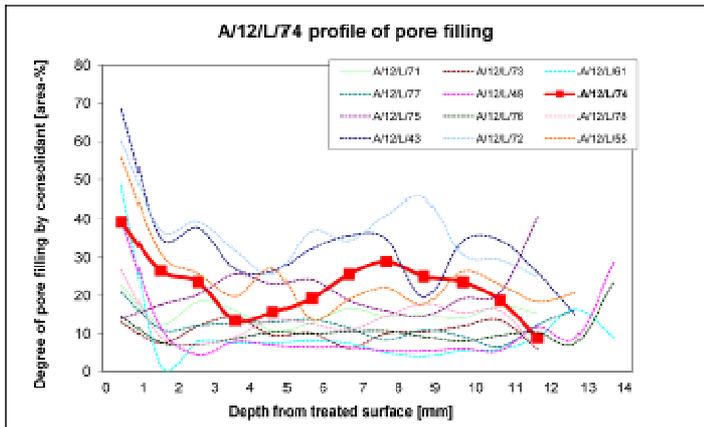


**Fig. 17** Bending strength of Maastrich limestone depending on the penetration depth and the numbers of applications of CaLoSiL<sup>®</sup> (ITAM AS CR, v.v.i, Prague)

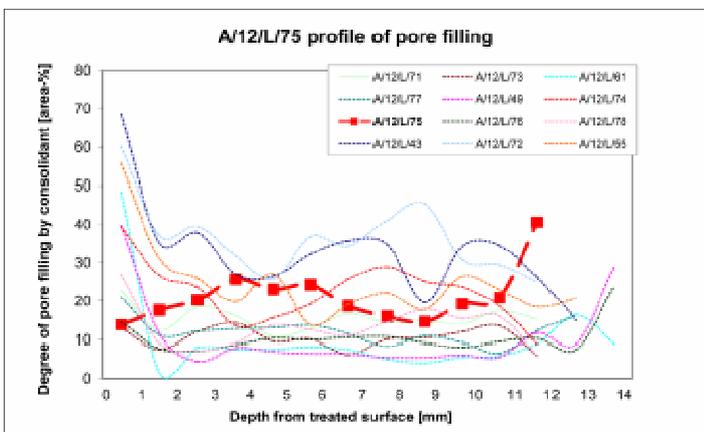
The formation of a white haze on the surface of the treated material depends not only on the penetration behaviour of CaLoSiL<sup>®</sup>, but also on the evaporation conditions of the alcohol. Fast evaporation is connected in many cases with a re-transport (back migration) of the nano-particles to the surface: there is not enough time for the fixation of the calcium hydroxide particles within the treated materials. SEM investigations in combination with digital image analysis have proven that slow evaporation, achieved for example by covering the treated samples, results in a more homogenous distribution of the calcium hydroxide nano-particles than when fast evaporation is allowed to occur. In these investigations, glass tubes (Fig. 18) with a height of 1,2 cm were filled with different aggregates having defined particle sizes. After saturation with CaLoSiL<sup>®</sup> and the subsequent evaporation of the solvent, the distribution of the nano-particles was determined by means of SEM-BSE/EDX (Fig. 19-21).



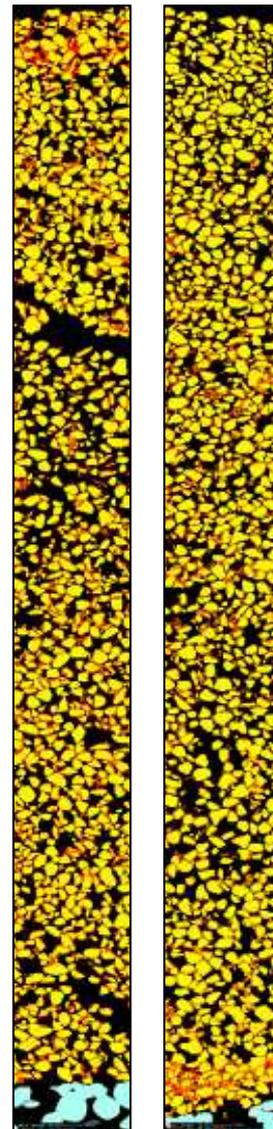
**Fig. 18** Test arrangements (University of Applied Arts, Vienna)



**Fig. 19** Depth distribution profile of calcium hydroxide nano-particles after fast evaporation of the solvent (University of Applied Arts, Vienna)



**Fig. 20** Depth distribution profile of calcium hydroxide nano-particles after slow evaporation of the solvent (University of Applied Arts, Vienna)



**Fig. 21** Samples for the digital image analysis:  
left: fast evaporation;  
right: slow evaporation

The treatment of mortar samples with CaLoSiL<sup>®</sup> has also shown that the back-transport of the nano-particles during the evaporation of the solvent, can result in an enrichment of calcium hydroxide at the surface (Fig. 22).



**Fig. 22** Distribution of calcium hydroxide nano-particles in mortar samples indicated by the red colour of the indicator phenolphthalein (University of Fine Arts, Dresden)

Left: Immediately after saturation with CaLoSiL<sup>®</sup>; Right: after 24 hours.

Apart from reducing the evaporation rate by covering the treated surfaces, the combination of CaLoSiL<sup>®</sup> with acetone followed by a post treatment with a weak ethanolic solution of hydroxypropyl cellulose or the combined application of CaLoSiL<sup>®</sup> together with coarser calcium hydroxide suspensions (CaLoSiL<sup>®</sup>-micro) are effective ways to prevent back-migration (Fig. 23).



**Fig. 23** Distribution of calcium hydroxide nano-particles in mortar samples after 24 hours indicated by the red colour of the indicator phenolphthalein (University of Fine Arts, Dresden)

Left: Modification of the solvent and after-treatment  
use of CaLoSiL<sup>®</sup> NP12,5 / 40% acetone  
after-treatment with HPC-gel in(ethanol)

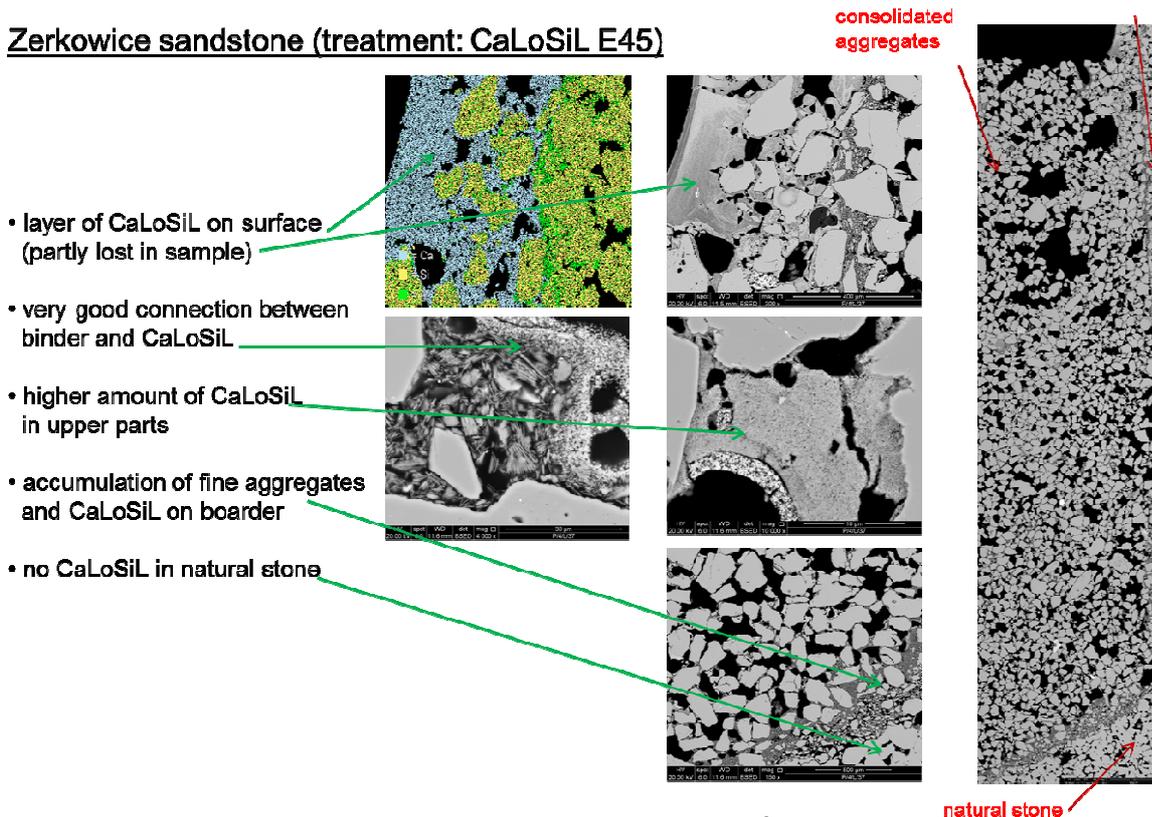
Right: Use of a bimodal dispersion containing  
CaLoSiL<sup>®</sup> E-45 and CaLoSiL<sup>®</sup> micro

Tests, in which a drill holes filled with powder of Zerkovice sandstone (as described on page 14) were treated with CaloSiL<sup>®</sup> E-45, have resulted in well-consolidated materials. The CaLoSiL<sup>®</sup> was able to penetrate down to the bottom of the drill hole. SEM-BSE investigations have proven the homogenous distribution of the consolidant within the stone powder (Fig. 24). The connection between the stone grains and CaLoSiL<sup>®</sup> was well established.

Generally, the consolidation achievable, the distribution of CaLoSiL<sup>®</sup> in the treated materials as well as the formation of white haze are determined by the:

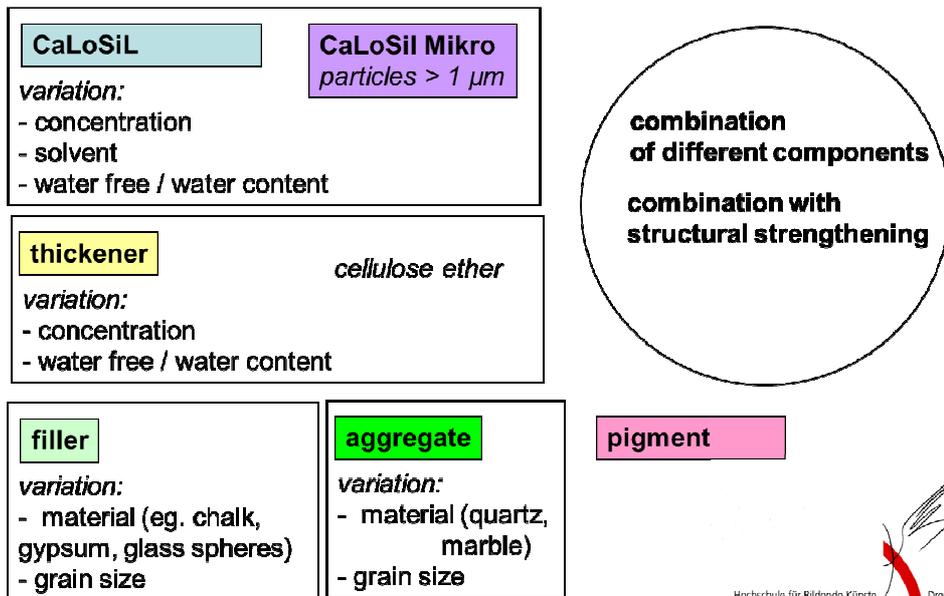
- deterioration characteristics
- application technique employed (brushing is in many cases less effective than injection, for example by using a syringe)
- concentration of the CaLoSiL<sup>®</sup> product used (repeated treatment with lower concentrated sols is, in most cases, more effective than a single treatment with highly concentrated sols)
- mineralogical composition of the material
- amount and concentration of additives incorporated into CaLoSiL<sup>®</sup>

**Zerkowice sandstone (treatment: CaLoSiL E45)**



**Fig. 24** SEM-BSE characterisation of the distribution of CaLoSiL<sup>®</sup> within aggregates of Zerkowice sandstone (Restauro, Torun, University of Applied Arts, Vienna)

The CaLoSiL<sup>®</sup>-products were used to develop a modular system of fully compatible consolidants for applications to manifold, composed materials (Fig. 25). Structural strengthening is combined with the filling of voids and cracks using CaLoSiL<sup>®</sup> modified with fillers and aggregates.



**Fig. 25** The concept of a modular system for consolidants based on CaLoSiL<sup>®</sup> (University of Fine Arts, Dresden)

### 2.3.3 Properties of materials after the combined application of calcium hydroxide nano-sols and silicic acid esters

The use of calcium hydroxide offers the possibility of the alkaline hydrolysis of silicic acid esters. This reaction should be much faster than the hydrolysis by moisture. The question is: will the silicic acid gel formed by this reaction produce a consolidation effect? To test such a conservation strategy, sand, treated with a first application of nano-lime suspensions (CaLoSiL<sup>®</sup>), was then treated using different, commercially available silicic acid ester-based products. The consolidation effect as well as the surface characteristics were assessed visually.

The treatment with CaLoSiL<sup>®</sup> produced a first consolidation: loose sand particles were bridged together and a solid, non-powdering surface was formed. The penetration behaviour of all of the silicic acid esters tested was not disturbed by the pre-treatment with CaLoSiL<sup>®</sup>. The sand was fully penetrated, both by Funcosil 300 and Wacker Silres BS-100 OH. As Fig. 26 shows, the loose sand particles were converted into a solid mass.



**Fig. 26** Loose sand particles consolidated by combined treatment with CaLoSiL<sup>®</sup> E-25 and Funcosil 300 (producer: Remmers, Germany), (IBZ-Freiberg)

**Table 3** Mechanical properties of mortar prisms after treatment with nano-lime sols and esters of silicic acid (all data are the mean values of 3 different samples); IBZ-Freiberg.

Test-No.	1. treatment	2. treatment	E-modulus untreated [kN/mm <sup>2</sup> ]	E-Modulus [kN/mm <sup>2</sup> ]	Compressive strength [N/mm <sup>2</sup> ]	Bending strength [N/mm <sup>2</sup> ]
0	reference sample		7,98	-	4,3 ± 0,3	1,3 ± 0,1
1	CaLoSiL IP 12,5	CaLoSiL IP 12,5	7,13	8,54	3,6 ± 0,3	1,4 ± 0,1
2	CaLoSiL IP 12,5	Wacker BS OH 100	6,66	11,88	8,2 ± 0,15	1,9 ± 0,1
3	CaLoSiL IP 12,5	Funcosil 300	7,17	12,47	6,7 ± 0,4	2,7 ± 0,15
4	CaLoSiL E 25	CaLoSiL E 25	7,52	8,26	4,3 ± 0,4	1,2 ± 0,1
5	CaLoSiL E 25	Wacker BS OH 100	7,61	11,81	8,8 ± 0,15	2,9 ± 0,3
6	CaLoSiL E 25	Funcosil 300	7,48	11,11	8,4 ± 0,3	2,7 ± 0,1
7	Funcosil 300	Funcosil 300	7,83	13,51	10,6 ± 0,15	2,6 ± 0,2

The lime/sand prisms used for the characterisation of the effect of a combined treatment with CaLoSiL<sup>®</sup> and silicic acid esters, were characterised by a compressive strength of 4,3 N/mm<sup>2</sup> and a bending strength of 1,3N/mm<sup>2</sup>. Two pre-treatments with either CaLoSiL<sup>®</sup> E-25 or CaLoSiL<sup>®</sup> IP-12,5 did not produce a measurable increase in the compressive and bending strength (tests 1 and 4, table 3). In the mortar prisms treated initially with CaLoSiL<sup>®</sup> E-25 followed by the application of Funcosil 300 and Silres BS-100-OH respectively, a significant consolidation effect was observed. The increase in compressive and bending strength correlates very well with the dynamic elasticity modulus determined by ultrasonic measurements.

Advanced granular disintegration of the building materials which a given monument consists of, is a common and serious problem in conservation. Comprehensive investigations were performed in order to determine the extent to which CaLoSiL<sup>®</sup> E-25 and E-45 preparations applied both separately and in compositions with silica acid ester, could be used as binders for particular grains of disintegrated, natural stones which lacked adhesion. The tests were conducted on samples of natural stones: Żerkowice sandstone, Gotland sandstone and Pińczów limestone. For this, the method already described in which the treatment of compacted, powdered stone aggregates within a drill hole in intact stone, was used. The tests performed are summarised in Table 4.

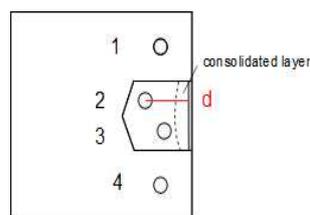
**Table 4** Materials and tests performed to characterise the combination silicic acid ester (KSE = Funicosil 300); (Restauro, Torun)

Materials	Aggregate	Binder	Consolidation treatments		
Zerkowice sandstone	quartz	siliceous	CaLoSiL <sup>®</sup> E45	KSE 300	CaLoSiL <sup>®</sup> E45, KSE 300
Gotland sandstone	quartz	clay + carbonate	CaLoSiL <sup>®</sup> E45	KSE 300	CaLoSiL <sup>®</sup> E45, KSE 300
Pinczow limestone	calcite	carbonate	CaLoSiL <sup>®</sup> E45	KSE 300	CaLoSiL <sup>®</sup> E45, KSE 300

The main aim was to find a direct relationship between the microstructure of a consolidated material and its properties. The following tests were implemented:

- Ultrasonic tests
- Porosity measurements
- Drilling resistance
- Microscopic analysis

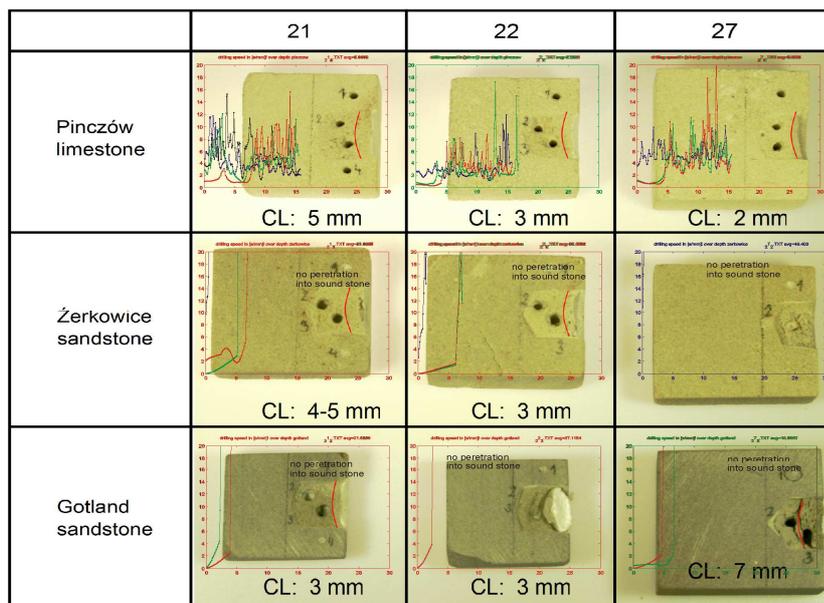
It was found that drilling resistance tests gave the most significant results. The GEOTRON drilling machine + Tersis SW was used for the investigations. The diameter of the drilling bit was 4 mm and the arrangement of the drill holes is summarised in Fig. 27.



**Fig. 27** Arrangement of the drill holes (ITAM AS CR, v. v. i, Prague)

The main results are (Fig. 28):

- In some cases, the strength of the material was so high that it was impossible to penetrate it with a given force on the drill.
- Some records from hole drilling were lost because of the material being too loose
- There was a tendency for strength to increase from the hole center to its perimeter
- The denser the aggregate, the higher was the strength achieved
- Average strength increase is the highest for #21 (treatment with CaLoSiL<sup>®</sup> E45 and KSE)



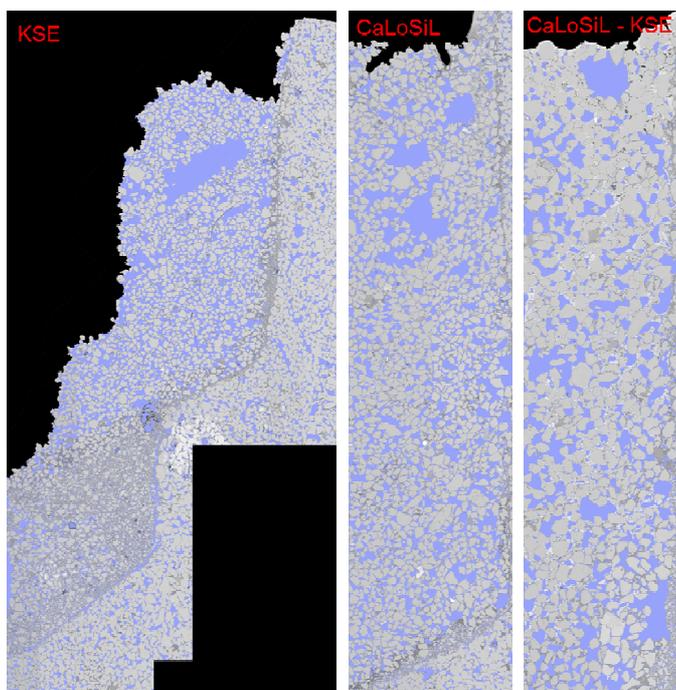
**Fig. 28** Drillhole resistance measurements (ITAM AS CR, v.v.i, Prague)

For microscopic characterisation, the whole compounds including the natural stone were vacuum-embedded in epoxy resin (Araldite® 2020). Polished sections were produced perpendicular to the surface of the treatment. The polished cross-sections were coated with carbon and studied by SEM (Philips XL 30 ESEM, 20 KV, high vacuum, back-scattered electron detector-BSE) fitted with an energy-dispersive X-ray analyser (Link-ISIS). The SEM-micrographs taken at low magnification had to be joined using image editing software (Photoshop®) in order to cover the whole sample diameter. Pores were edited in pseudo colour (blue) in order to improve their visibility and to allow a comparison of the different treatment methods. As Figures 29-31 clearly indicate, exceptionally good results were obtained for the samples in which CaLoSiL® E-45 and silicic acid ester were used in succession (Tab. 5). This is in excellent agreement with the results obtained by drill-hole resistance measurements.

#### Zerkowice sandstone

 = pore space

- layer on surface: CaLoSiL
- consolidant in stone: only KSE
- accumulation of fine aggregates: every sample; most with KSE
- distribution of consolidant:  
KSE very bad  
CaLoSiL good  
COMBINATION very good

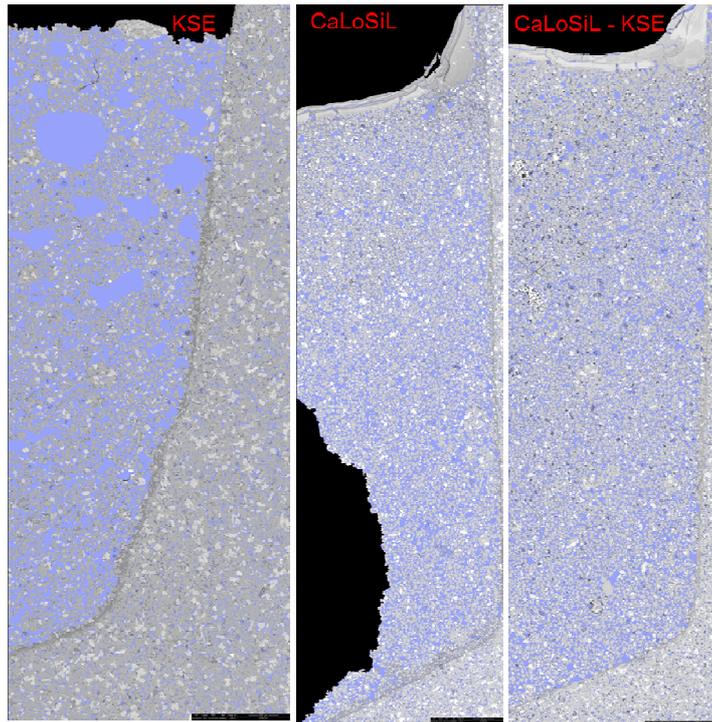


**Fig. 29** SEM Analysis of the consolidant distribution in Zerkowice sandstone (Restauero, University of Applied Arts, Vienna)

**Gotland sandstone**

 = pore space

- layer on surface: CaLoSiL
- consolidant in stone: only KSE
- accumulation of fine aggregates: every sample; most with KSE
- distribution of consolidant:
  - KSE very bad
  - CaLoSiL very good
  - COMBINATION very good

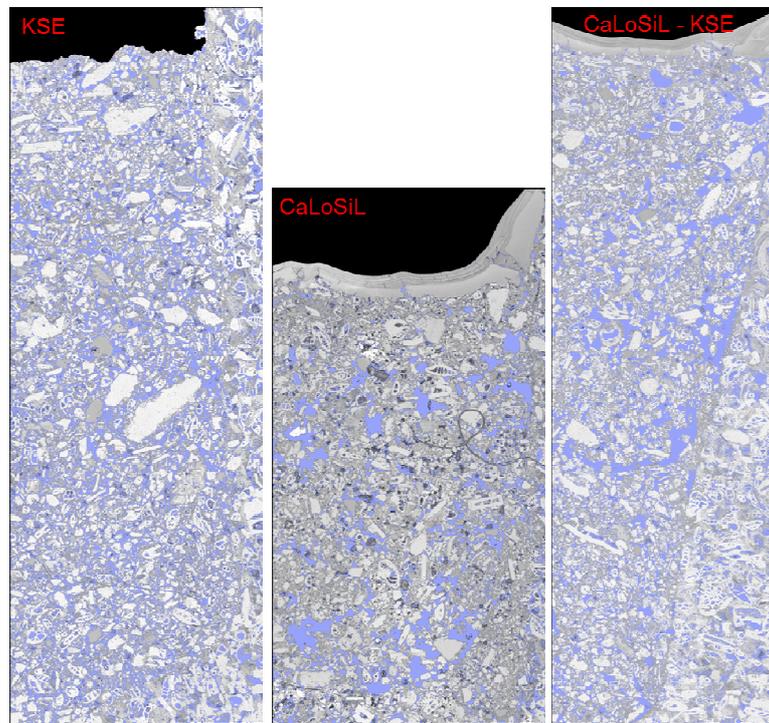


**Fig. 30** SEM Analysis of the consolidant distribution in Gotland sandstone (Restauro, University of Applied Arts, Vienna)

**Pinczow limestone**

 = pore space

- layer on surface: CaLoSiL
- consolidant in stone: none
- accumulation of fine aggregates: every sample; not that much
- distribution of consolidant:
  - KSE good
  - CaLoSiL very good
  - COMBINATION very good



**Fig. 31** SEM Analysis of the consolidant distribution in Pinczow limestone (Restauro, University of Applied Arts, Vienna)

The investigation into the effect of the consolidants on mechanical properties (bending strength) showed that both preparations used in two successive applications increased the mechanical properties by 80%, in the case of Pińczów limestone, and by 60%, in the case of Żerkowice sandstone. A comparable increase in the bending strength was observed when silicic acid ester was used.

Impregnation tests conducted using both natural stones with a pure CaLoSiL<sup>®</sup> preparation applied three times increased the mechanical strength by maximum of 17%. It was also noted that there was no difference whether the ester was applied directly after the introduction of CaLoSiL<sup>®</sup>, when the latter was highly reactive, or when it was applied after some time, when part of the lime had undergone carbonation. It is considered probable that the colloidal lime deposited in the inner pores of the stones, still contained enough reactive groups to catalyse the hydrolysis of the silicic acid ester.

Table 5: Summary of the microscopic investigations (University of Applied Arts, Vienna), KSE = silicic acid ester, Funcosil 300, producer: REMMERS; DE

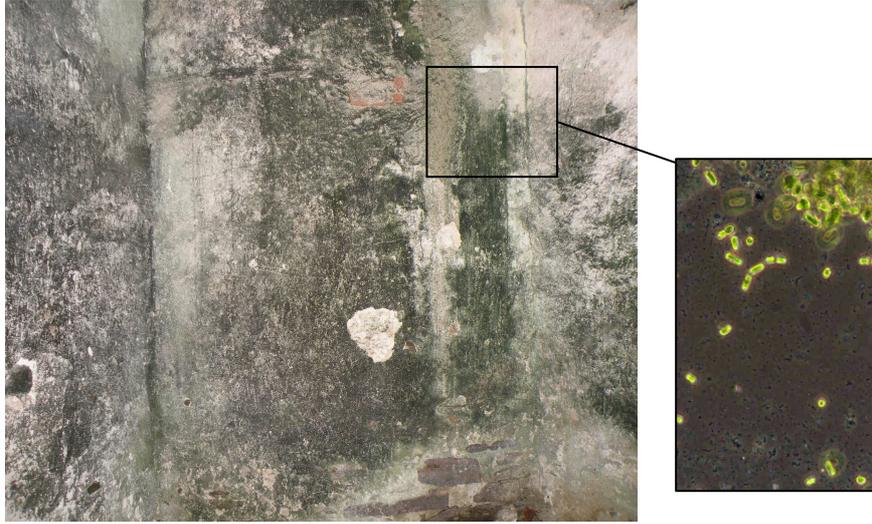
	consolidant in stone	layer on surface	accumulation of fine aggregates on boarder	distribution of consolidant	general assessment
Zerkowice sandstone KSE	yes!!!	no	Yes!!!	very bad	-
Zerkowice sandstone CaLoSiL <sup>®</sup>	none	yes	Yes	Good	++
Zerkowice sandstone CaLoSiL <sup>®</sup> + KSE	none	yes	Yes	very good	+++
Gotland sandstone KSE	yes	no	Yes	very bad	-
Gotland sandstone CaLoSiL <sup>®</sup>	none	yes	Middle	Good	++
Gotland sandstone CaLoSiL <sup>®</sup> + KSE	none	yes	Middle	Good	++
Pinczow limestone KSE	none	no	Middle	Good	-/+
Pinczow limestone CaLoSiL <sup>®</sup>	none	yes	Middle	very good	+++
Pinczow limestone CaLoSiL <sup>®</sup> + KSE	none	yes	Middle	very good	+++

## 2.5 The use of calcium hydroxide nano-sols to prevent biological growth (Industrial Microbiological Services, Ltd.)

The microbiological studies performed as part of Stonecore took 3 forms (survey, laboratory tests and field trial). Initial activity was focused on surveying objects in the field and using isolates collected from them to build a library of strains that could be used for testing the performance of the consolidants in the laboratory. During this a total of 53 fungal strains were isolated and purified. This yielded at least 13 unique species. Similarly, 25 algal strains were isolated and purified yielding at least 12 unique species. The data was stored and presented in a database and the further development of this is described in section 2.6 below.

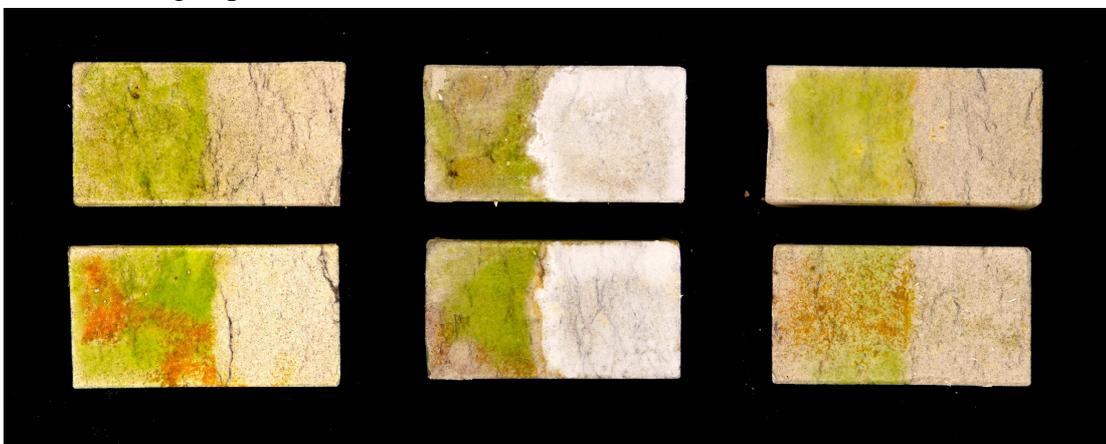
In a series of laboratory studies replicate samples of natural stone were inoculated with separate consortia of algae that had been isolated from historic monuments during the earlier phase of the project. Where conspicuous gaps in the spectrum of species that these consortia presented, additional stand-

ard test strains were added. The inoculated samples were then incubated for 4 months under conditions suitable for growth of the species employed. These were used to either examine the changes that the presence of the consolidants made to the susceptibility of the stone to colonization or to assess the performance at removing growth.



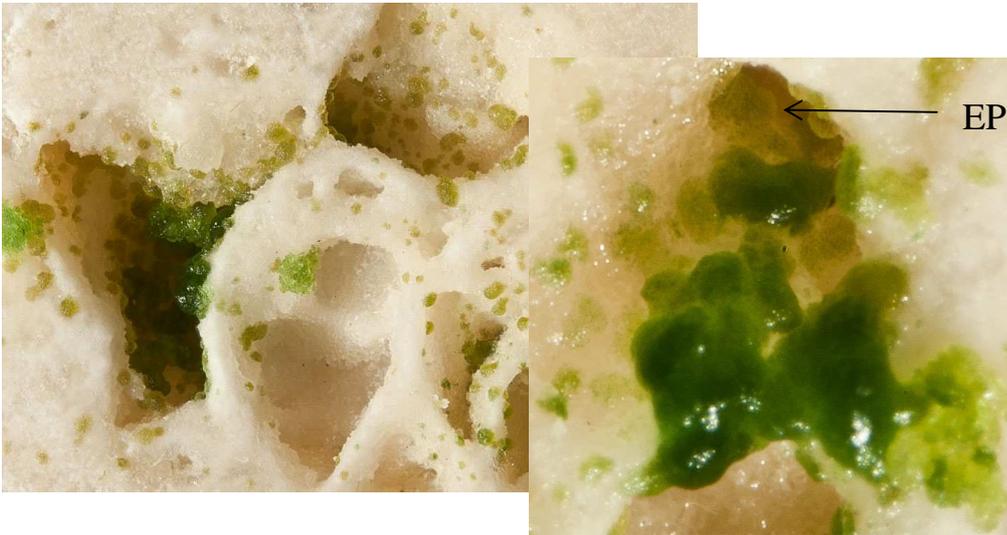
**Fig. 32** Fungal and Algal Growth on Render at Pernštejn Castle (IMSL)

The test the efficacy of CaLoSiL<sup>®</sup> as a disinfectant system for the removal of microbiological growth, the growth produced in the laboratory was removed by cleaning with water and then treated with either CaLoSiL<sup>®</sup> E25 (applied drop-wise), ethanol or a quaternary ammonium compound-based masonry disinfectant. The treated panels were then re-incubated. It was found that growth of algae could be remediated by cleaning and then treatment with either ethanol, CaLoSiL<sup>®</sup>E25 or a quaternary ammonium compound-based masonry disinfectant (QAC). In general, the elimination of growth using ethanol was only short-lived and the algae re-grew. Significantly reduced re-growth was observed on the systems treated with either CaLoSiL<sup>®</sup> or the QCA-based system although in one instance stronger growth was observed on blocks treated with the QAC-based system than on those treated with ethanol, presumably due to the selection and dispersal of a strain that was more tolerant of this chemistry (QAC-based systems demonstrate strong surfactant properties and can disperse resting a dissemination structures during their use). It is anticipated that the effects observed would be overwhelmed given time and in the field, where re-inoculation would occur, and growth would very likely resume as none of the systems retain significant residual antimicrobial activity. The performance of CaLoSiL<sup>®</sup> E25 as a disinfectant was similarly demonstrated during a field trial at the Ancient Theatre of Megalopolis.



**Fig. 33** Effect of CaLoSiL<sup>®</sup> as a Disinfectant on Sandstone (L-R: Untreated CaLoSiL<sup>®</sup> E25, QAC)

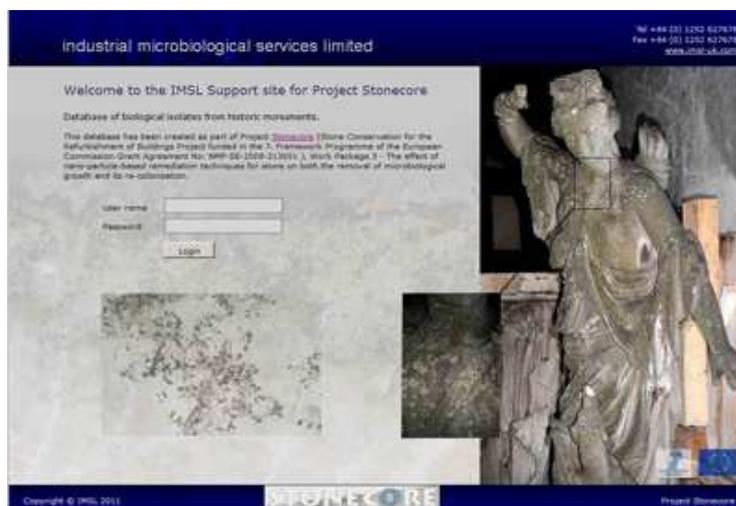
It is clear that CaLoSiL<sup>®</sup> has strong antimicrobial properties although it is not clear how long-lived these would be in all cases although it is likely that this would be no shorter than the products currently available. One interesting but, as yet, not fully explored possibility, is that CaLoSiL<sup>®</sup> may provide a unique solution to friable surfaces that are heavily colonized by microorganisms and where the resultant biofilm is ‘consolidating’ the surface through the production of exopolysaccharides (EPS) *etc.* The use of conventional disinfectants would result in loss of adhesion of the materials whereas it is possible that CaLoSiL<sup>®</sup> would be able to both kill the biofilm and provide a consolidation effect.



**Fig. 34** Algal Biofilm Growth in Fissures in Limestone showing EPS

## 2.6 Data Management System (Industrial Microbiological Services Ltd)

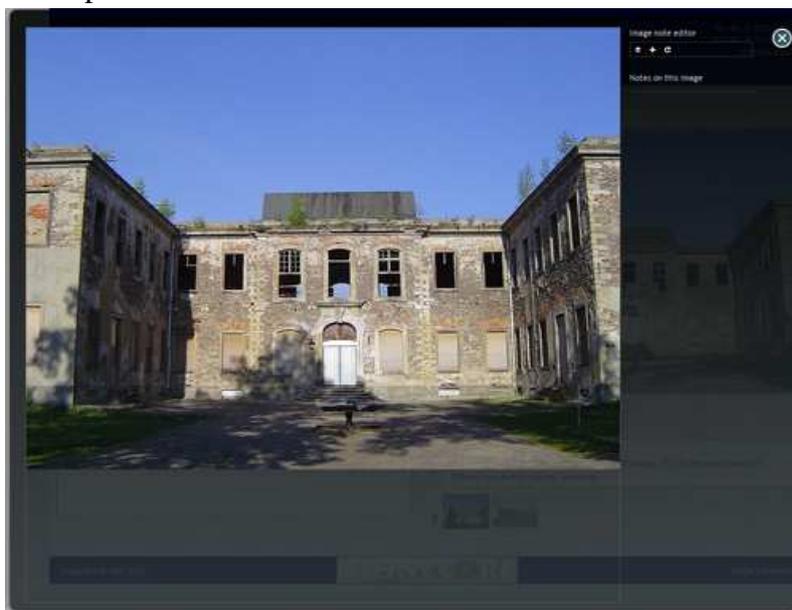
During the initial 18 months of the project an online database was created to manage and present the microbiological results of the surveys. At the mid-term review it was decided that there would be great value in extending this system to enable it to capture other data as well. Extending from this, a data management system was designed to capture and disseminate restoration process information about historical items. The development has led to a web based solution utilising a relational database as the data store. The application can host multiple projects with different users who log in with username and password credentials. Documents and links to external web sources can be uploaded to each project. Activity within the database is logged for audit purposes.



**Fig. 35** Main Data System Login Screen (<http://www.stonecore-data.com>)

The design incorporates a number of functions that will allow project management capabilities to be added to the system such that the work on a site, the flow of samples and the delivery of results can be managed in a single package. A very useful function would be for the system to be able to produce summary reports on both the progress of a project as well as technical results. The search capabilities are able of providing to provide data that this would require and it is anticipated that this would be augmented by custom reports formatted in a style to suit the project manager / restorer using the system. One of the unique aspects of the development is the ability to upload tag and drive the system from images relevant to the area under study.

The software is current in the process of first-stage commercialization and it is anticipated that the whole site will be transformed from a text-based interface with graphics to a graphical format with text displayed as and when needed. Leveraging the capability of the Annotation package could lead the way to a totally graphical approach to data capture and display, and thereby reduce the adherence to a fixed hierarchical process model.



**Fig. 36** Annotation System View

## **2.6 Non or minor destructive stone assessment methods**

### **2.6.1 Peeling test**

Peeling testing are defined as a method for making a quantified assessment of the adhesion of a surface or near-to-surface layer to a substrate. Adhesive tape is applied to the area to be investigated and the amount of material detached from the surface after peeling away the tape off is measured. In the conservation field, it is assumed that this amount corresponds to the cohesion characteristics of the substrate. Therefore, the peeling test is used for evaluating surface degradation or consolidation effects after strengthening interventions. In the past, some shortcomings of the test were a lack of standards and the unification of the evaluation procedure. As a result of the research carried out during the work in STONECORE, ITAM has established reliable procedures and a standardised protocol for testing the cohesion characteristics of brittle and quasi-brittle materials, mainly mortars and stones, by means of peeling tests. Also, recommendations for performing peeling tests on historic stone surfaces and for evaluating the results have been formulated by ITAM. A software application for peeling test evaluation has been developed and made generally available. Correlation between standard mechanical tests and established peeling test procedures was confirmed in an extensive study. The peeling test also proved useful in many on-site studies performed by project partners (Fig. 37).



**Fig. 37** Peeling test”- Experimental procedure (ITAM AS CR, v. v. i, Prague)

### 2.6.2 Karsten tube innovation

Water up-take capacity is an aggregate property of a material, integrating surface openness with capillarity and with the distribution and connection of pores within the material. This parameter is decisive for the ability of a liquid to penetrate into the material and to transport particles of consolidant. The so-called Karsten tube is often used for the determination of this property. In the literature and in the practice of restorers there are well known difficulties associated with the application of the Karsten tube. These issues have been substantially reduced by an innovative semi-automatic method which takes advantage of a micro-tube system. The approach to the portable device, developed mainly during the Stonecore project, has been driven also by its great versatility, robustness and simplicity, which results in a low production cost. It consists of a box containing a microprocessor which measures time and records the amount of liquid which has penetrated into the surface being investigated through the hand-held part. The water uptake velocity is followed on the scaled micro-tube kept in a holder which is fixed to a pistol grip with a magnet. The holder enables the fixing of other tubes also, for example the Mirowski tube or even a Karsten tube, when rotated into a vertical position, and the holding fixtures are replaced by those matching the applied tube. However, the advantage of using the horizontal capillary tube is that it can be used for measurements on inclined surfaces (e.g. vaults) or ceilings. The pistol trigger contains a micro-switch which controls the recording of the instantaneous, real-time values into the processor memory in the relevant set of the open group of measurement data (Fig. 38). The data records are then transferred into a computer and processed using a dedicated application that yields results in the form of easily-interpretable plots and numbers. The microtube proved its usefulness not only during field studies carried out during the work on the project, but also on other applications like the assessment of rock weathering. To conclude, the micro-tube electronic device can be successfully used as a non-destructive method for the reliable evaluation of the water sorption properties of a studied object.



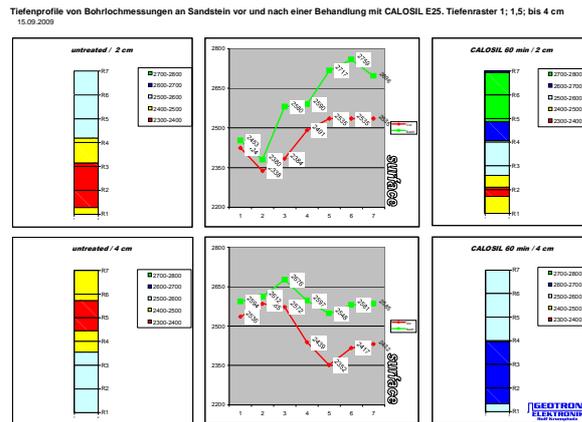
**Fig. 38** The developed micro tube testing device (ITAM AS CR, v. v. i, Prague)

### 2.6.3 Borehole ultrasonic measurement devices

A method and device for the determination of the stiffness profile of a material is based on the investigation of propagation velocity of ultrasound waves. This standard physical technique was innovatively redesigned by the Geotron company to be used in the confined spaces between two parallel holes drilled into the material to be studied (Fig. 39). The design adopted overcomes many technical obstacles of the typical transducer-receiver setup. Tests performed on real materials demonstrated excellent correlation between the developed device and standard ultrasound devices (Fig. 40). Very high sensitivity of the device also enables the use of this method for the determination of liquid content profiles and its evolution in time, which is a property of great importance for restorers and conservators who need to know whether the consolidant has reached a particular depth in the material.



**Fig. 39** Ultrasonic drill hole measurement device (GEOTRON)



**Fig. 40** Ultrasonic depth profile before (red) and after green) the treatment of sandstone with CaloSiL (GEOTRON)

### 2.6.4 Drilling resistance device

Mechanical and physical properties of the surfaces of objects vary significantly with depth. Also, the influence of treatment application is a function of the depth and therefore the characteristics of the depth profile are the best way to represent the properties of the studied object. In the course of the Stonecore project, an improved method and Tersis (Fig. 41) device for measuring drilling resistance were developed by Geotron in cooperation with ITAM. The innovation cycle was iterated several times and the device was improved significantly to meet the demands of users. Due to the built-in constant load, the Tersis drilling device is the ideally suited for the investigation of strength profiles of weak and soft materials; sensitively recording every detail and every minute obstruction in the path of the drill. Accordingly, a high frequency of data acquisition is obtained: about 30 records per second meaning approximately a hundred records per millimetre (based on a typical drilling speed) and several thousand data points from a typical hole depth of about three centimetres. During the extensive testing, a sound correlation between drilling resistance parameters and standard mechanical properties, such as compressive and flexural strength and hardness, were confirmed.



**Fig. 41** Developed drilling resistance device (GEOTRON)

### 2.6.5 The use of ground penetrating radar for the characterisation of cracks and fissures in stones

Comprehensive investigations were performed to develop new possibilities for the detection of fractures and voids in compact stones using Ground Penetrating Radar (GPR). Different, commercially available, pulse GPR systems operating at different central frequencies were used.

The use of GPR today is based in the traditional use of ground coupled antennas in the range of frequencies between 25 and 2400 MHz of various types of commercial instruments. These are adapted to a continuous recording mode, using a triggering device named a triggering wheel which produces pulses at predefined distance intervals that initiate the internal instrument data collection electronics. All modern commercial instruments have this interface so they can be used to collect data when a certain movement in the antenna is noticed. This interface between the antenna and the ground has the capacity to provide this pulse with a resolution of 2 mm in relation to the movement axis, providing a superior x-axis (axis of scanning) discretisation of the explored area. In addition, most modern instruments provide an interface to assign to each received reflection from the underground reflectors to its corresponding spatial coordinates (antenna location). This is achieved by connecting a precise GPS to the instrument that can attain accuracy in positioning down to 1 cm, when GNSS technologies are used. This type of scanning of the subsurface is convenient for flat grounds and related GPR applications like the scanning of asphalt and pavement, as the motion of the instrument antenna is uniform and does not produce inaccuracies at the total record. In archaeology, the use of GPR involves pulling the antenna over semi-rough surfaces, sometimes with minimal vegetation and small stones. This introduces significant noise to the records due to the non uniform scanning speed caused by obstacles in the path of the antenna and the difficulty of maintaining a constant speed by hand as well as the nonparallel motion of the antenna to the ground. The result is to collect medium quality data. In addition, the pulling speed is restricted to a minimum value as the operator cannot achieve very low, uniform motion of the antenna by hand. This problem appeared in the STONE-CORE project during attempts to scan rough limestone surfaces with high resolution antennas in order to visualise cracks of small size in the interior of the stone. A lot of effort and trial tests on site have shown that, in order to improve the signal quality, the transport mechanism for the antenna should be modified using external hardware in order to provide a commercial instrument with the capacity to discriminate smaller sized cracks in the body of the stone.

The problem was solved by GEOSERVICE by assigning an external device to the antenna that con-

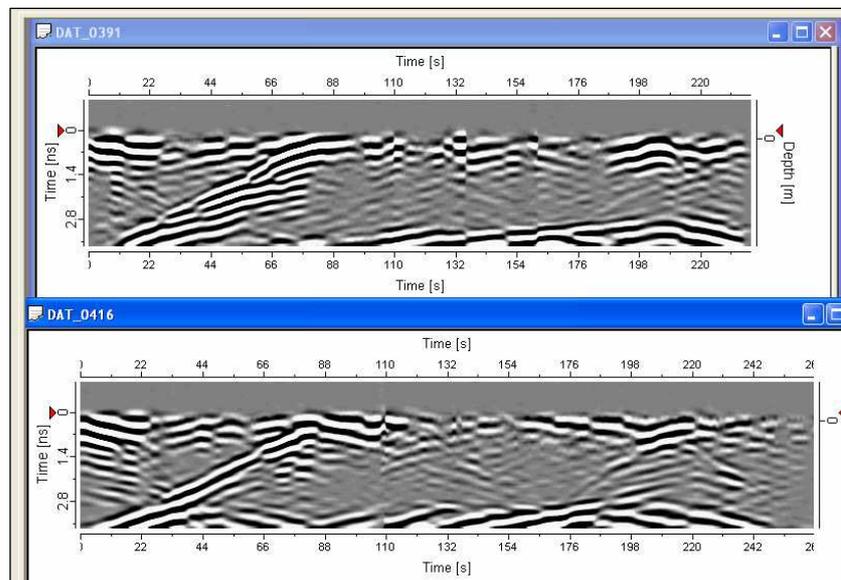


**Fig. 42** Positioner to operate the GPR system (Geoservice, TU Delft)

trolled its movement (Fig. 42), comprised of a custom designed positioner controlled by CNC software in order to achieve:

1. Uniform movement of the antenna at very low speeds
2. Accurate positioning of the antenna in relation to the target
3. Repeatability of scans in the same scanning line.
4. Increase the stacking capacity of the instrument from values of 2 to 4 for hand movement, up to 256 stacks through mechanically controlled movement.

An ultra wide band, stepped-frequency GPR was used with a dedicated antenna to operate in the frequency range from 3 to 8 GHz. The ultra-wide bandwidth is necessary for the detection and characterization of the fractures required, and for monitoring the progress of the ‘healing’ of them with the nano-sols. At first, a baseline measurement campaign was performed, followed by several measurements after injection of ethanol, which is the solute for the nano-sols that is used for the refurbishment treatments. Fracture images were constructed from the data recorded on the marble stones in the back seat at the Theatre of Megalopolis with the commercial GPR systems. These images give a good representation of the fractures inside the stone. It was found that the absence and presence of ethanol in the fractures of the marble stones in the back seat was detectable with the ultra wide band GPR, but not with the two commercial GPR systems in the frequencies between 800 MHz and 2.5 GHz. As a general conclusion, it was possible to demonstrate that using very low scanning speeds and the commercial GPR systems, available today, in combination with an additional facility to achieve low but uniform antenna movements, gives results that allow one to examine qualitatively the effectiveness of nanosols in the sealing of micro-cracks (Fig. 43). This is an experimental result based in on careful and sophisticated application of the stacking method through which it was possible to increase the S/N ratio by a significant degree, using stacks of 256 traces. These were values that were impossible to achieve using conventional hand movement.



**Fig. 43** Different response from the same target (back seat element) between the profile 391 (before CaLoSiL<sup>®</sup> consolidation) and the profile 416 (after CaLoSiL<sup>®</sup> consolidation). The difference is obvious at the left part of the scan where the inclined fracture shows much less thickness in comparison to the initial size (see upper part). Depth of penetration was 20 cm into the stone (GEOSERVICE; TU-Delft).

## 2.7 Results of trial testing and demonstration

One main subject of STONECORE was to demonstrate the successful application of the developed materials on real objects. For that, tests were realised on the following objects:

- Ancient Theatre of Megalopolis, seat and floor element (Geoservice, Greek Ministry of Culture, Strotmann&Partner)
- Leuben Castle, wall paintings (Strotmann&Partner)
- Leuben Castle, Facade Decoration (University of Fine Arts Dresden)
- Dahlen Castle, Gypsum Stucco Decoration (University of Fine Arts Dresden)
- Monastery Rosa Coeli in Dolní Kounice (University Pardubice)
- Statue of an Angel with Child from Kutná Hora, 1764 (University Pardubice)
- Xanten Cathedral, masonry in the cloister (Strotmann&Partner)
- Concrete-window of the church of Dahlem - Schmidtheim, 1960s (Strotmann&Partner)
- Gable of the rectory, Aachen-Orsbach, 1764 (Strotmann&Partner)
- Citadel of Mainz, coat of arms, Entry tunnel, 1659-1660 (Strotmann&Partner)
- Citadel of Mainz, coat of arms, tympanum (Strotmann&Partner)
- Cathedral of St. John the Evangelist and St. John the Baptist, 13-15th century (Restauro)
- Facade of the church of St. Joseph of the visitationists in Warsaw, Royal coat of arms and sculpture of St. Augustin) (Restauro)
- Consolidation of wall paintings and stucco at the Herculaneum Conservation Project (HCP, Ercolano, Italy); (University of Fine Arts Dresden, Germany)
- The Cathedral Basilica In Torun The Nave Corpus (Restauro)
- Nako gompa, Tibetan-Buddhist temple complex (University of Applied Arts, Vienna)
- Castle of Aschach, Austria, imitation of sgraffito (University of Applied Arts, Vienna, Strotmann&Partner)
- Copy of Holy Mary (byzantine mural) (Strotmann&Partner)

All objects were characterised and documented in detail before starting the tests. Comprehensive investigations were performed after the application of the consolidants. The tests included the use of the different types of CaLoSiL<sup>®</sup> alone and in combination with different types of silicic acid esters as well as the application of the developed injection grout and repair mortar. All tests were successful and have demonstrated the great potential of the developed materials.

The space available in this final report is, unfortunately, insufficient to present all objects in detail. However, the following three examples illustrate the variety of objects on which the use of CaloSiL<sup>®</sup> and its related products were tested.

### **Facade of the Church of the Visitation Order in Warsaw** (Realisation: Restauro, Poland, Fig. 44)

It is a remarkable creation of baroque sacral architecture; the only monument of the Royal Route in Warsaw that survived the devastation of World War II. Erected in the years 1727-33, it went through several thorough refurbishments and it also obtained a splendid stone and stucco decoration. The stucco decoration, consisting of full sculptures as well as floral and heraldic ornaments, was in a very bad condition. Numerous, and often improper from the technological point of view, interventions by conservators have contributed to the serious damage and destruction of the original. The lime and gypsum-lime mortars which had been repaired with tight and stiff cement mortars were very disintegrated, cracked and exfoliated in their structure. Also in this case, stabilisation of the disintegrated ground was the key procedure, on which the possibility of performing any further conservation works would depend. The choice of nano-particle calcium hydroxide in colloidal solution allowed simultaneous work with a system of lime-based materials for reinforcing, consolidating and filling stucco-work.

The observation of the results during the works, as well as the structural investigation of the mortars after the conservation, proved the effectiveness of the CaLoSiL<sup>®</sup> E-25 preparation in consolidating disintegrated mortars.



**Fig. 44** Restoration of the sculpture of St Martin on the Visitationist Church in Warsaw, Poland (before, during and after restoration), (Restauro, Torun)

**Statue of an Angel with Child from Kutná Hora, 1764,** (University Pardubice – Faculty of Art Restoration, UPFR, Czech Republic, Fig. 45)

Material: Kutná Hora limestone

Damages:

The main phenomena of damage based on the results of the preliminary investigation were:

- vast loss of the authentic surface of the statue caused by the sulphatisation of  $\text{CaCO}_3$ , the destruction of  $\text{CaCO}_3$  bonds by  $\text{CaSO}_4$  and, locally, by the formation of gypsum crusts
- crumbling and considerable loss of stone caused by improper, hard fillings of concrete during previous restoration treatments
- microbiological attack (green algae)



**Fig. 45** Sculpture before (left) and after (right) conservation (University of Pardubice)

Measures:

Consolidants base on calcium carbonate were selected for the structural consolidation of the sculpture. The worst damaged parts had to be fixed with grouting and provisional binder before treatment so that it would be safe to remove unfit repairs and reduce or displace the dark gypsum crusts. The sculpture was treated with a biocidal agent before consolidation to eliminate biological growth. The angel statue was consolidated using CaLoSiL<sup>®</sup> E25 and CaLoSiL<sup>®</sup> E50 and grouted with CaLoSiL<sup>®</sup> -paste-like. The whole surface was impregnated with CaLoSiL<sup>®</sup> products in two cycles; the most damaged parts in three cycles. After consolidation, the sculpture was freed of dusty deposits, algae and lichens and any residues of CaLoSiL<sup>®</sup>, which created a white haze on the areas where multiple applications had been made. The white haze was removable easily using wet cleaning methods. The sculpture was cleaned using micro- abrasive methods as well. Pieces of the broken bottom part were joined together using a spiral rustless peg called a Helifix. Missing parts of the bottom were reconstructed using a structurally suitable mineral modified binder chosen after several tests.

**Xanten Cathedral, masonry in the cloister** (Strotmann & Partner, Germany, Fig 46, 47)Material:

Masonry: brick, Weiberner Tuff

Window sill: Drachenfels Trachyte

Column: Baumberger Sandstone

Damages:

All stones showed a friable surface. Tuff and trachyte also were flaking and furthermore the trachyte showed an extreme formation of shells. Also black crusts were present.

Measures:

During the conservation, the stones were consolidated separately. Each stone was treated eight times with CaLoSiL<sup>®</sup> E25. The consolidant was injected with a syringe until the stone was saturated. Before the next run the consolidant was allowed to dry.



**Fig.46** Masonry, axis I and axis II before conservation (Strotmann&Partner)



**Fig. 47** Axis II after conservation (Strotmann & Partner)

After these measures, the cracks and voids were filled with an injection mass based on CaLoSiL<sup>®</sup>. After it had dried, the stones were additionally treated with silicic acid ester Funcosil 100. All materials were applied with a syringe. To achieve better penetration, the cracks were wetted with water prior to the application of CaLoSiL<sup>®</sup>.

After these measures, the stones were retouched with lime colours and new joints were made.

**Result:**

A peeling test as well as a drilling resistance measurement was performed and it showed that the stones had been stabilised.

### **3 CONCLUSIONS**

A range of new materials, based on calcium hydroxide nano-particles, including highly fluid consolidants, injection grouts and pastes were developed and are now commercially available. These proved to be highly successful when used both under laboratory conditions, on small-scale trials and on full-scale demonstration objects, demonstrating good penetration, substantial consolidation effects and a high degree of compatibility with the substrates to which they were applied. They were successfully combined with other consolidation materials and were incorporated into the working practices of a number of professional restorers as well as demonstrating the potential to act as a disinfectant for microbiological growth.

During the course of the project a number of techniques to study the characteristics of historic materials were either developed or improved. For example, a standardised method to assess surface friability was produced (Peeling Test) and a device for the semi-automated measurement of water uptake was produced which extended the applicability of the classical Karsten Tube method to non-vertical surfaces and ceilings. Similarly, the capabilities of existing ground penetrating radar systems were extended through the development of a motion control system that allowed both slower rate and more accurate scans to be performed while allowing the use of data-stacking to improve dramatically the signal to noise ratios and thus improve resolution. A new hand-held drilling resistance device was developed as well as a data management system and both are in the process of commercialisation.

STONECORE has fully achieved its objectives and technical goals. This has resulted in the development of new products and techniques that have already been adopted by restoration practitioners both from within the project and beyond, as well as increasing the business opportunities of the SME's involved. The new materials and techniques provide improved and safer restoration capabilities through the use of non-destructive measurement techniques, non-toxic materials and the opportunity to use materials that are fully compatible with those used in the original structure.

#### **4 Impact including the socio-economic impact and wider societal implications of the project**

##### **4.1 Impact and socio-economic impact of the STONECORE results on the refurbishment of buildings and the conservation of cultural heritage including wider societal implications**

STONECORE was aimed at the construction and conservation sector, a sector which is dominated by SMEs. It was the target of STONECORE to introduce nano-materials into this traditional and conservative business sector. This consistent with the EU policy aimed to “**generate step changes in a wide range of sectors and implementing decisive knowledge for new applications at the crossroads between different technologies and disciplines** (from work programme of NMP-call)”. The complex, interdisciplinary research and development has met the expected impacts of call NMP-2007-4.0-6 in which it is stated: “knowledge-based upgrading and retrofitting of the existing building stock has the potential for significant reduction in resources consumption - energy, water, raw materials. The construction sector achieves a new image of innovation and quality, creating new business opportunities and offering attractive working conditions.”

STONECORE has resulted in a completely new set of unique conservation materials based on colloidal calcium hydroxide nano-sols. Methodologies and techniques were developed to synthesise the calcium hydroxide nano-sols in batch sizes of 15 litres. It was shown that the quality of the products is equivalent to those obtained in laboratory scale processes. At the moment, the production capacities allow the synthesis of up 100 litres of CaLoSiL<sup>®</sup> per day, and an increase is possible whenever necessary. Thus, STONECORE has not only resulted in research results, but also in new products that are now available on the market.

The calcium hydroxide nano-sols developed offer many new possibilities. They allow the conservation of natural and artificial stone by the formation of compounds which were originally present. This is a significant improvement in the available conservation possibilities. Also today, many conservations are performed using components which are incompatible with natural stone or historic mortars or plasters. The use of plastics (epoxides, urethanes etc.) in particular must be regarded critically. The long term effects of such treatments are more or less unknown. The materials developed within STONECORE follow a completely different approach.

One of the oldest construction materials, lime or rather calcium hydroxide, has been modified by using sophisticated synthesis technologies. Nano-particles stably suspended in different alcohols were developed allowing the treatment of deteriorated stone, mortar or plaster with products having a penetration capacity similar to pure liquids. Thus a completely new approach in conservation science could be developed. Enhanced long-term stability and a reduction of the need for further conservation result. This advantage is connected with cost and time savings, which are always important. Nano-materials based on alcoholic sols do not mobilise salts present in the stone that has to be treated. All damage that can be caused by using, for example, lime-water as a consolidation agent can be prevented. Additionally, the construction season is prolonged by many months without danger from frost.

One main point which has developed within STONECORE was the combination of the calcium hydroxide nano-sols with already available products, especially silicic acid esters. This has expanded the application possibilities of silicic acid esters greatly. It could be shown that stones, such as weathered tuff or several types of sandstone, which could not be strengthened with silicic acid esters alone, can be consolidated successfully when pre-treatment with calcium hydroxide nano-sols is performed. The subsequent application of conventional silicic acid esters results in increases in mechanical strength far above what can be achieved by single applications of silicic acid esters alone. Another important point is that the time necessary for the conservation can be reduced significantly as the calcium hydroxide nano-particles accelerate the hydrolysis of the esters. Thus, the treated objects obtain faster hydrophilic properties. Faster post-treatments of the consolidated objects become possi-

ble. This obviously results in significant cost savings.

Biological growth, especially of fungi, causes huge problems, not only in the conservation of historic monuments but also in normal housing. Many fungi grow on natural and artificial stone as well as organic substances. They can present a serious danger for human health as fungal spores are very small and can easily be breathed deeply into the lungs. They cause a number of conditions from allergies producing cold-like symptoms, short-term respiratory difficulties, nasal and sinus congestion, asthma or sore throat, as well as true infections of the respiratory tract. The calcium hydroxide nano-sols developed in STONECORE combine successfully the safe removal of biological growth and the consolidation of corroded surfaces. They are ecologically benign materials, free of conventional fungicides, algicides, disinfectants and other toxic chemicals. A substantial improvement in the working and living conditions in buildings during and after refurbishment can be achieved.

Cost-effectiveness of the developed materials is given by the following points:

- Reduction of working time necessary for refurbishment and stone consolidation.
- Enhancement of the lifetime of conservation / refurbishment activity.
- Reduction of the material volume necessary for treatment.
- Reduction of the number of treatments steps necessary for the removal of mildew.
- Reduction of the volume of treatment agent necessary for the removal of algal und fungal growth.

Each refurbishment or restoration requires the comprehensive assessment of the damage present before intervention to enable the appropriate reconstruction and conservation activities to be selected. The same is true for to enable a realistic estimation of the costs to be performed. Similarly, characterisation of the conservation work, for example the structural consolidation achieved or the degree of filling of voids and fractures, is of great importance in order to assess the quality of the refurbishment. In both cases, the most favourable methods utilise non- or minor- destructive damage assessment technologies. Within STONECORE the following advances in this area were achieved:

- Development of a Peeling Test kit.
- Innovative digital Karsten tube measurement device
- New ultrasonic borehole measurement device
- New drilling resistance device.
- Enhanced resolution of existing commercial ground penetrating radar systems
- Development of a data handling system for restorers and conservators

All technologies / devices developed will be available after the end of STONECORE. Starting at the end of 2011, Geotron (Germany) will start the manufacture of the new drilling resistance device as a replacement for their current TERSYS system. The new TERSYS-2 device is the most sophisticated drilling resistance device available on the market worldwide. The Peeling Test kit will be manufactured by ITAM-Pargue and IBZ-Freiberg will distribute it together with the calcium hydroxide nano-sols. GEOTRON will also produce the new ultrasonic borehole measurement device. The commercialisation of the data handlings system and its further development is being explored.

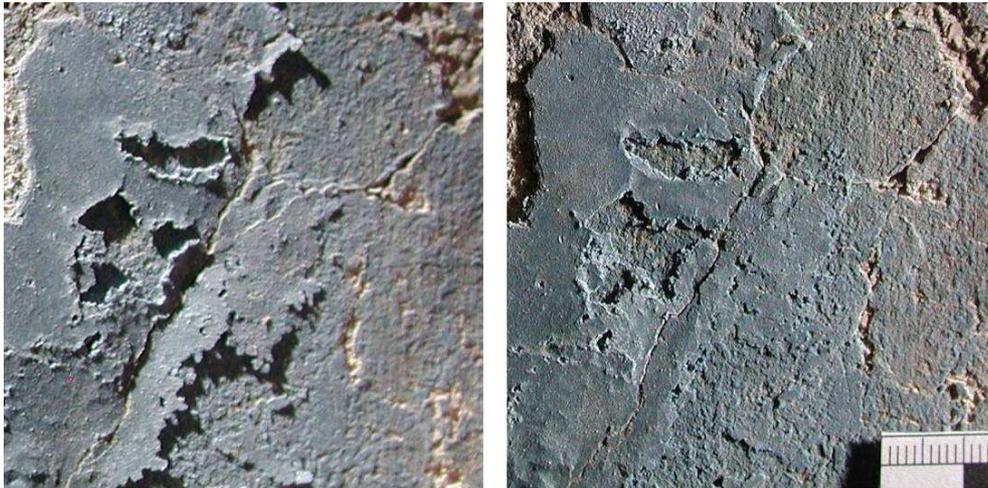
The results of the geophysical investigations have clearly demonstrated the potential of Ground Penetrating Radar in the detection of cracks and voids in stone. GEOSERVICE (Greece) will offer measurement services in this field, exploiting the enhancements in positioning and multiple scan technology that was developed during STONECORE.

An important outcome of the project is that there is increasing interest in the new calcium hydroxide nano-sols. During the whole project, samples of different CaLoSiL<sup>®</sup> products were sent to restorers worldwide. Examples of successful restorations outside of the STONECORE project include:

- Restoration of altars in the Capilla General de Ánimas (Spain: Realisation: by ALFAGÍA)

- Restoration of Globigerina stone in Malta (realisation: Sibylla Tringham, Courtauld Institute of Art, UK)
- Marble Memorial at Westminster Abbey, UK, (Realisation: Sabine Brandt, UK/Germany)

The successful application of CaLoSiL<sup>®</sup> on the Herculaneum-Project in Italy represents another example. The Herculaneum excavation site at Ercolano / Napoli (Italy) is famous for its antique wall paintings and stucco decoration. Conservation is being managed by the Herculaneum Conservation Project (HCP), an international consortium supported by grants. At Herculaneum, the presence of soluble salts (sulphates) is a special challenge. CaLoSiL<sup>®</sup> nano-sols were applied in October 2009 on a small test area in “Salone Nero” (Fig 48 - 50). The evaluation of the treated areas in spring 2011 has clearly indicated the great potential of calcium hydroxide nano-sols in ethanol for the consolidation of flaking paint layers which had been treated with hydrophobic consolidants during former conservation actions. Furthermore, cracks in stucco material have been fixed successfully with modified nano-sols.



**Fig 48,49** Flaking surfaces on wall paintings in the „Salone Nero“ before (left) and after the application of CaLoSiL (right). Picture: UFAD



**Fig. 50** Evaluation of the results by the HCP research group in May 2011



**Fig. 51, 52** Demonstration on the Greek test site at Megalopolis

Based on the successful demonstration tests at the ancient theatre of Megalopolis (Greece) (Fig 51, 52), the decision was made to use the developed materials and techniques for the conservation and restoration of the site. The Greek Ministry of Culture wrote:

“According to the experiences obtained by the Restoration Services of the Greek Ministry of Culture and after observing and recording the effects of the application of new materials and methods in the frame of Stonecore Project, the Scientific Committee of the Megalopolis site has concluded that the project has been successful in consolidation terms under the following perspective: The application of the introduced material (CaLoSiL<sup>®</sup>) succeeds in sealing small vacant spaces inside the stone, thus preventing further deterioration and development of biological growth. Generally it has been shown that the mechanism of using inorganic products applied in water solution for stone consolidation works only in small cracks (~50-100 mm), whereas for more distant cracks organic and stronger products are preferred. This conclusion is about to be presented in details by the President of the Committee Dr Giraud to its members, among which there are representatives of the Directorate for the Conservation of ancient monuments. At the ancient theatre of Megalopolis and while the restoration program was in process we had also the opportunity to apply two different methods of cleaning the surface of the stone in order to remove biological growth without harming the monument itself. The first method is the one introduced in the frame of Stonecore Project and the second is the typical method applied in most cases in Greek archaeological sites. The later involves the application of Desogen and Perhydrol. Bio-killer Desogen is usually applied on ancient stone monuments in order to constrain and if possible remove fungal and algal growth, while Perhydrol (H<sub>2</sub>O<sub>2</sub>) has been proven to remove different kind of microorganisms and in certain cases it dispatches a whitish substance which dissolves the coloured pigments caused by the lichen. Desogen was applied by brush on two samples. CaLoSiL<sup>®</sup> has been used as a novel treatment for the removal of fungal and algal growth. It contains calcium hydroxide nano particles suspended in different alcohols. CaLoSiL<sup>®</sup> has been applied by brush; injection and spraying on limestone samples as well as on selected parts of the theatre. The result of the application had positive effects on the removal of microbiological growth. In general terms it has been concluded that the treatment turned out to be successful since the applied material succeeded in penetrating deep enough in damaged zones and resulted in the stone stabilization as well as in the safe and environmentally compatible removal of mildew and algal growth. One of the most important benefits of the project is that the procedures and methods applied during the treatment are easy to learn and practice from the specialized staff (conservators) once demonstrated and explained. The whole conception and method can be passed on to other expertise related to the preservation of ancient monuments such as archaeologists, mechanics, artisans and skilled workmen. In that way the “know how” can be obtained by various experts involved in restoration programs and

the limited number of certain expertise in an archaeological project won't be a suspending factor for the realization of the application. The project of Megalopolis ancient theater has been recently re-financed in order to integrate the restoration of the monument. Our goal is to continue – in small scale at first - the application of consolidants introduced in the STONECORE program in certain architectural parts, which are preserved in situ and are not going to be moved during restoration. The whole procedure will be monitored in extended areas of application and in deeper time scale by specialized staff. The short and long term results, will define the decision of a wider application. “

**In summary**, STONECORE has resulted in the following three new approaches:

- Refurbishment by stone conservation with nano-materials leading to natural minerals compatible with stone, plaster and mortar.
- Safe and environmentally compatible removal of fungal and algal growth combined with stone or mortar stabilisation.
- Stone characterisation by non-destructive methods allowing both damage assessment and evaluation of the conservation at low costs

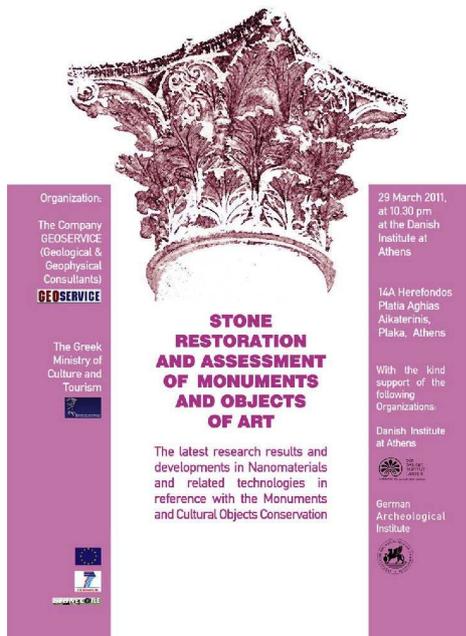
## 4.2 Dissemination activities and exploitation of results

During the three years of STONECORE many activities have been performed to publish and disseminate both the ideas and the results of the project. Each regular project meeting was accompanied by a public meeting in which the results were presented to interested restorers, scientists and authorities. In detail, the following meetings were organised:

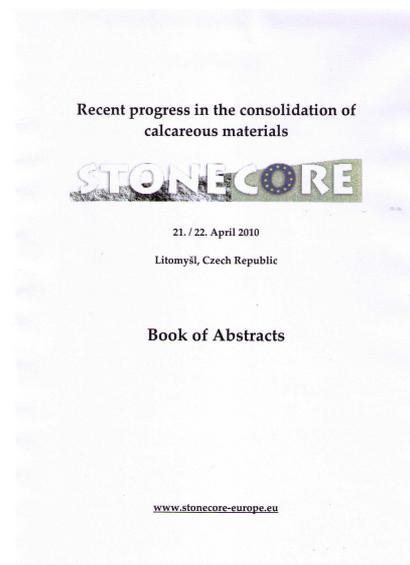
- March 2009, Vienna (Austria)
- September 2009, Athens (Greece)
- April 2010 Litomysl, (Czech Republic)
- October 2010, Torun (Poland)
- March 2011, Athens (Greece, Fig 55)
- August 2011, Freiberg (Germany, Fig 58)



**Fig. 53, 54** Litomysl meeting



**Fig. 55** Announcement of the 2011 public meeting in Athens



**Fig. 56** Cover of the Book of Abstracts

During the Litomyšl (Fig 53, 54, 61) meeting the scientific conference “Recent progress in the consolidation of calcareous materials” was held. The project partners discussed the outcome of STONECORE with experts from outside of the consortium. A special Book of Abstract was prepared summarising all contributions. Similar publications were prepared for the Freiberg meeting and a special meeting held in Peterborough, UK towards the end of the project.

Special events were organised in the United Kingdom and in Austria to disseminate the results of STONECORE in these countries. On June 7<sup>th</sup> and 8<sup>th</sup>, a special STONECRE meeting was held in Peterborough (UK) at which the outcome of the project was presented to, and discussed with, British restorers and scientists (Fig. 57). The meeting was organised together with Hirst Conservation, which will act as the distributor of CaLoSiL<sup>®</sup> in the United Kingdom and Ireland.



**Fig. 57** Peterborough meeting (UK)



**Fig. 58** Final public meeting in Freiberg (Germany)



**Fig. 59, 60** Workshop in Mauerbach (Austria)

In order to discuss the results with Austrian restorers a special workshop was organised by the Institute of Art and Technology/Conservation Sciences of the University of Applied Art, Vienna. The workshop was held in the “Kartause Mauerbach”, on May 9<sup>th</sup>, 2011. After the presentation of the main results, the handling, use and application of CaLoSiL<sup>®</sup> was demonstrated on-site (Fig 59, 60).

Comprehensive discussion of the removal of biological growth by using calcium hydroxide nano-sols has taken place on the autumn meeting of “The International Biodeterioration Research Group” (IBRG) which was held in autumn 2010 in Freiberg.

The project was presented by the coordinator at the following events:

- EURONANOFORUM 2009, 02.-04. June 2009 Prague (oral presentation: G. Ziegenbalg, M. Drdácáký;: “STONECORE - a European project to develop and apply nano-materials for the refurbishment of buildings”)
- Day of the open Monuments, Germany, 13. September 2009, Poster presentation at the Dahlen and Leuben castles
- Herculaneum-project: Napoli (Italy), 28./29. September 2009, 18. Mai 2011; oral presentation
- Exponatec, Cologne, Fair for restoration, Poster presentation
- FIRPA Restoration Fair, Granada, Spain, booth (Fig 62)
- AR&PA Innovation event, Valladolid, Spain, booth ECTP European Construction Platform, Brussels, 24., 25 November 2009; poster + oral presentation (Fig 63)
- ICOMOS meeting, Dresden, 16. January 2010, oral presentation
- DECHEMA meeting “nanotalks” Frankfurt/M. 25./26. January 2010, Poster
- Denkmal 2010; European Trade Fair for Conservation, Restoration and Old Building Renovation, Leipzig, Germany, booth (Fig 64)



**Fig. 61** Project discussion in Litomyšl



**Fig. 62** Presentation at FIRPA; Grenada, Spain



**Fig. 63** The STONECORE presentation at AR&PA Innovation event



**Fig 64** At the DENKMAL 2010, Leipzig

- *FP7 Session: Advances in materials under EU Framework Programmes* held within the 2010 European Materials Research Society, Warsaw, Poland, September 2010

- 2<sup>nd</sup> International Conference “Biocides in Synthetic Materials”, 28-29 September 2010, Berlin, Germany
- RILEM Technical Committee “Specifications for non-structural grouting of historic masonries and historic architectural surfaces”; Thessaloniki 10, 11 March 2011
- Swindon (UK); February 2011; Presentation of STONECORE to English Heritage;

The STONECORE–flyer and examples of posters developed to summarise the STONECORE project are given in Fig. 65 – 69.



Fig. 65, 66 The STONECORE flyer



Fig. 67, 68, 69 Examples of STONECORE posters

The results of the first reporting period were published on the CORDIS Technology Marketplace web-site (Fig. 70).

Technical leaflets as well as MSDS were prepared for all of the products developed. They are available on-line at [www.ibz-freiberg.de](http://www.ibz-freiberg.de) (Fig. 71, 72).

The results of the STONECORE project were presented in detail on the EWCHP-2011 – European Workshop on Cultural Heritage Preservation and Training Day (September 2011, Berlin) in a special session.

Legal Notice: The information in this website is subject to a disclaimer and a copyright notice

CORDIS: Technology Marketplace

Connecting people to technology

Home Business offers Search Other features News and events

■ ■ ■ Futuristic nanotechnology helps preserve history

A European-backed research project is developing revolutionary technology to identify, crack, and repair damage in historic stone buildings across Europe.

Europe is proud of its recent history and heritage, something that is clearly addressed in old stone buildings scattered around cities from the eastern Mediterranean to the North Sea, but many of these fine buildings are threatened by the ravages of time and need innovative solutions to keep them as beautiful as they once were.

The EU-funded 'Stone conservation for the refurbishment of buildings' (StoneCore) project is applying a new approach for renovating stone, mortar and plaster used in the construction of historic monuments and buildings. It is developing and testing nano-materials that are compatible with the stone and mortar used in these structures, as well as novel safe methods for the assessment of stone.

The project studied different types of nano-materials that would fit its needs, determining their suitability in preserving natural and artificial stones, mortars and plasters. It documented, sampled and categorised all the materials to be treated and studied, before investigating different fungal and algal growth on different stones, mortars and plasters.

StoneCore is developing sols (liquid-like suspensions) with calcium hydroxide particles at the nano-scale that could increase the strength of treated mortar and stone. These sols are white to white-tan and have a stability of several months. The dispersion modulus and concentration of the calcium hydroxide nano-sol have also been carefully selected.

At the same time, different species of mould and algae were isolated and identified in trials on buildings, to be neutralised with new nano-lime dispersions.

Novel non-destructive ways were also developed to assess and diagnose stone. These include non-invasive ground-penetrating radar (GPR) technology and innovative ultrasonic measurement systems. The system can detect even very fine fractures and cracks as well as monitor the renovation with nano-sols. Initial field results have shown that modern, high-frequency pulse radars are also capable of detecting thin fractures and fracture networks in stone structures.

In addition, an ultrasonic measurement tool has been developed to determine the stiffness of the stone material and identify loose surfaces. With this revolutionary technology the character and chem of European buildings will be preserved, and so will an important part of our history and heritage.

Country: GERMANY

Information Source: Result from the EU funded FP7-NMP programme

Contact Details  
ZIEGENBALG, Gerald (Dr.)  
IBZ-Salzchemie GmbH & Co.KG  
Former: Ingenieurouro Dr. Ziegenbalg GdR

Date: 2011-03-20

http://cordis.europa.eu/fetch?ACTION=D&SESSION=&DOC=1&TBL=EN\_OFFR&... 31.03.2011

CEO  
Hansbucker Strasse 34  
09399  
FREIBERG  
GERMANY  
Tel: +49 (0) 3731-200155  
Fax: +49 (0) 3731-200156  
Email: Contact  
URL: http://www.ibz-freiberg.de

View printable page View related result

Other ID: 6138

Back

http://cordis.europa.eu/fetch?ACTION=D&SESSION=&DOC=1&TBL=EN\_OFFR&... 31.03.2011

Fig. 70 Web-site of CORDIS Technology marketplace

IBZ-Salzchemie GmbH & Co.KG

Technical Leaflet

Sample box „Fresco“

Content

100 mL CaloSil® E5 (lime content 5g/L)  
100 mL CaloSil® IP5 (lime content 5g/L)  
100 mL CaloSil® E25 -grey (lime content 25g/L)  
20 mL CaloSil® paste-like

Use

The sample box contains selected types of CaloSil® which are suitable especially for the consolidation of powdering surfaces, wall painting and frescos.

CaloSil® E5, CaloSil® IP5

CaloSil® E5 is used especially for the consolidation of powdering surfaces. Loose particles as well as pigments are glued together on the surface.

CaloSil® IP5 needs longer time for the evaporation of the solvent. Deeper penetration and higher strengthening is possible. This depends, however, in many cases also on the structure of the material to be treated.

CaloSil® E25, CaloSil® E-25<sup>®</sup> -grey

Both products contain relatively high calcium hydroxide concentrations of 25 g/L. They are used for deep structural strengthening as well as for the consolidation of surfaces. Due to its low viscosity and thin consistency CaloSil® E25 -grey is especially suitable for applications on surfaces. The tendency to form white hazes is extremely low in comparison to other products.

CaloSil® "paste-like"

CaloSil® paste-like is a high concentrated nano-lime product. The solvent is ethanol as in all products of the CaloSil® E- series. It is used to fill small cracks, joints or openings. It can also be used to glue loose particles together or to stabilize detachments. Mixing with fillers such as marble or limestone powder offers the possibility to prepare special injection grouts or repair mortars.

Storage

All CaloSil® types have to be stored between + 5 °C and +30 °C. In unopened, original containers, storage for at least three months is possible. Settled particles can be re-dispersed by shaking the closed bottle or by ultrasonic treatment. The properties remain unaffected.

IBZ-Salzchemie GmbH & Co.KG  
Deuserbepark, Schwarze Kiefern • 09633 Halberstäde • Tel. +49 (0)3731 200155 • Fax: +49 (0)3731 200156 • www.ibz-freiberg.de • info@ibz-freiberg.de

IBZ-Salzchemie GmbH & Co.KG

Technical Leaflet

Test-Kit

Content

100 mL CaloSil® E25 (lime content 25g/L)  
100 mL Ethanol  
2 rings of Plexiglas  
2 different droppers  
1 Ficht 5dH  
10 mL Phenolphthalein in spray flask

Use

The Test-Kit is composed for first tests to characterize the action of CaloSil® E-25 on different materials. The results will give an overview about:

- penetration depth
- strengthening of the material
- white haze formation
- rate of carbonation

The Plexiglas rings are to fill with loose, original material. Then, saturation of the material with CaloSil® can be realized by dropping it on the surface until saturation is achieved. Repeated applications are possible after evaporation of the ethanol. The carbonation process can be followed by using the phenolphthalein solution. For that, phenolphthalein has to be sprayed on the surface that shall be characterized. A red color will be visible when unreacted calcium hydroxide is present. The sample is then still strongly alkaline (pH > 10) and further carbonation is possible.

An option is also the after treatment with silicic acid esters. That should be realized within one week after the treatment with CaloSil®.

If needed, CaloSil® E25 can be diluted with ethanol. Dilution with water, however, is possible only in limited extent. The addition of increasing amounts of water result in the gel like solutions followed by the flocculation of the calcium hydroxide particles.

Ethanol or Ethanol-water mixtures can be used also for pre-wetting of the materials to be consolidated.

Safety

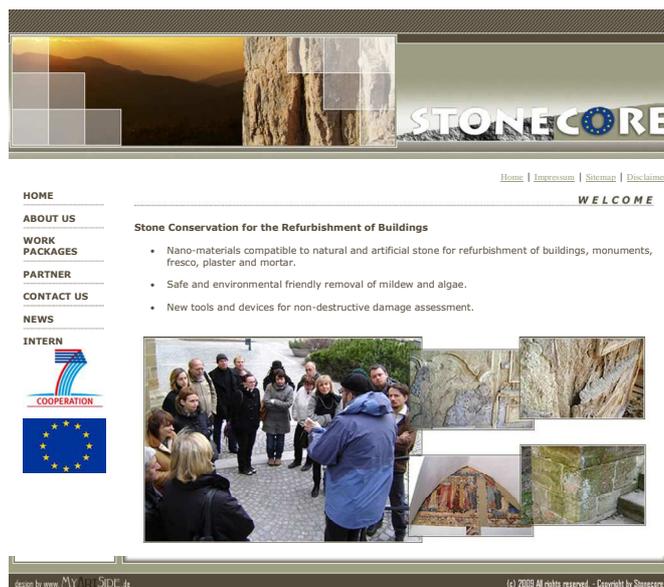
CaloSil® is flammable/combustible. Keep away from oxidizers, heat, sparks and flames. Avoid spilling, skin and eye contact. Ventilate well, avoid breathing vapour. CaloSil® reacts strongly alkaline. Do not breathe vapour or mist. Do not smoke. Keep container closed. Use with adequate ventilation. Wash thoroughly after handling. Keep away from sources of ignition. Please store in a cool, dry place and in a tightly closed container.

IBZ-Salzchemie GmbH & Co.KG  
Deuserbepark, Schwarze Kiefern • 09633 Halberstäde • Tel. +49 (0)3731 200155 • Fax: +49 (0)3731 200156 • www.ibz-freiberg.de • info@ibz-freiberg.de

Fig. 71, 72 Examples of technical leaflets

### 4.3 STONECORE Website + Logo

The web-site [www.stonecore-europe.eu](http://www.stonecore-europe.eu) has been online since April 2009 (Fig 73). There is a continuous increase in the interest of the web site, as the usage statistics indicate. The web-site has an internal section which allows the publication of results which are of importance for the STONECORE consortium only. The web-site is updated regularly.



**Fig. 73** Start website of the STONECORE-project



**Fig. 74** Project-Logo

#### 4.4 Partner in STONECORE and contact addresses

##### **IBZ-Salzchemie GmbH & Co.KG**

Mr. Prof. Dr. Gerald Ziegenbalg  
Gewerbegebiet „Schwarze Kiefern“  
09633 Halsbrücke, Germany,

Tel. +49-3731-200155; Fax +49-3731-200156

E-mail: [gerald.ziegenbalg@ibz-freiberg.de](mailto:gerald.ziegenbalg@ibz-freiberg.de)  
[www.ibz-freiberg.de](http://www.ibz-freiberg.de)

##### **Geoservice**

Mr. Klisthenis Dimitriadis  
Lykaiou 35  
114 76 Athens, Greece

Tel. +30-210-6469865; Fax +30-210-6469865

E-mail: [info@geoservice.gr](mailto:info@geoservice.gr)  
[www.geoservice.gr](http://www.geoservice.gr)

**Strotmann & Partner**

Ms. Dr. Ewa Piaszczyński  
Hauptstrasse 140  
53721 Siegburg, Germany

Tel. +49-2241-916774; Fax +49-2241-916549

E-mail: [werkstatt@restaurierung-online.de](mailto:werkstatt@restaurierung-online.de)

<http://www.restaurierung-online.de>

**Restauro Sp.z.o.o.**

Ms. Malgorzata Musiela  
Lazienna 4  
87-100 Torun, Poland

Tel. +48-56-621 1240; Fax +48-56-621 1240

E-mail: [restauro@restauro.pl](mailto:restauro@restauro.pl)

<http://www.restauro.pl>

**GEOTRON ELEKTRONIK**

Mr. Rolf Krompholz  
Leite 2  
01796 Pirna, Germany

Tel. +49-3501-762 367; Fax +49-3501-792 733

E-mail: [service@geotron.de](mailto:service@geotron.de)

<http://www.geotron.de>

**Industrial Microbiological Services Ltd.**

Mr. Peter Askew  
Pale Lane,  
Hartley Wintney,  
Hants.  
RG27 8DH  
United Kingdom

Tel. +44-1252- 627 676; Fax +44-1252-627 678

E-mail: [peter.askew@imsl-uk.com](mailto:peter.askew@imsl-uk.com)

<http://www.imsl-uk.com>

**University of Fine Arts Dresden**

Mr. Prof. Christoph Herm  
Güntzstrasse 34  
01069 Dresden, Germany

Tel. +49-351-4402 107; Fax +49-351-4402 250

E-mail: [herm@serv1.hfbk-dresden.de](mailto:herm@serv1.hfbk-dresden.de)

<http://www.hfbk-dresden.de>

**Hellenic Ministry of Culture**

Mr. Dr. Demosthenes Giraud  
Karytsi Square 12  
105 61 Athens, Greece

Tel. +30-210-3232 922; Fax +30-210-3242 509

E-mail: [dziro@culture.gr](mailto:dziro@culture.gr)

<http://www.culture.gr>

**Ustav teoreticke a aplikovane mechaniky, Akademie ved Ceske Republiky****Verejna Vyzkumna Instituce**

Mr. Prof. Miloš Drdáký  
Prosecka 76  
190000 Praha, Czech Republic

Tel. +42-0286-885 382; Fax +42-0286-884 634

E-mail: [drdacky@itam.cas.cz](mailto:drdacky@itam.cas.cz)

<http://www.itam.cas.cz>;

<http://www.arcchip.cz>

**Technische Universiteit Delft**

Mr. Claudio Patriarca  
Stevinweg 1  
2628 CN Delft, The Netherlands  
Tel. +31-152-788 732; Fax +31-152-781 189

E-mail: [C.Patriarca@tudelft.nl](mailto:C.Patriarca@tudelft.nl)

<http://www.tudelft.nl>

**Univerzita Pardubice, Faculty of Restoration/Department of Chemical Technology of Restoration**

Mr. Karol Bayer  
Jiráskova 3  
57001 Litomyšl, Czech Republic

Tel. +42-046-603 6594; Fax +42-046-161 2565

E-mail: [karol.bayer@upce.cz](mailto:karol.bayer@upce.cz)

<http://www.upce.cz/fr>

**University of Applied Arts, Vienna, Institute of Art and Technology/Conservation Sciences**

Mr. Prof. Johannes Weber  
Salzgries 14/1  
1013 Vienna, Austria

Tel. +43-1-71133 4825; Fax +43-1-5321447 4829

e-mail: [Johannes.weber@uni-ak.ac.at](mailto:Johannes.weber@uni-ak.ac.at)

<http://www.dieangewandte.at>