CZECH TECHNICAL UNIVERSITY IN PRAGUE

Faculty of Civil Engineering

Performance Evaluation of Consolidants for Friable Inorganic Building Materials

Habilitation Thesis

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Field of study: Theory of Building Structures and Materials

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Declaration

I hereby submit for the evaluation and defence the habilitation thesis elaborated at the Institute of Theoretical and Applied Mechanics of the Czech Academy of Sciences.

I declare I have accomplished my final thesis by myself and I have cited all the sources that I used.

Prague, 24. August 2018

Zuzana Slížková

Annotation

The habilitation thesis is based on a collection of published journal articles and conference papers that the author has substantially contributed to. All of the presented articles deal with the topic of performance evaluation of possible consolidants for disintegrated inorganic building materials: plasters, renders and stone. The consolidation treatments aim to improve stone or mortar cohesion in relation to conservation or restoration of historic buildings and monuments to be preserved. The thesis is divided into two parts. Part I deals with plaster and render consolidation in relation to historic buildings. Part II focuses on porous stone (limestone and sandstone) consolidation treatment evaluation.

Key words: consolidation; plaster; render; mortar; stone; consolidant; conservation

Anotace

Habilitační práce je souborem uveřejněných vědeckých článků, který je doplněný komentářem.
Všechny prezentované články se zabývají tématem hodnocení efektů možných konsolidantů pro rozpadající se anorganické stavební materiály: omítky a kámen.

Práce je rozdělena do dvou částí. Část I se zabývá konsolidací omítek historických staveb. Část II se zaměřuje na vyhodnocení konsolidačního ošetření porézního kamene (vápence a pískovce). Cílem konsolidačního ošetření je zlepšení soudržnosti kamene a omítek, které tvoří povrch konzervovaných a restaurovaných historických staveb a umělecko-řemeslných děl.

Klíčová slova: konsolidace; omítka; malta; kámen; kosolidant; konzervace

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Introduction

This thesis is based on a collection of published journal articles and conference papers that the author has substantially contributed to. All of the presented articles deal with the topic of performance evaluation of possible consolidants for disintegrated inorganic building materials: plasters, renders and stone. The consolidation treatments aim to improve stone or mortar cohesion in relation to conservation or restoration of historic buildings and monuments to be preserved. The author of the thesis has been interested in this topic for years, including her diploma thesis and her practice in the State Studios for Restoration and later in the National Heritage Institute in Prague. The research presented in this habilitation thesis she conducted at the Institute of Theoretical and Applied Mechanics of the Academy of Sciences of the Czech Republic in Prague.

The thesis is divided into two parts. Part I deals with plaster and render consolidation in relation to historic buildings. Part II focuses on porous stone (limestone and sandstone) consolidation treatment evaluation. The whole thesis is comprised of the opening chapter, six chapters reporting individual research studies, and the final results summary followed with results applied in practice. The individual chapters are introduced with brief comments by the author, printed in italics, that explain the research study objective and the link with previous parts of the research. Some articles are included as a shortened version, focusing on the author's contribution on a joint article.

Part I contains two chapters. Chapter One presents the methodology for the selection of a suitable consolidant for a particular mortar. This chapter also outlines the properties, advantages and disadvantages of possible consolidants, and introduces the guideline for evaluation of consolidant performance in relation to plaster/render strengthening.

Chapter Two presents the results of the experimental studies; mainly a quantitative assessment of the strength gain achieved after the mortar specimen impregnation with different consolidants.

Part II focuses on stone, and is comprised of four chapters. Chapter Three deals with performance evaluation of commercial nanolime CaLoSiL as a consolidant for porous limestone. The impact of different concentrations of calcium hydroxide nanoparticles on stone strengthening and porosity reduction is discussed.

Chapter Four describes the use of the radiography method for imaging and mapping of the newly created binder within the consolidated limestone. It is an evaluation of the new binder’s deposition in the limestone over time.

Chapter Five focuses on the sandstone consolidation treatment using tetraethoxysilicate consolidant modified by different additives. The sandstone’s mechanical and textural characteristics after impregnation with the modified tetraethoxysilicate are evaluated and discussed.

Chapter Six also deals with consolidants based on tetraethoxysilicate and their impact on sandstone’s mechanical properties after impregnation. The investigation had two aspects; the effect of the consolidant’s active substance (silica gel) quantity on the resulting stone strength and the influence of testing method on obtained strength data.

Chapter Seven is the final commentary, which contains a summary of the results.

Examples of how these research results can be and have been applied in practice are presented in Chapter Eight and in Appendix I and II.

Part I. Consolidation of renders and plasters

Chapter 1

Requirements and methods for the choice and consolidation of plasters and renders

This chapter is based on two publications, that resulted from the author´s work on the topic "Consolidation of renders and plasters" in the frame of the Technical Committee RILEM 243-SGM „Specifications for non-structural grouting of historic masonries and architectural surfaces".

1. Slížková, Z., Veiga, R., van Hees, R. (2016). Requirements and methods for the choice and consolidation of plasters and renders in situ. Proceedings of the 4th Historic Mortars Conference - HMC2016. Thessaloniki: Laboratory of Building Materials Department of Civil Engineering Aristotle University of Thessaloniki, 2016 - (Papayianni, I.; Stefanidou, M.; Pachta, V.), s. 556-563. ISBN 978-960-99922-3-7.

2. van Hees, R., Veiga, R., & Slížková, Z. (2017). Consolidation of renders and plasters. Materials and Structures, 50(1), 65.

1.1. Aim of the consolidation treatment

In many cases, degraded renders and plasters will just be replaced with new materials. However, in case historic mortars are concerned, a specific, heritage related, value of the ancient mortar may exist and should be assessed: for example, the mortar may be furnished with mural paintings that are to be preserved or else the material of the mortar itself can be important as a document of ancient technology. In those cases, conservation of the ancient material is important and a consolidation treatment may be the way to ensure this.

Consolidation is in this context a treatment meant to re-establish the material's cohesion in a mortar (render or plaster). This action usually requires the introduction of a new binding agent into the degraded layer. The binding agents applied for this purpose, in a liquid state, on degraded materials, are called consolidating agents, consolidating products, consolidants or strengtheners. The products can be applied to the surface using different procedures (coating, spraying, pouring, sometimes using compresses, i.e. poulticing or injection) and tools (brush, sprayer, syringe, pipette etc.) and should penetrate the degraded layer for an appropriate depth, which is related to the degraded zone.

This paper addresses the consolidation of plasters and renders for a depth of several mm up to several cm. After absorption of the liquid product by the mortar, drying, setting and hardening processes will start and reactions, which are typical for the specific consolidant, will take place. The final distribution of the new binding agent in the mortar depends on the consolidant type in combination with the treatment conditions and mortar properties.

The efficiency of a consolidation treatment depends on the product, on the mortar characteristics, on the application procedure and on the ambient conditions during and after the product application. A consolidation treatment should therefore be chosen and applied, taking into account all relevant aspects such as:

- mortar characteristics and conditions (physical, chemical properties, water content, form and cause of degradation, geometry of the surface to be treated, depth of degradation);
- product characteristics (chemical composition, concentration and strengthening capacity, penetration capacity/(particle size and viscosity), setting time, type of solvent or medium;
- application procedure and regime (process of application, applied amount in one application, number of applications, time intervals between applications);
- ambient conditions during and after treatment (temperature, humidity, wind speed).

It is necessary to select the appropriate materials and procedures for a correct consolidation treatment. The main aim of this paper is offering a guideline for the selection and assessment of consolidation treatments for renders and plasters, taking into account possible risks or harmfulness of the consolidation products and offering information on how to assess their efficiency, compatibility and durability under given conditions.

1.2. Identification of the type of damage

Before deciding on any treatment, it is important to first identify the type of degradation and its origin, i.e. the conditions that can be the cause of damage to the render / plaster. This means that an assessment of the current condition (state of conservation) of the construction to be restored/repaired (see Fig. 1, left) and gathering data about previous maintenance and treatment is necessary. The technical assessment includes:

- damage assessment (decay forms and quantification);

- exposure conditions, including moisture and salt content of the substrate;
- material characterization;
- analysis of the mechanism(s) of decay and risk assessment.

Fig. 1 Example of a situation in practice: disintegrated and partly detached aerial lime render before consolidating treatment (l), hydraulic lime render after consolidation and repairing (r)

Decay forms of the to be treated plaster, render or mural painting may include (Fig. 2, 3):

- crumbling
- powdering
- sanding
- chalking

Other damage types, more related to layering or loss of adhesion are not typically treatable with consolidants. In practice, a combination of decay forms may be found, which might need a combination of treatments, like consolidation in combination with (non structural) grouting. The analysis of the decay mechanism and the exposition conditions will not be further discussed here.

Fig. 2 Crumbling and sanding of plasters

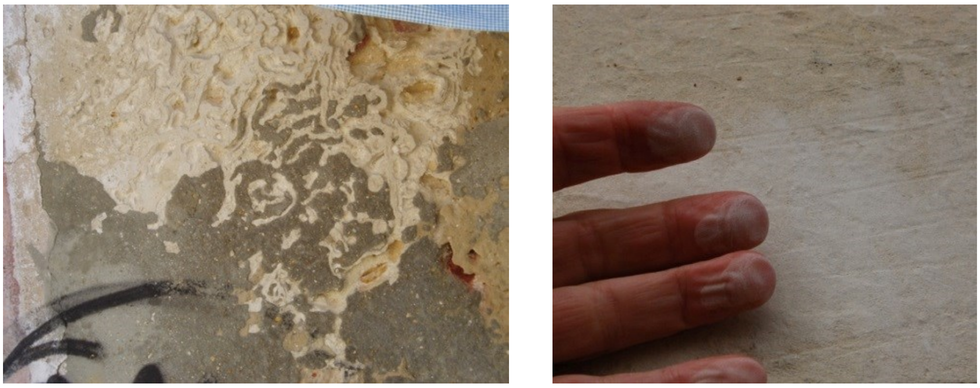


Fig. 3 Powdering (resulting in alveolisation) and chalking of plasters

Apart from the type of damage also the extent and depth of the decay have to be assessed, as well as at least some of the properties of the material, i.e. the to be treated, decayed mortar, and for which sampling of a small quantity of material may be necessary. These properties include:

- physical properties, such as porosity, pores sizes, water absorption rate;
- mechanical properties; due to the conservation state of the mortar, conventional test methods can in general not be applied, but simple methods like surface hardness and cohesion (for example shore hardness, Scotch tape/peeling test) and/or drilling resistance measurement may be performed;
- stratigraphy and micro-structural identification: a cross section of the affected plaster layer may provide important information to base the treatment on.

1.3. General requirements

Requirements are mainly related to compatibility and performance of treatments and the mortar substrates [van Hees et al. 2014]. In case of decorated surfaces, such as mural paintings, also the risk of impairing colours should be carefully considered. The consolidation treatment should be effective (improving the cohesion of the degraded mortar) and compatible with the existing mortar.

A consolidation treatment can be considered compatible if it does not lead to technical (material) or aesthetic damage to the existing materials; the treatment as such should further be as durable as possible. Criteria and requirements can be defined on this basis. The compatibility requirements can be subdivided in physical, chemical, mechanical and aesthetic requirements; next to those there are performance and durability requirements.

1.4. Selection of consolidant – aspects to be consider before decision

The preliminary selection of consolidants to be used for testing in a specific case should be done considering several aspects. Generally, chemical similarity between the consolidant and the mortar binder is favourable owing to maintain the original composition of the historical material and to achieve similar physical-chemical characteristics between non-treated and treated mortar.

In specific cases, is not necessary to have the same chemical composition between the consolidating compound and the mortar binder if the consolidation treatment meets other criteria of compatibility. The new binder should not be prone to fast weathering and biodeterioration in particular atmospheric conditions.

Regarding the reactivity of the consolidant with the mortar, it is advantageous if the consolidant can form chemical bonds with the mortar particles (for example ethyl silicate reacting with the OH- groups of silicate minerals present in mortar). The consolidation treatment can be more durable and effective in these cases.

The consolidated plaster/render should be re-treatable, i.e. allow the application of other required conservation materials, e.g. repair mortars, paints or protective treatments. Therefore, hydrophobic consolidating materials may be problematic if it is foreseen the application of water based materials in following conservation steps.

The penetration ability of the consolidating liquid depends on its viscosity and surface tension. Low viscosity and high surface tension (low contact angle) are favourable characteristics for a good penetration and fast absorption of the consolidant by the mortar. The particles size of the consolidating material is another important parameter, particularly in the case of consolidants, that are based on the dispersion of nanoparticles in water or alcohol, e.g. nanolime, nanosilica, dispersions of synthetic resins in water. The particles of the consolidating material need to be significantly smaller (ten to hundreds of times) than the pores of the mortar to be able to penetrate into the mortar effectively. The penetration ability of consolidant is also strongly affected by the porosity of the render or plaster. Mortars with small and thin pores are expected to absorb the consolidating liquid more difficultly than porous mortar with relatively large pores and eventually also cracks. The contact time of the consolidating liquid with the surface of the plaster or render has to be adapted according to the penetration ability of the consolidant into the specific plaster or render and to the required penetration in view of the expected consolidating effect.

The goal of the consolidation treatment is to improve the cohesion of the degraded material, aiming at returning the original structural and strength properties to the mortar.

Therefore, the concentration of the effective binding substance present in the consolidating liquid has to be carefully adapted to the requirements related to the strengthening effect. The strength increment resulting from the consolidation treatment should not be very high because, in most cases the strength of historical plasters/renders is in the order of a few MPa. In some consolidating liquids, the concentration of the effective substance is very low, for instance lime water containing only 0.16% w. of calcium hydroxide must be repeatedly applied to achieve a satisfying consolidation effect. On the other hand, there are consolidants with a high concentration of the effective substance, e.g. nanolime products containing up to 5% w. of calcium hydroxide, where one or a few applications can be sufficient.

The penetration ability of a consolidant also depends on its concentration, which should also be considered, as the penetration ability is reduced with increasing concentration. It is often better to apply a less concentrated consolidant repeatedly and/or progressively increasing its concentration than to apply a high concentrated product only once. Consolidants used mainly for stone consolidation (ethyl silicate or nanosilica) have relatively high content of SiO_2 (dozens of percent) and this fact should be considered to avoid the risk of over-strengthening. Low concentrated (diluted) variations of up to 10% w. should be more appropriate for the consolidating treatment of historical mortars.

The method of application should be practicable, considering the given conditions (damage type, geometry of the surface to treat, ambient temperature and moisture, required contact time).

The distribution of the consolidant in the mortar layer after consolidation should be checked. For the assessment of penetration depth, methods with indicator liquids can be used (Fig. 4) or microscopic examination of the cross section (Fig. 5).

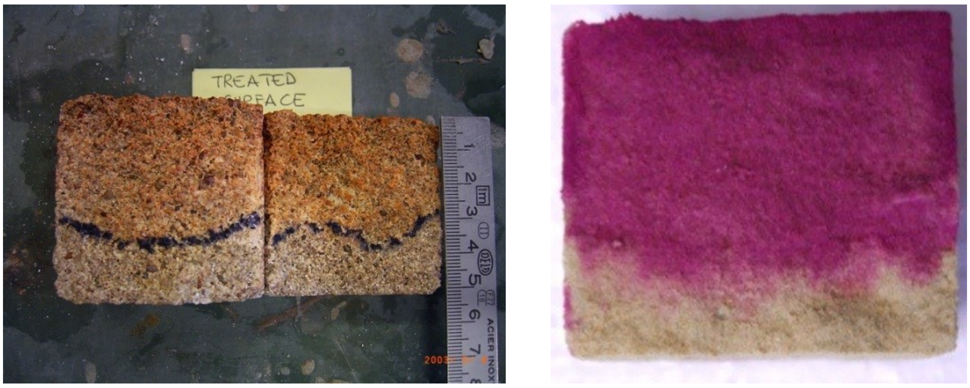


Fig. 4 a,b Use of indicator liquids to assess the presence of a product in a substrate. Left – dithizon, used for ethyl silicate; right – phenolphthalein used for the assessment of the penetration of a nanolime consolidant [Borsoi G. et al. 2015]

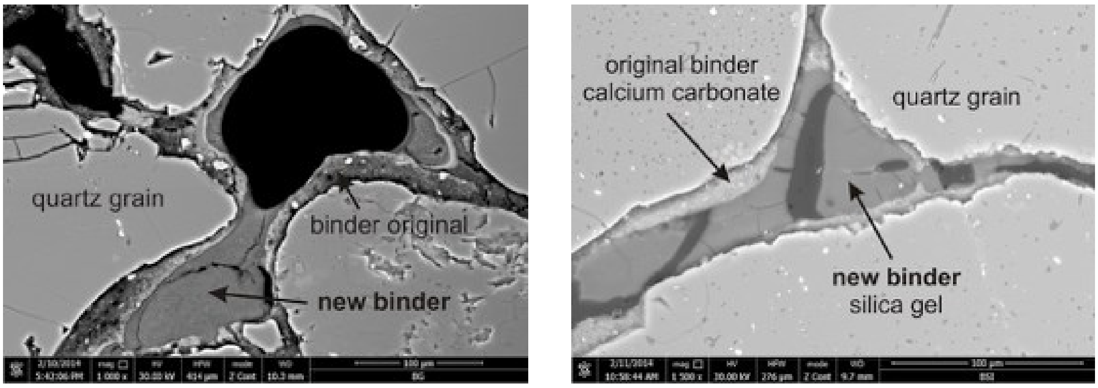


Fig. 5 a,b Use of SEM- BSE microscopy to detect the presence of a product in a substrate. Left – nanolime treatment result: new calcium carbonate layers detected in pores near the treated mortar surface; right – silica sol treatment result: silica gel detected at the depth of 2 mm under the treated mortar surface

Especially in the case of precious painted substrates it will be almost impossible to obtain enough sample material in order to perform laboratory tests for all compatibility and durability related requirements. In this case artificially degraded substrate materials, with a composition, coherence and porosity comparable with those of the degraded mortar [Borsoi et al. 2012; Lubelli et al. 2015; Pascoal et al. 2015] could be used, or artificially prepared mortar with parameters similar to degraded mortar [Drdácký, Slížková 2012].

1.5. Consolidation products – characteristics relating the consolidation treatment

Historically, the available conservation materials for building materials were mainly lime, gypsum and natural organic compounds based on vegetal oils, waxes, polysaccharides (vegetal gums and starch), proteins and natural resins. (In several regions of the world, traditional plaster materials exist, in which natural additives were added, based on for example gluten from wheat flour glutinous (sticky) rice or jaggery (from cane sugar after boiling) and several authors state [Papayianni, Singh 1990; Satish 2013] that these kinds of adhesives have been used also as consolidants for this type of mortars). Later, with the development of chemistry, barium water, ethyl silicate, synthetic polymers came into building materials conservation practice [Siegesmund, Snethlage 2011]. Many of these natural and synthetic substances failed to satisfy compatibility and performance requirements for the consolidation treatment.

Recently, more attention has been paid to the use of inorganic consolidating materials. An important advantage is that hydrophilic inorganic products are free of the problems caused by hydrophobic properties of organic-polymeric products [Matteini 2011] and are less susceptible to microbiological attack than organic compounds.

Limewater was recommended in some literature of the 20th century [Denninger 1958] for consolidation of mural paintings, particularly for fixation of released surface paint layers. Useful contributions dealing with limewater applications on mortar have been given during the last 20 years [Brajer and Kalsbeek 1999; Hansen et al. 2003; Tavares et al. 2008;

Girsa et al. 2009; Borsoi et al. 2012; Slížková et al. 2015; Drdácký and Slížková 2015]. Silica based consolidants, mainly utilized for (sand)stone consolidation, can be used also for consolidation of specific types of mortar, particularly earthen mortars. Calcium hydroxide sols (nanolimes) were developed in recent years in order to get improved efficiency of lime-based consolidants [Dei, Salvadori 2006; Ziegenbalg 2008; Baglioni et al. 2009; Borsoi et al. 2012]. The natural conversion of calcium carbonate to calcium oxalate led to experiments in Italy, using a treatment based on ammonium oxalate to protect stone and lime plaster against acid rain [Matteini et al. 1994; Matteini, Giovannoni 1996]. Later, ammonium phosphates were proposed for consolidation of calcareous substrates and tested on limestone [Sassoni et al. 2011] and mortars. The most important physical-chemical characteristics of common consolidation products are given in Table 1. Some positive and negative aspects, which should be considered in relation to consolidation treatment, are mentioned in Table 3.

1.6. Application methods and procedures

The application procedure of the consolidant depends on the consolidant penetration properties, on the mortar suction ability, on the type and location of the element to be treated and on the exposition (for example interior or exterior). It is not possible to give one standard application method and procedure, which could cover all mortar substrates, degradation types and environmental conditions. A very general indication on the most appropriate application method is given in Table 2.

In most cases the consolidant must be applied on site, without removing the element. In those circumstances the application is done by: i) spraying (or squeezing from a bottle) the mortar surface: several repetitions with small intervals, until the mortar is saturated to the required depth (thickness); ii) brushing: several brushing operations with small intervals, until the substrate is saturated to the required depth; or even by iii) poultice application.

In laboratory, for comparison of the effect of different treatment products or concentrations, vertical capillary absorption of the liquid, may under circumstances be the most adequate application method.

1.7. Assessment of the consolidation treatment compatibility – general guideline

The selection of the product to be used and the verification of its fitness in the specific situation should be done through laboratory testing and/or in situ assessment. The following sequence of actions should preferably be carried out:

- Preliminary selection of consolidants based on the characteristics of the mortar to be consolidated and requirements for selection (as refered to in 1.4.)

- Testing of different application procedures and regimes (method of application, applied amount of consolidant per mortar surface unit during one application, number of applications, time intervals between applications).
- Testing the consolidation agents previously selected on trial specimens and subsequent comparison of the test results:
    - Preferably on site (but not on the object)
    - Alternatively on mortar specimens in lab: simulation of composition and porosity of mortar (render / plaster) to be treated; simulation of ambient conditions (T, RH) – can be important for the final distribution of the consolidant in the substrate and for the resulting strength profile. Porosity of the artificially degraded mortar can be fine-tuned by adapting binder content and grain size distribution of the aggregate. For practical reasons the use of this procedure may be limited to very important plaster and wall painting surfaces.
- Assess properties on treated and not-treated mortar and compare results
- Apply accelerated ageing (climatic cycles and salt crystallization cycles) on part of the specimens and evaluate the behaviour under these actions, in comparison with not decayed mortar.

1.8. Parameters to measure and measuring methods

The performance of the treatment should be assessed *in situ* or on model substrates following evaluation based on comparison with the untreated material. Standardized measuring methods for testing mortars or modified methods for testing historical mortar [Veiga et al. 2004; Válek and Veiga 2005; Drdácký 2011; Drdácký 2012; Drdácký and Slížková 2013; Drdácký and Slížková 2015] should be applied to determine mortar parameters. When such a method is missing, adoption of a method for testing stone [Tabasso and Simon 2006; Bläuer et al. 2012] can be considered. Requirements, parameters and proved test methods are given in Tables 4 and 5. After such an assessment the consolidant should be applied to the object.

Table 1. Characteristics of consolidation products for renders, plasters and wall paintings

Common name	Active phase chemical composition	System	Active phase size and concentration		Solvent or Dispersion medium
			Size	Concentration	
Lime water	$Ca(OH)_2$	Solution, homogeneous mixture, dissolved phase (Ca^{2+} cations, OH^- anions) in water	0.11 nm (Ca^{2+}) 0.14 nm (OH^-)	maximum (saturated sol.) 0.16 % w. (1.6 g/l)	Water
Barium water	$Ba(OH)_2\ 8H_2O$	Solution,homogeneous mixture, dissolved phase (Ba^{2+} cations, OH^- anions) in water	0.15 nm (Ba^{2+}) 0.14 nm (OH^-)	maximum (saturated sol.) 5.6 % w. (56 g/l)	Water
Nanolime	$Ca(OH)_2$	Colloid, Sol, dispersed phase (calcium hydroxide particles) in alcohol	50-300 nm	max. in products about 8 % w. (80 g/l) usually used 5-25 g/l	Ethanol, Isopropyl alcohol, etc.)
Nanosilica	SiO_2	Colloid, Sol, dispersed phase (silica particles) in water	7-125 nm	max. in products 50 % w. (500 g/l) usually used 30-100 g/l	Water
Silicic acid ester, TEOS, Ethylsilicate	Tetraethoxy silane or tetraethoxy orthosilicate	Homogenous phase, Monomer	1.5-3 nm	about 28 % w. SiO_2	None
	Ethoxy oligomeric siloxane or ethyl polysilicate	Homogenous phase, oligomer, partly pre-condensed	<15 nm	about 40 % w. SiO_2	None
	Tetraethoxy silane or ethoxy oligomeric siloxane	Solution, homogeneous mixture, dissolved phase-ethyl(poly)silicate molecules- in solvent	<15 nm	about 10 % w. SiO_2	Organic solvent e.g. ketone, ethanol
Acrylic resins	Acrylate/ methacrylate (co-)polymer	Solution (homogeneous mixture), dissolved phase - acrylate (co)polymer molecules-in solvent	<10 nm	35-100 % w. usually used 1-5 % w.	Acetone, Toluene, Xylen, Ethanol, Isopropyl-alcohol etc.
Acrylic dispersions	Acrylate/ methacrylate (co-)polymer	Colloid, Sol, dispersed phase -acrylate (co-)polymer particles-in water	170-200 nm	40-50 % w. usually used 5 % w.	Water
Ammonium oxalate	$(NH_4)_2C_2O_4$	Solution,¨homogeneous mixture dissolved phase (NH_4^+ cations, oxalate anions) in water	0,14 nm (NH_4^+) <1 nm (oxalate)	usually used 2,5- 5 % w.	Water
Ammonium phosphates	Di-ammonium hydrogen phosphate (DAHP) $(NH_4)_2HPO_4$ or Ammonium di-hydrogen phosphate (ADHP) $(NH_4)H_2PO_4$	Solution, homogeneous mixture, dissolved phase (NH_4^+ cations, phosphate anions) in water	0,14 nm (NH_4^+) <0,5 nm (PO_4^{3-})	usually used 5 % w.	Water

Table 2. Application methods for different circumstances. General indications

	Practice large surface, interior	Practice large surface, exterior	Practice small surface or ornaments	Laboratory large surface	Laboratory small surface
Spraying	x	x		x	
Brushing	x	x	x	x	x
Poulticing			x		
Capillary absorption					x

Table 3. Positive and negative aspects of consolidants in relation to consolidation treatment

Common name	Advantages	Disadvantages	Risks
Lime water	- good chemical match with lime mortar - little change of all mortar characteristics (porosity, water absorption, …) after consolidation	- low content of the active phase and resulting low strengthening effect after one application - repeated water saturation of mortar due to treatment -high pH of lime water	- salts crystallization and damage - white haze after many cycles - instability of some pigments due to high pH of the water - reduced strength of wet mortar - freezing in cold climatic periods
Barium water	- sufficient content of the active phase - chemical stability of the $BaCO_3$ -stabilization of sulphates in mortar	- created $BaCO_3$ differs from $CaCO_3$ - high pH of barite water	- raising of colour intensity after more cycles (yellowing, whitening) - instability of some pigments due to high pH of the water - reduced strength of wet mortar - freezing in cold climatic periods
Nanolime	- sufficient content of the active phase - good chemical match with lime mortar - non-aqueous system (may be suitable for salt laden mortars)	- particle size of nanolime may be a limiting factor for some fine porous mortars - fast evaporation of alcohol from nanolime may cause agglomeration of $CaCO_3$ near the surface	- white haze due to fast evaporation of alcohol resulting from high temperature or high air ventilation during the treatment, high product concentration or too many applications or too fine pores in treated mortar
Nanosilica	- good strengthening effect - economic product	- created SiO_2 differs from $CaCO_3$ - particle size of silica sols may be limited for some fine porous layers of mortar - high content of the active phase (often need to be diluted for mortar consolidation)	- white haze, glossy surface - surface over-strengthening due to wrong choice of the product concentration, and limited penetration etc.
Silicic acid esters	- good strengthening effect - good penetration depth; - good chemical compatibility with the earthen mortar binder	- created SiO_2 differs from $CaCO_3$ - reduction of mortar water absorption after treatment (persisting hydrophobic features)	- white haze, glossy surface - surface over-strengthening due to wrong choice of the product concentration or due to application on wet or salt laden mortar - detachment
Acrylic polymers	- good strengthening effect - good adhesion effect	- acrylate resin differs from $CaCO_3$ (no chemical match) - drying and water vapour permeability retardation after treatment - low penetration depth	- increase of degradation of surrounding not treated zones due to significant changes of moisture behaviour - detachment of the surface layer due to low permeability of water vapour - differential weathering by comparison with untreated material
Ammonium oxalates	- an increase in cohesion was observed after treatment - the wetting properties are retained and the passage of water is not prevented - the treated surface is more resistant to acid attack	- created calcium oxalate phases differ from $CaCO_3$ - the nature of the reaction determines its spontaneous termination only a few microns below surface [Matteini 1996] - not enough data are available to evaluate the consolidating effect on mortars/plasters	- ammonium affects copper based pigments such as malachite, verdigris, and azurite.
Ammonium phosphates	- sufficient content of the active phase - absence of toxicity - very low solubility of the reaction products (calcium phosphate compounds) - low viscosity = good penetration into the stone - good strengthening effect	- created calcium phosphate phases differ from $CaCO_3$ - not enough data are available to evaluate the consolidating effect on mortars/plasters	- ammonium affects copper based pigments such as malachite, verdigris, and azurite.

Table 4. Laboratory tests on a render/plaster (simulated mortar) before and after consolidation treatment

Parameter	Requirement	Test method
Application		
Product application	Comparison of different application techniques	--
Physical		
Porosity	Small/moderate decrease of porosity acceptable, generally max up to the porosity of the sound material	RILEM 25-PEM 1.1. 1980, EN 1936: 2007, MIP, microscopy (image analysis)
Pore size distribution	Not significantly different from sound material	MIP, SAXS, CT
Water absorption	Moderate decrease (20-50%) of water absorption compared to mortar before consolidation	EN 1015-18:2002 or EN1925: 1999
Drying behaviour / rate	Limited decrease in drying velocity (rate). After 24h moisture content treated mortar =<80% of saturation	RILEM 25-PEM II.5 EN 16322:2013
Water vapour permeability	Limited decrease	EN 1015-19:1998 ISO 12572:2001
Thermal and hygric dilation	Limited change, maximum 30% change [Veiga et al. 2007]	EN 14581: 2004 (thermal) RILEM 25-PEM II.7 (hygric)
Mechanical		
Hardness	Improvement, but not surpassing the sound material Homogeneous effect over depth of treated zone	DRMS Shore hardness Ultrasonic velocity Bending test (Nb thickness plaster layer) Compression strength
Cohesion	Improvement, but not surpassing the sound material Homogeneous effect over depth of treated zone	DRMS Shore hardness Ultrasonic velocity Bending test (Nb thickness plaster layer) Compression strength Peeling test (strip test)
Deformability	No significant reduction	(Dynamic) modulus of elasticity EN 14146: 2006 (Frequency of resonance)
Aesthetic		
Colour change and general appearance	No visible / significant change of colour and/or appearance (except if render/ plaster is to be painted or to have chromatic reintegration after consolidation)	Naked eye, Spectrophotometry (also to be used for long term monitoring): acc. to EN 15886: 2010 Colour measurements of surfaces
Performance & durability		
Penetration depth	Full decayed zone should be reached Homogeneous distribution	DRMS Indicator liquid Microscopic examination
Resistance to weathering	Improvement of the treated render/plaster compared to the untreated one	Frost-thaw cycles Salt crystallization cycles Wet-dry cycles Ageing in climatic chambers (T,RH, gases) Resistance to sunlight / UV

Table 5. In situ tests on a render/plaster before and after consolidation treatment

Parameter	Requirement	Test method
Application		
Product application	Comparison of different application techniques	-
Physical		
Water absorption	Moderate decrease of water absorption	Karsten or micro tube [Drdácký, Slížková 2015] Drip method (droplet test) [Bläuer et al. 2012]
Chemical		
Chemical, mineralogical composition and chemical reactivity	Stability of new compounds should be assessed considering environmental factors	Methods of determination of chemical or/and mineralogical composition (Portable XRF, portable FTIR, Raman spectroscopy, etc.)
Mechanical		
Cohesion, hardness	Improvement, but not surpassing the sound material Homogeneous effect over depth of treated zone	DRMS Shore hardness Ultrasonic velocity Peeling test (strip test)
Deformability	No significant reduction	(Dynamic) modulus of elasticity by ultra sound method
Aesthetic		
Colour change and general appearance	No visible / significant change of colour and/or appearance (except if render/ plaster is to be painted or to have chromatic reintegration after consolidation)	Naked eye, Spectrophotometry (also to be used for long term monitoring): acc. to EN 15886: 2010 Colour measurements of surfaces
Performance & durability		
Penetration depth	Full decayed zone should be reached Homogeneous distribution	DRMS After sampling: with use of indicator liquid and/or microscopic examination
Resistance to weathering	After consolidation improvement when compared to before consolidation	Assessment effect of natural weathering on medium to long term (monitoring physical, chemical and mechanical properties)

Conclusion of the testing can be an (scientific) assessment of effectiveness, risks and durability of tested treatments under natural and artificial conditions and a list of aspects, which should be taken into account before decision making.

Fig. 6 In situ testing of the plaster parameters: water absorption rate by means of micro-tube (left) and drilling resistance using DRM system (right).

Chapter 2

Comparative tests of consolidants´ strengthening effects on weak mortars

This chapter focuses on experimental testing of various consolidants´ effects on mortar specimens imitating friable historical mortar/plaster. The chapter is based on three publications dealing with this topic, which resulted from a research conducted in the frame of the project GAČR 103/09/2067 *managed by the author of the thesis.*

Slížková, Z., Drdácký, M., & Viani, A. (2015). Consolidation of weak lime mortars by means of saturated solution of calcium hydroxide or barium hydroxide. Journal of Cultural Heritage, 16(4), 452-460.

Slížková, Z., Frankeová, D., Drdácký, M. (2013). Strengthening of poor lime mortar with consolidation agents. The 3rd Historic mortars conference. Glasgow: University of the West of Scotland, (Hughes, J.), ISBN 978-1-903978-44-3.

Slížková, Z., Frankeová, D., & Drdácký, M. (2018, June). Comparative Tests of Strengthening Effects on Weak Mortars Consolidated with Various Agents. In International Conference on Theoretical, Applied and Experimental Mechanics (pp. 21-26). Springer, Cham.

2.1. Consolidation of weak lime mortars by means of saturated solution of calcium hydroxide or barium hydroxide

2.1.1. Research aims

Discussions on the use of a solution of calcium hydroxide in water (often referred to as "lime water") for consolidating weak inorganic porous materials have been going on for decades. In the Czech Republic, multiple applications of lime water have frequently been prescribed by the central national conservation office as the only acceptable consolidation treatment for lime renders. Such massive application of lime water as a consolidation agent for conserving historic rendered façades has raised much discussion, and has aroused the resistance of some regional authorities and practicing restorers, leading to the involvement of our team in laboratory research on this contentious issue. The research presented in this subchapter aims to offer an objective evaluation of the influence of adding lime water to friable mortar, and to ascertain the degree of consolidation. The consolidating effects not only of lime water but also of multiple applications of some other treatments were investigated: distilled water, lime water blended with metakaolin, and barium water (a barium hydroxide saturated solution in water). In this study, barium hydroxide was considered as an alternative "traditional" consolidant to calcium hydroxide, and potentially more effective, because it is much more *soluble in water than calcium hydroxide. With respect to the distilled water, its effects were investigated with reference to the type of mortar and the shape of the specimens. The lime water with added metakaolin was tested in accordance with recently-published research results.*

2.1.2. Lime water treatment of renders

Until the publication the paper "Lime-water consolidation effects on poor lime mortars" in APT Bulletin [M. Drdácký, Z. Slížková 2012], there was a lack of experimentally supported publications and detailed information about the effects of lime water treatment on weak lime mortars. Some papers presented only marginal data [L. Mora et al. 1977] or the results attained under certain limited conditions may be too broadly interpreted [S. Peterson 1982], and may be arbitrarily extrapolated into conditions where no knowledge is available, and thus no justification or evidence exists [B.L. Clarke, J. Ashurst 1972]. Though the number of relevant articles is quite small, a detailed literature review is beyond the scope of this paper. Only the most relevant experimental studies are mentioned, leaving aside reviews [E. Hansen et al 2003], theoretical works analysing, for example, very important questions of binding mechanisms [D.T. Beruto et al. 2005], [M. Giordani, D. Beruto 1987], and also papers illustrating confusions in terminology (lime water against lime wash) [W. Millar 1998] or presenting discussions and arguments against the application of lime water for consolidating mortar and stone [N.J.T. Quayale 1996].

The effect of lime water applied in situ for restoring wall paintings on lime mortar rendering has been investigated by I. Brajer and N. Kalsbeek [I. Brajer, N. Kalsbeek 1999]. These researchers systematically tested lime water treatments from the point of view of the application procedure, the number of applications (20-70 cycles), dosage and maturation. They concluded that continuous "wet" applications bring about a consolidation effect, unlike applications with "drying" breaks, which do not consolidate the wall painting. However, the observed consolidation tended to concern fixation of a released surface paint layer, for which lime water was recommended in some older literature [E. Denninger 1958]. (It is interesting to note that the so-called "traditional" lime water was not included by Friedrich Rathgen in the list of consolidation techniques that he compiled in 1898. In former Czechoslovakia, F. Petr added lime water to the list of recommended treatments in 1953, without any reference [F. Petr 1953]). I. Brajer and N. Kalsbeek did not carry out any objective measurements of mechanical characteristics in their study.

In the field of measuring the mechanical characteristics important results were published by C. Price [C.A. Price 2004] and his team [C. Price et al. 2008]. Although this work concerns limestone restoration, it has helped considerably in the presented study. C. Price applied lime water in 40 cycles on stone and also on crushed limestone sand. He found a very small increase in the amount of calcite in the material, no observable change in the mechanical characteristics, and no consolidation effect on the crushed material.

Lime water effects and the use of metakaolin as an additive in limewater were studied by M. Tavares, R. Veiga and A. Fragata [M. Tavares et al. 2008]. They recommended the use of limewater and limewater with metakaolin for consolidating old rendering with low cohesion on the basis of laboratory and in-situ tests results, and concluded that the tested consolidants increase the mechanical resistance of the superficial layers.

Notwithstanding the research referred to above, there has been a considerable lack of knowledge concerning the method of lime water treatment of renders. A thorough experimental programme was therefore carried out, aimed at revealing the fundamental behaviour of weak lime mortars when subjected to multiple saturations and evaporation of distilled water, a saturated solution of calcium hydroxide in water ("lime water"), lime water with added metakaolin, and saturated solution of barium hydroxide.

2.1.3. Experimental

2.1.3.1. Lime mortar test specimens

On the basis of a literature survey indicating very slight effects of multiply wetted historic mortars or stone with lime water, as regards both penetration depth and strengthening, the authors designed and prepared specific test specimens in the form of short tubes for compressive tests and plates for tensile tests, Figure 7, Table 7. The specimens were made of lime mortar prepared in laboratory from powdered lime hydrate and river sand. The white air lime hydrate (CL90) Čertovy schody, Czech Republic, of a great purity (98.98% of CaO + MgO) was used. The most frequent particle diameter found in lime was 15 μm and 90% of particles were smaller than 38 μm (the particle size distribution was measured using a Laser analyser CILAS 920). The specific surface area of used lime was 16.5 m^2/g (by means of gas adsorption, BET method, using the device Micromeritics ASAP 2020).

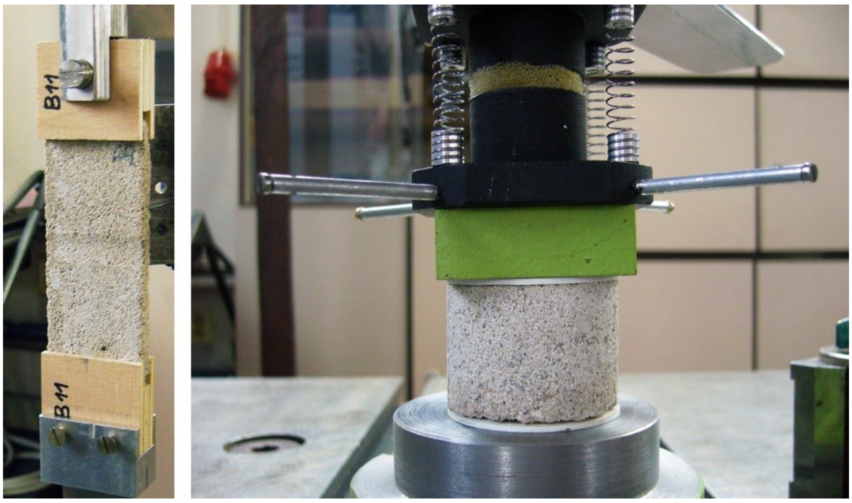


Fig. 7 Testing specimens - thin plates for tensile tests (left) and tubes for compressive test (right)

As the aggregate of the mortar a quartz sand was used (sand quarry Borek, Czech Republic). Mineralogical composition of the sand was determined by means of optical microscopy (thin section of the sand was investigated by the polarizing microscope Zeiss NU2) and XRD analysis (Bruker D8 Advance system with Cu-anode (λ Kα = 0.15418 nm) and variable divergent apertures at convention Bragg-Brentano para-focus Θ – Θ reflective geometry, step 0.02°2 Θ, step time 188 s). The sand consisted mainly of quartz, but particles of quartzite, marlstone, granitic rocks, K-feldspar and plagioclase were also determined using petrographic microscope. XRD analysis identified quartz, feldspars, illite, and/or muscovite, and chlorite. Particles of the sand Borek were sorted in grain size fractions by means of sieving before preparing the laboratory mortar. The grain size distribution of the aggregate for mortar specimens, Table 6, was designed so that it reproduced the grading of the historic render aggregate. For this purpose, the historic lime render with quartz aggregate was sampled from a medieval castle and the sample of 200 g was dissolved by the acid dissolution. The aggregate separated from a disintegrated mortar by filtration was dried and sieved to obtain the grading curve of the mortar aggregate. In accordance with the grain size distribution of the historic render the various size fractions of the sand Borek were mixed and used for preparation of the model laboratory mortar.

Table 6. Grain size distribution of the lime mortar sand (sieving analysis)

Size (mm)	<0.063	0.063-0.125	0.125-0.25	0.25-0.5	0.5-1	1-2
% w.	0.2	0.7	4.8	36.4	43.6	14.3

The quartz sand and the commercial air lime hydrate CL 90 in a ratio of 1:9 by volume (2.5 kg of the dry sand mixture, 0.1 kg of the lime hydrate and 0.25 kg of water by weight) were mixed in the laboratory to prepare a poor weak lime mortar. First, water was poured into the mixing bowl then the lime hydrate was added and the lime mixture was mixed for 5 minutes in a laboratory mortar mixer. After that the sand was poured into the lime and finely, mortar was mixed 20 minutes. The fresh mortar was stored in a closed plastic bag to prevent the mortar from carbonation.

The specimens were fabricated by casting of the fresh mortar in a stainless steel cast, with no separation treatment of steel walls, and were well compacted. This enabled the specimens to be pushed out from the cast immediately after moulding, and prevented the development of shrinkage defects. The tubular cast shape of specimens for the compressive test increased the surface-to-cross-section area ratio and intensified the measurable compressive strengthening effect. The plates for the tensile tests were provided with wooden (plywood) heads to enable them to be fixed into the special flexible loading grips, ensuring correct alignment without disturbing bending and without eccentricity, Figure 6. As the study was focused mainly on compressive strength of consolidated mortar, five tubes for compressive strength and one plate for the tensile strength testing were prepared for each consolidation treatment mode (consolidation agent, number of applied cycles, application regime). Mortar specimens were left to harden for six months before consolidation substances were applied. The specimens were cured by slight spraying of distilled water for about one month to support a carbonation process.

Table 7. Specimens parameters

Specimen shape	Length cm	Width cm	Thickness cm	Volume cm^3	Treated surface cm^2	Porosity(MIP) %
tube (compression test)	3	4	0.55	17.3	37.7	27
plate (tension test)	10	4	0.5	20	40	

All specimens were conditioned before testing in a controlled environment (20 °C, RH 65%). Then the consolidation agents were applied, and after completion of the consolidation treatment the specimens were left to mature for another 60 days, which was sufficient to allow carbonation of the calcium or barium hydroxides applied into lime mortar specimens by lime water. In both cases (before consolidation substances application and before testing of treatments effects, the level of carbonation was checked by phenolphthalein testing.

The tubes for compressive strength testing were used for peeling tests before their destruction. The other tests (MIP, microscopic examination, water drop absorption, colour parameters) were carried out on samples prepared from the broken test specimens after compressive strength testing because the authors maintain a policy of testing as much as possible identical materials. Therefore, the tests follow a sequence from non-destructive to destructive ones.

2.1.3.2. Consolidation of mortar specimens

The following consolidation substances were applied: distilled water, calcium hydroxide saturated solution in water (“lime water”), lime water + metakaolin and barium hydroxide saturated solution in water (“barium water”). The applied consolidation substances are listed in Table 8 together with data relating the consolidation procedure applied on the tube specimens for the compressive test.

Water solutions of calcium hydroxide and barium hydroxide were prepared using chemical products p. a. (pro analysi) and distilled water. For the lime water solution 2 g of $Ca(OH)_2$ p. a. were put in 1 L of distilled water; for the barium water solution 5 g of $Ba(OH)_2.8H_2O$ p. a. were add in 1 L of distilled water and slightly mixed. The solubility of $Ba(OH)_2$ in water made it possible to prepare “barium water” with a higher concentration of barium hydroxide (5% weight) than for the lime water (0.16% weight). The lime water with metakaolin was prepared by mixing of 2 g of calcium hydroxide pro analysi and 2 g of metakaolin in l L of distilled water. Metakaolin used in our study for modification of the lime water was a finely ground burnt claystone, commercial name Mefisto L05 (České lupkové závody Inc., Nové Strašecí, Czech Republic) with relatively high amount of alumina (52.1% SiO_2, 43.4 % Al_2O_3). The metakaolin has the particle diameter at 50% of particles equal to 4 µm, 90% of particles size was smaller than 11 µm (Laser analyser CILAS 920). The specific surface area of the metakaolin was determined at 12.7 m^2/g using BET method (gas adsorption device Micromeritics ASAP 2020). The pozzolanic activity of the used metakaolin was determined as the important characteristic of this pozzolanic material using the modified Chapelle test [G. Cordeiro et al. 2008 and T. Perraki et al. 2005]. The obtained value was 1002 mg, which represents the amount of $Ca(OH)_2$ fixed by 1 g of metakaolin. The used method is based on the evaluation of reactivity of the metakaolin with calcium oxide in water. The mixture was kept at the temperature of 85 °C for 16 h., after that time the mixture was filtered and the remained CaO content was determined by means of sucrose extraction and titration with HCl solution [CSN EN 459-2 2010].

Lime water, barium water and lime water with added metakaolin were prepared one week before consolidation treatments and stored in closed glass barrels at laboratory conditions (25 °C, 40% RH) during the all experiment. For consolidation treatments a solution above the solid sediment was poured off and used.

Each agent was applied by continually dripping it from a syringe on to tubes fixed in a horizontal position on a rotating shaft, Figure 8, or lying on supports in a horizontal position (tensile specimens). The mortar specimens were fully saturated during each application of the distilled water or consolidating agent, and we recorded the amount of the agent that was applied. Two treatment schedules were intended for lime water, which was the main subject of the study: 50 resp. 160 series of application of lime water. The lower number of applications (50) represented the level recommended in the older literature, whilst the higher number (160) the maximal level of applied cycles followed the recent recommendation how to consolidate historic renders by means of many applied cycles of sprayed lime water into lime renders [Drdácký and Slížková 2012]. The same schedule (50/160 applications) was used for the distilled water treatment to study the difference between effects of lime water and distilled water. In respect to other two studied agents (lime water with metakaolin and barium water), the lower number of applications only was realized with a purpose to compare the obtained effects with lime water applied at the same condition. Particularly in case of barium water, where better effect on mechanical properties of consolidated mortar was expected with individual application, the higher number of applications (160) was consider as needless.

Two different variations of the drying time interval between two following saturations were tested for the lime water: first, 2 applications per day were performed, and the mortar tubes were allowed to dry completely before the following saturation (wet to dry alternative); and second, 3 applications per day were performed, and the new dose of the lime or destilled water was applied as soon as the mortar was capable of absorbing it, but before it dried out completely (wet to wet alternative). In case of the lime water with metakaolin and the barium water, only 3 applications per day (wet to wet alternative) were performed.

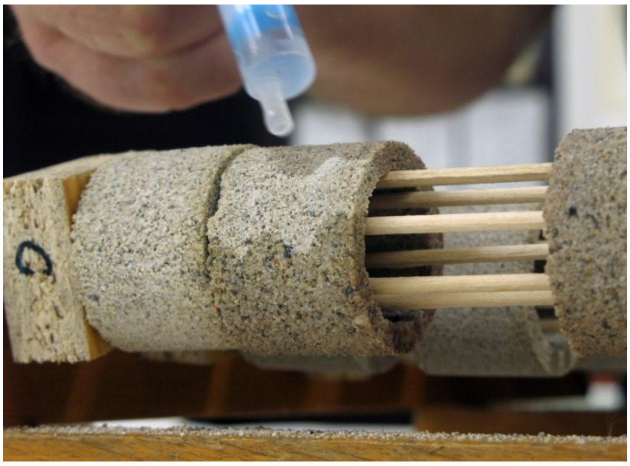


Figure 8. Impregnation of short tubes, using a syringe

Table 8. Data related to consolidation treatments applied on mortar tubes

Tested agent	Active substance	Number of applications per 1 day	Total number of applications	Total amount applied (l/m^2)	Total treating time (days)	Applied agent to specimen mass ratio (g/g)	Applied agent volume to the treated volume ratio (ml/cm^3)
Distilled water	Distilled water	2 (dry)	51	55	25	6.94	11.7
Distilled water	Distilled water	2 (dry)	161	180	80	22.83	38.4
Lime water	$Ca(OH)_2$ p.a.	2 (dry)	50	52	25	6.38	11.1
Lime water	$Ca(OH)_2$ p.a.	3 (wet)	58	58	19	7.12	12.2
Lime water	$Ca(OH)_2$ p.a.	2 (dry)	161	156	80	19.74	34.0
Lime water	$Ca(OH)_2$ p.a.	3 (wet)	160	155	54	18.72	32.2
Lime water + Metakaolin	$Ca(OH)_2$p.a. +Mefisto L 05	3 (wet)	58	55	19	6.50	11.7
Barium water	$Ba(OH)_2.8H_2O$ p.a.	3 (wet)	58	57	19	6.77	11.8

However, the intended number of application has not been managed in the experimental work precisely and really applied cycles of consolidating agents have slightly varied from the original schedule (58 cycles instead of 50 were realized for the wet to wet alternatives and 161 instead of 160 cycles for the wet to dry alternative). Also for the treatment of plates intended for the tensile strength test the number of applications was modified slightly. The purpose to study the influence of lower and higher repeated applications number for lime and distilled water was kept.

2.1.3.3. Mechanical characteristics

All mechanical tests were carried out on an electromechanical loading frame TESTATRON with the maximum loading capacity of 100 kN at laboratory conditions (RH 65%, T 20 °C), load cell Lucas 2 kN (typically for tension tests) or 10 kN (typically for compression tests) and crosshead velocity movement of 0.45 mm × min^{-1}. The short mortar tubes were loaded along the tube axis in compression, Fig. 7 right. The attained compressive strengths were checked against those measured on a set of rectangular specimens. The average compressive strength determined from the untreated tubular reference specimens was 0.260 MPa, and the average compressive strength measured on the rectangular specimens was 0.549 MPa, which corresponds after a low slenderness ratio correction [Drdácký 2011] to the cube compressive strength of 0.365 MPa. In fact, such a relation is not necessary for a comparative study of this type, because the effect of the individual agents was tested on identical specimens and the overall behaviour was compared. However, it follows from the results that the tubular specimens provide lower compressive strength - approximately 50% of the values measured on the rectangular 40 × 40 × 27 mm (non-standard) specimens, and that the poor mortar that was used really is weaker than usual historic masonry lime mortars, e.g. [Drdácký and Slížková 2008]. Of course, this “weak” mortar was very well compacted and integrated, and was not intended to model the typical sand-like disintegration of degraded mortars. In spite of the fairly good cohesion of the tested mortar, a quite extensive loss of surface material during treatment was observed, even though the treatment was very delicate. The same effect is typical for in situ applications, when the ancient mortar is sprayed with lime water (see further). The average compressive strength was calculated from tests on five specimens.

Tensile strength was tested on a small number of specimens (from one to two), and the values given here should be considered only as informative. The results of mechanical tests are presented in Figs. 9 and 10. In the Figure 9 all tested specimens are displayed with the average values (black colour fill). Mostly five specimens were tested, in few cases the fragile model mortar did not sustain treatment and movement and was damaged before testing. Then only four specimens were tested. It is seen in the Fig. 9 that the scatter of results was mostly very narrow.

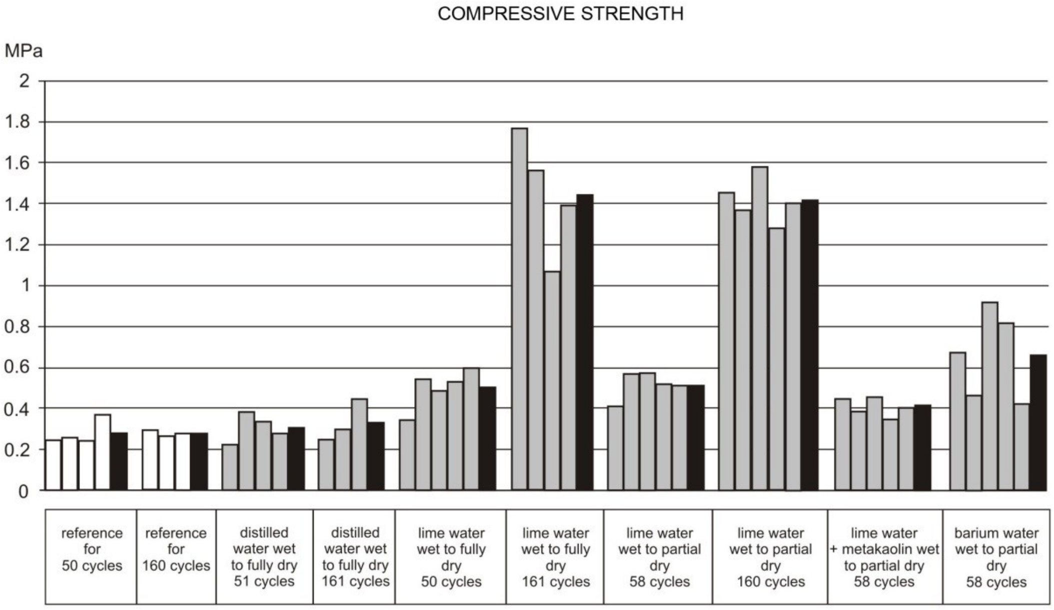


Figure 9. Results of compressive tests on tubes consolidated by various agents

Figure 10 shows that barium water treatment is about three times more efficient than lime water treatment, when the efficiency is measured by the change in the tensile strength, which corresponds to a higher concentration of the active compound (barium hydroxide) in the solution. The greater density of the newly crystallized tissue is apparent in the figures mentioned above. Both agents penetrate easily into such a porous mortar.

Fifty cycles of lime water with drying (two saturations per one day) and also 58 cycles of lime water applied more often (three saturations per one day), led to an increase in the compressive strength of the thin-walled tubes. However, this gain was very small. The results further show that there is no apparent difference in compressive strength between lime water application with total drying and with partial drying. There is a considerable increase in the compressive strength of a poor lime mortar after 160 cycles (in the case of two saturations per day, and also in the case of three saturations per day).

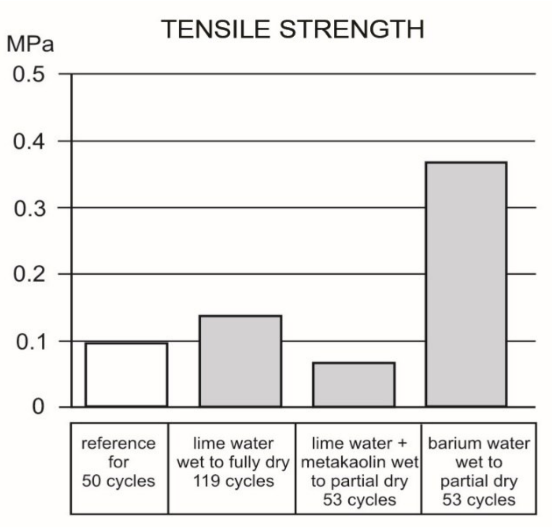


Figure 10. Results of tensile tests on thin plates consolidated by various agents

The combination of lime water with metakaolin did not provide any benefit. No detectable improvement of the lime water due to modification with metakaolin was observed. This indicates that the products of the pozzolanic reaction of metakaolin and calcium hydroxide in lime water were not water soluble, did not penetrate throughout the mortar, and therefore did not improve its compressive strength. The lime present in the lime-metakaolin suspension was partially consumed due to a pozzolanic reaction with metakaolin, and the following consolidation treatment of the mortar with lime-metakaolin water was less effective than simple lime water treatment.

Better results were achieved with barium water, although a direct comparison in terms of effectiveness of the active agent is biased by the higher concentration of $Ba(OH)_2$. Samples undergoing the same number of treatments (58) show a higher compressive strength when barium water was employed with respect to lime water. Although the observed improvement in mechanical properties is not as large as might have been expected considering the higher concentration of $Ba(OH)_2$ in the saturated solution, this allowed for a lower number of treatment and lower amount of water introduced into mortar to achieve the same result. As far as the tensile strength is considered, barium water granted much better results. In fact, the strength after consolidation was more than three times higher than that of the untreated reference mortar.

Distilled water didn’t show any consolidating effect on the tested mortar with a low lime content. In this case only compressive strengths were measured, and the difference from the reference specimens was insignificant. Probably the repeated dissolution and precipitation of the calcium carbonate presented in the treated mortar with a low content of lime, was not accompanied by a significant redistribution within the volume of the specimen and no relevant microstructural changes occurred.

2.1.3.4. Peeling tests results

The peeling method involves peeling off the surface material by sticking some scotch tape to the surface and then removing it [P. Mora and G. Torraca 1965]. The peeling test method is very sensitive to surface roughness, which leads to difficulties when testing mortars. Though the results correlate with the mechanical characteristics of the material, the relationship between the released material and strength has not been appropriately explained. However, this test can be used for a very rough check on the consolidation effect.

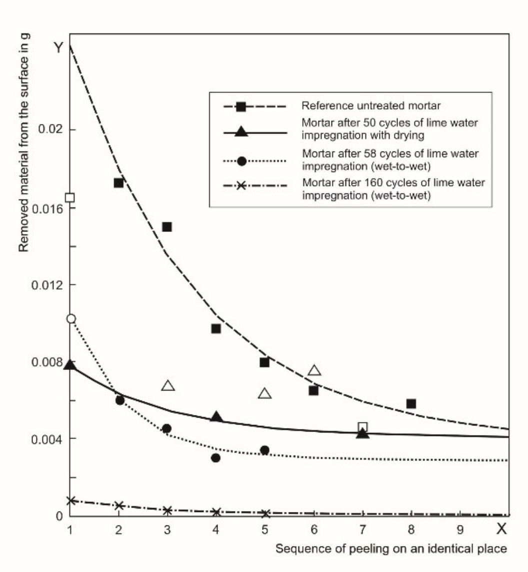


Figure 11. Peeling test on tubes after mature consolidation

In the authors’ experience, it is only necessary to keep to the recommended procedure, which consists of repeating the test on the same surface area several times (optimally 10 times) before applying the treatment, and doing the same again after the treatment. The recommended and correct procedure has been suggested in [Drdácký, Lesák et al. 2012]. Figure 11 shows that after 50 cycles of treatment with lime water no significant effect was observed. After 160 cycles, a positive effect is apparent. For the measurement a two-sided tape fix o moll®, 40 mm in width was used.

2.1.3.5. Change in structure

Solutions with higher amount of the active agent deliver a much greater amount of the resulting salt into the mortar, and help to form a stronger binding structure. Figure 12 illustrates the basic differences between untreated mortar and mortars treated with lime water and barium water, respectively, from the macroscopic point of view. (Pictures taken by an optical microscope SZP 11-TH, magnification 10×).

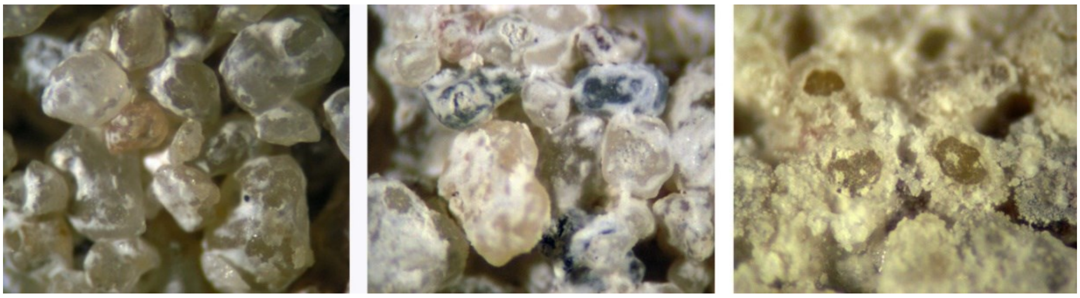


Figure 12. Macroscopic structure of the untreated weak lime mortar substrate: a (left) reference, b (central) 161 lime water saturations, c (right) 58 barium water saturations

At microscopic scale, Figure 13 shows a comparison on an identical scale of SEM (MIRA II LMU by Tescan Corporation) SE images of typical $CaCO_3$ and $BaCO_3$ formation after various treatments. It seems that calcium carbonate has grown in the columnar form in the untreated mortar, together with tabular crystals. The matrix is quite thin, with weak bridges. After 161 cycles of lime water treatment in the mode of full drying between subsequent applications, the matrix is filled with layers of newly-formed calcium carbonate in platelet form. However, the new material forms discontinuous clusters without regular and dense bridging. Figure 13c clearly illustrates the differences between the consolidating matrices of lime and barium water. Barium water obviously yields a denser and better-connected microstructure, which is reflected in the reported higher efficiency of barium hydroxide consolidation treatment. In fact, in both cases a nano-sized precipitated phase of carbonates is apparent.

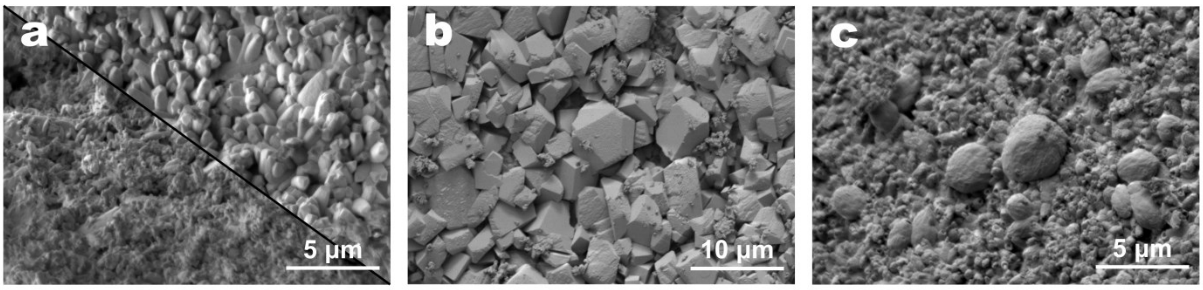


Figure 13. SEM-SE micrographs of the binder morphology: a (left) reference, b (central) 161 lime water saturations, c (right) 58 barium water saturations

A microscopic study of the cross sections by means of SEM-BSE, Figure 14, focused on the distribution of consolidants into the mortar specimen depth profile. External surface of the samples is in the upper part of each SEM-BSE micrograph. Figures 14a,b show calcium carbonate on the surface layer of the mortar, in the first case for the reference mortar, and in the second case for the mortar treated with 161 cycles of lime water, where a much thicker layer of calcium carbonate is visible. Figure 14c depicts the dense structure of the barium carbonate on the treated mortar surface.

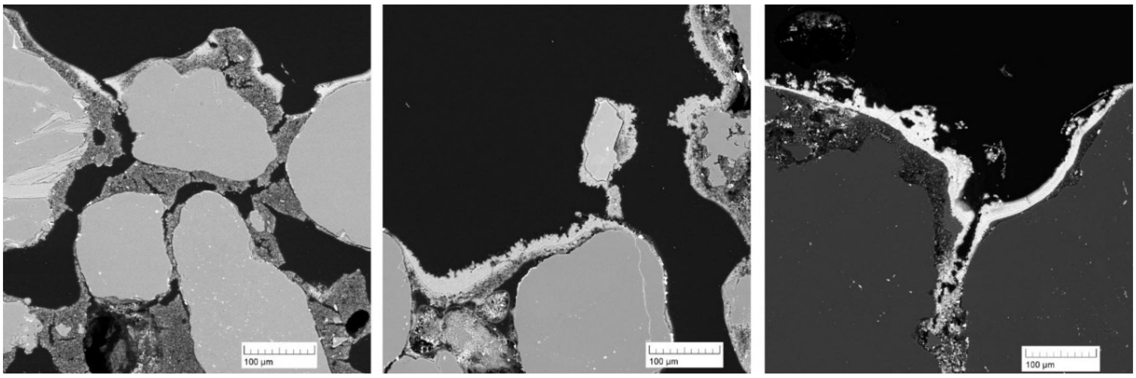


Figure 14. SEM-BSE micrographs of the structure of the new binder layer (cross section): a (left) reference, b (central) 161 lime water saturations, c (right) 58 barium water saturations, magnification 700x

The SEM-BSE investigation was supplemented by SEM-EDX (EDX by Bruker Corporation) elemental mapping of the cross sections. SEM-EDX investigations confirmed that the distribution of calcium (calcium carbonate) in the reference mortar and in the treated mortar with distilled water and lime water is rather uniform, and any difference between the different consolidation regimes could not have been distinguished by this method in the magnification that was used. Only the barium water treated specimens presented a significantly higher deposition of Ba (barium carbonate) on the mortar surface layer, Figure 15.

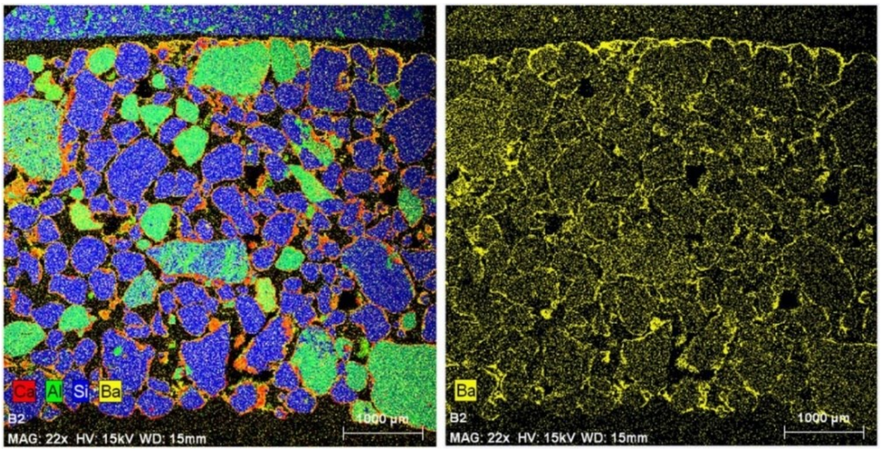


Figure 15. SEM-BSE micrographs of the lime mortar treated with barium water, magnified 22×:
a (left) distribution of Ca, Al, Si, Ba elements, b (right) distribution of Ba element

2.1.3.6. Change in porosity

The mercury accessible porosity and the distribution of pore sizes in the reference and consolidated mortars were determined by Mercury intrusion porosimetry, using a AutoPore IV 9500 (Micromeritics Corporation), with pressure range of 0.005-413 MPa. The mercury parameters were set to values of 485 erg/cm^2 for the surface tension of mercury and 130 degrees for the contact angle. Five samples were measured for each consolidation treatment and average values were calculated. It can be concluded from MIP data that all evaluated consolidation treatments slightly reduced the mercury accessible porosity of treated mortars (Table 9). For the lower number of consolidants applications (50-58 cycles) the porosity decreased by about 1 %, while for the higher number of application cycles (160) by approximately 3%. No significant difference was found for lime water with metakaolin compared to simple lime water. Barium water treatment decreased mortar porosity slightly more than lime water applied at the same condition.

Table 9. Porosity by MIP and a change of porosity due to consolidation treatment

Consolidant	Cycles	Regime	M porosity (% vol.)	M porosity change (% rel.)	Standard deviation (±) [%]	Variation coefficient [%]
Reference	0		27.22		0.36	1.33
Lime water	50	wet to fully dry	26.21	-3.7	0.42	1.60
Lime water	58	wet to partial dry	26.66	-2.1	0.78	2.93
L.w.+ metakaolin	58	wet to partial dry	26.47	-2.8	0.45	1.70
Barium water	58	wet to partial dry	26.4	-4.0	0.51	1.96
Lime water	160	wet to partial dry	24.48	-10.1	0.68	2.76

Concerning the mortar pore size distribution, the effects after treatments with lime water, lime water with metakaolin and barium water, are quite small, Figure 16. The volume of most frequent pores in mortar specimens decreased with increasing number of applied cycles of the lime water. Barium water treatment influenced the pore structure mainly in the range of pores from 0.005-1 µm creating more uniform pore size distribution. The lime water with metakaolin treatment did not show any significant difference compared to the reference mortar, Fig.16b.

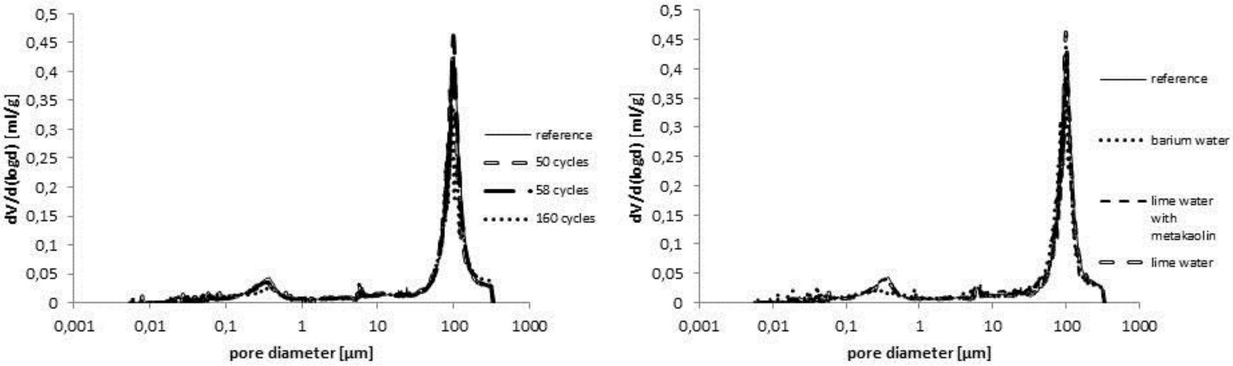


Figure 16. Pore size distribution of the lime mortar by MIP: a (left) the lime water treatments (various application cycles), b (right) other consolidants treatments (58 application cycles)

2.1.3.7. Water drop absorption results

The water drop absorption rate is defined as the time taken for a limited amount of water to be absorbed by the surface of the material [RILEM II. 8b (1980)]. A laboratory pipette filled with 0.01 ml of water was used in this experiment. The water drop was applied to the tube mortar specimen surface and the change in the behaviour of the untreated (reference) specimen and the specimen treated with a specific consolidant was evaluated. The time required for total absorption of the water dripped on to surface of the tube specimen from a height of 1 cm was observed by naked eyes and recorded using stop watch. A minimum of five measurements were performed for each consolidation treatment. The mean values of the absorption times for each treatment are reported in Table 10.

Table 10. Water drop absorption rate for individual treatments

Tested agent, active substance	Total amount of applied consolidant (l/m^2)	Applied agent to specimen mass ratio (g/g)	Applied agent volume to the treated surface ratio (ml/cm^2)	Applied agent volume to the treated volume ratio (ml/cm^3)	Absorption time of water drop (s)
Untreated reference specimen	0				< 1
Distilled water	55	6.94	5.52	11.7	< 1
Distilled water	180	22.83	18.17	38.4	< 1
Lime water, $Ca(OH)_2$	52	6.38	5.22	11.1	< 1
Lime water, $Ca(OH)_2$	58	7.12	5.84	12.2	< 1
Lime water, $Ca(OH)_2$	156	19.74	16.13	34.0	< 1
Lime water, $Ca(OH)_2$	155	18.72	15.36	32.2	< 1
Lime water + metakaolin	55	6.50	5.54	11.7	< 1
Barium water, $Ba(OH)_2.8H_2O$	57	6.77	5.68	11.8	358

For each of the tested water solutions, the change in the absorption rate was only observed for specimens treated with saturated solution of barium hydroxide. Although porosity and pores size of mortar specimens were relatively large, the barium water treatment of 58 cycles caused the significant reduction of water absorption rate. This founding corresponds with SEM-EDX observation, which proved a significantly higher deposition of Ba (barium carbonate) on the specimen surface (Figure 15).

2.1.3.8. Colour change and other application problems

Calcium hydroxide based consolidants require impregnation with a large number of applications or saturations, which may be accompanied by a colour change after carbonation, so-called whitening, white hazing or a blooming effect. Colour change was determined with a spectrometer Avantes AvaSpec 2048 equipped with Avasphere-IRRAD system for collecting reflected light from the surface of samples. Data were collected from the external surface of cylindrical specimens and expressed in compliance with the CIE L*a*b* standard notation. The mean values of three measurements for each point of analysis over three different samples for each treatment and for the untreated sample are listed in Table 11.

Table 11. *L*a*b** coordinates for the investigated specimens.

Tested agent	Number of applications per 1 day	Total number of applications	*L**	*a**	*b**
Untreated sample	0	0	66.8	1.7	7.2
Lime water	3	58	65.5	1.6	7.1
Lime water	3	160	70.1	1.5	5.1
Barium water	3	58	73.8	0.9	3.8

Although the sample surface was not flat, irregular and rather inhomogeneous (due to the presence of aggregates of different colour), the scattering of the data was relatively small and comprised between ± 0.5.

This allows for drawing the following conclusions: the effect of 58 treatments with lime water didn't appreciably change the colour of the sample. However, after 160 treatments, a clear whitening effect can be appreciated. Impregnation with barium water is much more effective in this respect, because lightness is 6 points higher than the untreated samples, and both a* and b* coordinates are much lower adding a clear white hue to the original sample. The intensity of such effect can be ascribed to the amount of $Ba(OH)_2$ introduced in the samples, much higher even than that of $Ca(OH)_2$ after 160 treatments.

Laboratory application and also practical application of lime water treatment is characterised by a remarkable loss of loosened material from the mortar or render surface.

This amount is influenced by the surface cohesion and the composition of the surface layers. On ancient historic façades, a rather compact and hard crust covers the more disintegrated or even "sandy" subsurface render layer. In these situations, the crust provides natural protection for the original subsurface substance. Repeated wetting with lime water very rapidly degrades the crust layer, opens the systems and makes the crust layer more vulnerable to weathering effects. The achievable consolidation of the sandy layer does not compensate for this negative consequence of the lime water treatment [Drdácký and Slížková 2014].

2.1.4. Conclusions

Lime water treatment of a specific lime mortar was shown to be effective after a sufficiently large number of applications (160 saturations) into a weak lime mortar. Some poor mechanical characteristics (compressive strength and surface cohesion) were improved substantially after such a large number of saturations. No consolidating effect of distilled water on the compressive strength of tested mortars with a low lime content (1:9) was observed. The higher concentration of barium hydroxide in its saturated solution resulted in higher compressive strength than in specimens treated in the same mode with lime water, but the increase was not as large as would have been expected according to the concentration of the barium water. The improvement in tensile strength, however, was much better: the strength after consolidation was more than three times higher than the strength of the untreated reference mortar. A microscopic study found differences between the consolidating matrices of lime and barium water – barium water clearly built a denser and better-connected substance. There was no detectable benefit of modifying lime water with metakaolin in terms of the mechanical characteristics of the treated mortar.

All evaluated consolidation treatments slightly reduced porosity of mortar. For the lower number of applications (50-58 cycles) the porosity decreased by 1 %, while for the higher number of application cycles (160) by approximately 3%. The presence of pores in the range 0.003-1 µm was detected in mortar treated with barium water. Concerning the distribution of the consolidants into the mortar specimens, a higher deposition of Ba (barium carbonate) on the surface layer of the mortar was detected by SEM-EDX. This finding corresponds with the results of the water absorption test, which showed a reduction in the water absorption rate for this consolidation treatment. On specimens after barium water impregnation, some whitening was slightly observable, while lime water tended to cause less remarkable whitening effect which was also confirmed by spectrometric measurements.

In studies of the behaviour of consolidants, trials on real objects and also laboratory experiments using model substrates representing a certain type of deteriorated material are an important tool. The task is very complex, and the reader should bear in mind that the tested mortar was cured in the laboratory – there was no surface crust layer or paint present, and there were no soluble salts in the treated material. This is not a common case in most practical situations. The research reported here did not aim to optimize the application of various agents, only to make a comparison under specific conditions. This should be understood in order to avoid misinterpretation of the results.

2.2. Consolidation of weak lime mortars by means of nano-lime and non-lime agents

2.2.1. Research aim

Lime water treatment on a specific lime mortar was tested and evaluated for effectiveness, showing that after a sufficiently high number of applications (160 cycles, 54-80 days of a permanent consolidation treatment) some of the poor mechanical characteristics (compression and surface cohesion) were substantially improved. The research presented in this paper (subchapter) aimed to test effects of other consolidation agents, mainly lime nanosuspensions and other consolidating agents: ammonium oxalate, silica nanosuspension (sol), silicic acid ester. The goal of the study was to compare the lime water treatment with some other less labour-intensive consolidation technologies.

2.2.2. Experimental

The specimens for testing were made of lime mortar prepared from powdered air lime hydrate and river quartz sand in a ratio of 1:9 by volume and were left to harden for six months. Then the consolidating agents were applied, and after the consolidation treatment, the specimens were left to mature for 60 days further. The same methodology, mortar and testing specimens parameters, as described in the chapter 2.1.3.1., was used for this experiment.

2.2.2.1. Consolidation of mortar specimens

The following consolidation substances were applied: calcium hydroxide colloidal solutions in alcohols ("nanolime" CaLoSiL E15, CaLoSiL IP25), calcium sulphate saturated solution in water ("sulphate water"), ammonium oxalate solution in water (2.5% resp. 5% w/w), colloidal solution of silica in water (silica sol), silicic acid ester (SAE) solution in ethanol (ethyl silicate) and various combinations of lime and silica based consolidants. Calcium sulphate solution treatments should resemble the phenomenon that occurs where the gypsum crust developed on the historical surface dissolves during the consolidation treatment from repeated watering and redistributes in the treated mortar layer. The applied consolidation substances are listed in Table 12 together with data of the consolidation procedure.

Commercial nanolime products CaLoSiL E15 and IP25 were applied without any adjustment. Silica-based products Dynasylan 40 and Kostrosol 0830 containing comparatively higher levels of silica were dissolved obtaining SiO_2 concentrations more suitable for poor lime mortar consolidation. Dynasylan 40 was dissolved with ethanol (1:4 weight parts) and Kostrosol 0830 with distilled water (1:9 w.). The final silica content in these products adjusted for mortar specimens treatment was about 8 % w. and

3% w. for Dynasylan and Kostrosol, respectively. Water solutions of calcium sulphate and ammonium oxalate were prepared using chemical products p.a. (pro analysi) and distilled water.

Table 12. Substances and consolidation treatment used in the experiment

Tested agent, active substance *% w.*	Commercial product (*d = diluted)*	Number of applications per 1 day	Total number of applications	Total amount applied (l/m^2)	Total time treatment (days)
Lime water + Silica sol	+Kostrosol 0830 *d.*	3	58 + 5	56 + 3.5	19 + 2
Sulphate water, $CaSO_4$ 0.26%	$CaSO_4.2H_2O$ p.a.	2	50	51	25
Sulphate water, $CaSO_4$ 0.26%	$CaSO_4.2H_2O$ p.a.	3	58	58	19
Barium water, $Ba(OH)_2$ 5%	$Ba(OH)_2.8H_2O$ p.a.	3	58	57	19
Ammonium oxalate water, 5%	$(NH_4)_2C_2O_4.H_2O$	3	58	27	19
Ammonium oxalate water, 2.5%	$(NH_4)_2C_2O_4.H_2O$	3	38	32	13
Nanolime, $Ca(OH)_2$ 1.5%	CaLoSiL E 15	12	40	30	3.5
Nanolime, $Ca(OH)_2$ 1.5%	CaLoSiL E 15	7	7	6.5	1
Nanolime, $Ca(OH)_2$ 2.5%	CaLoSiL IP 25	12	40	24	3.5
Silica sol, SiO_2 3%	Kostrosol 0830 *d.*	3	5	3.5	2
Silicic acid ester (SAE), SiO_2 8%	Dynasylan 40 *d.*	2	2	1.5	1
Silica sol 3% + Nanolime 2.5%		3/ 4	5 + 4	3.5 + 3.5	2 + 1
SAE 8% + Nanolime 2.5%		2 /4	2 + 4	1.5 + 3.5	1 + 1

Two different variations of the drying time interval were tested: first, 2 applications per day were performed and the tubes were allowed to dry completely before each new application; and second, 3 applications per day were performed with each additional treatment completed on partially wet mortar. Sulphate, barium, ammonium oxalate water and nanolime dispersions were applied in 38-58 cycles. Some consolidating treatments were performed to study the effect of agents after 2 to 7 applications made during 1 or 2 days (silicic acid ester, silica sol, lime nanodispersion). When combining two products, the second consolidating agent was applied 24 h after the first product application. Two months after the completion of the mortar consolidation treatments, compression strength tests were then performed.

2.2.2.2. Mechanical characteristics

The short mortar tubes were loaded along the tube axis in compression (chapter 2.1.3.3., Fig. 7 right). Results are illustrated in the graphs depicted on Figures 17 and 18.

The consolidation effect of lime water was substantially improved when it was combined with colloidal silica (silica sol). 5 cycles of 3% solution of silica were applied at the beginning of this treatment and then 58 cycles of lime water followed. This approach significantly increased the effect of lime water impregnation.

Ammonium oxalate (2.5% concentration, 38 applications), showed strengthening similar to lime water after 58 applications. The lower concentrated solution (2.5%) penetrated better than the higher concentrated solution (5%) where accumulation of salt crystals in the mortar surface layer was evident. The sulfate water treatment provided a negligible increase in compressive strength of the mortar.

The most significant increase in strength was achieved using nanolime products CaLoSiL, which was applied in multiple cycles for comparison with lime water treatment. Very good results were found in mortars consolidated with CaLoSiL E 15, with 7 applications. Because ethanol evaporates quickly, the 7 cycles of the product were applied in one day. The least labourious (2 cycles) consolidation treatment was completed using diluted Dynasylan 40 (SiO_2 content in the applied agent 8% w.). The combined treatment of silicic acid ester with low content of SiO_2 (diluted Dynasylan 40) following the application of nanolime product (CaLoSiL IP 25) was shown to be effective in terms of both time and strength increase. Comparing the effects of CaLoSiL E 15 and IP 25, the tests concluded that a higher concentration of the active substance does not always lead to higher strengthening. Consolidation with CaLoSiL IP 25 is likely to lead to reduced (less uniform) distribution of the new binder in mortar specimens, when compared to lower concentrated CaLoSiL E 15 treatments.

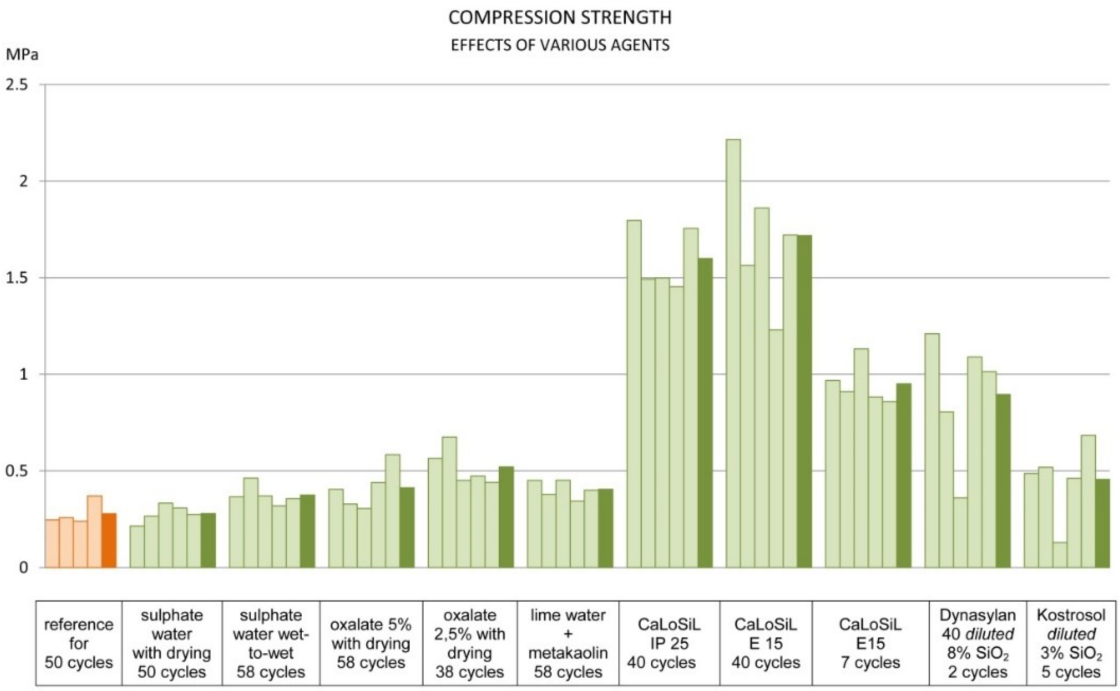


Figure 17. Selected consolidation treatment influence on compression strength of specimens

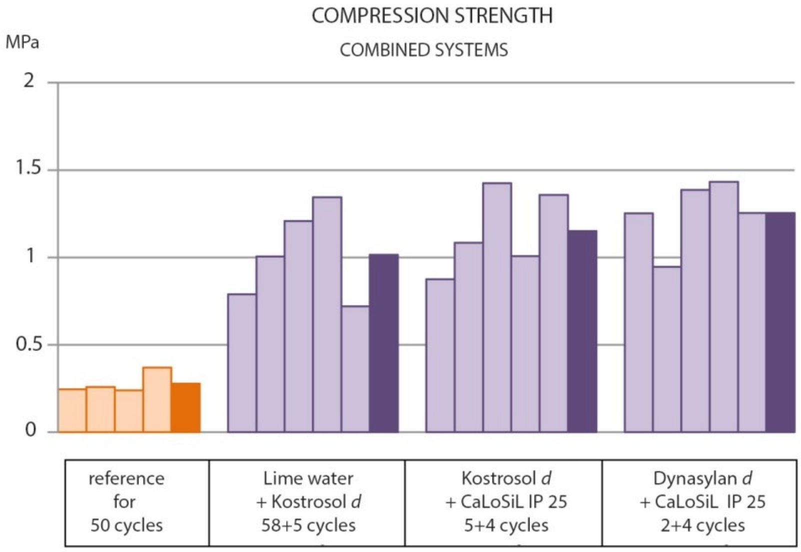


Figure 18. Influence of consolidation treatment based on combination of two agents

2.2.2.3. Peeling tests results

The peeling test, also known in the literature as the Scotch Tape test, established by Drdácký [Drdácký, Lesák et al. 2012] has been used for assessing the surface consolidation or strengthening efficiency of treatments (see also the chapter 2.1.3.4.). Main application strategy of this procedure exploits repeated peeling in the same place on a surface in order to eliminate the effect of the natural decrease in the detached material from the subsurface layers, which might be incorrectly interpreted as a consolidation effect. When sticking and peeling is repeated several times, the amount of detached material starts to become almost constant and characterizes the cohesion of the material.

For the evaluation of the weight measurements of detached material amounts a nonlinear approximation model was adopted. This model type was necessary namely if the data converge to some positive, i.e. non zero value, which is typical for testing of consolidation effects on degraded mortars. Then the constant A could be considered as a value describing the cohesion quality of the near surface material layer. Three parameters – A, B and C – described the cohesion quality and they were computed using the following approximation:

$$m(n) = A + B * e^{-C*n}$$

where m(n) denotes the removed material’s weight (mg). According to the peeling-test model, unperturbed material’s cohesion manifests itself as a constant amount of removed material in peeling sequence, denoted as ***A*** in the formula. This weight corresponds to the fragments broken apart from the surface in the process of affixing the strip on the surface.

It assumes that this component would remain constant if the peeling is repeated again and again.

In the experiment, areas without gross defects and imperfections were selected and the tape, sized 10 mm × 45 mm, was placed on the measured surface. The tape was smoothed into place by finger. After approximately 90 seconds of application the tape was removed by seizing the free end and pulling it off steadily at rate of about 10 mm/s and at angle of 90°. Then the sampler was weighted with stuck material. The test was then repeated ten times at the same location. For the each consolidation treatment, 5 mortar specimens were tested and the mean value of computed constants ***A*** of the individual specimens was evaluated. Results for the all assessed treatments are listed in the Table 13.

The treatments tested provided favourable results and considerable reduction in removed surface material are listed as follows: diluted silicic acid ester (81% reduction), diluted silica sol (85%), nanolime CaLoSiL E 15, 7 cycles (87%), sulfate water (93%). All other consolidation treatments caused 100% change, where any material was removed from the mortar surface during the test with the used tape. The efficiency of the consolidation treatments in relation to the surface cohesion was characterized well by the peeling test, however the results are different from the compressive strength results, which refer closer to the structural characteristics.

Table 13. Results of water drop absorption and peeling test

Tested agent, active substance % w.	Total amount of applied consolidant (l/m^2)	Absorption time of water drop (s)	Peeling test *A* constant (mg)
Untreated reference specimen	0	< 1	4.720
Lime water + Silica sol	56 + 3.5	< 1	0
Sulphate water, $CaSO_4$ 0.26%	51	< 1	0.326
Sulphate water, $CaSO_4$ 0.26%	58	< 1	0.125
Ammonium oxalate water, 5%	27	1,6	0
Ammonium oxalate water, 2.5%	32	< 1	0
Nanolime, $Ca(OH)_2$ 1.5%	30	394	0
Nanolime, $Ca(OH)_2$ 1.5%	6.5	50	0.634
Nanolime, $Ca(OH)_2$ 2.5%	24	610	0
Silica sol, SiO_2 3%	3.5	< 1	0.694
Silicic acid ester (SAE), SiO_2 8%	1.5	13	0.910
Silica sol 3% + Nanolime 2.5%	3.5 + 3.5	2	0
SAE 8% + Nanolime 2.5%	1.5 + 3.5	< 1	0

2.2.2.4. Water drop absorption results

The water drop absorption rate is defined as the absorption time of a limited and finite amount of water by the surface of the material (RILEM 1980), the same methodology as described in the chapter 2.1.3.7 was used for the experiement. The water drop was applied on the tube mortar specimen surface (Fig. 19) and the change in the behaviour of untreated (reference) specimen and the specimen treated with a specific consolidant was evaluated.

The most significant reduction in water absorption due to a consolidation treatment was achieved with nanolimes CaLoSiL when the products were applied in 40 cycles. The CaLoSiL IP 25 applied in 7 cycles also caused noticeable change in the water absorption behaviour. A slight decreasing effect was found after consolidation with silica sol and CaLoSiL (5 + 4 cycles) and after silicic acid ester application. The reason of the reduction in the second case (SAE) is probably a change of the wettability of the treated mortar in consequence of the higher contact angle of water (> 90°) on the slightly hydrophobic mortar specimen. The low reduction of the absorption rate was observed also for specimens treated with 5 % solution of ammonium oxalate. It was proved in the presented experiment, that the water drop absorption test is a simple, fast method, giving reasonable information about the change of water behaviour when water is applied on untreated and treated surface.

Figure 19 Test of the water drop absorption rate

2.2.3. Conclusions

The lime water treatment was compared with some other technologies that are less labour-intensive. The most efficient agents were suspensions of calcium hydroxide in alcohols, which are marketed under the trade name CaLoSiL by the German producer IBZ Freiberg. Their major advantage is that they can be applied much more rapidly than tens to hundreds of lime water cycles and that they deliver higher amount of lime in a one cycle. The efficiency of suspensions in alcohol is signalled by a one-day application of CaLoSiL E15 (7 cycles), where there is a significant strengthening effect.

In terms of chemical composition, calcium hydroxide water solution (lime water) and also nanolimes (alcohol colloidal solutions) are supposed to be suitable for consolidation of calcitic porous materials, such a limestone, lime mortar and marlstone. Besides the different lime content and solvent, these lime agents differ in the particle sizes resulting in penetration ability. This should influence their application preference. While lime water contains calcium ion, sized about 0.1 nm, calcium hydroxide particles in CaLoSiL are considerably larger (50-200 nm). This property defines the use of nanolime dispersions for structural consolidation of porous material with a sufficiently large pore diameter. On the other hand, the content of calcium hydroxide in lime water is very low (1.7 g/l at 20 °C) and therefore in cases where it is necessary to add larger quantities of lime in a shorter time, or where repeated watering of the wall could be risky, CaloSiL products with higher lime content (5-25 g/l) could be the preferred agent. It seems from the results that lower concentration of CaLoSiL (E 15) provided a better distribution of the new binder in the mortar structure and higher compression strength than the more concentrated CaLoSiL (IP 25).

Like lime water and nanolime dispersions applied calcium hydroxide into mortar, silica sol and silicic acid ester introduced into the treated material amorphous silica. The amount of active substance (SiO_2) in the commercially available products is generally 100 to 500 g/l, which is a much higher content compared to lime based agents. Also when taking the required strength of mortar into account, diluted solutions of these products are more suitable for the consolidation of deteriorated mortar. Diluted, 8% silicic acid ester applied in two cycles was shown to be equally effective as CaLoSiL E 15 applied in 7 cycles. Silica sol, diluted down to 3 %, was found be less effective, but in combination with lime water or CaLoSiL led to substantial improvement in strength. The combination of CaLoSiL and diluted silicic acid ester also appeared to be promising.

Surface cohesion of mortar was achieved with most of the tested consolidation agents. When ammonium oxalate was applied in two different procedures, the lower concentrated solution (2.5%) gave better strength results. 5% concentrations of ammonium water in context with its multiple applications (58 cycles) caused a reduction in water drop absorption. As expected, the most significant reduction in water absorption due to consolidation treatment was found after 40 cycles of nanolimes CaLoSiL treatment. When CaLoSiL IP 25 was applied in 7 cycles it also caused noticeable change in the water absorption behaviour. A slight decreasing effect in the water absorption rate was found after consolidation mortar with silica sol and CaLoSiL (5 + 4 cycles) and after the silicic acid ester application. In the second case the reason of the reduction was probably the residual hydrophobic character of the mortar specimens.

Success of the consolidating process is influenced by many factors. The basic characteristics and parameters need to be taken into account when designing optimal consolidation treatment, such as chemical, mineralogical composition, strength, size, shape of pores, porosity of treated material, further size of ions, molecules or particles of the active substance in the consolidation product, chemical composition and concentration of the active substance in the product, the drying rate and setting time of the new binder during and after expected ambient conditions.

Knowledge of these parameters is a good basis for the design of a consolidation treatment (type of consolidation agent, the concentration of active substance, method of application, the number of repeated applications during a consolidation process, the method of treating the substrate after impregnation). An important tool in the study of the behaviour of consolidants are trials on real objects as well as laboratory experiments using model substrates representing certain type of deteriorated material. The task is very complex and the reader should bear in mind that the tested mortar was cured in laboratory - there was no surface crust layer or paint present and there were no soluble salts in the treated material, which is not a common case in most practical situations. The research reported here did not aim to optimize the application of various agents, only to make a comparison under specific conditions. This should be understood in order to avoid misinterpreting the results.

2.3. Comparative study of strengthening effects on weak mortars consolidated with various consolidants; study on various types of mortar

2.3.1. Research aim

While previous studies (chapters 2.1. and 2.2.) have focused on the effects of consolidation treatment under the conditions that consolidants were applied according to conservators´ recommendations or according to recommendations published in the literature, this study has focused on the comparison of consolidants´effects under testing condition assuring unified amount of a solid consolidant (30 mg) application within 1 cm^3 of mortar specimen. The solid consolidant means the binder forming component contained in the applied consolidation product (e.g. calcium hydroxide in lime water or silica in silica sol). The strengthening capacity of various consolidants applied at conditions of unified quantity of the solid consolidating component per the volume unit of the mortar specimen was investigated.

Also, the range of consolidated mortar was extended in this study. Not only one type of lime mortar was used for the experiment but various mortars with different sand were impregnated.

2.3.2. Experimental

Commercial products (CaLoSiL IP 15, KSE 100) and chemical solutions prepared in laboratory by dissolving chemicals in water (barium hydroxide, ammonium oxalate, ammonium phosphate) or by dilution more concentrated products (Syton X 30) were used for the experiment. Also some combinations of lime based and silica based consolidating liquids were tested to study synergetic effects of both products. Consolidants were applied on specimen surface using an automatic manual pipette. The volume of the consolidant to be applied within the mortar specimen during one „cycle“ (usually in one day) was chosen individually for each specimen in order to reach full saturation of mortar. In case the consolidant needed to be applied more than once, the following dose was applied after the previous one had dried. Table 14 gives names and abbreviations of solid components contained in various consolidants tested. The term ‘‘cycle’’ is used for the impregnation of the mortar specimen with a consolidant and following the subsequent drying out of the treated mortar. The required amount of a consolidant for total impregnation cycles was calculated based on the mortar specimen volume and the consolidant concentration. The amount of 30 mg of the binder forming solid component was applied per 1 cm3 of mortar regarding all consolidants tested and all mortar specimens.

After completion of impregnation, the mortar specimens were left for at least 90 days at laboratory conditions and then subjected to mechanical tests. In addition to the mechanical properties that were the main subject of study, also microstructure and water transport properties (the water absorption rate, vapor permeability) of mortars were observed.

2.3.2.1. Testing specimens

Former experimental studies for testing efficiency of lime water on mechanical characteristics of lime mortars successfully used thin-walled mortar specimens in the shape of tubes for compression strength and thin plates for tension test [Slížková et al. 2015; Moreau et al. 2010; Drdácký & Slížková 2012].

Thin specimens enable even distribution of the consolidation agent across the entire volume of the test specimen, and shorten the time for maturing. The same specimen shapes were therefore used also in the present study. In addition to the thin specimens, beams for measuring the bending strength of mortars were prepared and tested. Figure 20 illustrates shapes of specimens for different strength testing, the specimens parameters were following: tube 29 × 39 × 5.5 mm, plates 60 × 40 × 6 mm, beams 101 × 20 × 20 mm.

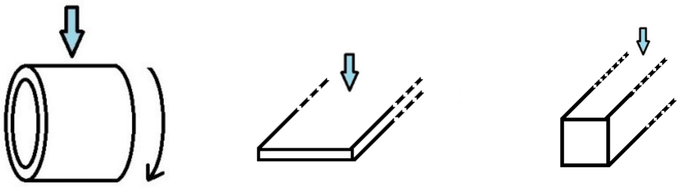


Fig. 20 Specimens shape: tube for compression, plate for tension, beam for flexural strength.

The specimens were fabricated from a weak lime mortar which was previously prepared using sand (9 volume parts) and small quantity of lime hydrate (1 volume part) with water. Six specimens of the same shape and same mortar composition were tested as reference samples to found out mechanical characteristics of the specific mortar and then sets of six specimens were tested for each consolidation liquid after the consolidation treatment of the mortar. In order to study the influence of the mineralogical composition of the mortar, various sorts of sand were alternatively used in the experiment for the mortar preparation: siliceous (mainly quartz) sand with semiangular to semirounded grains, quartzite crashed sand and limestone crashed sand. Possible chemical reaction of used sands with the lime binder was studied in special research by conducting of pozzolanic activity test [Frankeová & Slížková 2016]. All mortar sorts were prepared using the same part of sand of the same granularity and the same part of lime hydrate and water. Besides three sorts of lime mortar with different type of sand, one sort of earth mortar was prepared and tested in the study.

Table 14. Binder forming components in tested consolidants

Binder forming solid component	Consolidant	Symb.	Solvent
Calcium Hydroxide	Lime water, 0.16 w%	L	Water
Calcium Hydroxide	Nanolime CaLOSiL IP 15, 15g/L	CL	Isopropyl alcohol
Barium Hydroxide	BH -water solution, 4 w%	B	Water
Silica	Syton X 30, dil. to 10 w%	S	Water
Silica	KSE 100	KSE	Organic solvent
Ammonium Oxalate	AO water solution, 2.5 w%	AO	Water
Dihydrogen Ammonium Phosphate	DAP water solution, 5 w%	AP	Water

The consolidation treatment of prepared mortar specimens was conducted after all lime mortar specimens were fully carbonated. The carbonation rate of lime mortars was checked by means of thermal analysis. The illustration of the consolidated tubes is documented in Figure 21.

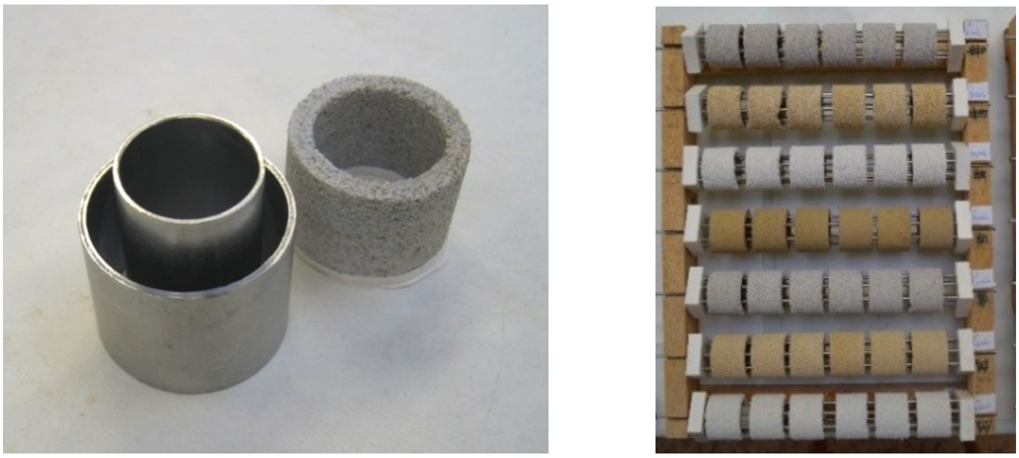


Fig. 21 Mortar tubes: specimen production (left) and arrangement of the consolidation treatment

2.3.3. Results and discussion

The experiments conducted on various types of mortar composition brought the knowledge that the strengthening efficiency due to consolidation treatment is influenced significantly by the characteristics of consolidated mortar. In terms of lime mortars and especially the mortar with limestone aggregate, the “nano-lime” (dispersion of calcium hydroxide nanoparticles in alcohol), marketed under the trade name CaLoSiL IP 15, proved to be very effective strengthening agent. Also the combined applications of lime-based consolidants (lime water or CaLoSiL IP 15) with silica- based consolidants (diluted

Syton X30 or KSE 100) have shown very good consolidation effects on lime mortars. Results are given in Figures 22 to 24.

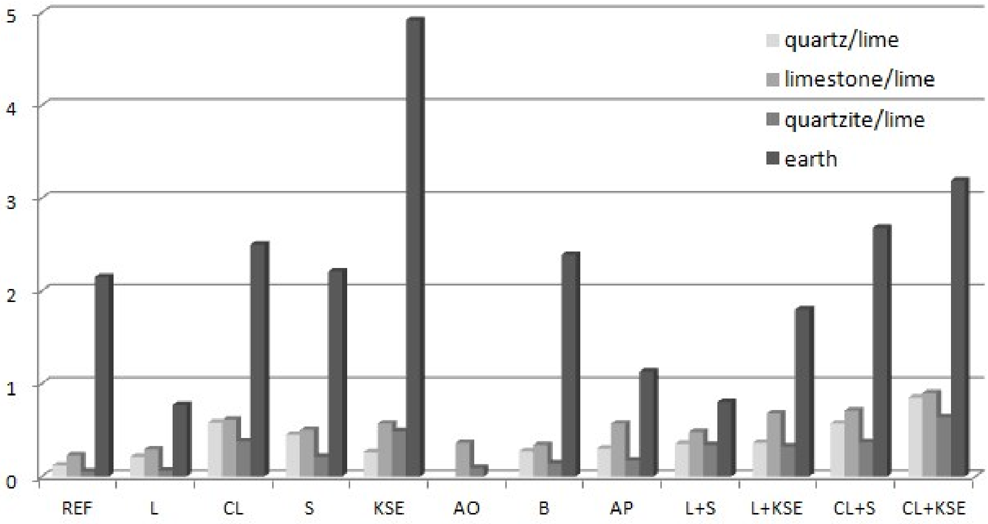


Fig. 22 Compressive strength (MPa) of mortar tubes: non-treated (REF) and treated with different consolidants (see abbreviations in Table 14). Mortars caption: aggregate composition/ binder composition

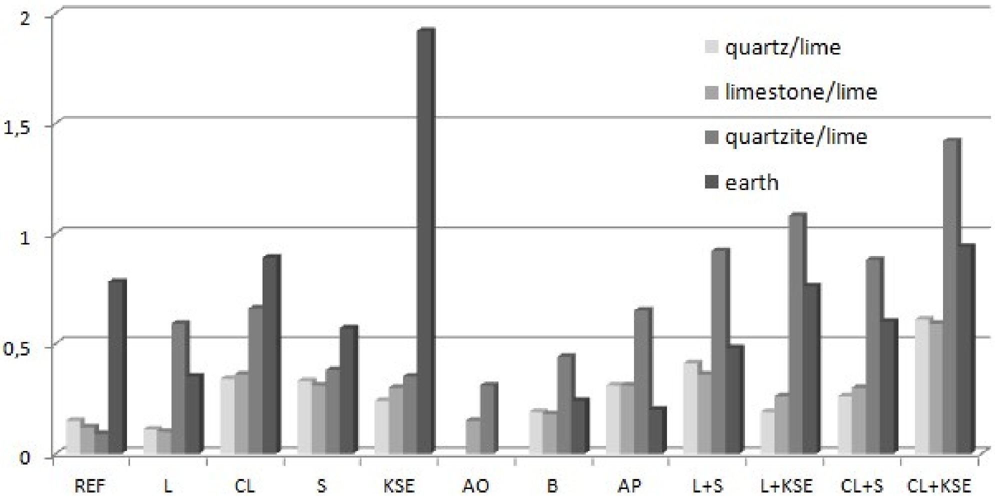


Fig. 23 Flexural strength (MPa) of mortar beams: non-treated (REF) and treated with different consolidants (see abbreviations in Table 14). Mortars caption: aggregate composition/ binder composition

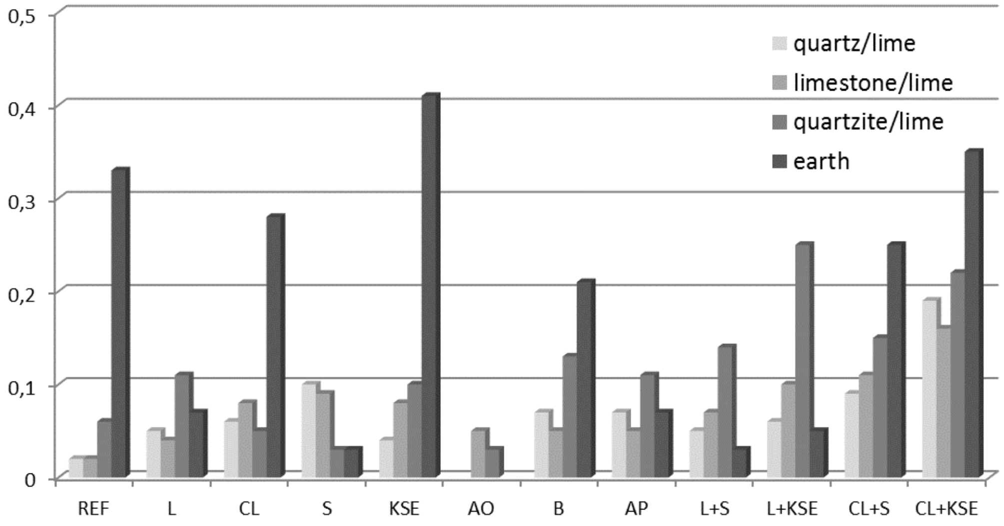


Fig. 24 Tension strength (MPa) of mortar plates: non-treated (REF) and treated with different consolidants (see abbreviations in Table 14). Mortars caption: aggregate composition/ binder composition

Entirely different results were achieved when the same consolidants were used for strengthening of earth mortar. For that mortar, KSE 100, product based on TEOS, was the most efficient consolidant in relation to strength improvement. Unfortunately, KSE 100 treatment caused significant inhibition of the water drop absorption into the treated mortar due to the change of the surface tension. However, water vapour permeability of tested mortars was not significantly changed after the consolidation treatments.

Contrary to the lime mortars results, only slight effect was found in the case of the earth mortar for CaLoSiL IP 15, probably due to low penetration of the consolidant into the material.

For the practical use, the financial costs of consolidation intervention represent one of the most fundamental aspects. Table 15 shows that treatments including lime water are several times time demanding than other.

Table 15. Total period of treatment (in days) of beam samples

sand/binder mortar composition	L	CL	S	KSE	AO	B	AP	L+S	L+KSE	CL+S	CL+KSE
quartz/lime	108	18	2	2		3	3	57	57	16	16
limestone/lime	108	10	2	2	8	3	3	57	57	9	9
quartzite/lime	108	13	2	2	13	4	3	57	57	9	9
earth	64	23	2	2		5	4	66	66	15	15

2.3.4. Conclusions

All the tested consolidation agents showed positive strengthening effect when they were used for consolidation of the poor lime mortar, with the exception of the influence of lime water on the flexural strength. Study of the pozzolanic activity of various types of sand in mortars showed that the grains of sand may be reactive with calcium hydroxide and can participate in the formation of hydraulic compounds when they are subjected to calcium hydroxide for a long time (several months at room temperature). In treated lime mortar samples, however, the products of this reaction were not detected, probably because of the relatively small amount of these substances in mortar and their X-ray diffraction amorphous character.

PART II. Consolidation treatment of stone

Chapter 3

Consolidation of porous limestone with nanolime products

The thesis´author focused on this topic intensively during her work as a researcher of the European project STONECORE dealing with the development and application of nano materials for consolidation and conservation of stone.

Performance evaluation of nanolime with the trade name "CaLoSiL" on Maastricht limestone was described in the article of Zuzana Slížková and Dita Frankeová, that was presented in 12th International Congress on the Deterioration and Conservation of Stone, Columbia University, New York (2012) and published on-line at http://iscs.icomos.org/pdf-files/NewYorkConf/slizfran.pdf: "Slížková, Z., & Frankeová, D. (2012). Consolidation of porous limestone with nanolime: laboratory study."

3.1. Research aim

The recent outburst of nanotechnologies has influenced the conservation science and has brought nanoparticles of calcium hydroxide dispersed in alcohols as a new form of treatment product based on $Ca(OH)_2$*. Nanolime products are an attractive choice mainly for the consolidation of substrates containing calcite considering the intended chemical similarity between the treated substrate and the treatment product. CaLoSiL® (introduced in October 2006) has been the first commercially available stone treatment product based on calcium hydroxide sol [*Ziegenbalg 2008; Drdácký et al. 2009*]. Another commercial product Nanorestore® was developed at the University of Florence (CSGI Consortium) and has been also studied by conservation scientists [e.g.* López-Arce et al. 2010*]. Consolidation action depends on the products' characteristics but also on procedures adopted for their application [*Ferreira Pinto et al. 2008*]. This chapter presents the influence of the repeated application (1 to 6) of CaLoSiL products of the lower and the higher concentration of* $Ca(OH)_2$ *on the limestone with high and large porosity.*

3.2. Consolidation of limestone with nanolime product CaLoSiL®

The treatment product CaLoSiL® is available in various concentration of $Ca(OH)_2$ from 15 to 50 g/l in different alcohols. However this product brings a much more effective alternative in relation to lime water [Drdácký and Slížková 2008], the concentration of the effective substance in the product is low when compared to the products based on silicic acid ester (100-500 g/l). Multiple applications of the CaLoSiL product can be considered when a higher consolidation effect is required [Drdácký and Slížková 2011]. This can be achieved either by multiple application of a low concentrated CaLoSiL or using a high concentrated product. The presented research studied differences in the both approaches when applied on a porous limestone. The assessment of the consolidating efficiency of the products was based on performance of both the destructive and the non-destructive laboratory tests: bending and compressive strengths, ultrasound velocity measurement and porosity determination. Except of the compressive strength the other characteristics were investigated in the depth profile of stone specimens in order to find the distribution of the treatment product within the stone layer. The testing aimed at a quantitative evaluation of the product strengthening effect and at a recommendation of an optimal treatment procedure for the selected type of stone and treatment condition (dry condition T 20-25 °C, RH 30-40 %).

3.3. Materials and Methods

3.3.1. Treatment products

Three variants of the commercial product CaLoSiL were used in the present study. The products contain $Ca(OH)_2$ particles dispersed in different alcohols (ethanol and isopropyl alcohol types were investigated). The particles size ranges from 50 to 150 nm. The producer of the agent is IBZ-Salzchemie GmbH & Co. KG, Germany. In the study an ethanol based type with two different concentrations of dispersed lime particles (25 g/L, 50 g/L respectively) and an isopropyl alcohol based type with concentration 25 g/L were examined. Trade names of the selected types are CaLoSiL E 25, CaLoSiL E 50 and CaLoSiL IP 25. The behaviour of differently concentrated CaLoSiL and the influence of a different alcohol medium were studied at consolidation of a highly porous limestone aiming improvement of material (calcite crystals) cohesion.

3.3.2. Stone

The laboratory experiment was carried out on the Maastricht limestone (Tab. 16), which is a material with low mechanical characteristics, a high open porosity and large pore sizes. These stone characteristics seemed to be suitable for such a consolidation study focused on the stone strength enhancement. Upper Cretaceous Maastricht limestone ("mergel") outcrops in the provinces of Dutch and Belgian Limburg. Formation represents one of the few native Dutch natural stones used for building and construction. The Maastricht limestone is very homogeneous, and layering is rarely observed. The only location where the Maastricht limestone can be quarried today is in Sibbe, Holland. Under the optical microscope [Rescic et al. 2010] the Sibbe variety shows a good sorting with grain dimension of about 100 μm. The grains, subangular in shape, are constituted mainly by sparitic calcite (shell fragments and skeletons of sea organisms) and secondarily by micritic calcite. There are also rare silicatic grains. The binder is scarce and constituted by sparitic calcite. The porosity is high (≈ 50%) and mainly constituted by macroporosity (most of all pores have a diameter ≈ 48 μm). The petrographic classification is grainstone and intrasparite. The decay of historic stone develops mainly through the detachment of the crust.

Table 16 Physical characteristics of Maastricht limestone

Stone	Water absorption by immersion	Water absorption coefficient	Bulk density	Open porosity	Main pore diameter
	% wt.	$kg/m^2 \, min^{1/2}$	g/cm^3	% vol.	μm
Maastricht limestone	34.4	20.2	1.3	50	48

3.3.3. Application procedure

Stone specimens were conditioned in the laboratory before the experiment. The treatment was performed on 5 × 5 × 3 cm^3 prismatic specimens and only one face of the specimen was treated with a certain volume of the product (30 ml). The product was applied by syringe pouring the stone surface until the total volume of 30 ml of the product has been soaked. The volume (30 ml) was chosen as a result of a preliminary test when the amount of the product needed for the wetting of 75 cm^3 (5 × 5 × 3 cm^3) stone specimen had been determined. The selected volume (30 ml) does not refer to the volume needed for full saturation of the stone but for its impregnation by capillary absorption when the front of the product (visible by darkening of the impregnated stone material) reaches the bottom of the stone specimen. The time needed for the first and for the successive applications (2-6) was measured.

Specimens for the bending test, US and porosity investigated in depth profile were treated on the face 5 × 3 cm^2. Since the multiple application of the products was studied, two specimens were impregnated twice, another two specimens four times and the last two specimens six times. The break between every single impregnation represented 4 days. This time was sufficient for drying out of impregnated stone under the laboratory condition which had been found on the basis of an individual preliminary test. Stone specimens were not covered by any impermeable coating which should control evaporation of alcohol from the impregnated material and so the drying process of the stone went through all specimen faces and was relatively fast thanks to alcohol medium of the nanolime and also to a high and large stone porosity. Stone specimens were able to absorb 30 ml of the nanolime product even in the case of the sixth application but the time needed for the repeated impregnation increased for some types of the CaLoSiL product.

Specimens for the compressive test had the same parameters (5 × 5 × 3 cm^3). These specimens were impregnated by the same manner like the previous specimens with one difference that the product was applied through the face 5 × 5 cm^2 to the depth of 3 cm.

The maturing of impregnated stone specimens occurred in dry conditions (laboratory environment, 20-25 °C, 30-40 % RH) without any special care. The testing of impregnated specimens started one month after the consolidation treatment.

The stone specimens were analysed with several techniques in the following order: propagation of US velocity, bending test and open porosity distribution by MIP – all in the depth profile, and water accessible porosity and compressive strength.

Results from the performed tests are expressed as an average value gained from individual measurements of two specimens treated with the same procedure.

3.3.4. Methods

The US velocity was measured with a portable instrument USG 20 (Krompholz Geotron Elektronik, FRG) with a 250 KHz transmitter (USG-T) and receiver (USE-T). The measurement was taken in a direct transmission/reception mode, across opposite parallel sides of the specimen. In a first step, the untreated stone specimens were measured in all three spatial directions (one measurement for the one axis) so that the difference between X, Y and Z axes was found for each specimen and an unified geometric orientation for all specimens could be set before the treatment. Only one geometric plane was selected for a more detailed study. Then the depth profile of ultrasound velocities was measured with a step of 7 mm in the direction from the treated top surface to the bottom (Figure 25a). The measurement points were marked on the stone specimens and the comparative test after the specimen treatment could be taken using the same points and tracks. The diameter of the flat contact area on the transducer was 2 mm.

The bending strength values in the depth profiles of not treated and treated specimens were tested on thin plates. The 50 mm depth was cut to slices and so 8 rectangular thin plates of the depth 3.7 mm ± 3 mm with the top side parallel to surface were created (Figure 25b). Slides were marked 1 to 8 and their specific positions relating the original surface were registered. Bending strength and the Young's modulus of elasticity were then tested on these small-size partial specimens, which resulted in the knowledge of strength values in relation to the location of a stone layer in the original stone specimen.

This way of testing enabled to determine the strength values distribution along a depth profile perpendicular to the surface. The specimens were tested in three point bending in a special rig after long term conditioning in laboratory (20-25 °C /RH 30-40%) using load cell Lucas 100 kN for the load measurement, LVDT 1 mm sensor for the deflection measurement, at the cross head speed of 0.15 mm/min.

Even tough the destructive character of this method does not allow the performance of these tests before and after the treatment on identical specimens, a quite good homogeneity of stone along the selected axis enabled the evaluation of the strengthening effect by means of comparing the strength values obtained on different not treated specimens and different treated specimens of the same type of stone.

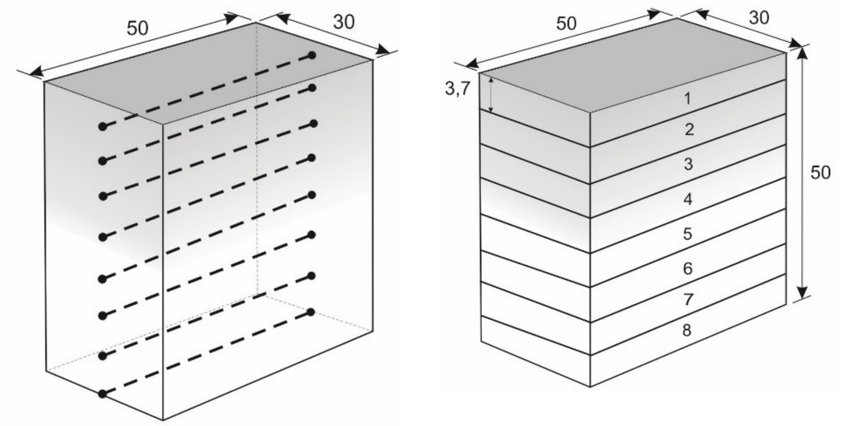


Fig. 25 a (left) Layout of the US velocity measurements from top to bottom, b (right) Layout of a specimen cutting to slices for detailed bending strength tests.

The open porosity and its distribution in the studied materials were determined by Mercury intrusion porosity, using a Quantachrome porosimeter, model Poremaster PM-60-13 with pressure range of 0.005-413 MPa. The mercury parameters were set to values of 480 erg/cm^2 for the surface tension of mercury and 140 degrees for the contact angle. The samples were dried out before the test and a penetrometer of 1 cm^3 was used for the measurement. After performing the bending test the broken stone slices were used for porosity characterization.

The hydric behaviour through the stone was studied on specimens 50 × 50 × 30 mm^3 (treated surface 50 × 50 mm^2). The determination of the porosity accessible to water was carried out following RILEM recommendation [RILEM 1980]. The compressive strength was tested on the same specimens like hydric characteristics using load gauge Lucas 50 kN, sensor Megatron 25 mm, load speed 0.45 mm/min.

3.4. Results and Discussion

The time needed for the first and for the each successive application (2-6) indicates a possible change of transport characteristics of the CaLoSiL within the stone in case of the repeated applications. The best results were obtained for the CaLoSiL E 25 which needed roughly the same time (around 300 s) to penetrate the specimen from the top to the bottom for the first and for the following applications. Simple measurement showed that even in case of the 6th application the penetration coefficient of this product did not change significantly.

Figure 26 illustrates that a different behaviour was found for CaLoSil IP 25 and E 50. After the first three applications the time needed for specimens impregnation increased as the product penetration ability got worse especially in case of the highly concentrated CaLoSiL E 50. The accumulation of these products in some parts of the stone specimen is probable the reason for the rise of the penetration time in cases of the 4th to the 6th application.

The determination of the ultrasonic (US) velocity profiles seems to be a suitable tool for the estimation how an even or uneven distribution of the product's effective compound (calcium carbonate in this case) has developed within the stone specimen after the treatment. The US velocity in the untreated specimens was 1.7-1.8 km/s and the profile was quite homogenous (see Fig. 27). Most of the treated specimens showed an increased velocity in the surface area (top and bottom), probably as a result of the cumulation of the consolidation product during the evaporation period.

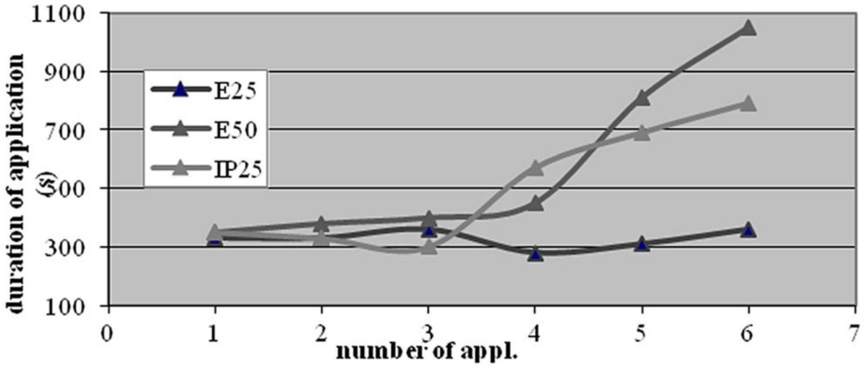


Fig. 26 Times needed for wetting of a stone specimen with 30 ml of CaLoSiL in relation to the successive number of application.

The increased US velocity in the bottom region gives an evidence that products penetrated the all depth of the specimen (5 cm). The rise of US velocity due to the treatment represents about 5 % of the original value in a central part of a specimen for the lower concentration and about 13% for the higher concentration after 2 applications. In the surface area the increase of velocity was 2-3 times higher compared to the central part of the stone. The consolidating effect (US velocity) increased more after successive applications (4-6) but more intensively in the area near the surface. It seems from the US velocity measurements that multiple applications of the CaLoSiL products lead to cumulation of the product within the surface region and this trend is more significant in case of the higher concentrated studied type - CaLoSiL E 50. The optimal procedure for consolidation of the investigated stone seems to be 2 applications of the lower concentrated types - CaLoSiL E 25 or IP 25. Different behavior of the products E 25 and IP 25 has not been found in case of the US velocity tests: the differences between the velocity profiles are quite low for the both products with a different alcohol medium.

The US velocity corresponds with the stone modulus of elasticity and characterizes its change resulting from the consolidating treatment very sensitively. Bending strength profiles (see Fig. 28) brought similar results but in detail these data have a higher scatter, which is probably influenced by local defects. Considering the distribution of the strength in the profile the better results were found on stone consolidated by 2 applications only. The higher number of applications went to an uneven distribution of the product in the stone which was followed by an increase of the strength in the surface part.

The strength rise considering overall stone specimens is illustrated in Figure 29 for both the bending and the compressive strengths. The distribution of the strength in the stone specimen profile is not considered in these graphs: the average values of the specimen strength are shown (for the bending the average is calculated from individual slices strength of 2 specimens and the compressive strengths were determined by testing 2 specimens 5 × 5 × 3 cm^3). The increase of the average bending strength value of a specimen represented 45% after 6 applications for E 25, 63% for IP 25, and 100% for E 50. The rise of the compressive strength was 93% for E25, 47% for IP 25, and 126 % for E 50 after 6 applications. After 2 applications (which seems to be a suitable treatment amount relating the even distribution of the product in the stone) the bending strength increase represented 20% (E 25), 18% (IP 25) resp. 54% (E 50) and the compressive strength increase 50 % (E 25), 23% (IP 25) resp. 73% (E 50). The presented test results support conclusions that two applications of the CaLoSiL products seem to be the optimal procedure for the treatment of porous limestone. When a stronger strengthening is needed the higher concentrated product E 50 applied with care may be useful.

The porosity investigations correspond with previous results. The values of the open porosity obtained on specimen 5 × 5 × 3 cm^3 were quite optimistic: the porosity decreased due to the treatment (Tab. 17) but not dramatically. MIP method used for the testing of porosity in the depth profile showed its uneven distribution coming from a bigger influence on pores near the surface (see Fig. 30) even after 2 applications.

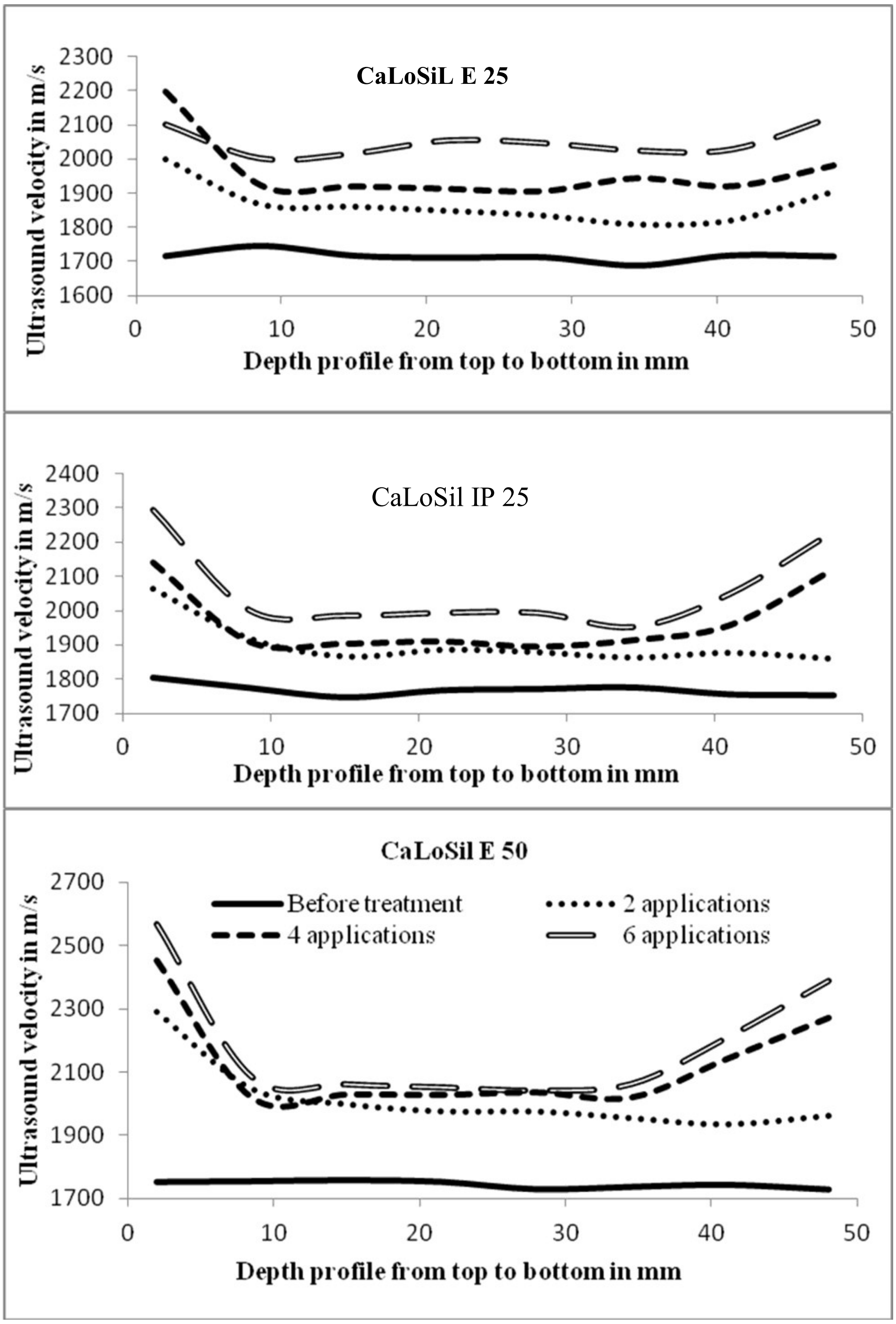


Fig. 27 US velocity in depth profile for the Maastricht limestone before and after treatment with CaLoSiL IP 25, E25 and E 50.

Concerned the stone color the local white hazes appeared on the surface of some specimens (IP 25 and E 50 after 6 applications of the products). White staining was not found for specimens treated with the CaLoSiL E 25.

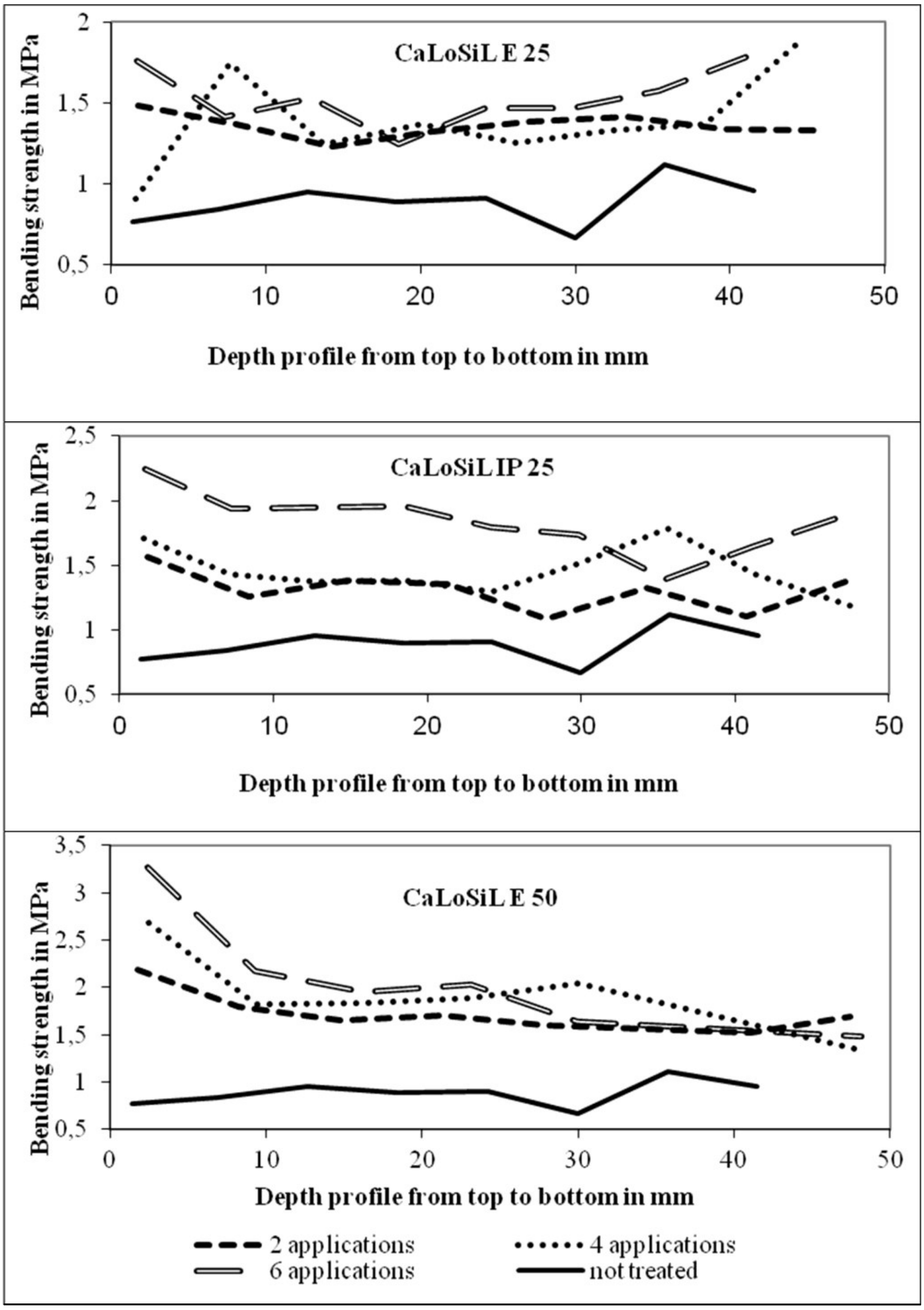


Fig. 28 Bending strength of stone slices in the depth profiles for not treated specimens and the specimens treated with E 25, IP 25 and E 50.

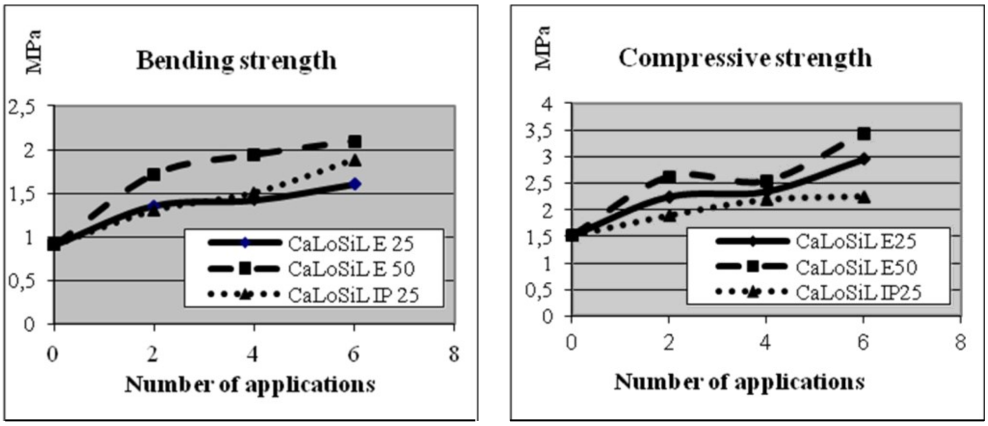


Fig. 29 Increase of bending strengths (left graph) and compressive strengths (right graph) of the Maastricht limestone due to consolidation with multiply applied the CaLoSiL products.

Table 17. Reduction of water accessible porosity of the Maastricht limestone due to consolidation with 6 applications of the CaLoSiL products

Maastricht limestone	Water accessible porosity (RILEM I/1)	Decrease of porosity	
	%	% abs.	% rel.
untreated	50.3		
treated by 6 cycles E 25	47.4	2.9	5.8
treated by 6 cycles IP 25	47.4	2.9	5.8

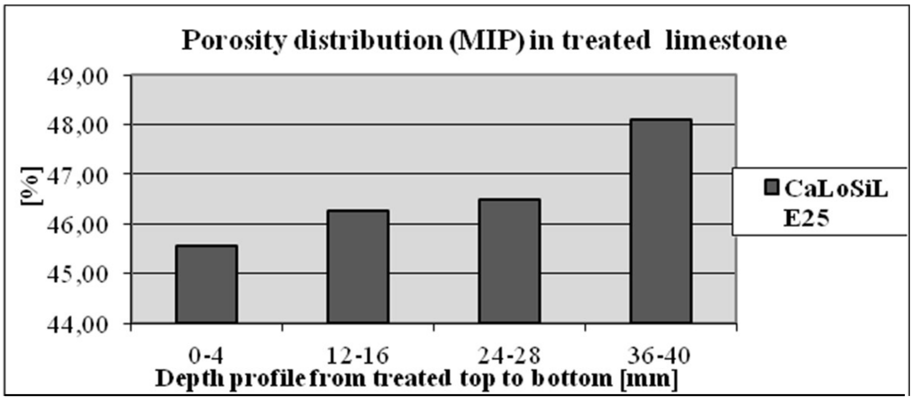


Fig. 30 Distribution of open porosity values (MIP) within the treated specimen depth profile (CaLoSiL E 25, 2 applications).

3.5. Conclusion

The appropriate amount of the product (both the concentration of the effective compound and the sum of applications) has to be chosen in relation to the stone porosity and the treatment condition in order to achieve the regular distribution of the product in the substrate. The optimal procedure for consolidation of investigated stone seems to be 2 applications of the lower concentrated types CaLoSiL E 25 or IP 25. Application of the products with a different alcohol medium (CaLoSiL E 25 and IP 25) generates rather low observed differences measured by the US velocity and the strength in the depth profiles. The higher sum of performed applications resulted in an uneven distribution of the product in the stone specimen which was followed by the increase of the strength in the surface part. The local white hazes appeared on the surface of some stone specimens after 6 applications of the products IP 25 and E 50.

Chapter 4

Modifying the consolidation depth of nanolime on Maastricht limestone

This chapter proposes a new method to achieve an in-depth homogeneous deposition of calcium hydroxide nanoparticles in Maastricht limestone, which consists of applying water immediately after the application of the consolidant. The work also demonstrates the reliability of an imaging technique using differential X-ray transmission radiography for the mapping of the consolidation action without requiring the use of labeling substances.
The chapter is based on a publication: "Niedoba, K., Slížková, Z., Frankeová, D., Nunes, C. L., & Jandejsek, I. (2017). Modifying the consolidation depth of nanolime on Maastricht limestone. Construction and Building Materials, 133, 51-56". The article presents results of the project „NAKI DF 11P01OVV012 researched at the ITAM CAS (2011-2015) under leadership of the thesis´author.

4.1. Distribution of the consolidant inside the stone porous structure

Building materials exposed to weathering agents deteriorate gradually from the surface inwards. A degradation intensity gradient is formed, which is characterized by e.g. differences in mechanical strength and porosity. The knowledge of the properties of this gradient is useful when investigating consolidation treatments to reestablish the material properties to its sound condition, i.e. non-gradient condition. There are several methods of analysis that can be used for the estimation of the degradation and consolidation depth profile, e.g. drilling resistance [Rodrigues, 2002], X-ray tomography [Dewanckele et al. 2012], ultrasound wave velocity [Pinto & Rodrigues 2008]. Some authors use labeling substances to follow the consolidant transport and its final distribution using neutron and X-ray radiography [Slavíková et al. 2012 and 2014]. However, in some cases, especially in samples with fine pores and large internal specific surface area, the material acts as a chromatography column and the motion of the marker may differ from the movement of the consolidant. Thanks to recent advances in technology e.g. [Boone et al. 2014 and Banerjee et al. 2015], it is now possible to follow the consolidants' distribution without the need of markers e.g. [Cnudde et al. 2007, de Argandoña et al. 2009] and avoid results' inaccuracies.

The consolidation of deteriorated porous stone and mortar using the capillarity absorption of liquid compounds has been a straightforward method in conservation science for decades [Torraca 2008]. The impregnation method is governed by physical principles and can only be controlled by the restorer up to a limited degree. Moreover, the presence of moisture in the porous materials in natural exposure conditions can interfere with the strengthening agent. Thus, it would be desirable to have more control over the final distribution of the consolidant.

Calcium hydroxide nanosuspensions have been proved to be efficient consolidants [Natali et al. 2014; Slížková & Frankeová 2012], and there are several methods for their manufacture e.g. [Daniele & Taglieri 2012; Liu et al. 2010], including a new environmentally-friendly method [Asikin-Mijan 2015]. There are at least two commercial products available and its particle size spans from tens to hundreds of nanometers; the carrier medium is alcohol-based. However, the consolidation efficiency of these nanolime suspensions can be compromised by several aspects. The essential requirement for a successful consolidation treatment with nanolime is the adequate accessibility of the pore size of the substrate to the consolidant. It has been reported that if the pore diameter is of one order higher than that of the nanoparticles in the suspension, a penetration depth of about 5 cm can be reached [D'Armada & Hirst 2012]. However, problems arise during the evaporation of the solvent leading to partial back-migration of the nanolime particles towards the exposed surface. Borsoi et al. [Borsoi 2016] observed a dense nanolime deposition at 0.5 mm from the exposed surface of a limestone treated with nanolime, although the stone (Maastricht) had been saturated with nanolime up to 4 cm depth. This phenomenon is obviously affected by the environmental conditions, e.g. high temperature and high air flow velocity lead to a rapid evaporation of the solvent and, con-sequently, to the increment of lime deposition close to the surface.

One of the most important features of nanoparticle suspensions is its dispersion stability. In the case of lime nanoparticles suspensions in alcohols, sedimentation of the nanoparticles takes place over time, which can lead to its aggregation. Obviously, if the particles aggregate, they lose the penetration ability. Thus, the stability of nanosuspensions is another important parameter that can influence the consolidation efficiency, which is irrelevant in the case of non nano-structured consolidants. This paper focuses on a new method to modify the distribution of nanolime inside the porous structure of limestone (Maastricht) by using water to disperse the nanoparticles and to reduce the solvent evaporation rate. The consolidation action was directly monitored through label-free X-ray radiography. Drilling resistance measurements were also performed to assess the in-depth strengthening effect.

4.2. Materials and methods

4.2.1. Materials

The nanolime product used in this study was CaLoSiL pro-duced by IBZ-Salzchemie GmbH & Co. KG, Germany. CaLoSiL is available in various concentrations of $Ca(OH)_2$, from 15 to 50 g/l, in different alcohols and is ‘‘ready to use.” In this study, an ethanol-based product with two different concentrations of nano-lime particles (25 g/L and 50 g/L, labeled CaLoSiL E25 and CaLoSiL E50, respectively) was employed; the average particle size of CaLoSiL products is 150 nm [Technical Leaflet, CaLoSil, 2016].

Maastricht limestone was selected for this study given its homogenous structure characterized by low mechanical strength, high open porosity (ca. 50%) and unimodal pore size distribution (see Fig. 31). These properties were considered suitable for this consolidation study focused on the stone in-depth strength enhancement. Moreover, in practice, it is very difficult to obtain stone material weathered in natural exposure conditions for laboratory testing, and Maastricht limestone shows physical characteristics that are, in general, close to natural deteriorated stone. The Maastricht limestone samples used in this study were quarried in Sibbe (The Netherlands), which is the only place available nowadays for quarrying this stone. The specimens’ dimensions were 20 × 20 × 20 mm and 20 × 20 × 40 mm. In all experiments, the samples were coated with silicone to have unidimensional absorption and drying through one of the 20 × 20 mm surfaces.

4.2.2. Methods

Differential X-ray transmission radiography was used to map directly the consolidant distribution inside the stone. The X-ray source was set to a voltage of 90 kV and a current of 500 lA. The X-ray detector used was a scintillation Flat Panel with a resolution of 2048 × 2048 pixels, the size of one pixel corresponding to 200 × 1 m. The geometry of the imaging system was set to achieve 2× magnification. The experimental apparatus is shown in Fig. 32.

Drilling resistance measurements were performed with a TER-SIS T1 system from Geotron-Elektronik (Germany). The drilling resistance test consists of drilling a hole and measuring the force required for the drilling under controlled rotation speed and perforation rate. The drilling holes (ca. 5 mm in diameter) were made perpendicular to the exposed surface, i.e. across the nanolime impregnation path. Three specimens were tested and at least three holes were performed in each sample.

4.2.3. Testing procedures

4.2.3.1. Unmodified consolidant distribution in Maastricht limestone

The investigation of the Maastricht limestone consolidation was firstly carried out using X-ray radiography to follow the drying process and characterize the final distribution of the nanoparticles within the stone matrix. Six cubic specimens, 20 × 20 × 20 mm in size

(Fig. 33), were impregnated with several solutions. The reference specimens, labeled R, did not receive any treatment and were used for the normalization of the images to suppress errors caused by the inevitable fluctuation of the X-ray radiation. Specimens #1 and #4, treated with pure solvents (water and ethanol, respectively), were used to verify if the solutions introduced had evaporated completely at the end of the experiment. A special sample holder was manufactured to position the specimens and allow its image acquisition at the same time (Fig. 32). The first image was acquired with the specimens in the dry condition. A determined volume of each consolidant (1.3 ml) were then poured into the top containers (Fig. 32). The volumetric amount of consolidant was pre-determined experimentally, used volume corresponded to the one-third of the pore volume. In order to achieve high image statistics and suppress image noise, the automatic image acquisition time was set to one frame per 30 s, thus allowing to observe small changes in the material density. The analysis was performed at room temperature and the entire experiment took 24 h.

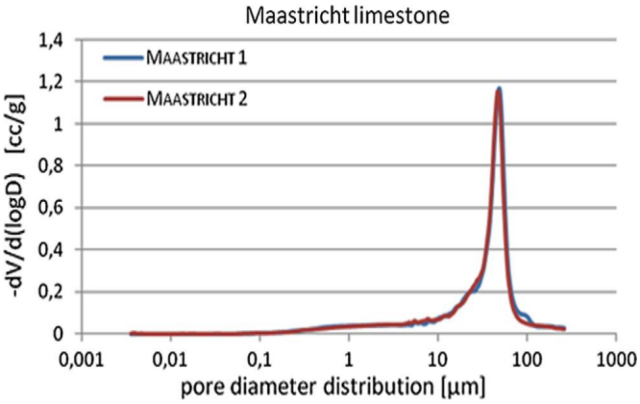


Fig. 31 Pore size distribution of Maastricht limestone

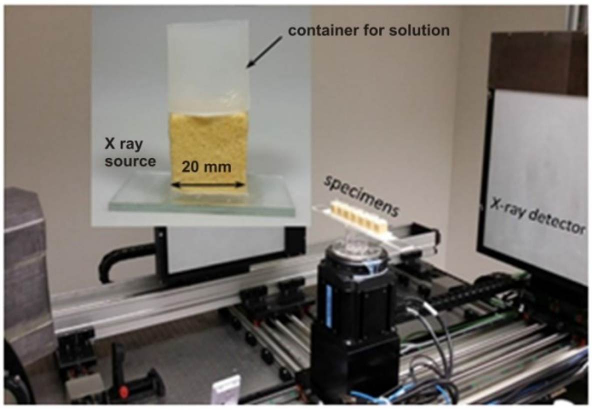


Fig. 32 Experimental apparatus of the X-ray radiography measurement

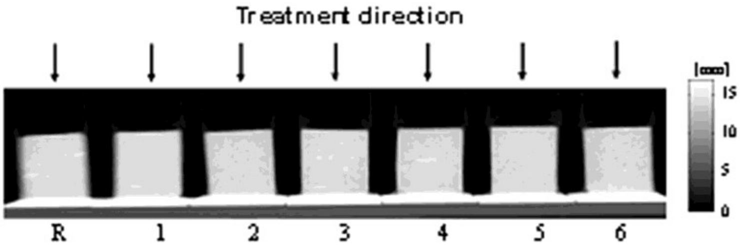


Fig. 33 Limestone samples (with a container on the top) attached to a glass slide; R - reference, #1-water, #2 - lime water, #3 - barium water, # 4 - ethanol, #5 - CaLoSiL E25, #6 - CaLoSiL E50.

The X-ray images were normalized by the intensity of the reference specimen. Subsequently, they were corrected for beam hardening effect using a set of aluminum filters. The resulting image after performing the corrections is shown in Fig. 34. In order to evaluate the increment in density assigned to the presence of consolidant, the results were processed through the following equation:

$$I_{DIFF} = \frac{I - I_0}{I_0} \qquad (1)$$

where I_0 is the initial pixel intensity (reference specimens), I is the pixel intensity from the specimens with consolidant, and I_{DIFF} is the differential pixel intensity, which expresses the increment in density. However, this operation is only possible if the initial imaging geometry is maintained throughout the entire experiment. Unfortunately, the sample holder cracked during the experiment causing slight shifts on the samples' images. To tackle this problem, an image matching method based on the Lucas-Kanade algorithm [Lucas & Kanade 1981]. An iterative image registration technique with an application to stereo vision was employed. Each specimen was matched individually throughout the image sequence; Fig. 34 shows a diagram of the image matching process for specimen #1.

4.2.3.2. Modified consolidant distribution in Maastricht limestone

In this experiment, larger samples were used to be able to perform drilling resistance measurements. Prismatic specimens 20 × 20 × 40 mm in size were coated with silicone leaving one side exposed (20 × 20 mm). CaLoSil and distilled water were applied, water immediately after CaLoSil , by immersion of samples in the given volume of the liquid. The volume of CaLoSiL was con-stant (2 ml) while the water volume was either 0.5 ml or 1 ml.

Next, the samples were left to dry with the treated surface facing up. The X-ray radiography imaging was done using the reference (non-treated) samples and the treated samples after drying.

The drilling resistance measurement is not as sensitive as X-ray imaging in detecting the consolidant; one application is visible on the X-ray images, but would be barely identifiable by the drilling method. Therefore, eight subsequent applications were performed to detect reliably the consolidant by the drilling method. Each application was done after evaporation of the ethanol; the time interval between applications was one day. The carbonation of CaLoSiL took place in laboratory conditions during the subsequent application process and, after finalizing the application sequence, the samples were stored in CO_2 chamber (25 LC, 65% RH, 3% CO_2) for one week to accelerate the carbonation process.

4.3. Results and discussion

4.3.1. Unmodified consolidant distribution in Maastricht limestone

Fig. 35 shows the average density evolution over time of the sam-ples treated with CaLoSiL. The ethanol in the reference specimen (#4) evaporated completely after 10 h. Ethanol is the carrier medium of CaLoSiL nanoparticles and has no contribution to density increment, so the final increment in density is only attributable to the nanolime consolidation effect. The comparison between the density distribution in the sample treated with CaLoSiL E25 (#5) and in the sample treated with CaLoSiL E50 (#6) is given in fig. 36. Three main zones can be clearly distinguished by their differences in density. The higher density at the surface (superficial layer) is probably formed by the movement of the suspension towards the surface where the solvent evaporates and the nanoparticles deposit. The two other zones, located deeper inside the material, were probably formed by the decrease in the amount of ethanol while diffusing into the deepest empty pore structure of the material, thus contributing to the deposition of nanoparticles and creating interfaces between treated and non-treated areas. The difference between CaLoSiL E25 and E50 (Fig. 36) is quantitative, which is in line with the concentration of nanoparticles in each product.

4.3.2. Modified consolidant distribution in Maastricht limestone

The idea of applying water over the samples treated with CaLoSiL was to promote the dispersion of the nanoparticles within the stone matrix, thus avoiding heterogeneous differences in density. Fig. 37 shows a sample treated with CaLoSiL E25 and the sample treated with CaLoSiL E25 and water. Disregarding the intrinsic stone heterogeneity, it is possible to observe significant differences in the final distribution of the nanolime particles. First and most importantly, the water treatment prevents the formation of the high density layer at the surface. This can be partially attributed to the expected slower drying process in comparison with the CaLoSiL treatment alone, because water is less volatile than ethanol. Moreover, the application of water immediately after the nanolime treatment promotes the dispersion of nanoparticles throughout the porous structure, thus contributing to the homogenization of the consolidation action.

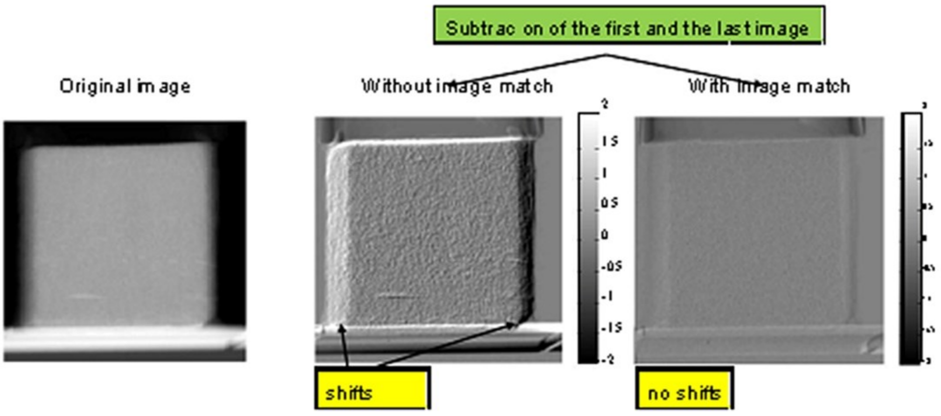


Fig. 34 Diagram of the image matching process in Maastricht limestone (specimen #1).

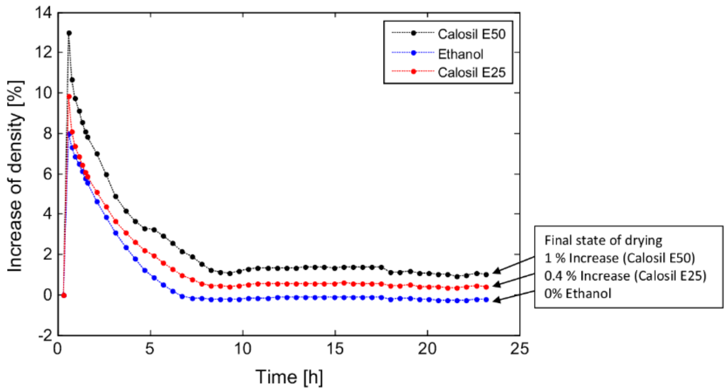


Fig. 35 Density evolution over time in the reference (blue – sample #4 treated with ethanol) and CaLoSiL-treated samples (red – sample #5 treated with CaLoSiL E25, black – sample #6 treated with CaLoSiL E50).

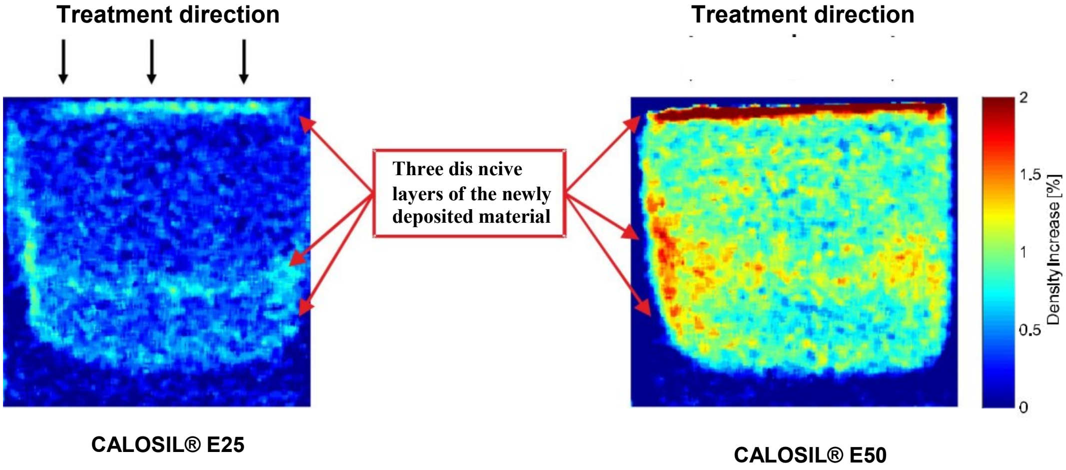
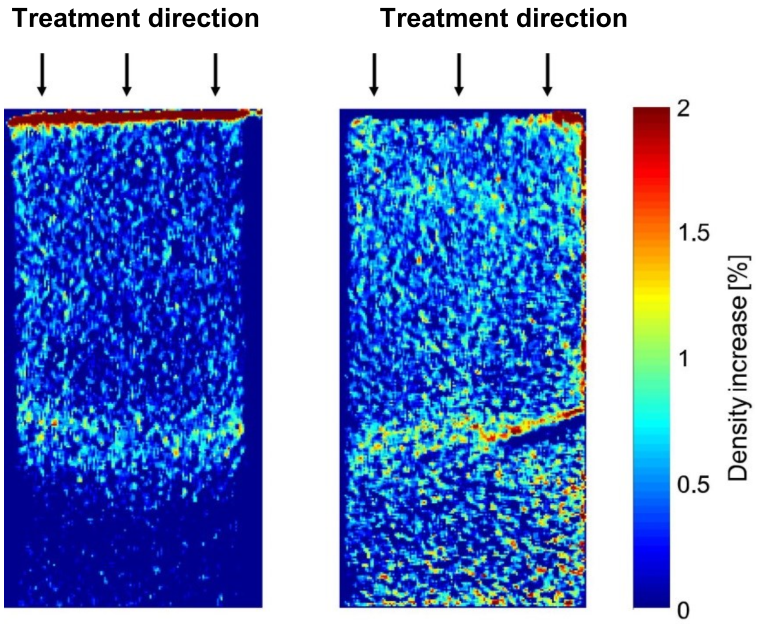


Fig. 36 X-ray radiographic images: comparison between samples treated with CaLoSiL E25 and E50.



2 ml CaLoSil®E25

2 ml CaLoSil®E25 + 0.5 ml H_2O

Fig. 37 X-ray radiographic images of samples treated with CaLoSiL (left) and CaLoSiL and water (right).

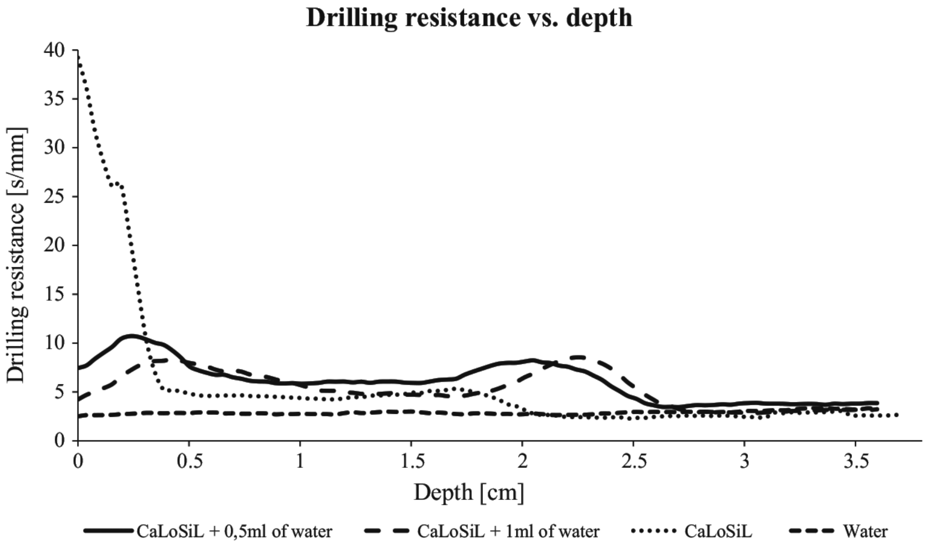


Fig. 38 Consolidation effect of CaLoSiL on the drilling resistance of Maastricht limestone

Fig. 38 shows the consolidation effects on the stone drilling resistance between the different treatments. The results obtained in the sample treated with CaLoSiL (without water) show a high increment of the drilling resistance nearby the surface. Moreover, the surface showed a white coloration, which is not acceptable in conservation interventions. In contrast, the samples treated with CaLoSiL showed an in-depth consolidation profile. The results are in line with those obtained by X-ray radiography and indicate that the water treatment procedure is a promising method to overcome the limitations assigned to the use of nanolime suspensions. The method can be optimized for a given substrate by varying the amount of nanolime and water according to the type of porous structure.

4.4. Conclusions

The consolidation of porous building materials with nanolime suspensions can result in the heterogeneous deposition of the nanoparticles within the treated stone matrix, partially due to the migration of the particles towards the surface during the solvent evaporation process leading to the formation of a high density superficial layer. This phenomenon is caused by the high volatility of the solvent (alcohol) and can be enhanced by environmental conditions, which are extremely important in practice. In this study, a new method of treatment was proposed to induce an in-depth mass consolidation effect and promote an homogeneous dis-tribution of the consolidant. The imaging method for mapping the distribution of the consolidant in the stone matrix provided reliable evidence of the proposed treatment method efficiency. The main results can be summarized as follows:

- The imaging method based on differential X-ray radiography was successfully applied for mapping the consolidant action inside the Maastricht limestone matrix without requiring marking agents that can lead to imprecise results.
- A two-step procedure based on nanolime application followed by application of water was investigated. The method proved to be efficient on the in-depth modification of the consolidation depth profile in Maastricht limestone.
- The combination of X-ray radiography and drilling resistance allowed confirming the efficiency of the new proposed consolidation procedure.
- The new consolidation method can be optimized for a specific substrate by varying the amount of nanolime and water according to the type of porous structure.

For future work, the investigation of the role of the moisture content present in substrates should give important insight on the success of nanolime treatments in practical conditions.

Chapter 5

Modified ethylsilicate consolidants effects on the sandstone mechanical properties

Ethylsilicates (also called silicic acid ester or ethyl polysilicate) are widely used consolidants for disintegrated sandstone. The ethylsilicates drawbacks, the shrinkage and cracking, can be reduced according Mosquera et al. [2003 and 2008] *by the formation of wider pores within the gels, or by ethylsilicate modification with particles, that was suggested by* Miliani et al. [2007] *and* Xu *et al. [2012]. This chapter discusses reducing the shrinkage and cracking using various nanoparticles or using organic amines as an ethylsilicate additive. Both nanoparticles and amines were tested in the experimental laboratory study focused on the Hořice and Mšené sandstone impregnation and mechanical properties assessment. However, clearly positive impact of aditives on ethylsilicate behaviour in relation to sandstone consolidation were not proved.*

The thesis´ author worked on this topic as a leading researcher of the research project NAKI DF 11P01OVV012 at ITAM CAS. The project was solved in cooperation with J. Heyrovský Physical Institute of CAS under leadership of J. Rathouský.
The colaboration of both research teams of CAS (JHI and ITAM) resulted in a joint publication: Monika Remzová, Petr Šašek, Dita Frankeová, Zuzana Slížková and Jiří Rathouský. Effect of modified ethylsilicate consolidants on the mechanical properties of sandstone. Construction and Building Materials, (2016), 112, 674-681.

5.1. Shrinkage and cracking of the ethylsilicates gels

Silicon alkoxides, such as silicon ethoxide or its oligomers (generally called ethylsilicates), are excellent consolidants for the weathered silicate materials [Wheeler & Goins 2005]. However, they suffer from two major drawbacks. First, the shrinkage and cracking of the formed gels due to the syneresis and residual drying stress lead to their decreased mechanical strength [Scherer 1996]. Due to their compact microporous texture (pores narrower than 2 nm), the capillary pressure, which is reciprocally proportional to the pore width according to the Young-Laplace equation, is very high, what the relatively brittle framework of the siliceous gel cannot withstand [Scherer 1997, Scherer 2001]. Second, the physical properties of the gel phase do not match those of the treated stone (such as the dynamic elastic modulus, hardness, thermal expansion coefficient, porosity etc.).

The shrinkage and cracking of the gel can be reduced by the formation of wider pores within the gels [Mosquera et al. 2003a,b; Mosquera et al. 2008] or by the modification with particles [Miliani et al. 2007; Xu et al. 2012]. We have found that the shrinkage and cracking of the gel films due to drying is drastically reduced because of the presence of incorporated nanoparticles smaller than about 10 to 20 nm and the formation of mesopores about 10 nm in width. We have recently developed a novel preparation strategy called "brick and mortar" based on the fusion of preformed nanocrystals with surfactant-templated sol-gel material, which acts as a structure-directing matrix and as a chemical glue [Szeifert et al. 2009; Fattakhova-Rohlfing et al. 2009; Rathouský et al. 2010]. We have found that this technique is not only suitable for the preparation of thin layers for the application in solar cells, photocatalysis or sensors, but also enables to obtain consolidants with very promising properties.

The modification of gels can be expected to have a substantial effect on their physico-chemical and especially mechanical properties, depending on the properties of nanoparticles (e.g., their size and the nature of their surface), and the character of porosity created. It can be anticipated that the characteristics of the modified gels containing embedded particles and wider pores will be closer to those of the consolidated stone than the properties of purely polymeric gels.

This communication aims at the determination and analysis of the effect of the addition of nanoparticles and formation of pores on the elastic modulus and hardness of the gels formed either without space restrictions in a Petri dish or within the pores of sandstone. Elastic modulus and hardness of the sandstone specimen are obtained from load-displacement measurements in nanoindentation tests. In these tests, the depth of penetration beneath the specimen surface is measured as the load is applied to the indenter. By this technique also the distribution of the consolidant applied on the sandstone sample can be determined. Nanoindentation is a versatile method for material characterization at scales where classical mechanical tests are inadequate. Additionally the effect of the consolidation of sandstones with modified gels on their bending strength was determined.

5.2. Materials and methods

5.2.1. Preparation of modified ethylicate consolidants

Chemicals used include Dynasylan40 (Evonik), di-n-butyltin dilaurate (Alfa Aesar), isopropanol (Lach Ner), 1-octylamine (Alfa Aesar), 1-dodecylamine (Fluka), 1-hexadecylamin (Aldrich). Particles of silicon dioxide were obtained from Evonik and Cabot, including pristine hydrophilic nanoparticles 13.5 nm in size and hydrophobized ones either methylated or octylated 24 nm and 18 nm in size, respectively. The particle size given was provided by the corresponding producers. However, these primary nanoparticles tend to cluster forming aggregates several hundreds of nanometers in size.

Adsorption measurement using nitrogen as adsorptive showed the aggregates consisted of a lose, unconsolidated assemblage of primary nanoparticles. The particle size distribution of aggregates of hydrophilic nanoparticles exhibited a maximum at ca 375 nm without any marked change even after the storage time of eighteen months. There was a very small percentage of particle aggregates larger than ca 800 nm.

The gels were prepared from Dynasylan40, which is a mixture of monomeric and oligomeric ethoxysilanes, the average chain length being about five Si-O units. First a suspension of nanoparticles and catalyst in isopropanol was prepared. Nanoparticles were added at the concentration of 5%. As a catalyst, either dibutyltin dilaurate (DBTDL) or organic amines at the concentrations of 2% and 0.4%, respectively, were used. Second Dynasylan40 was diluted with isopropanol at the ratio of 1:1 (v/v). Finally the diluted Dynasylan solution was added to the suspension of nanoparticles and catalysts in isopropanol. After 24 hours the sol was suitable for the application. An overview of samples prepared is given in Table 18.

The samples prepared were designated as follows (see Table 18): D, from pristine Dynasylan40 with DBTDL as catalyst, DA, modified with hydrophilic nanoparticles, DBTDL as catalyst, DTS, modified with hydrophobized methylated nanoparticles, DBTDL as catalyst, DR, modified with hydrophobized octylated nanoparticles, DBTDL as catalyst, DO, catalyzed by octylamine, DD, catalyzed by dodecylamine, DH, catalyzed by hexadecylamine.

Table 18. Compositions of consolidants under study

Sample	Concentration of nanoparticles / wt.%	Size of primary nanoparticles/ nm	Surface modification of nanoparticles	Catalyst / vol. %
D	-	-	-	DBTDL (1%)
DA	5	13.5	Hydroxyl groups	DBTDL (1%)
DTS	5	24	Methyl groups	DBTDL (1%)
DR	5	18	Octyl groups	DBTDL (1%)
DO	-	-	-	Octylamine (0.4%)
DD	-	-	-	Dodecylamine (0.4%)
DH	-	-	-	Hexadecylamine (0.4%)

5.2.2. Physico-chemical characterization of the gels obtained from modified ethylsilicate consolidants

The porosity of gels dried at 60 °C was determined by the analysis of adsorption isotherms of nitrogen at the boiling point of liquid nitrogen (ca 77 K). Before the adsorption experiment the samples were outgassed at 60 ºC for 24 hours to ensure the complete cleaning of the surface. The experiments were carried out using an ASAP2010 apparatus (Micromeritics). Because of the complex character of the samples' porosity the obtained isotherms were analyzed by a combination of several methods, especially the Broekhoff-de Boer t-plot and several variants of the NLDFT. The pore width is described using the IUPAC nomenclature, micropores, mesopores and macropores corresponding to the width of less than 2 nm, 2-50 nm and more than 50 nm, respectively.

5.2.3. Properties of sandstone substrates used

Consolidants were tested on two types of sandstone, namely Mšené and Hořice (locations of quarries in the Czech Republic), with different porosity and strength. Sandstone Hořice is significantly stronger (bending strength almost 3 times higher) than sandstone Mšené (Table 22) and less porous (Table 19). Sandstone Mšené represents a porous stone with low bending strength and in this study it was used as a material with characteristics similar to deteriorated sandstone. The mineralogical composition is similar in both tested sandstones. Hořice sandstone is an ocher colored fine-grained clastic sedimentary rock consisting mainly of quartz clasts (98%) and containing clay matrix (kaolinite, often impregnated with iron-oxyhydroxides). Mšené sandstone is a white-greyish fine-grained sedimentary psamitic rock [Slížková 2002] containing quartz as a major mineral (99%) and muscovite and feldspar clasts as accessories. The matrix is formed by clay minerals (kaolinite, chlorite) but its content is very low (<0.5 %). Both stones have been widely used as building, architectural and sculptural materials in the Czech Republic. Texture properties of stones obtained by mercury porosimetry are given in Table 19.

Table 19. Characteristics of sandstones

Sandstone	Bulk density / kg/m^3	Porosity / % vol.	Median pore diameter / µm
Hořice	2043	25	34
Mšené	1925	32	24

Table 20. The formation of porosity in modified xerogels

Consolidant	Porosity	Vmi/cm^3/g	Vme/cm^3/g	Mesopore width/nm
D	Microporous	0.10-0.12	-	-
DA	Microporous	0.16-0.18	-	-
DTS	Microporous	0.16-0.18	-	-
DR	Microporous	0.16-0.18	-	-
DO	Micro-mesoporous	0.06	0.54	6
DD	Micro-mesoporous	0.11	0.22	4.5
DH	Micro-mesoporous	0.10	0.28	4.5

Vmi, volume of micropores, Vme, volume of mesopores.

5.2.4. Testing the mechanical properties of consolidated sandstones

5.2.4.1. Nanoindentation

The goal of nanoindentation testing is to obtain elastic modulus and hardness of the specimens. It can be carried out by contacting an indenter tip of known geometry with the sample surface. The samples were tested with Hysitron TI 750L Ubi nanoindentation instrument. A three-sided pyramidal diamond Berkovich indenter and the Oliver-Pharr method were used to get the elastic modulus and hardness. In a typical test, force and depth of penetration are recorded. Figure 39 shows typical load (P)-depth (h) curve, where P_{max} is the maximum load. Initial unloading stiffness S is defined as follows [Fischer-Cripps 2011]:

$$S = \frac{dP}{dh} = \frac{2E^*\sqrt{A}}{\sqrt{\pi}} \Rightarrow E^* = \frac{1}{2}\frac{\sqrt{\pi}}{\sqrt{A}}\frac{dP}{dh} \qquad (1)$$

$$\frac{1}{E^*} = \frac{(1-\upsilon^2)}{E} + \frac{(1-\upsilon_i^2)}{E_i} \qquad (2)$$

where A is the projected contact area at load values peak, E^* is the reduced elastic modulus and E and ν are Young´s modulus and Poisson’ ratio for the sample and E_i and ν_i are the same parameters for the indenter tip [Oliver 2004]. For Berkovich indenter used in these our experiments the elastic modulus E_i and Poisson’ ratio ν_i are 1140 GPa and 0.07, respectively. Each gel sample was scanned by in-situ Scanning Probe Microscopy (SPM) imaging to select a suitable place for experimental testing with minimum roughness. Maximum load was P_{max} = 1.0 mN, load was increased linearly for 5 s to reach maximum, which was held for 2 s and then full unloading was achieved within 5 s. Load curve is shown on Figure 39.

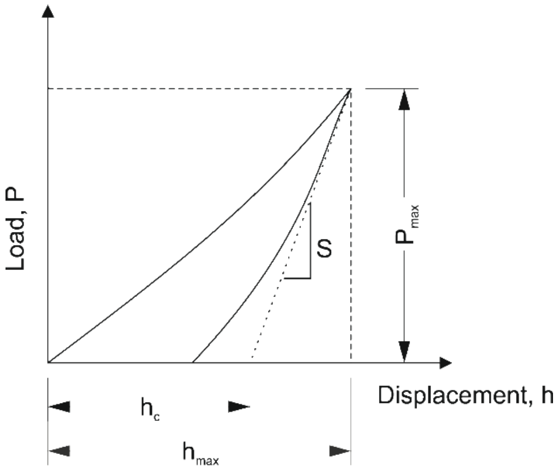


Fig. 39. Compliance curves, a typical loading unloading curve with maximum P_{max} and depth beneath on specimen surface h_{max}, depth of contact h_c and slope of the elastic unloading S.

A cylindrical sample of xerogel prepared from ethylsilicate consolidants 20 mm in diameter and ~ 4 mm in height was prepared for nanoindentation testing. Sandstone samples which were treated with ethylsilicate consolidants were prepared by cutting out of a bigger slab (lower part of the specimens). Samples were embedded in resin, after 24 hours they were grinded with SiC paper (up to grit #2000) and polished. Finally, the surfaces were cleaned by sonication following the procedure presented elsewhere [Velez 2001]. The xerogels (natural maturing) were tested in a matrix 5 × 5 μm in size, the distance between the indents and the total test area being 1 μm and 25 μm^2, respectively. For naturally matured xerogels 25 indents for each sample were performed. Indentation was performed using the scan surface SPM probe with a scanned area of 20 × 20 μm, scanning frequency being 0.5 Hz. Because of the embedding in resin and porosity of samples, single indents were made to distinguish the resin from the gel in pores. The location of single indents was selected with the aid of optical microscope and for each sandstone sample at least 30 indents were made. All naturally matured samples were analyzed by using SPM probe to detect any overlap effects (pile-up or sink-in). Based on these tests 1 micron spacing between indents was chosen.

5.2.4.2. Bending strength of stone plates

Bending strength of stones was tested 3 months after the consolidation treatment on small-size specimens, namely rectangular plates with nominal dimensions of 20 × 50 × 3 mm. This way of testing enabled to determine the strength value distribution along a depth profile perpendicular to the surface (Fig. 40) [Drdácký, Slížková 2008, Slížková, Frankeová 2012]. Six cut plates were marked by numbers from 1 to 6, where numbers 1 and 6 indicated the top and bottom layers of the specimen, respectively. Four specimens were consolidated, matured, sliced and measured for each consolidation treatment. Two specimens (12 plates) were measured as reference samples at the untreated condition.

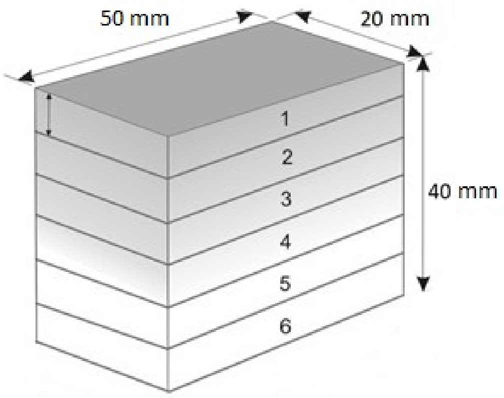


Fig. 40. The specimen layout preparation for bending strength measurement. The depth of the gray shade depicts the amount of consolidant deposited.

Stone specimens were conditioned in a climatic chamber (25 °C / 50% RH) before the experiment. The consolidation treatment was performed on 2 × 5 × 4 cm^3 prismatic specimens and only one face of the specimen (2 × 5 cm^2) was treated with a certain volume of the respective consolidation agent (2.5 ml). The agent was applied by pipette on the stone surface (2 × 5 cm) until the total volume of the product was soaked (5 applications of 0.5 ml each). The applied volume (2.5 ml) was chosen as the amount of consolidant which penetrates into the stone specimen in certain depth (2-3 cm) so that only a part of the stone specimen was consolidated and the bottom part of stone remained untreated. Consolidated stones were laid on a tray and placed outside without cover in order to be exposed to natural climatic conditions (average temperature 20 °C, average humidity 70% RH, Fig. 41). After 1 month specimens were placed back in the chamber (25 °C / 50% RH) for conditioning and then were sliced for bending strength measurements.

Fig. 41. Treated samples' storage in natural climatic conditions

5.3. Results and discussion

5.3.1. The influence of the modification on the gel porosity

From the character of the type IV isotherms on xerogels prepared by drying the wet gels at 60 ºC in the air, which were catalyzed by amines (0.4%), and the corresponding pore width distributions it is apparent that these xerogels contain besides a smaller content of micropores also an important percentage of mesopores. This content is especially large if octylamine is used as a catalyst, the pore width corresponding to the maximum of the distribution being 6 nm.

The findings obtained from the extensive adsorption study can be summarized as follows:

The addition of nanoparticles to sols whose gelation was catalyzed by dibutyltin dilaurate does not lead to the formation of mesoporosity in corresponding xerogels. The probable explanation of this observation is that the nanoparticles function as defects around which narrow corona is formed, which was identified as a micropore. Actually only slight increase in the micropore volume was observed.

The surface properties of added particles, i.e. their hydrophilicity for the surface covered with hydroxyl groups and hydrophobicity if methyl or octyl groups are grafted to the surface, does not have much effect on the character of porosity, as presented in Table 21. Therefore it can be concluded that there is no formation of chemical bonds between the surface of particles and the surrounding gel. If that would be the case, there should be a difference. While bonds could be formed only in the case of the presence of reactive hydroxyl groups on the surface, the surface covered with alkyl groups must be completely inert.

If instead of dibutyltin dilaurate an organic amine was used as catalyst, a substance with a higher basicity, which however does not reach that of inorganic bases (such as ammonia or hydroxides of alkaline metals), important changes in the porosity occurred [Mosquera et al. 2008]. The formation of micropores was substantially suppressed and a substantial proportion of mesopores was formed their width achieving 5-10 nm depending on the type and concentration of the organic amine used. Due to the structure of their molecules some primary amines with a longer alkyl chain (such as octyl or dodecylamine) can function as non-ionic surfactants, which can e.g. decrease the surface tension.

To sum up, in order to suppress the formation of micropores, which have a negative effect on the cracking of gels due to a high capillary pressure, and the formation of more advantageous, substantially wider mesopores an organic amine are preferable as catalysts [Mosquera et al. 2008]. The role of primary amines with a longer alkyl chain seems more complex than that of mere catalysts.

5.3.2. Nanoindentation experiments

Three types of nanoparticles were used for the modification of Dynasylan40. While the particle size of all the three materials is similar, their surface properties substantially differ. The surface of unmodified nanoparticles A is covered with hydroxyl groups, that of hydrophobized ones either with smaller methyl groups (R) or much longer octyls (TS).

The mechanical properties of gels formed in Petri dishes modified by embedding nanoparticles are expected to differ substantially from those of the unmodified ones. First the hardness of the gels has increased. The increase depends on the surface properties of nanoparticles. For the nanoparticles with hydroxylated surface (i.e. the unmodified nanoparticles) the increase in the hardness is the greatest, namely by 48 %. While the hardness of pristine Dynasylan gel equals 1.04 ± 0.09 GPa, that of modified with A particles 1.54 ± 0.04 GPa. If methylated and octylated nanoparticles are incorporated, the increase is smaller, namely by 37 % (1.43 ± 0.05 GPa) and 8 % (1.12 ± 0.02 GPa), respectively. Data are presented in Table 21.

The increase in hardness for the modified gels is due to the higher hardness of the added nanoparticles. There seems a stronger affinity of the surface of hydroxylated nanoparticles with the gel than for the hydrophobized ones. The affinity of methylated and octylated nanoparticles with the sandstone matrix is weaker, especially in the case of octylated ones. As the surface of methylated particles is less covered with alkyl groups than that of octylated ones, the hardness of gels is lower. On the other hand, the surface of octylated nanoparticles is completely covered with alkyl chains and completely chemically inert, which leads to similar hardness. Concerning the Young's modulus, the trends are similar. The modulus of gels modified with hydroxylated nanoparticles is increased, by 72 % (from 7.74 ± 0.52 GPa for unmodified gel to 13.29 ± 0.16 GPa for the gel modified with hydroxylated particles). For gels with embedded methylated nanoparticles, the increase equals is less 45 % (11.26 ± 0.26 GPa). On the other hand, the modulus of gels with incorporated inert octylated nanoparticles is lower than that of the unmodified gels, namely 7.15 ± 0.07 GPa.

The formation of mesoporosity within the gels leads to a decrease in both the hardness and the Young's modulus of the gels. Such a decrease is due to the formation of mesoporosity within the gels. The hardness of gels catalyzed with octylamine, dodecylamine and hexadecylamine decreased from 1.04 ± 0.09 GPa for unmodified gel to 0.41 ± 0.02 GPa, 0.11 ± 0.01 and 0.66 ± 0.02 GPa, respectively. Similar trend was observed for the Young's modulus – a decrease from 7.74 ± 0.52 GPa for unmodified gel to 6.08 ± 0.08, 4.49 ± 0.14 and 7.64 ± 0.23 GPa for modified samples, respectively. Actually, the decrease in both properties was the smallest for the gel catalyzed with hexadecylamine.

The properties of the gel formed in the pores of sandstone are much more difficult to interpret as the size and shape as well as the surface of pores are not uniform within the samples. Concerning the effect of the embedded nanoparticles on the hardness of the gels, a much greater increase was observed in samples not prepared with Petri dishes. The hardness of the unmodified gel is almost the same in the samples gelled in a Petri dish (1.04 ± 0.09 GPa) and in pores of the sandstone (0.96 ± 0.16 GPa). In comparison with unmodified gel in pores of the sandstone, an increase as high as 122 % was obtained for gel modified with hydroxylated nanoparticles (to 2.13 ± 0.18 GPa). Even for methylated and octylated nanoparticles the increase is substantial, 49 % (1.43 ± 0.10 GPa) and 92 % (1.84 ± 0.12 GPa), respectively.

Concerning the Young's modulus, for all the samples are larger than the values obtained for gels formed in the Petri dishes. Comparing with the sandstone consolidated with pristine Dynasylan (12.33 ± 1.68 GPa), a marked increase was observed for gels modified with hydroxylated nanoparticles, by 79 % (to 22.09 ± 1.23 GPa). For the methylated (10.62 ± 0.75 GPa) and octylated (14.25 ± 0.85 GPa) nanoparticles some decrease and increase, respectively were observed, but the data seem rather ambiguous.

Generally, it seems that the gel with mesoporosity formed in pores of sandstone differs from the gel formed in the Petri dishes but the data are rather scattered and no clear trend was observed. The hardness and the Young's modulus are the highest for the gel catalyzed with dodecylamine (1.39 ± 0.26 and 24.04 ± 3.12 GPa), respectively, i.e. an increase in comparison with unmodified gel was observed for both properties. For the gel catalyzed with octylamine both parameters are lower than those for unmodified gel (0.61 ± 0.09 and 9.66 ± 2.56 GPa, respectively). Finally for the gel catalyzed with hexadecylamine the values of both parameters are roughly comparable with those for the unmodified gel (0.82 ± 0.14 and 16.22 ± 0.88 GPa, respectively).

Table 21. Hardness and Young's modulus of gels prepared in Petri dishes and those gelled within pores of Mšené sandstone.

	Gel in Petri dish		Gel in sandstone Mšené	
Sample	Hardness/GPa	Young's modulus /GPa	Hardness /GPa	Young's modulus/GPa
D	1.04	7.74	0.96	12.33
DA	1.54	13.29	2.13	22.09
DR	1.43	11.26	1.43	10.62
DTS	1.12	7.15	1.84	14.23
DO	0.41	6.09	0.61	9.66
DD	0.11	4.49	1.39	24.04
DH	0.66	7.64	0.82	16.22

Designation of samples see Table 19

5.3.3. The bending strength experiments

The treatment with both pristine Dynasylan and modified consolidants on both Hořice and Mšené sandstones led to an increase in the bending strength values. As regards the quantity of the strengthening effect of the consolidation treatment, it was significantly higher for the weaker sandstone Mšené. The strength gain was approximately 200 % for the most strengthening consolidants applied in this stone and the highest increase was achieved with pristine Dynasylan (D), which raised the strength most effectively (230%). The stronger sandstone Hořice was strengthened with the same consolidants moderately: maximal strength gains were around 100%, for pristine Dynasylan40 (D) and for Dynasylan modified with nanoparticles (DA, DR and DTS). The results indicate a potential strengthening effect of tested variants after application into quartz sandstone with a specific porosity and the strength gains values should be assessed according to the needs of specific situations in stone consolidation practice.

In general, not only the strength increase but also the achieved strength distribution (gradient) represents important characteristics in relation to evaluation of consolidation treatment performance. For this reason, strength values in the depth profile (from the surface to the bottom of treated stone specimens) were measured (see Table 23) and evaluated. The continuous, moderate strength decrease was evaluated positively, while sharp decline in strength (when adjacent stone layers differed by more than 50%) was assessed negatively.

The graphs in Fig. 42 and 43 illustrate that the tested variants can be divided into two groups, in terms of the depth profile of the strength. For the first group – namely pristine Dynasylan40 (D) and consolidants with nanoparticles (DA, DR and DTS) – the uneven strength distribution with sharp drops in the strength was found. These variants exhibited much higher strength increase in the surface part of stone specimens compared to inner or bottom stone areas. This phenomena is not in agreement with the recommendations for optimal consolidating intervention given in recent literature [Tabasso & Simon 2006]. The requirement of moderate strength changes due to consolidating treatment was better fulfilled by the second group of consolidants – DO, DD, and DH. Hořice sandstone performed the bending strength increase between 35% and 57% and differences between adjacent layers did not exceed 50% for this group of consolidants. Positive results were obtained also for Mšené sandstone treated with these modifications (DO, DD, DH): upper parts of specimens showed strength increment from 46% to 86%, while remaining parts of specimens were strengthened by 15% to 35%.

In general, the distribution of strength values in the depth profile after consolidation is influenced by two factors: by possible inhomogeneity in the rock structure and by the consolidant distribution in stone, which depends on the stone porosity and on quantity and penetration ability of the liquid consolidant. In presented study, the amount of applied consolidating agents was chosen so that the greater part of stone specimens was impregnated and the difference between more and less penetrated stone parts was obvious. The lower or bottom parts of treated stone specimen were not or poorly penetrated with tested consolidants and the strength of these layers is similar to the strength of untreated stones.

Table 22 An overview of bending strength data obtained on Hořice and Mšené sandstones

Treatment	Slice No.	Sandstone				Treatment	Slice No.	Sandstone			
		Hořice		Mšené				Hořice		Mšené	
		Strength (MPa)	SD	Strength (MPa)	SD			Strength (MPa)	SD	Strength (MPa)	SD
non-treated		4,21	0,74	1,45	0,25						
D	1	8.34	0.75	4.74	0.32	**DTW**	1	7.10	0.44	3.70	0.46
	2	8.11	0.85	4.80	0.69		2	8.05	0.45	3.96	0.46
	3	7.81	0.71	4.08	1.18		3	7.20	0.07	3.85	0.53
	4	5.15	0.59	4.79	1.83		4	4.60	0.76	3.60	0.32
	5	4.30	0.67	2.85	1.15		5	4.54	0.27	1.43	0.20
	6	4.49	0.36	1.49	0.21		6	4.53	0.66	1.30	0.13
DA	1	8.61	0.42	4.12	0.16	**DO**	1	6.61	1.36	2.74	0.74
	2	8.49	0.43	4.23	0.28		2	6.51	0.88	2.57	0.33
	3	5.75	0.46	2.16	0.35		3	5.76	1.00	2.31	0.89
	4	4.45	0.66	1.33	0.20		4	4.53	0.80	1.80	1.26
	5	4.91	1.12	1.27	0.22		5	4.52	0.55	1.93	0.70
	6	4.86	0.87	1.12	0.16		6	4.79	0.18	1.70	0.20
DR	1	8.42	0.56	3.61	0.81	**DD**	1	6.06	0.23	2.26	0.26
	2	5.02	0.76	3.10	1.22		2	6.08	0.93	2.12	0.22
	3	4.06	0.78	1.34	0.57		3	5.87	0.29	1.58	0.22
	4	4.38	0.40	1.00	0.07		4	6.45	0.78	1.48	0.26
	5	4.44	0.46	1.19	0.25		5	4.59	1.01	1.66	0.50
	6	4.55	0.15	1.35	0.35		6	4.71	0.92	1.45	0.54
DTS	1	8.45	0.49	4.36	0.29	**DH**	1	5.67	0.39	2.12	0.29
	2	5.64	0.61	4.29	0.21		2	6.46	0.12	1.86	0.15
	3	5.05	0.69	3.00	0.44		3	6.20	0.70	1.70	0.27
	4	5.15	0.39	1.35	0.21		4	5.55	0.40	1.76	0.37
	5	4.80	0.20	0.98	0.07		5	4.84	0.32	1.77	0.52
	6	5.10	0.39	0.81	0.03		6	4.11	0.05	1.78	0.47

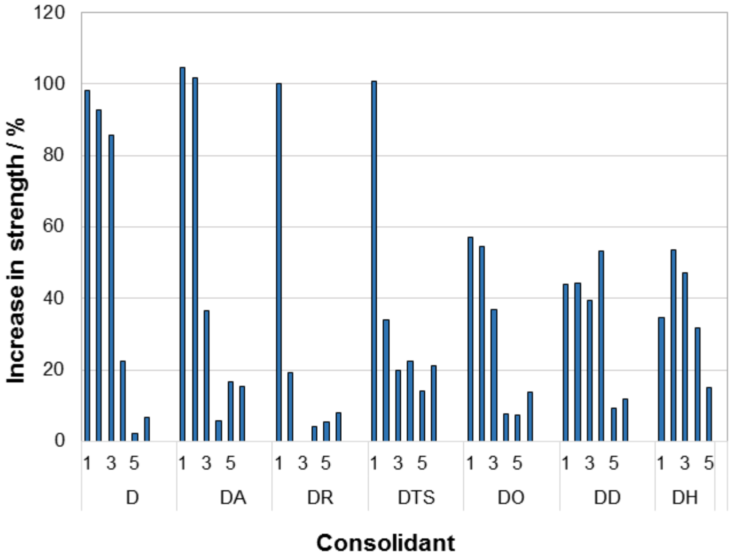


Fig. 42. Sandstone Hořice – bending strength increase in depth profile; layers order in direction from the treated surface to the bottom of stone specimens.

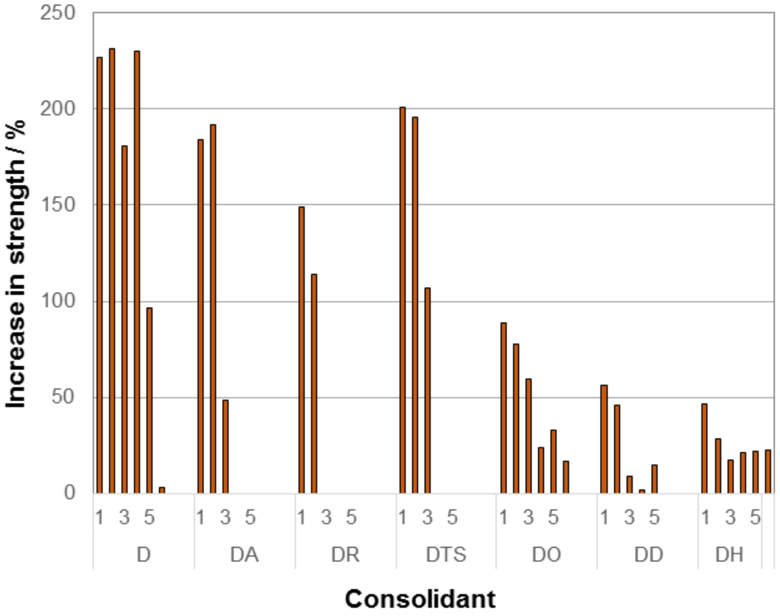


Fig. 43. Sandstone Mšené – bending strength increase in depth profile; layers order in direction from the treated surface to the bottom of stone specimens.

5.4. Conclusions

The sol-gel process was found to depend on the properties of particles added, especially on their size and surface properties. While the hydrophobization of the particle surface has decelerated the process, the hydroxylated particles have had only a slight effect on the polycondensation process.

In order to suppress the formation of micropores and to support the formation of more advantageous, substantially wider mesopores, organic amines are preferable as catalysts. The role of primary amines with a longer alkyl chain seems more complex than that of mere catalysts. If nanoparticles were added, no substantial effect on the character of the porosity was observed.

The mechanical properties of gels modified by embedding nanoparticles or by creating mesoporosity were substantially changed. Due to the embedding of nanoparticles both the hardness and Young's modulus were increased. On the other hand, the formation of the mesoporosity within the gels had an opposite effect.

The modification of consolidants by the creation of mesopores in the gels enables to achieve an even consolidation of the stone. Concerning the modification with nanoparticles, these variants exhibited much higher strength increase in the surface part of stone specimens compared to inner or bottom stone areas. This phenomena is not in agreement with the recommendations for optimal consolidating intervention. In this experiment, the strengthening effects of modified variants TEOS were primarily assessed. In terms of the evaluation of the compatibility of the consolidation treatment, also other characteristics of treated stones need to be assessed, mainly capillary absorption, drying rate, dilatations and color of stone.

Chapter 6

Laboratory verification tests on consolidation effects on stone

As the previous chapter, also this chapter focuses on the Czech sandstone mechanical characteristics in relation to the consolidation treatment with ethylsilicates. The experiment presented in this chapter aimed to compare material data acquired using circular discs and rectangular plates as tested stone specimens. At the same time the influence of silica content in tested ethylsilicate based consolidants was taken into account. Furthermore, cylinders and cubes cut from sandstone were treated with ethylsilicates in order to determine their depth penetration ability. Differences in consolidation effects are discussed in relation to the chemical characteristics of the applied consolidation agents.

This chapter is based on a joint publication: "Leal L. N. P., Drdácký M., Slížková Z. (2018). Flexural tests on consolidation effects on stone. Proceedings from SAHC conference in Cusco 2018.

6.1. Bending strength tests

The impact of impregnation with chemical agents supporting stone consolidation should be tested and described in terms of the physical and chemical characteristics of the stone after the intervention. For this purpose flexural tests represent a suitable method capable of providing information on the impregnation efficiency as well as on the change of mechanical properties for the sake of assessing the intervention compatibility. Typically small-size specimens – rectangular plates or circular discs – made of material extracted from the treated stone are tested to acquire the bending strength and Young's modulus of elasticity. The advantage of the use of rectangular plates is that several physical characteristics of identical test specimens can be tested gradually, which reduces errors originating from material non-homogeneities (see [Drdácký, Slížková 2008c], for example). Plates with typical nominal dimensions of 15 × 40 to 50 × 4 mm are ideally cut from blocks previously treated on one surface with the consolidation agents being tested, which makes it possible to observe changes in material characteristics along a depth profile perpendicular to the treated surface. The specimens are typically tested in three-point bending. Biaxial flexure tests have been developed for ceramic and glass testing, for which several testing arrangements are available and have even been standardized – piston-on-three-ball, piston-on-ring, ball-on-ring and ring-on-ring (see for example [Danzer et al. 2006]) or for concrete plates (see for example [Kim et al. 2013]). There are few studies focused on the relationship between the bending strength attained using rectangular plates in three- or four-point bending and that acquired using circular discs subjected to biaxial loading. The effect is naturally influenced by the homogeneity and isotropy of the material tested as well as by the size of the test specimens. Biaxial testing of stone in the mode of a ring-to-ring arrangement for conservation efficacy assessment was recommended by Wittmann and Prim [Wittmann et P. Prim 1983]. The method is very effective and rather fast for strength testing. However, the circular discs are not practical for determining other material characteristics which are decisive for application in the conservation of porous materials. In this paper, the results of a comparison of uniaxial and biaxial tests on almost isotropic sandstone specimens are presented.

6.2. Experimental programme

6.2.1.Test specimens and arrangement

Plates with nominal dimensions of 15 × 40 to 50 × 4 mm made of quartz sandstone were loaded in a three-point bending. Comparative biaxial bending tests were carried out using plates with a diameter of 55 mm and a thickness of about 4 mm in a special fixture (Fig. 44). The supporting rig had the form of a circular ring with a diameter of 40 mm, on which the specimen tested was centrally placed. The position was controlled with an alignment cap which had a central hole for defining the position of the loading ring (a cylindrical hollow piston). The supporting rig carries an LVDT sensor for the measurement of the central deflection of the plate in the course of loading. For a uniaxial flexural test arrangement a special fixture placed on the upper surface of the rectangular plate (Fig. 45) makes it possible to eliminate deformation of the plate in contact with its support, which is not possible in the case of a circular disc.

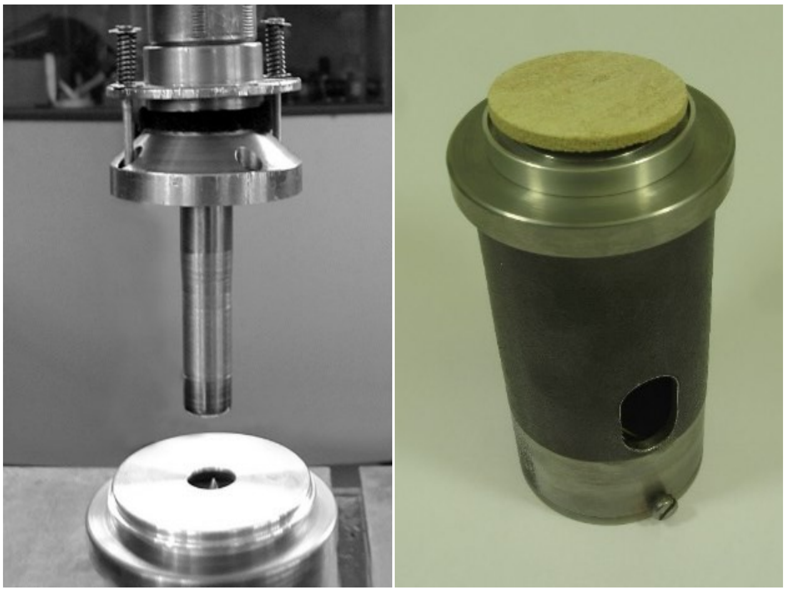


Fig. 44 Test arrangement at biaxial bending (left). Thin disc supported with a special rig (right).

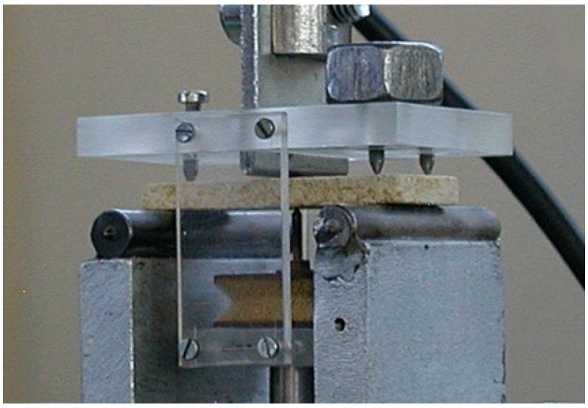


Fig. 45 Flexural test of thin rectangular plates.

6.2.2. Treatment of test specimens

Three different consolidating products were used to treat the samples: Porosil Z designated as product A; KSE 300 designated as product B and KSE 510 designated as product C. Deposition of silica gel inside the pores of the stone creates consolidation effects. The three products were applied by absorption on the rectangular and cylindrical plates. Further, stone cubes and cylinders were treated with two different techniques in order to study efficiency.

6.3. Test results - mechanical characteristics

The measured strength in biaxial bending is calculated according to Wittmann & Prim [1983] using the eq.

$$\sigma = \frac{3\,F}{4\pi\,(h^2)} * \left\{2 * (1+\nu) * ln\left(\frac{a}{b}\right) + \frac{(1-\nu)*(a^2-b^2)}{a^2}\right\}$$

where F is the maximum force reached during the test, h is the thickness of the plate, ν is the Poisson number, b is the loading ring radius and a is the supporting ring radius. The Young modulus is calculated as [4]:

$$E = 1{,}5\frac{F}{f_0}\frac{1}{h^3} * (1-\nu^2) * \left\{b^2 * ln\left(\frac{b}{a}\right) + \frac{(a^2-b^2)(3+\nu)}{2*(1+\nu)}\right\}$$

where F is the value of the force; f_0 is the total displacement at the span middle in the last point of elastic behavior; ν is the material Poisson modulus; h is the thickness of the plate; b is the ring load application radius and a is the support ring radius.

The flexural strength of the rectangular plate specimen is the highest stress registered on the outer surface of the specimen at the failure moment and it is calculated as:

$$\sigma = \frac{3\,P\,l}{2b\,(h^2)}$$

where σ denotes bending strength; P ultimate load; l span length; b specimen width and h specimen height.

Fig. 46 shows a comparison of the flexural strength attained on rectangular plates subjected to three-point bending and the biaxial flexural strength from the tests using circular discs. It may be observed that both methods give identical tendencies in the determination of the material characteristics of different qualities of stone, here achieved by means of impregnation with different ethylsilicate-based consolidants. Therefore, both methods are applicable for assessing the efficiency of various strengthening agents, with almost the same results. Kim et al. [Kim et al. 2013] described a similar situation between the unidirectional bending test and bidirectional bending test. In their research they achieved the ratio of 0.64:1 of the strengths measured in a four point and bidirectional bending test. Shetty et al. reported the same behaviour with the unidirectional and bidirectional bending tests, too.

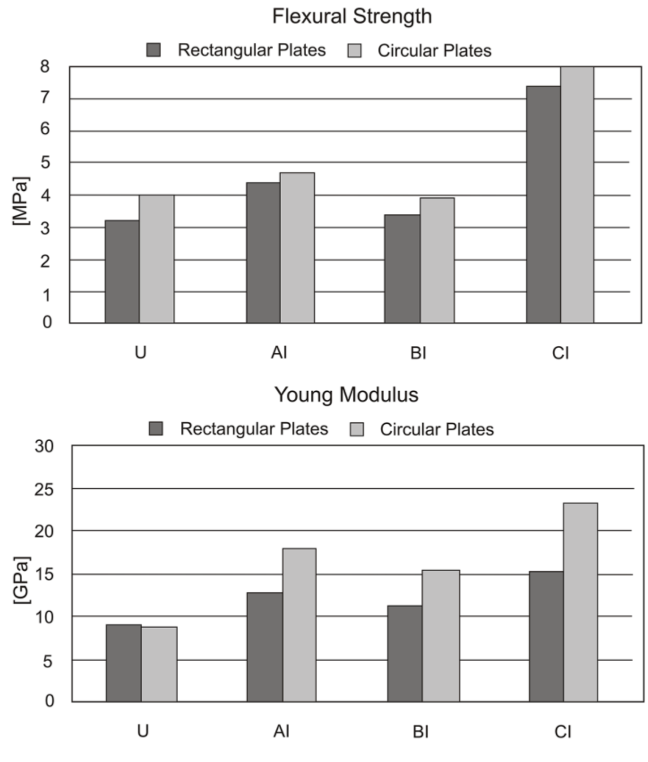


Fig. 46 Comparison of uniaxial and bi-axial bending test results (u denotes untreated reference specimens).

Fig 47 represents flexural strength distribution along the depth profile in cubes or cylinders as measured on the rectangular and circular plates cut as thin plates from them and tested in unidirectional and bidirectional bending. The results illustrate at the same time average depths of penetration of the consolidation products, which attained values between 18 mm and 35 mm.

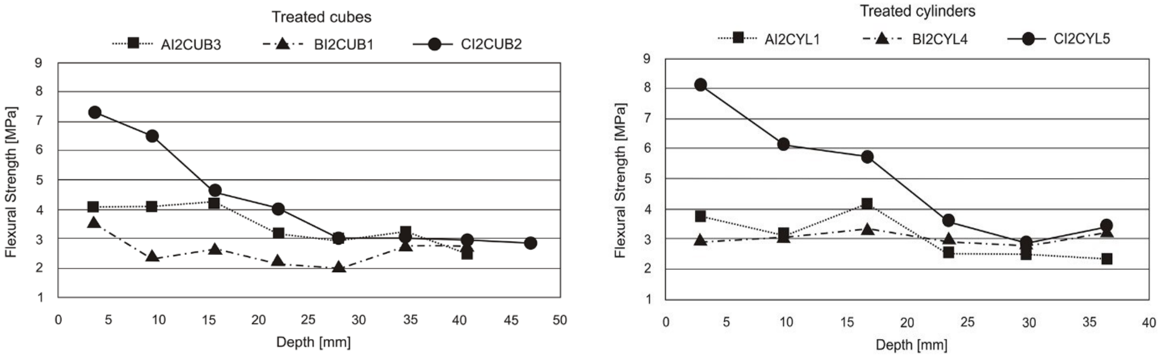


Fig. 47 Penetration profile in cubes and cylinders.

Product A in both cases exhibited a rather even strengthening effect up to a depth of about 25 mm to 35 mm and then the material characteristics did not change. Product B created a rather constant but very low strength profile in the case of the bidirectional behavior and with some oscillations in the case of a unidirectional bending test. This means that the product acts along all the depth without remarkable differences in each zone. Product C presents a remarkable difference near the surface compared to the others products, and due to the high values attained in the first 20 mm in depth a possible problem of incompatibility of mechanical behavior between the consolidated and the untouched zone is open to discussion. The penetration depth reached a value of 25 mm.

The penetration depth of the consolidants was studied by Drdácký and Slížková [Drdácký, Slížková 2008c] by means of unidirectional bending tests. The fact that the maximum flexural strength along the profile of the cubes and cylinders is not located at the external face being treated is not a surprising situation. In their research the maximum bending strength was at the maximum penetration depth, which is between 20 mm and 30 mm. Furthermore, the maximum penetration depth (in products A and C) is visible because the difference of the flexural strength between two consecutive levels is important and below this value the strength is almost constant. Any big difference in the flexural strength in a short distance may generate compatibility strength problems between the external zone being treated and the internal zone not reached by the consolidants. Not only is the strength strongly affected, but examination of the plates treated by capillary absorption also shows important increases in the Young modulus of the material.

Regarding the two techniques used to the application: capillary absorption (I) and brushing (II); the similarity of the profile achieved with both techniques is interesting. 48 describes the flexural strength profile in depth on four cylinders (random choice) treated with product A and product C using the two techniques. They represent a pattern of shadow between the method I profile and method II profile. Both methods present the same penetration depth. Brushing method II is one of the main methods presently used in the practice. After these results, it is possible to affirm that both methods are similar in effectiveness.

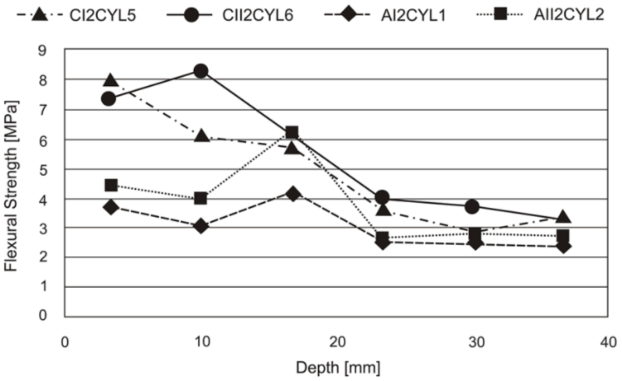


Fig. 48 Treated cylinders with different techniques.

6.4. Consolidant characteristics

Due to their chemical similarities to sandstones in particular and their simple application, silicic acid esters (SAE) are one of the mostly and successfully applied materials in stone conservation [Ziegenbalg, Piaszczynski 2012]. The most important silicic acid ester used in conservation is tetraethyl orthosilicate (TEOS) $Si(OC_2H_5)_4$. It is a clear liquid with low viscosity and a typical smell. Esters decompose when they react with water, producing alcohols and acids. This reaction can be induced by acidic as well as alkaline conditions (and catalysts). Tetraethylorthosilicate is sold as ”pure” TEOS, as partially pre-hydrolysed mixtures, or diluted with different types of organic solvents. Under the conditions of stone consolidation, hydrolysis of TEOS is induced in reactions with humidity. Hydrolysis results in the formation of polymeric networks consisting of Si-O-Si bonds. Complex reactions leading to the release of ethanol and the formation of silicic acid gel are typical. The hydrolysis of silicic acid esters is, under normal conditions, a slow process. Special catalysts are added in order to increase the reaction rate and to determine the nature of gels within reasonable times. Typically, tin-organic compounds are applied, but also acid catalysed products are produced. Unfortunately, the compositions of the catalysts used are often not published by producers. Stone consolidants based on SAE are often characterised by their gel deposition potential. For example, pure TEOS will theoretically result in the formation of about 300 g/L SiO_2; the gel deposition potential is about 30%.

Three SAE based products tested in the experiment were first characterized using information from the manufacturer: Remmers KSE 300 – without solvent, 30% gel deposition potential; Remmers KSE 510 – without solvent, 45% gel deposition potential; Porosil Z – containing solvent (ethanol), acid catalyst, 30% gel deposition potential. Then, the gel deposition of each product was measured experimentally: a gravimetrical method was used to monitor 10 of ml consolidant, which was poured into a Petri dish and allowed to react with the atmospheric humidity in the laboratory (T 21 °C, RH 50%) for 36 days. Residual water and organic compounds in the gel obtained were determined by thermal analysis with an SDTQ 600 (TA Instruments), at two times: after 1 week and after 5 weeks. An example of the DTA/TG analysis result for KSE 300 gel is illustrated in Figure 49. The gel compound data as measured and calculated are summarized in Table 23. The gel structures formed depend not only on the type of used TEOS, but also strongly on temperature, moisture and the catalyst used. Figure 50 shows structures of gels formed from the consolidants tested.

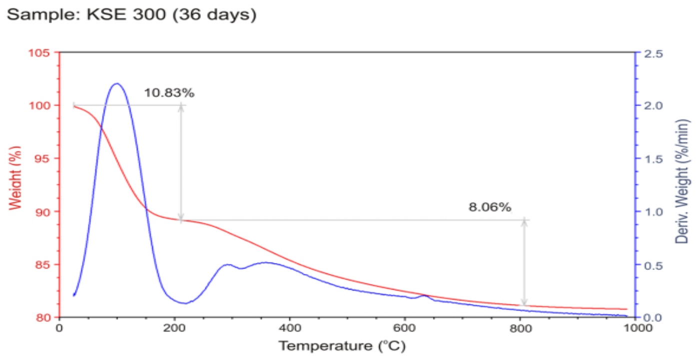


Fig. 49 Water and alcohol content (weight %) in the gel formed from KSE 300, determined by DTA after 5 weeks.

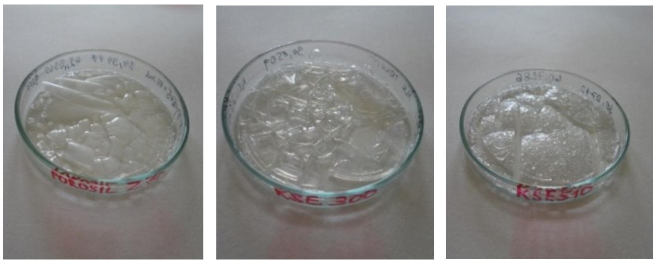


Fig. 50 Structures of gels formed from the consolidants tested after 1 week.

Table 23. Amount of SiO_2 formed from SAE products in laboratory condition on a Petri dish

SAE liquid product	SiO_2 content after 5 week	
	weight %	g/L
POROSIL Z 30	14.3	123
KSE 300	26.0	248
KSE 510	42.3	438

6.5. Conclusions

The paper presents a comparison of two methods for testing the flexural strength of stone samples in laboratory conditions – i.e. biaxial testing of thin discs and uniaxial testing of thin beam-like plates. Both techniques studied using quartz sandstone test specimens yielded results adequately describing the changes in the stone after consolidation treatment and their choice in practice is determined by aspects other than mechanical testing modes – namely, the sample extraction techniques – core drilling or saw cutting – and the planning of other types of tests, for example, for dilation behavior under various moisture and temperature conditions.

The general deterioration of the sandstone over time is an inevitable process. This research had demonstrated that the flexural strength and flexural Young modulus may be recovered by a consolidant treatment. However, the increase in flexural strength and Young modulus is strongly related to the amount of silica gel generated inside the pores.

The flexural strength profile along the depth of the element treated exhibit remarkable differences between consecutive levels; it depends on the efficiency of the consolidants used. The same is valid for the modulus of elasticity. Important differences in mechanical characteristics along short lengths inside the stone may generate compatibility problems between the superficial strengthened zone and the inner zone.

Part III.

Chapter 7

Final comments

7.1. Results and recommendations based on comparative tests of consolidants on mortars

Before deciding on the consolidation treatment of disintegrated plaster or render, it is important first to identify the mineralogy and porosity of the mortar. It has been proven that the success of consolidation is significantly influenced by the characteristics of mortars, and not only those of the consolidants.

Regarding the lime mortars and especially mortar with limestone aggregate, the nanolime "CaLoSiL 15" proved to be a very effective strengthening agent. Also, the combined applications of lime-based consolidants (nanolime Calosil 15 or lime water) with silica based consolidants (ethylsilicate KSE 100 or diluted Syton) led to very good consolidation effects on lime mortars.

The results indicate that a lower concentration of CaLoSiL (E 15) provided a better distribution of the new binder in the mortar structure and led to higher compression strength of the mortar than a more concentrated CaLoSiL (IP 25). From this, it can be assumed that uniform distribution of the consolidant in the mortar layer is very important for the effective strengthening of the mortar and, in some cases, the effect of the uniform distribution of a consolidant can overcome the effect of the concentration of the consolidant.

Lime water treatment of a friable lime mortar was shown to be effective after a sufficiently large number of applications (160 subsequent saturations) of lime water into a mortar. The initial poor mechanical characteristics (compressive strength and surface cohesion) of mortar were improved substantially after the large number of mortar saturation steps with lime water.

The study of the pozzolanic activity of various types of siliceous sand in mortars showed that the grains of siliceous sand may react with calcium hydroxide and can contribute in the formation of hydraulic compounds when they are exposed to calcium hydroxide for a long time (several months at room temperature). In treated lime mortar samples, however, the products of this reaction were not detected, probably because of the relatively small amount of these substances in the mortar and their amorphous character which prevents its identification with X-ray diffraction. The hydraulic compounds resulting from the reaction of lime consolidants with siliceous mortar components can contribute to mortar strengthening, but they have not been proven directly in the treated mortar with the applied analytical methods.

In the case of tested earth (clay) mortar, only consolidation with ethylsilicate (KSE 100) was beneficial; good results were also achieved with ethylsilicate combined with a nanolime product. Unfortunately, KSE 100 treatment significantly inhibited mortar´ water absorption by capillarity due to the changed surface tension after the treatment. However, water vapour permeability in tested mortars was not significantly changed after the consolidation treatment. Contrary to the lime mortars results, only a slight strengthening effect was found in the case of the clay mortar for the nanolime product (CaLoSiL IP 15). The reason was probably attributed to the low penetration ability of the nanolime into the clay mortar, which contained finer pores compared to tested lime mortar. Generally, the influence of consolidants dissolved or dispersed in water was minimal or did not have any effect on the strength of tested clay mortar´ specimens. This is probably due to erosion of mortar´ specimens by water supplied during multiple impregnations of aqueous solutions.

Often, a higher number of subsequent treatments is needed to achieve an adequate consolidation effect. Some examples of consolidation treatments for specific plasters/renders are given in Table 16 [van Hees, Veiga, Slížková 2017]. The term ‘‘cycle’’ is used for the impregnation of the decayed mortar layer with a consolidant and following the subsequent drying out of the treated layer. The required amount of a consolidant for one impregnation cycle can be derived from the mortar water accessible porosity.

Table 24. Indication of the number of treatments for the consolidation treatment for different mortar types and condition

Render/ plaster type	Lime water (saturated solution)	Nanolime in alcohol 15-25g $Ca(OH)_2$/l	Ammonium oxalate 25g/l, or Ammonium phosphate 50g/l, or Barium hydroxide 40g/l	Ethylsilicate (TEOS) 100 g SiO_2/l	Nanosilica (SiO2) in water 30- 100 g SiO_2/l
lime mortar, very weak cohesion, salt-free	100 cycles	5-7 cycles	3-4 cycles	2 cycles	2 cycles
lime mortar, quite good cohesion, pores > 10 µm, salt- free	50 cycles	3-5 cycles	2 cycles	1 cycle	1 cycle
lime mortar, fine pores (1 µm), salt –free	30-50 cycles	-	2 cycles	1 cycle	-
lime mortar, contaminated with salts	-	3-7 cycles	-	1 cycle	-
earthen mortar	-	3-7 cycles	-	1-2 cycles,	1-2 cycles

The preliminary selection of consolidants to be used for a mortar consolidation in a specific case should be done considering several aspects. Generally, chemical similarity between the consolidant and the mortar binder is favourable to maintain the original composition of the historical material and to achieve similar physical-chemical characteristics between non-treated and treated mortar.

In specific cases, it is not necessary to have the same chemical composition between the consolidating compound and the mortar binder if the consolidation treatment meets other criteria of compatibility. The new binder should not be prone to fast weathering and biodeterioration in particular atmospheric conditions.

Regarding the reactivity of the consolidant with the mortar, it is advantageous if the consolidant can form chemical bonds with the mortar particles (for example ethylsilicate reacting with the OH- groups of silicate minerals present in a mortar). The consolidation treatment can be more durable and effective in these cases.

The consolidated plaster/render should be re-treatable, i.e., allow the application of other required conservation materials, e.g., repair mortars, paints or protective treatments. Therefore, hydrophobic consolidating materials may be problematic if it is foreseen the application of water-based materials in the following conservation steps.

The penetration ability of the consolidating fluid depends on its viscosity and surface tension. Low viscosity and high surface tension (low contact angle) are favourable characteristics for a good penetration and fast absorption of the consolidant by the mortar. The particles size of the consolidating material is another important parameter, particularly in the case of consolidants that are based on the dispersion of nanoparticles in water or alcohol, e.g. nanolime, nanosilica, dispersions of synthetic resins in water. The particles of the consolidating material need to be significantly smaller (ten to hundreds of times) than the pores of the mortar to be able to penetrate into the mortar effectively. The penetration ability of the consolidant is also strongly affected by the porosity of the render or plaster. Mortars with small and thin pores are expected to absorb the consolidating liquid more difficultly than porous mortar with relatively large pores and eventually also cracks. The contact time of the consolidating liquid with the surface of the plaster or render has to be adapted according to the penetration ability of the consolidant into the specific plaster or render and to the required penetration in view of the expected consolidating effect.

The goal of the consolidation treatment is to improve the cohesion of the degraded material, aiming at returning the original structural and strength properties to the mortar. Therefore, the concentration of the effective binding substance present in the consolidating liquid has to be carefully adapted to the requirements related to the strengthening effect. The strength increment resulting from the consolidation treatment should not be very high because, in most cases, the strength of historical plasters/renders is in the order of a few MPa. In the case of some consolidants, the concentration of the effective substance is very low, for instance lime water containing only 0.16% w. of calcium hydroxide must be repeatedly applied to achieve a satisfying consolidation effect. On the other hand, there are consolidants with a high concentration of the effective substance, e.g. nanolime products containing up to 5% w. of calcium hydroxide, where one or a few applications can be sufficient.

The penetration ability of a consolidant also depends on its concentration, which should also be considered, as the penetration ability is reduced with increasing concentration. It is often better to apply a less concentrated consolidant repeatedly and/or progressively increasing its concentration than to apply a high concentrated product only once. The consolidants used mainly for stone consolidation (ethyl silicate or nanosilica) have relatively high content of SiO_2 (dozens of percent) and this fact should be considered to avoid the risk of over-strengthening. Low concentrated (diluted) variations of up to 10% w. should be more appropriate for the consolidating treatment of historical mortars.

The method of application should be practicable, considering the given conditions (damage type, geometry of the surface to treat, ambient temperature and moisture, required contact time).

7.2. Results and recommendations based on evaluation of stone consolidation treatment

Many claims mentioned in the previous subchapter regarding the general aspects, which should be considered before a choice of a possible consolidant for a specific mortar (plaster, render), should also be considered in case when someone intends a stone consolidation treatment. Mainly these parameters and aspects should be taken into account before choosing a specific consolidant for a specific stone: chemical similarity between components of both consolidant and stone, possible chemical reactions in stone after intended stone treatment and possible character (beneficial or risky) of expected reaction´ products; requirements for the needed strength gain in the specific case; porosity of stone, stone absorption capacity, stone pores or cracks diameter and penetration ability of possible consolidant; consolidant solid component properties such as particles´ size and amount, then properties of consolidant liquid medium (water or organic solvent) such as surface tension, dynamic viscosity, boiling point and evaporation rate influencing consolidant transport and required favour deposition into stone structure; possible stone colour change and its possible acceptance.

The performance of the treatment should be assessed in situ or in laboratory using specific stone specimens or model substrates imitating the stone to be treated following evaluation based on comparison with the untreated material.

The thesis presents several laboratory experiments investigating the effects of various consolidants on stone. The results of the experiments can be briefly summarized as follows.

The study of nanolime based consolidant CaLoSiL applied on porous Maastricht limestone´ surface proved that lime nanoparticles can be transported by capillary absorption within relatively large distance below the absorption surface (5 cm was detected) when stone pores are of favour (large) size. It should be considered, that Maastricht limestone consists of pores with diameter 48 μm (measured by MIP), that exceeds transported lime nanoparticles (with diameter 0.1-0.25 μm) of about 200-500 times.

Results based on quantitative evaluation of the strength gain achieved after performed consolidation treatment of Maastricht stone with nanolime has been following: bending strength after two subsequent treatments improved by 20% for CaLoSiL E 25, 18% for CaLoSiL IP 25 resp. 54% for CaLoSiL E 50 and compressive strength by 50 % (CaLoSiL E 25), 23% (CaLoSiL IP 25) resp. 73% (CaLoSiL E 50). However, it was found that the higher number (4-6) of subsequent applications led to irregular deposition of applied lime within stone and the accumulation of nanolime at or just beneath the surface. This trend was more significant when the more concentrated nanolime product (50 g/L) was used. Therefore, less concentrated nanolime products with a $Ca(OH)_2$ content of up to 25g/L is recommended to use for consolidating porous limestone.

Flexural strength, ultrasound velocity and open porosity were investigated in the depth profile of Maastricht limestone specimens in order to study characteristics´ variability caused by inhomogeneous nanolime deposition within the stone block (dimensions 3x5x5 cm). Applied methodology was evaluated as successful. The porosity measurements corresponded with the mechanical characteristics results, showing that multiple applications of the CaLoSiL nanolime resulted in the accumulation of nanolime near the stone evaporation surfaces, particularly in case that more concentrated nanolime was used. On average, the open porosity of treated stone decreased due to treatment, but reduction was relatively modest (MIP porosity dropped from 50% to 46,5% after two subsequent treatments with CaLoSiL E 25).

Two another method was successfully applied for mapping the consolidant distribution inside the Maastricht limestone; the imaging method based on differential X-ray radiography and the drilling resistance measurement system.

Concerning the stone colour, white hazes appeared on the Maastricht limestone surface after six repeated treatments with nanolime (CaLoSiL IP 25 or E 50). This phenomenon relates to the described accumulation of lime particles at stone evaporation surface. White hazes were not found for specimens treated with CaLoSiL E 25. Regarding the choice of a solvent, the ethanol based product (CaLoSiL E) showed better results compared the isopropanol type (CaLoSiL IP) in terms of favourable deposition of nanolime within the stone structure.

It was concluded, that consolidation of porous limestone with nanolime suspensions can result in the heterogeneous deposition of lime nanoparticles within stone pores network, partially due to the back migration of the particles towards the surface during the solvent evaporation process leading to the formation of a high density superficial layer. A new technique was suggested to achieve an in-depth homogeneous distribution of calcium hydroxide nanoparticles in Maastricht limestone, which consisted of applying water immediately after the application of the consolidant.

In response to published and orally disseminated Maastricht limestone results in relation to nanolime consolidation treatment, studies dealing with a similar topic were published in the next years by other researchers, e.g. by G. Borsoi [Borsoi et al. 2016 a, b, c].

In the frame of the *STONECORE* project and following *NANOLITH* project, where the thesis´ author participated as a researcher, another application of nanolime products for stone conservation was investigated and suggested. Consolidation techniques based on combined treatment of stone with nanolime and then with ethylsilicate (silicic acid ester) achieved very promising results and were recommended for consolidation of porous limestone [Ziegenbalg & Piaszczynski 2012]. Application of nanolime products not only for limestone strengthening but also as a component of the protective painting system or as a grouting material was studied, and outputs from conducted testing including practical examples of stone monuments restoration was published [Macounova at al. 2016].

Strengthening of disintegrated renders and stone represents an important intervention during conservation or restoration of our building and architectural culture heritage. In the same time, it remains to be a current research theme and a topic of European and national research projects.

Although many questions have been answered by scientific investigations, many questions remain. One of them is the task of designing and optimization of specific application conditions for a given material to ensure required deposition of consolidant within a degraded surface layer.

Chapter 8

Research application in technical practice

In practise, conservators, restorers and other experts dealing in the field of conservation of culture heritage are very interested in research results, that can improve conservation procedures and technologies. Some of research projects solved by the thesis´ author were focused on a development and publishing the applied research outputs. Examples of these results are as follows:

- Contract for utilization of research and development results with the restoration company GEMA ART GROUP a.s. regarding two developed culture heritage procedures, proven by the Ministry of Culture of the Czech Republic: "Consolidation of the historical lime plaster by suspension of calcium hydroxide nanoparticles in alcohol" and "Consolidation of the porous limestone by suspension of calcium hydroxide nanoparticles in alcohol" [Slížková and Frankeová 2015 a, b].
- Certified methodology for determining the decisive material characteristics of historical materials for the purpose of the planning of restoration intervention [Slížková et al. 2016].

The mentioned publications were written in Czech. As illustration of these outputs, one conservation procedure and one certified methodology are annexed to the thesis.

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Appendix I

The certified methodology is presented in the Czech language with original numbering of tables and used references.

METODIKA URČENÍ ROZHODNÝCH MATERIÁLOVÝCH CHARAKTERISTIK HISTORICKÝCH STAVEBNÍCH MATERIÁLŮ PRO PLÁNOVANÝ RESTAURÁTORSKÝ ZÁSAH

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Metodika je výsledkem výzkumného projektu s názvem „Podmínky a požadavky kompatibilní péče o historické anorganické porézní materiály“ (DF12P01OVV018), podporovaného v letech 2012-2015 Ministerstvem kultury ČR v rámci výzkumného programu NAKI.

Oponenti

Ing. arch. Miloš Solař
Pracoviště: Generální ředitelství Národního památkového ústavu
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Anotace

Metodika předkládá výčet materiálových vlastností, které je důležité posoudit při navrhování postupu určitého konzervačního nebo restaurátorského zásahu na stavebním památkovém objektu. Jsou popsány materiálové vlastnosti, jejichž zhodnocení by mělo být východiskem pro navržení určitého postupu povrchové úpravy, čištění, konsolidace, doplnění chybějící hmoty nebo hydrofobizace památkového objektu, aby restaurátorský zásah splňoval nároky na kompatibilitu materiálů. Tyto vlastnosti jsou zjišťovány při předprojektové přípravě nebo restaurátorském průzkumu v rámci obnovy památkových objektů nebo předmětů kulturního dědictví. Metodika je určená pracovníkům památkové péče, restaurátorům, architektům a projektantům pro přesnější zadávání zkoušek a analýz materiálových vlastností.

I. Úvod

Základním předpokladem pro stanovení potřeb, metod a postupů odborného ošetření (konzervace/restaurování) každého objektu kulturní povahy je jeho poznání, jež dovoluje v prvé řadě specifikovat předmět ochrany. Předmětem ochrany se pro účely této metodiky rozumí hmotná podstata objektu (materiál), jež je nositelem estetické nebo historické hodnoty díla a dílčích informací různého charakteru.

Podle současného pojetí, vycházejícího z Benátské charty z roku 1964, je cílem restaurování zachovat a odhalit estetické a historické hodnoty památky [13]. Restaurování je založeno na respektu k originálnímu materiálu. Otázky, jaká část nebo povrchová vrstva materiálu má kulturní hodnotu, a tím právo na památkovou ochranu, a co všechno přispívá ke komplexní hodnotě památky a musí být při restaurování zohledněno, nejsou jednoduché a jejich řešení často vyžaduje potřebnou diskuzi odborníků. Konečné rozhodnutí o cílech a rozsahu restaurování/konzervace je v kompetenci odborné organizace státní památkové péče.

Cílem této metodiky je předložit seznam materiálových vlastností, které mají být zjištěny a/nebo hodnoceny v rámci materiálového průzkumu památkových objektů a předmětů kulturní povahy v souvislosti s připravovaným restaurátorským nebo konzervačním zásahem. Tyto vlastnosti jsou zjišťovány při předprojektové přípravě nebo při restaurátorském průzkumu v rámci obnovy památkových objektů nebo předmětů kulturního dědictví. Metodika je určená pracovníkům památkové péče, restaurátorům, architektům a projektantům pro přesnější zadávání požadavků na zkoušky a analýzy materiálových vlastností, aby výsledky průzkumu byly efektivně využitým informačním podkladem pro upřesnění cílů, rozsahu a metod konzervačního/restaurátorského postupu.

II. Potřebnost metodiky

Pro zjištění rozsahu restaurátorských průzkumů vypracovaných v posledních letech byla provedena analýza několika desítek průzkumů uložených v archivu NPÚ ÚOP HMP. Analýza odpověděla na otázky: jaké materiálové vlastnosti se v praxi nejčastěji zjišťují, jaké výstupy poskytly provedené průzkumy, jak jsou tyto výstupy použitelné pro restaurování či záchranu památky.

Nedostatečná kvalita analyzovaného souboru průzkumů potvrdila potřebu vypracování metodiky obsahující přehled materiálových vlastností, jejichž znalost je zásadní pro navržení technického provedení určitého konzervačního nebo restaurátorského zásahu.

III. Výběr materiálových vlastností na základě experimentálních studií

Vzhledem k rozsahu tématu se metodika soustředila na stanovení rozhodných materiálových charakteristik pro čtyři základní restaurátorské zásahy, prováděné na anorganických stavebních materiálech, jmenovitě na tyto zásahy:

- konsolidaci
- čištění
- doplnění vybraných typů hornin umělým kamenem (tvárnými směsmi)
- hydrofobizaci.

Při aplikaci metodiky je třeba věnovat zvláštní pozornost objektům s nehomogenní materiálovou skladbou, např. vícevrstvým omítkám, povrchům se zbytky polychromie apod., které mohou ovlivnit rozsah restaurátorského zásahu a tím i rozsah a skladbu průzkumu.

III.1. Čištění

Záměrem čistícího zásahu je odstranění sekundárně deponovaného materiálu podle požadavků památkové péče. Jedná se obvykle o materiál, který mění barvu, strukturu, složení a další vlastnosti původního materiálu památky. Ke změně dochází u porézních materiálů postupně ve směru od povrchu do hloubky, u kompaktních materiálů skokem s ostrou hranicí mezi původním materiálem a sekundárním (krustou).

Důležité jsou strukturní vlastnosti posuzovaného materiálu v blízkosti povrchu a je výhodné je vyšetřit mikroskopicky, na leštěném výbrusu příčného řezu povrchovou vrstvou zkoumaného materiálu. Tentýž výbrus může posloužit k určení mineralogického složení materiálu (hlavní a vedlejší složky) pomocí optické polarizační mikroskopie a dále k určení prvkového chemického složení materiálu pomocí skenovacího elektronového mikroskopu s EDX analyzátorem. Pokud je potřeba provést detailnější studium některých složek (stanovení uhlíkatých povrchových nečistot [11,12], zbytky nežádoucích povrchových úprav, podezření na přítomnost objemově nestabilních jílových minerálů), používají se analytické instrumentální metody: (pyrolýzní) plynová chromatografie s hmotnostní detekcí (GC/MS), infračervená (FTIR) a/nebo Ramanova spektrometrie, rentgenová difrakce (XRD), termická analýza. Výše uvedené metody se použijí i pro vyšetření povrchových úprav a konzervačních látek, které mají zůstat zachovány (zbytky polychromie, hodnotné povrchové úpravy). Zejména při použití chemických látek pro čištění je nutno znát a posoudit chemické a mineralogické složení čištěného materiálu včetně vedlejších složek, tmelů a povrchových úprav. Před použitím vody pro čištění povrchu je nutné zvážit rozpustnost složek materiálu ve vodě a smáčivost povrchu pro vodu [10]. Pokud formy poškození materiálu ukazují na přítomnost vodorozpustných solí, je na místě vyšetřit, kvantifikovat a monitorovat obsah solí.

Také při použití čisticích metod využívajících chemické látky (např. uhličitan a hydrogenuhličitan amonný, fluorid amonný, slabé organické kyseliny) je možné zkontrolovat obsah zbylých chemikálií v materiálu po čištění (např. amonné, fluoridové ionty).

Po selektivním odstranění nečistot by mělo následovat hodnocení změny materiálových vlastností. Z fyzikálních vlastností jsou to především rychlost vsakování vody do materiálu (koeficient kapilární absorpce) a rychlost vysychání, které referují o návratu k původním transportním vlastnostem materiálu pro vodu. Pokud šlo v procesu čištění o redukci nebo odstranění vrstvy, která omezovala prostupnost vodní páry (např. některé historické konzervační prostředky, syntetické pryskyřice nebo kompaktní krusta), je možné zkontrolovat také faktor difuzního odporu. Orientační míru paropropustnosti lze také pouze odvodit z četnosti, velikosti a propojenosti pórů v hloubkovém profilu vzorku zjištěných při mikroskopickém vyšetření strukturních vlastností. Pro posouzení změny povrchové soudržnosti materiálu před a po čištění je v případě potřeby možné využít metodu odtržení lepicí pásky, tzv. peeling test [19]. Hodnocení změn strukturních vlastností a složení ve směru od povrchu do hloubky materiálu po čistícím zásahu se provede opět mikroskopickým vyšetřením výbrusu příčného řezu (OM, OPM a SEM-EDX). Barvu lze hodnotit makroskopicky, subjektivně okem nebo instrumentálně s využitím spektrometru. Mikroskopické vyšetření nábrusu nebo výbrusu příčného řezu v odraženém světle poskytne informaci o barvě, příp. odlišnostech barvy materiálu v hloubkovém profilu.

III.2. Konsolidace

Cílem konsolidačního zásahu je zlepšení soudržnosti degradovaného materiálu. Proto se nejprve zjišťuje profil vlastností materiálu ve směru od povrchu do hloubky a podle výsledku se určí, do jaké hloubky je třeba materiál impregnovat konsolidačním prostředkem. Může se jednat o stovky µm (fixace degradované povrchové vrstvy) až po jednotky cm. Hloubkový profil vlastností materiálu je možné zjistit více způsoby. V některých případech lze soudržnost materiálu do hloubky posoudit orientačně přímo na objektu škrabáním pomocí skalpelu. V laboratoři je možné stanovit hloubkový profil vlastností přesněji, ale na odebraném vzorku. Na základě mikroskopického vyšetření (SEM, OM) nábrusu nebo výbrusu příčného řezu vzorkem se zjistí strukturní vlastnosti i spojení jednotlivých zrn materiálu směrem od povrchu do hloubky. Mechanické vlastnosti lze odvodit z hloubkového profilu rychlosti šíření ultrazvukového signálu. Jednotlivé rychlosti se měří ve směru paralelně s povrchem na odebraném tělísku ve tvaru válce nebo kvádru. Vzorek je postupně proměřován v různých vzdálenostech od povrchu tělíska a pevnostní profil je odvozen z hodnot rychlosti šíření UZ signálu zjištěných v různých vzdálenostech od povrchu. Pokud je odebraný vzorek natolik soudržný, že jej lze dále rozřezat na dílčí plátky paralelní s povrchem, je možné změřit pevnost v ohybu u jednotlivých plátků, lišících se vzdáleností od povrchu. Mezi částečně destruktivní způsoby patří zkouška odporového vrtání, jejíž smysluplné užití je však limitováno na materiály jemnozrnné a homogenní z hlediska tvrdosti jednotlivých složek (problémem je např. vápenná malta s relativně tvrdým křemenným pískem a měkkým vápenným pojivem).

Z hlediska výběru vhodného konzervačního prostředku pro konsolidační zásah je důležitá znalost chemického a mineralogického složení materiálu (výhodou je, pokud má konsolidant stejné nebo podobné složení, jako má pojivo nebo tmel degradovaného materiálu). Z hlediska penetrační schopnosti prostředku je důležité posoudit velikost pórů materiálu, protože některé konsolidační produkty nemusí vyhovovat z hlediska velikosti částic (experimentálně bylo zjištěno, že velikost póru materiálu musí být 100x větší než je velikost částic konsolidačního prostředku, aby prostředek dosáhl potřebné penetrační hloubky). Např. disperzní produkty (koloidní roztoky) obsahující částice s velikostí v řádu stovek nanometrů penetrují dostatečně hluboko pouze do materiálů s velikostí pórů nad 10 mikrometrů. Velikost pórů degradovaného materiálu je možné stanovit rtuťovou porozimetrií, v tom případě však získáme jednu celkovou hodnotu pro objem vzorku cca 1 cm3 bez zohlednění případných odlišností materiálu v hloubkovém profilu. Je proto vhodné tuto zkoušku doplnit mikroskopickým vyšetřením nábrusu nebo výbrusu příčného řezu potřebnou vrstvou materiálu, které poskytne informace o struktuře pórů v hloubkovém profilu a odhalí případné tenké kompaktní vrstvy na povrchu materiálu, které by mohly bránit penetraci konsolidačního prostředku. Studium mikrostruktury s využitím SEM-EDX, ev. OPM může být zacíleno vedle strukturních vlastností také na chemické a mineralogické složení materiálu.

Před konsolidací by měl být degradovaný materiál odsolený a neměl by mít vysoký obsah vlhkosti. Obsah ev. přítomných solí v materiálu a obsah vlhkosti musí být před konsolidací známý a uvažovaný před výběrem konsolidační technologie. Dále je žádoucí vyhodnotit smáčivost materiálu vodou nebo organickým rozpouštědlem (ethanol, isopropylalkohol) a zjistit, zda povrch materiálu má hydrofilní nebo hydrofobní vlastnosti [10].

Rychlost vsakování vody do materiálu se zjistí Karstenovou trubicí nebo mikrotrubicí [20]. Tento parametr rovněž vypovídá o hydrofilním nebo hydrofobním chování povrchu a navíc z něho lze odvodit časové nároky na konsolidační ošetření: materiály s nízkým koeficientem absorpce potřebují delší čas pro ošetřování (sprejování, natírání, polévání, obklad), zatímco pro materiály s vysokým koeficientem absorpce stačí pro dosažení určité hloubky penetrace výrazně kratší čas smáčení povrchu konsolidačním prostředkem. Protože konsolidační ošetření degradovaného materiálu by nemělo výrazně měnit transportní vlastnosti materiálu pro vodu, tato vlastnost materiálu se kontroluje s různým časovým odstupem také po provedeném zásahu a hodnotí s přihlédnutím ke konkrétním požadavkům a vlhkostním podmínkám objektu.

Hodnota otevřené (efektivní) pórovitosti materiálu umožňuje odhad potřebného množství konsolidačního prostředku při zvolené penetrační hloubce. Materiály s vyšší pórovitostí absorbují více konsolidantu a naopak. Otevřená pórovitost se zjišťuje nasáknutím vzorku vodou a jeho vážením na vzduchu a ve vodě (hydrostatické vážení) nebo pomocí rtuťové porozimetrie (v tomto případě získáme pórovitost pouze pro rozsah pórů 3 nm až 300 μm). Otevřenou pórovitost je možné stanovit také obrazovou analýzou mikroskopických snímků nábrusů připravených z odebraných vzorků materiálu.

Konsolidační zásah je založen na dodání nového pojiva do degradovaného materiálu. Toto pojivo by mělo být rovnoměrně rozptýleno v ošetřené vrstvě materiálu. Obvykle dochází v důsledku konsolidace k zúžení pórů materiálu (snížení velikosti pórů, ve kterých se prostředek ukládá), a také ke snížení otevřené pórovitosti. Míra těchto změn se po zásahu kontroluje zkoušením sledované vlastnosti na vrstvě konsolidovaného materiálu a hodnotí se ve vztahu k parametrům stejného materiálu v dobrém stavu nebo v požadovaném stavu. Velikost pórů a pórovitost ovlivňuje transportní vlastnosti vody materiálem, proto by se nové hodnoty po konsolidaci neměly výrazně odchýlit od hodnot charakteristických pro daný materiál a od hodnot, který má daný materiál pod ošetřenou zónou. Rizikem vysokého zaplnění pórů a výrazného snížení pórovitosti materiálu v povrchové ošetřené vrstvě je např. zadržování vody pod ošetřenou vrstvou v důsledku zpomalení vysychání vody zevnitř materiálu přes ošetřený povrch, což může vést k poškození materiálu mrazovými cykly nebo solemi.

Konsolidace by měla vést k nárůstu pevnosti degradovaného materiálu, i nárůst pevnosti však musí mít určité limity. Kontrola nového pevnostního profilu se provádí stejným způsobem jako před konsolidačním zásahem. Vedle rychlosti absorpce a vysychání vody (ev. i vodní páry), mechanických vlastností (pevnosti v ohybu, rychlosti šíření UZ signálu, modulu pružnosti [27]), je nutno kontrolovat také vliv konsolidace na vlhkostní a teplotní roztažnost materiálu. Tyto vlastnosti lze měřit na malých vzorcích s využitím komerčních nebo speciálně vyvinutých dilatometrů [31, 32].

Limitujícím faktorem pro zkoušení vlastností ošetřené vrstvy po zásahu je tloušťka a lokalizace této vrstvy: v případě tenké vrstvy je stanovení některých vlastností obtížné vzhledem k malému objemu posuzovaného materiálu, zejména in situ. Jednodušší disciplínou je zkoušení vlastností ošetřené vrstvy na modelových laboratorních vzorcích, které napodobují „zdravý a degradovaný“ materiál. V případě hodnocení zásahu na objektu se přednostně využívají nedestruktivní nebo semi-destruktivní metody zkoušení: hodnocení soudržnosti materiálu tzv. peeling testem, hodnocení pevnosti a modulu pružnosti ultrazvukovým vyšetřením, pevnostního profilu odporovým vrtáním (tloušťka vrtáku 3 mm), sorpčních vlastností kapkovou zkouškou nebo využitím trubic nebo mokrých houbiček), mikroskopické vyšetření odebraného vzorku upraveného do nábrusu nebo výbrusu příčného řezu.

Pořadí důležitosti jednotlivých zkoušek se může lišit podle konkrétní situace.

III.3. Doplňování (tmelení, náhrada poškozeného materiálu novým)

Při návrhu složení doplňků bychom měli vycházet ze základního požadavku, který uvádí i Benátská charta (Mezinárodní charta o konzervaci a restaurování památek a sídel), tj. že ideální opravná malta pro doplňování přírodního kamene by měla být dostatečně trvanlivá, avšak měla by časem podléhat přirozenému stárnutí, a to rychleji než stárne originál. O rychlosti stárnutí rozhodují vlastnosti porézních materiálů, a je zřejmé, že některé z nich jsou pro rychlost degradace a živostnost porézních materiálů zásadní, tj. kritické.

Z literatury i ověřovacích studií je však zřejmé, že na vlastnosti tvárné směsi má určující vliv typ pojiva; je známo, že malty ze vzdušného vápna jsou méně pevné oproti hydraulickým pojivům, avšak vyznačují se vyšší propustností pro vodu, vodní páru i elasticitu malt. Při doplňování historických omítek je složení pojiva opravné malty zřejmé; problém nastává při optimalizaci složení pojiva malty pro opravu hornin, které se svými vlastnostmi od omítkových substrátů značně odlišuje. Plnivová složka ovlivňuje kvalitu a do určité míry i vlastnosti malt zvoleným mineralogickým složením, distribucí a tvarem částic. Parametry plniva významně ovlivňují strukturu malty a její vizuální podobu. Při výběru plniva v případě doplňků na kámen jsou však tyto parametry dány strukturou doplňované horniny a zpracovatelskými vlastnostmi. Běžnou praxí při volbě kameniva je využívání drcené horniny, která požadavky na shodu ve struktuře i zpracovatelské vlastnosti nejčastěji nejlépe splňuje. Vlastnosti opravných malt lze také ´řídit´ nastavením poměru jednotlivých složek, tj. pojiva a plniva a dále množstvím záměsové vody. Navýšením obsahu pojiva i množstvím záměsové vody se zvyšuje porozita malty a s ní související ostatní vlastnosti. Nadbytek vody nebo pojiva v maltě je na druhou stranu příčinou smrštění malt a vzniku prasklin a trhlin. Také podmínky přípravy malty a jejich expozice mohou zásadně ovlivnit trvanlivost opravy.

Při provádění oprav na porézní podklad je zřejmé, že složení doplňovacího materiálu na kámen musí vycházet z poznání tmelené horniny, tj. jejího mineralogického složení a její mikrostruktury. Její charakterizaci lze provádět nejlépe pomocí mikroskopických technik, zejména optické mikroskopie v polarizovaném a nepolarizovaném světle a dále pak skenovací elektronové mikroskopie s EDX mikrosondou (SEM-EDX). Další možností je využití rentgenové difrakce nebo tzv. termické analýzy. Mikroskopické techniky využívají pro charakterizaci vzorek upravený do formy nábrusu nebo výbrusu, který se pozoruje v procházejícím a odraženém světelném režimu. Kromě informace o mineralogickém složení poskytuje informaci o stavu materiálu, korozních fenoménech, příp. chování konzervačních látek v porézním systému. Může dále poskytnout informaci k mikrostruktuře a porézním systému a tak doplnit informaci o mikrostruktuře.

Mikrostrukturní vlastnosti materiálu (celková pórovitost, velikost pórů a jejich distribuce, spojitost pórů) ovlivňují transport vody a vodní páry materiálem (rychlost absorpce a vysychání vody z materiálu). Nejčastěji se stanovuje rtuťovou porozimetrií a přináší zásadní informaci ke skladbě pórů, jejich velikosti a zastoupení. Z hlediska interakce materiálu s vodou jsou nejzásadnější tzv. kapilární póry, které se podílejí na transportu vody v porézním systému. Naopak příliš malé póry ´mikropóry´ nebo naopak póry veliké, tzv. makropóry, vzniklé např. zvětráváním materiálu, průchod vody porézním systémem zpomalují. Se skladbou pórů a jejich přístupností souvisí další rozhodný parametr, tj. kapilární absorpce, která se měří jako množství vody, které je schopné daný materiál pojmout v rámci časového intervalu. Tato nasákavost tedy zjednodušeně souvisí s kapilární aktivitou materiálu a její poznání je zásadní pro hodnocení chování materiálu při jejich zavlhčení a naopak vysýchání. Mezi rozhodné charakteristiky patří i vlastnosti související s pevností materiálu a jeho pružností, tj. pevnost v tlaku, tahu za ohybu a dynamický modul pružnosti. Z ověřovacích studií i dat z literatury však jednoznačně vyplývá, že pevnostní charakteristiky jsou rozhodné pouze v případech doplňků omítek nebo malt opravnými maltami, nikoliv však při doplňování hornin, které představují substrát se zcela odlišnými mechanickými vlastnostmi.

III.4. Hydrofobizace

Hydrofobizace (hydrofobní úprava nebo vodoodpudivá úprava povrchu) je postup, při kterém je na porézní materiál aplikován hydrofobní prostředek, který má výrazně zvětšit úhel smáčení materiálu pro vodu a tím snížit nasákavost tohoto materiálu. Hydrofobizace se obvykle provádí na exteriérových površích, které jsou značně exponovány srážkám nebo stékající vodě a kde je cílem tuto vodu rychle z povrchu odvést a minimalizovat její vsáknutí. Z povahy věci nejde o opravný zásah, ale o preventivní opatření.

Výsledný efekt aplikace hydrofobizačního prostředku, tj. změna smáčecího úhlu pro vodu, je dána souhrou řady faktorů, jako je obsah vlhkosti v substrátu, teplota prostředí, atmosférický tlak, rychlost odparu prostředku, velikost pórů substrátu, hrubost povrchu substrátu a další. Jak již bylo naznačeno, při rozhodování, zda hydrofobizaci provést a v jakém rozsahu, hrají zásadní roli vlastnosti konstrukce, jejího geometrického uspořádání, stav materiálu i konstrukce z hlediska zatížení vlhkostí a vodorozpustnými solemi (momentálního i možného budoucího), popřípadě další skutečnosti (např. výskyt nových vápenných omítek, výskyt uměleckých děl na obou stranách konstrukce, výskyt starších konzervačních prostředků atd.).

Dopad provedené hydrofobní úpravy se hodnotí zejména dosaženým snížením nasákavosti. To je dáno v zásadě změnou úhlu smáčení pro vodu a hloubkou penetrace hydrofobního prostředku. Čím je úhel smáčení a hloubka penetrace větší, tím více je snížena nasákavost materiálu. Úhel smáčení je v terénu poměrně obtížně měřitelný. Základní představu si lze udělat při vhodném uspořádání (horizontální rovná plocha) při vyfocení kapky vody a následném odečtení úhlu z fotografie. To je schůdné zejména u leštěných, málo nasákavých materiálů, kde není kapka příliš deformována nerovnostmi podkladu a materiál (byť mikroskopicky heterogenní) lze popsat jedním úhlem smáčení. V případě porézního materiálu s nerovným povrchem je obtížné z deformovaného tvaru kapky aproximovat úhel smáčení a jeho hodnocení je problematické i laboratorně. S výhodou lze využít měření tzv. dynamického úhlu smáčení, kdy je pořízen videozáznam nebo sekvence fotografií vsakující se kapky. Měření lze využít i pro nasákavé materiály a vypovídá nejen o úhlu smáčení suchého materiálu, ale také o chování materiálu již smočeného.

V praxi se obvykle přistupuje přímo k hodnocení nasákavosti materiálu, kterou je možné měřit buďto in situ nebo jako standardizovanou veličinu laboratorně. Pro in situ měření nasákavosti byla vyvinuta řada metod, které se liší požadavky na měřený povrch, citlivostí k nehomogenitám i citlivostí ke změně nasákavosti. Naměřená data jsou nejčastěji zpracována ve formě diference před a po ošetření, srovnání mezi různými materiály je možné s přihlédnutím k různorodosti materiálů (jejich hrubosti, velikosti a tvaru pórů atd.). Pro orientační zjištění, které je v praxi nejčastější, se používá jednoduché smočení povrchu a sledování, zda dochází ke sbalování kapek a zda je část tekutiny postupně sorbována materiálem. O něco složitější metoda spočívá v měření stopy, kterou zanechá kapalina po bodovém smočení vertikálně orientovaného povrchu materiálu. Metoda je vhodná i na poměrně hrubé povrchy a dokáže zachytit velmi malé rozdíly nasákavosti materiálu. Pro nesmáčivé materiály je obvykle stopa neměřitelná, neboť dochází ke sbalení vody do kapek.

Tradiční metodou pro zjištění in situ nasákavosti je Karstenova trubice, která umožňuje získat časovou závislost vsakování vody definovanou plochou. Vzhledem k testované ploše je metoda použitelná i na značně hrubozrnném materiálu, limitující však může být fixace trubice na málo pevném materiálu (degradovaný kámen či omítka). Velmi přesné měření lze získat pomocí mikrotrubice pracují na podobném principu, avšak s o několik řádů menšími objemy a řádově menší kontaktní plochou. Na rozdíl od Karstenovy trubice se v tomto případě téměř neuplatňuje gravitační síla a absorpce vody je závislá pouze na kapilárních silách. V případě středně a hrubozrnných materiálů je metoda vzhledem k malé kontaktní ploše omezena heterogenitou materiálu a je třeba hodnotit větší množství míst. Pro málo porézní a tedy málo nasákavé materiály byly vyvinuty další kontaktní metody, které jsou založeny na hodnocení změny hmotnosti houby nasáklé destilovanou vodou po přiložení definovanou plochou na definovaný čas na měřený materiál. Metoda je vhodná zejména na hladké rovné povrchy jako například leštěný mramor nebo žula. V praxi může být hydrofobním prostředkem dosaženo takového snížení nasákavosti, že uvedená měření, respektive časy potřebné k dosažení měřitelných objemů vsáklé kapaliny jsou příliš dlouhé. Pro hodnocení pak postačuje skutečnost, že povrch je pro vodu nesmáčivý.

Pro laboratorní měření nasákavosti lze postupovat v souladu s normou ČSN EN 13755: Zkušební metody přírodního kamene - Stanovení nasákavosti vodou za atmosférického tlaku.

Hloubku průniku hydrofobizačního prostředku, která je důležitým faktorem účinnosti hydrofobizace a její životnosti, lze v praxi určit poměrně snadno, avšak téměř výhradně vždy destruktivně. Nejjednodušší metoda spočívá v odebrání materiálu do dostatečné hloubky (vyseknutí vzorku omítky, jádrový vývrt kamene apod.) a změření nenasákavé vrstvy po ponoření vzorku do vody. Hloubku průniku prostředku lze sledovat dále řadou sofistikovanějších metod, které jsou založeny například na barvení ošetřeného vzorku (např. nástřik roztokem s indikátorem diphenylthiocarbazonem, který reaguje s nejběžnějším katalyzátorem organokřemičitanů –dibutylcíndilaurátem).

Další vlastnosti, které jsou při aplikaci hydrofobizace v praxi sledovány, jsou barevná změna materiálu a změny lesku (odrazivosti) povrchu materiálu. V obou případech je žádoucí, aby docházelo k minimálním změnám, v praxi však hydrofobní ošetření většinou vede k různě intenzivnímu probarvení (zvýraznění) barevnosti materiálu v souvislosti s uzavřením mikroprasklin na jeho povrchu a tedy se snížením rozptylu světla na povrchu materiálu. Změny lesku materiálu jsou obvykle vnímány jako více nežádoucí, ale dochází k nim spíše v souvislosti s technologickou chybou (rychlé vyschnutí prostředku, aplikace přílišné koncentrace prostředku apod.), vhodnými podmínkami aplikace je lze téměř zcela minimalizovat. Tyto barevné a další změny se v praxi nejčastěji hodnotí vizuálně. V případě potřeby objektivnějšího hodnocení je (opět s určitými omezeními danými kvalitou a morfologií povrchu) možné absolutní celkovou barevnou změnu vyhodnotit exaktně pomocí přenosného spektrometru. Podobně lze objektivizovat změny lesku měřením změny reflektance povrchu.

Paropropustnost je z hlediska povrchových úprav porézních materiálů důležitá veličina, kterou lze však získat pouze laboratorním měřením na standardizovaných vzorcích.

Měření probíhá například dle normy ČSN EN 15803 Stanovení paropropustnosti vodní páry. V praxi nebývá v souvislosti s prováděním hydrofobizace testována, tyto testy jsou prováděny v rámci certifikace komerčních hydrofobizačních prostředků a dopad aplikace prostředku na paropropustnost materiálu by měl být uveden v technickém listu produktu. V případě hydrofobizantů na bázi alkylalkoxykřemičitanů je dopad ošetření na paropropustnost materiálu obvykle malý, pokles nepřesahuje přijatelných 10 % a změna je při porovnání s ostatními typy hydrofobizačních prostředků (oleje, vosky, pryskyřice atd.) zanedbatelný.

Vedle paropropustnosti je důležité měření rychlosti vysychání vody z materiálu a vyhodnocení míry případného snížení rychlosti vysychání po hydrofobizaci povrchu (viz metoda č. 21).

V následující tabulce (Tab.1) jsou uvedeny materiálové vlastnosti, jejichž zhodnocení by mělo být východiskem pro navržení určitého postupu čištění, konsolidace, doplnění chybějící hmoty nebo hydrofobizace památkového objektu, aby restaurátorský zásah splňoval nároky na kompatibilitu materiálů.

Tab. 1. Materiálové vlastnosti pro návrh konzervačních a restaurátorských zásahů
(X – vlastnosti s vyšší prioritou, o – vlastnosti s nižší prioritou)

Vlastnost	**Symbol Jednotka**	**Čištění**	**Konsolidace**	**Doplnění**	**Hydrofobizace**	**Metody č.**
Hloubka degradované vrstvy, která má být zpevněna	- [mm]		X	o		1, 2, 4, 25, 26
Mikrostrukturní vlastnosti: četnost, velikost, tvar a propojenost pórů, množství pojiva/ tmelu, popis a lokalizace defektů (praskliny, trhliny)	popis mikroskopického nebo rentgenového obrazu příčného řezu	X	X	o	o	1, 2, 6, 7
Velikost pórů stanovená rtuťovou porozimetrií	- [µm]		O	X		4
Smáčivost pro vodu a org. rozpouštědla (úhel smáčení nebo doba vsáknutí kapky)	- [° nebo s]	X	X	X	X	23, 24
Koeficient kapilární absorpce vody	w [kg·m^{-2}·hod$^{-1/2}$]	X	X	X	X	20
Otevřená (efektivní) pórovitost	P_o [% obj.]		O	o	X	3
Chemické složení složek	-	X	O			2, 11-18
Přítomnost sekundárních vodorozpustných solí v hloubkovém profilu	- [% hm.]	o	X	X	X	10
Obsah vlhkosti v hloubkovém profilu	- [% hm.]		O		X	9
Minerální (fázové) složení materiálu v hloubkovém profilu	-	X	X		X	1, 2, 11, 13, 15,

						16
Rychlost vysychání vody	- [kg·m^{-2}·hod$^{-1/2}$]	o	o		X	21
Faktor difuzního odporu pro vodní páru	μ -	o	o		X	22
Povrchová soudržnost (hmotnost odtrženého materiálu)	- [g/m^{2}]	o	o			27
Odpor proti vrtání (pokud metoda poskytuje jednoznačně interpretovatelné výsledky)	- [N] nebo [s]		X			25
Přídržnost	f_u [N.mm^{-2}]			X		29
Rychlost šíření UZ signálu	V [km/s]		X	O		26
Modul pružnosti	E [MPa]		X	X		26, 28
Pevnost v tahu za ohybu	R_f [N·mm^{-2}]		X	X		28
Pevnost v tlaku	R_c [N·mm^{-2}]			X		28
Teplotní roztažnost	α_T [µm/K]		o	O		30
Vlhkostní roztažnost	α_H [µm/m]		o	O	o	31
Mrazuvzdornost	počet cyklů		o	O	o	32
Odolnost vůči vodorozpustným solím	počet cyklů		o	O	o	33
Přítomnost organických látek	-	o			o	13, 15,16, 18, 19
Přítomnost mikroorganismů v případě osídlení povrchu (bakterie, plísně, řasy, mechy, lišejníky)	-	o			o	1,2
Barva exponovaného (znečištěného) povrchu a referenční barva materiálu (barva lomové plochy materiálu, dohodou stanovená barva)	slovně nebo souřadnicemi barvy: L^*, a^*, b^*	X				38
Změna barvy a lesku	slovně nebo $\Delta E^* = \sqrt{\Delta L^{*2}+\Delta a^{*2}+\Delta b^{*2}}$	X	X	X	X	38

IV. Metody pro zkoušení materiálových vlastností

Metody používané pro stanovení materiálových charakteristik (tab. 1., sloupec vpravo), jsou v následující tabulce (tab. 2) rozčleněny do skupin podle cíle analytické nebo zkušební metody. Podrobnější popisy jednotlivých metod jsou uvedeny v příloze této metodiky.

Tab. 2. Metody a zkoušky pro charakterizaci materiálových vlastností

Metody pro studium mikrostrukturních charakteristik

Metoda č.	Název	Cíl analýzy	Možnost in situ
1	**Optická mikroskopie**	určení tvaru a velikosti zrn a pórů, popis počtu vrstev	**ano**
2	**Skenovací elektronová mikroskopie**	studium morfologie povrchu, tvaru, velikosti a četnosti částic	ne
3	**Stanovení pórovitosti přístupné vodě**	určení otevřené pórovitosti, nasákavosti a objemové hmotnosti	ne
4	**Rtuťová porozimetrie**	určení velikosti a distribuce pórů, pórovitosti v intervalu 3 nm – 200 µm	ne
5	**Sítová analýza**	zastoupení jednotlivých velikostních frakcí zrn v sypkém materiálu	ne
6	**Rentgenová tomografie**	zjištění prasklin, makropórů, poruch či přítomnost vnitřních konstrukcí z různých materiálů	ne
7	**Obrazová analýza**	určení velikosti, tvaru a četnosti částic, poměr složek	ne
8	**Plynová absorpce (metoda BET)**	stanovení velikosti měrného povrchu materiálu	ne

Metody pro studium materiálového složení

Metoda č.	Název	Cíl analýzy	Možnost in situ
11	**Rentgenová difrakční analýza**	identifikace anorganických krystalických fází materiálu i sekundárně vytvořených látek	ne
12	**Silikátová analýza**	chemické složení pojiva, poměr pojivo:plnivo	ne
2	**Skenovací elektronová mikroskopie s EDS detektorem**	prvková mikroanalýza fází přítomných ve vzorku	ne
13	**Termická analýza**	fyzikální nebo chemické vlastnosti pevných látek, zastoupení složek materiálu	ne
14	**Iontově výměnná chromatografie**	stanovení aniontů a kationtů vodorozpustných solí	ne
15	**Infračervená spektrometrie**	identifikace organických a anorganických sloučenin	ne
16	**Ramanova spektroskopie**	identifikace organických a anorganických sloučenin	**ano**
17	**X-ray fluorescenční spektroskopie**	chemická (prvková) analýza kovových i nekovových materiálů	**ano**

18	**Hmotnostní spektrometrie**	identifikace organických sloučenin	ne
9	**Stanovení obsahu vlhkosti**	zjištění vlhkostních poměrů objektu	**ano**
10	**Stanovení obsahu vodorozp. solí**	identifikace a distribuce rozpustných solí	**ano**
19	**Průzkum v UV světle**	zviditelnění složek, které nemusí být viditelné v denním světle	ne

Metody pro zjištění interakce porézního materiálu s vodou (vodnými roztoky)

Metoda č.	Název	Cíl analýzy	Možnost in situ
20	**Stanovení kapilární nasákavosti**	stanovení množství vody, které je vzorek schopen absorbovat kapilárním systémem	**ano**
21	**Stanovení rychlosti vysychání**	stanovení rychlosti vysychání vzorků	ne
22	**Stanovení paropropustnosti**	určení prostupnosti vodní páry zkoumaným materiálem	ne
23	**Měření kontaktního úhlu**	Zjištění smáčivosti povrchu pomocí měření kontaktního úhlu mezi kapkou vody a povrchem	ne
24	**Kapkový test**	hydrofobita povrchu, rychlá srovnávací metoda	**ano**
31	**Vlhkostní dilatometrie**	určení změny délkových rozměrů při nasycení tělesa vodou	ne

Metody pro stanovení mechanických charakteristik

Metoda č.	Název	Cíl analýzy	Možnost in situ
28	**Zkouška pevnosti**	určení pevnosti materiálu při ohybové a tlakové zkoušce, lze současně stanovit modul pružnosti	**ano**
26	**Ultrazvuková transmise**	lokalizace poškození, dlouhodobé monitorování stavu, srovnávací metoda, lze současně stanovit modul pružnosti	**ano**
25	**Odporové vrtání**	měření hloubkového pevnostního profilu materiálu, ověření účinnosti konsolidace	**ano**
27	**Peeling test**	zjištění povrchové soudržnosti, jako srovnávací metoda	**ano**
29	**Zkouška přídržnosti**	určuje přídržnost doplňku k podkladu	**ano**

Stanovení charakteristik souvisejících s odezvou materiálu vůči změnám vnějších podmínek

Příloha č.	Název	Cíl analýzy	Možnost in situ
30	**Teplotní dilatometrie**	určení změny délkových rozměrů při zahřátí/ochlazení tělesa	ne
31	**Vlhkostní dilatometrie**	určení změny délkových rozměrů při nasycení tělesa vodou	ne

32	**Zkouška mrazuvzdornosti**	určení změny vlastností materiálu před a po absolvování zmrazovacích cyklů	ne
33	**Zkouška odolnosti vůči působení solí**	určení změny vlastností materiálu před a po vystavení cyklickému působení solí	ne
34	**Stanovení tepelné vodivosti**	určení hodnoty koeficientu tepelné vodivosti materiálu v suchém stavu	ne

Metody pro stanovení vlastností materiálu v makroměřítku			
Příloha č.	**Název**	**Cíl analýzy**	**Možnost in situ**
35	**Teplotní analýza povrchu (termokamera)**	diagnostika podpovrchových defektů (trhliny, dutiny) pomocí měření teplotních polí	**ano**
36	**Měření georadarem**	detekce velkých prasklin a inkluzi, zkoumání struktury zdiva, zjištění vlhkosti objektu	**ano**
37	**Detekce kovů**	detekce kovových prvků uvnitř objektů	**Ano**
38	**Stanovení barevnosti povrchu pomocí spektrometru**	Porovnání barevnosti povrchu před a po restaurátorském zásahu	**Ano**

V. Množství a velikost vzorků pro materiálové zkoušky

Odběr vzorků historického materiálu z kulturních památek za účelem jeho charakterizace během všech stadií konzervátorského procesu popisuje norma EN 16085 (2012) Conservation of Cultural property - Methodology for sampling from materials of cultural property - General rules. Tato norma upozorňuje na skutečnost, že vzorkování je invazivní a nevratně poškozuje kulturní památku, jakkoliv málo. Odběr vzorků má být proto proveden pouze v silně zdůvodněných případech a v nejtěsnější konzultaci s osobami odpovědnými za památku a s osobami, které budou vzorky studovat. Je nutné vzít v úvahu, zda lze stejnou informaci získat neinvazivním způsobem. Tato evropská norma nepředepisuje žádný konkrétní počet vzorků nebo množství materiálu ke zkoušení. Odběr vzorků je ve smyslu této normy prováděn při místním šetření dohodou mezi osobami odpovědnými za památku a osobami, které mají zkoušky provádět způsobem neinvazivním tak, aby nedošlo k nevratnému poškození památky. V tabulce 6 jsou vyznačeny metody, které je možné provést in-situ na objektu bez invaze.

Výše uvedená evropská norma pro odběr vzorků z památky je i hlavní překážkou pro případnou plnou aplikaci řady technických norem, neboť obvykle nelze zajistit množství a objem materiálu, potřebný pro výrobu zkušebních těles v normou určených rozměrech a počtech. Zkušební postupy je nutno v takových případech modifikovat a zjistit vliv odlišných parametrů vzorku na naměřené hodnoty zjišťované vlastnosti, aby mohl být výsledek zkoušky případně upraven korekcí na velikost vzorku a správně interpretován [6].

Normalizací v oblasti zkoušení historických materiálů a památek obecně se zabývá technický výbor CEN/TC 346 - Conservation of Cultural Heritage, který dosud zpracoval pouze zlomek potřebných norem. Pro hodnocení stavu historického materiálu je možno využít především normu EN 16096 (srpen 2012) Conservation of cultural property - Condition survey and report of built cultural heritage. Jedná se o dokument, který má obecnou povahu a průzkum je založen na "hodnocení dochovaného stavu vizuální prohlídkou, kombinovanou v případě potřeby jednoduchým měřením". Norma se neodvolává na žádnou další technickou normu a jejím základním posláním je dokumentace stávajícího stavu. Pro zkoušení historických materiálů z kulturních památek se vedle CEN norem používají normy Českého normalizačního institutu ČSN, EN, dále normy WTA (Vědecko-technická společnost pro sanace staveb a péči o památky) a organizace RILEM (International Union of Laboratories and Experts in Construction Materials, Systems and Structures), která vydává tzv. technická doporučení pro řešení jednotlivých problémů v oblasti konstrukčních materiálů.

VI. Srovnání „novosti postupů“ oproti původní metodice, příp. jejich zdůvodnění, a jejich srovnání s postupy v zahraničí

Nároky na provádění materiálového průzkumu v ČR jsou v různém rozsahu zmiňovány v publikacích architektů, historiků umění, technologů a dalších pracovníků památkové péče [13-18]. Jsou doporučeny metody zjišťující složení materiálu (chemické a fázové), mikrostrukturu, velikost a tvar částic (mikroskopická analýza, granulometrická analýza) a dále jsou jmenovány některé metody pro zjištění příčin poškození díla (stanovení vlhkosti gravimetrickou metodou nebo exaktními vlhkoměry, stanovení obsahu vodorozpustných solí kapalinovou chromatografií, zjištění biotických škůdců mykologickou mikroskopickou analýzou, strukturální poškození ultrazvukovým, příp. radarovým vyšetřením, rentgenografií, počítačovou tomografií. Nová metodika se zaměřuje na materiálové vlastnosti, které charakterizují anorganické stavební materiály, a které je třeba posoudit před navržením postupu čištění, konsolidace, doplnění chybějící hmoty, hydrofobizace památkového objektu, aby zásah splňoval nároky na kompatibilitu materiálů. Metodika vznikla na základě studia zahraničních odborných publikací [1-12] a výzkumu provedeného v rámci projektu NAKI DF12P01OVV018.

VII. Uplatnění Certifikované metodiky

Metodika je určená pracovníkům památkové péče, restaurátorům, architektům a projektantům pro přesnější zadávání zkoušek a analýz materiálových vlastností. Tyto vlastnosti jsou zjišťovány při předprojektové přípravě nebo restaurátorském průzkumu v rámci obnovy památkových objektů nebo předmětů kulturního dědictví.

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Appendix II

The conservation procedure is presented as it was published, in the Czech language with original numbering of tables, figures and used references.

ZPEVNĚNÍ HISTORICKÉ VÁPENNÉ OMÍTKY DISPERZÍ NANOČÁSTIC HYDROXIDU VÁPENATÉHO V ALKOHOLU

Památkový postup

Zuzana Slížková a Dita Frankeová

1. Úvod

Tento památkový postup je výsledkem výzkumného projektu s názvem „Nové materiály a technologie pro konzervaci materiálů památkových objektů a preventivní památkovou péči“, č. NAKI DF11P01OVV012, podpořeném Ministerstvem kultury ČR. Jedním z úkolů projektu bylo vypracování a ověření postupu konsolidace historických materiálů památkových objektů. Předkládaný postup se týká zpevnění historických vápenných omítek.

2. Cíl památkového postupu

Cílem památkového postupu je záchrana historické vápenné omítky na stavebním objektu, který je kulturním dědictvím, přičemž poškození omítky se vyznačuje dezintegrací (oddělováním zrn nebo shluků zrn). Záchrana omítky spočívá v její impregnaci kapalným vápenným zpevňujícím prostředkem, který prosákne omítku a po vytvrdnutí vrátí omítce potřebnou soudržnost. Cílem postupu je zvýšit soudržnost omítky jen do takové míry, aby omítce zůstaly vlastnosti charakteristické pro omítku s vápenným pojivem.

3. Popis památkového postupu

Vymezená plocha dezintegrované omítky (např. 1 m^2) se rovnoměrně zkrápí kapalným zpevňujícím prostředkem, kterým je vápenná disperze obsahující hydroxid vápenatý ve formě částic rozptýlených v etanolu, přičemž vápenné částice mají velikost 50-150 nm. Disperze, nanesená na povrch omítky, penetruje různě rychle (v závislosti na velikosti pórů omítky) z povrchu omítky do její hloubky. Zkrápění povrchu omítky trvá tak dlouho, dokud se vápenná disperze ještě do omítky vsakuje a přeruší se v okamžiku, kdy již jsou póry omítky disperzí naplněné a prostředek do omítky již nepenetruje. Kromě jemného kropení se aplikace disperze na omítku může provádět postřikem nebo pomalým poléváním až do nasycení omítky. Obvyklá dávka nutná pro prosáknutí vrstvy omítky do hloubky 1,5 cm je 2,5 litru prostředku naneseného na 1m^2 povrchu.

Pro zpevnění vápenných omítek se použije vápenná disperze s koncentrací v rozmezí 10 až 25 g/l (hodnota koncentrace udává obsah hydroxidu vápenatého v disperzi). Na jemnozrnné a jemněji porézní omítky se aplikuje disperze s nižší koncentrací (10 až 15 g/l), zatímco na hrubé omítky s velkými póry (desítky až stovky µm) je možné použít více koncentrovanou disperzi (25 g/l). Při aplikaci méně koncentrované disperze (10g/l) je obvykle potřebné omítku napustit dvakrát až třikrát, při vyšší koncentraci (25 g/l) jedenkrát až dvakrát. Druhá a každá další aplikace (prosycení vrstvy omítky disperzí) se provádí až po vyschnutí zpevňované omítky.

Zpevnění omítky se projeví do několika dní (podle teploty a vlhkosti vzduchu) nárůstem soudržnosti omítky. Po každé aplikaci by měly být zhodnoceny alespoň in-situ měřitelné parametry (soudržnost omítky a rychlost absorpce vody do omítky). Vlastnosti ošetřené omítky by se měly postupně (po dílčích zpevňujících krocích) přibližovat vlastnostem nepoškozené vápenné omítky.

Aplikace vápenné disperze se provádí za vhodného počasí, kdy je omítka vyschlá, obsah vlhkosti v omítce odpovídá rovnovážné vlhkosti, relativní vlhkost vzduchu je do 75% a teplota vzduchu od 10 do 22°C. K postřiku omítky se využívají běžné ruční nebo tlakové postřikovače. Tlak dopadající disperze musí být nízký přiměřeně stavu degradované omítky, aby nanášení kapalného prostředku nezpůsobovalo odpadávání zrn nebo shluků zrn omítky z fasády.

4. Příklady použitelných vápenných disperzí (disperzí nanočástic hydroxidu vápenatého v alkoholu)

Jsou dostupné vápenné disperze od více výrobců. Na základě výsledků provedeného výzkumu má v současné době nejlepší vlastnosti vápenná disperze CaLoSiL E (výrobce IBZ - Salzchemie GmbH & Co.KG). Informace o výrobku jsou dostupné v technickém listu na http://www.ibz-freiberg.de/. Koncentrace vápna v prostředku je udána v názvu prostředku, např. CaLoSiL E 25 obsahuje 25g hydroxidu vápenatého v litru prostředku, zatímco CaLoSiL E 15 pouze 15 g hydroxidu vápenatého v litru prostředku. Prostředek se před aplikací nijak neupravuje.

5. Optimální dávkování zpevňující disperze

Objemové množství disperze, které se má nanést na omítku během jedné impregnace a také odhad času, potřebného k prosycení potřebné tloušťky omítky je vhodné optimalizovat na základě zkoušky nasákavosti omítky přímo na objektu. Na malé zkušební ploše (10x10cm nebo 20x20cm podle možností) se zjistí objemové množství vápenné disperze, které je potřebné pro prosycení omítky (např. 250ml). Kontrola hloubky penetrace vápenné disperze se provádí odseknutím malého vzorku napuštěné omítky (plocha 2x2 cm, hloubka 2 či více cm podle tloušťky omítky) a následným natřením nebo pokapáním plochy kolmé k povrchu omítky fenolftaleinem (indikátorem pH). Omítka prosáklá vápennou disperzí se barví fialově, neprosáklá omítka zůstává beze změny barvy. Podle zjištěné spotřeby vápenné disperze na zkušební ploše se zpřesní objem disperze nanesený na 1m^2 omítky. Nanesené přebytky disperze, které se nevsakují do omítky, se odsávají savým materiálem (např. buničinou).

6. Barva ošetřené omítky

Jako při každém zásahu, kterým se sytí omítka hydroxidem vápenatým s následnou tvorbou uhličitanu vápenatého, který má bílou barvu, může dojít ke změně barvy omítky (zbělání povrchu). Tato případná změna nevyžaduje žádnou další úpravu u omítek, které mají být následně opatřeny vápenným nátěrem nebo přeomítnuty.

U pohledových (nenatíraných) omítek a zejména v případech, kdy se jedná o umělecká a umělecko-řemeslná díla, je nutno respektovat požadavek NPÚ, aby po zpevnění nedošlo ke změně optických vlastností povrchu zpevňované omítky, tedy ke vzniku nežádoucího bělavého zákalu. Riziko zbělání se technologicky vždy sníží pečlivým dodržováním památkového postupu, volbou spíše nižší koncentrace disperze s nanášením ve více dílčích aplikacích, dodržováním vhodných aplikačních podmínek a odstraňováním nevsáklých přebytků disperze z povrchu omítky, aby nedošlo k jejich zasychání na povrchu. Dalším preventivním opatřením je provedení vzorků zpevnění na omítkách v konkrétních situacích s následným vyhodnocením barvy povrchu omítky pracovníkem NPÚ a stanovením přijatelné intenzity konsolidace pro danou situaci, tedy stanovením přijatelného množství aplikované vápenné disperze.

7. Meze využitelnosti

Památkový postup není vhodný pro zpevňování omítek, které neobsahují póry nebo praskliny větší než 1 µm z důvodu nedostatečné penetrace disperzního prostředku. Může se stát, že póry omítky jsou na povrchu zúženy v důsledku zasolení omítky síranem vápenatým nebo v důsledku přítomnosti jiných depozitů či zbytků kompaktní povrchové úpravy. Strukturu povrchové vrstvy zpevňované omítky (velikost a četnost pórů) je proto vhodné před zásahem posoudit (nejlépe mikroskopickým vyšetřením příčného řezu odebraným vzorkem omítky).

8. Přínos památkového postupu

Přínos památkového postupu spočívá ve vyšší efektivnosti zpevňujícího procesu oproti dosavadním řešením. Podstata řešení je ve využití nového vápenného prostředku, který díky optimální koncentraci vápna (10-25g/l), velikosti vápenných částic 50-250 nm a absenci vody umožňuje efektivní, kompatibilní a šetrný zpevňující zásah během relativně krátké doby (1 až 3 týdny). Památkový postup je možné aplikovat i na vápenné omítky chudé na pojivo (s obsahem pojiva pod 10 hm%), které není vhodné zpevňovat vápennou vodou. Tím dochází k rozšíření aplikační sféry vápenných zpevňujících prostředků pro historické vápenné omítky.

9. Závěr

Laboratorní výzkum potvrdil účinnost vápenné disperze s velikostí částic 50-150 nm v etanolu pro zpevnění dezintegrované vápenné omítky. Dezintegrovaná vápenná omítka dosáhla po zpevnění standardních hodnot mechanických vlastností vápenné omítky, aniž by došlo k nežádoucím změnám dalších fyzikálních vlastností. Přílohou památkového postupu je protokol o ověření postupu v praxi, při zpevňování historické omítky na hradě Karlštejn s obrazovou dokumentací.

10. Návrh konkrétních uživatelů

Památkový postup je určen pro restaurátory, technology a pracovníky památkové péče.

11. Způsob využití výsledku

Památkový postup je určen pro využití bez omezení.

Byla uzavřena smlouva o využití výsledku mezi vlastníkem výsledku, kterým je ÚTAM AV ČR, v. v. i. se sídlem Prosecká 76, 190 00 Praha 9, IČ:68378297, DIČ:CZ68378297 a uživatelem výsledku, kterým je společnost GEMA ART GROUP a. s. se sídlem Haštalská 760/27, 110 00 Praha 1, IČO:26437741, DIČ:CZ2643774.

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V Praze 16. 6. 2015

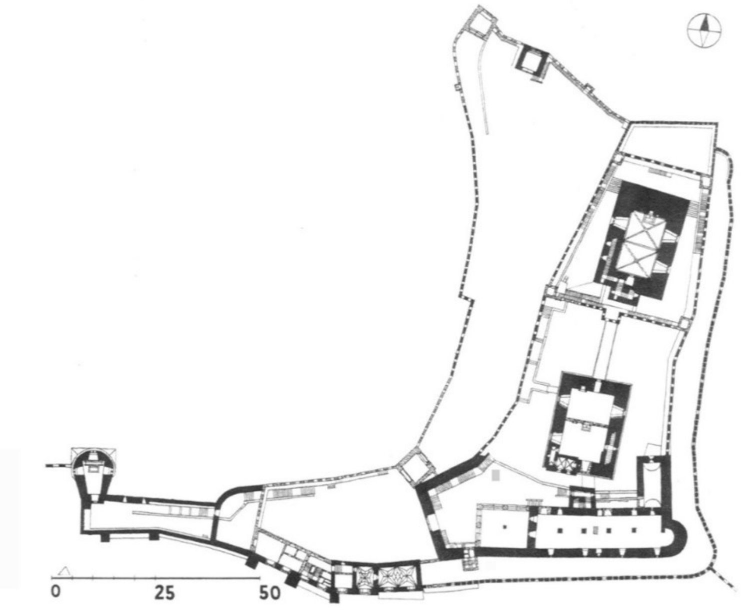
Ústav teoretické a aplikované mechaniky Akademie věd České republiky, v. v. i.

PROTOKOL O OVĚŘENÍ PAMÁTKOVÉHO POSTUPU V PRAXI

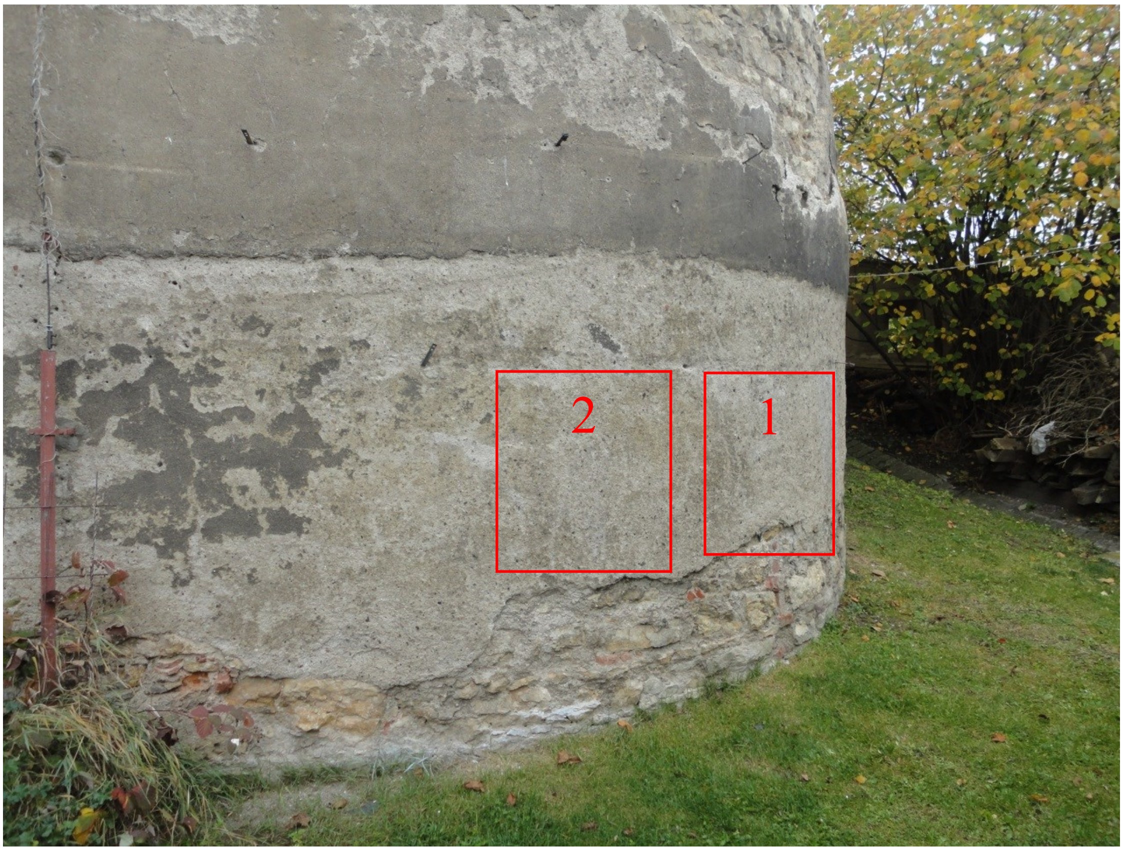
Památkový postup Zpevnění historické vápenné omítky disperzí nanočástic hydroxidu vápenatého v alkoholu byl ověřen Ing. Petrem Justou, restaurátorem a technologem firmy GEMA ART GROUP a. s. (Haštalská 760/27, 110 00 Praha 1, IČO:26437741, DIČ:CZ2643774 e-mail: restaurovani@gemaart.cz).

Postup byl ověřen při zpevňování vnější historické vápenné omítky objektu Císařský palác na hradě Karlštejn (obr. 1) v letech 2013-2014. Ověření proběhlo na základě aplikace popsaného památkového postupu (v září roku 2013) a zjištění výsledků zpevnění omítky (v říjnu 2013 a listopadu 2014).

Vymezená plocha dezintegrované omítky (plocha č. 2 na obr. 2) byla konsolidována rovnoměrným zkrápěním vápennou disperzí, obsahující hydroxid vápenatý ve formě částic velikosti 50-150 nm. Koncentrace disperze byla 10 g/l, disperzním prostředím byl etanol. Během jedné aplikace bylo naneseno na 1m^2 omítky 2,5 litru disperze. Po vyschnutí omítky byl s časovým odstupem cca 1 měsíce zjištěn efekt prvního konsolidačního kroku na mechanické vlastnosti omítky, její pórovitost a nasákavost. Bylo zjištěno, že po jedné aplikaci vápenné disperze došlo k prokazatelnému zvýšení soudržnosti omítky (72 % úbytek odtrženého materiálu lepicí páskou), zvýšení tlakové pevnosti o 68 %, zvýšení ohybové pevnosti o 64 %. Otevřená pórovitost klesla o 11 % a přiměřeně se snížila také rychlost absorpce vody do omítky. Absolutní hodnoty pevnosti ošetřené omítky po jednom zásahu (pevnost v tlaku 0,4 MPa, pevnost v tahu za ohybu 0,2 MPa) byly nadále nižší oproti pevnosti standardní vápenné omítky. Zjištěné fyzikální vlastnosti zpevněné historické omítky byly vyhodnoceny jako vyhovující a zpevňování omítky bylo po jedné aplikaci vápenné disperze ukončeno.



Obr. 1. Půdorys hradu Karlštejn, aplikace pam. postupu na vnější omítce jižní strany Císařského paláce



Obr. 2. Pohled na plochu referenční (1) a plochu ošetřenou vápennou disperzí (2)

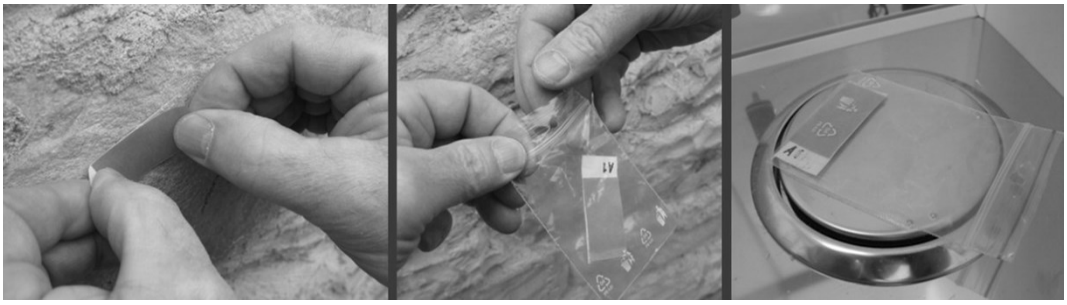
Metodika ověření

Odběr vzorků referenční (neošetřené) i ošetřené omítky a in-situ měření soudržnosti a nasákavosti omítky proběhlo dne 25. října 2013, asi jeden měsíc po aplikaci památkového postupu. Soudržnost omítky byla hodnocena pomocí tzv. peeling testu a rychlost absorpce vody do omítky pomocí mikrotrubice a Karstenovy trubice. Odebrané vzorky omítky byly v laboratoři upraveny do potřebných rozměrů a následně byla zjištěna jejich pórovitost a pevnost v tlaku a v tahu za ohybu. Hodnoty vlastností zjištěné na ošetřené omítce byly porovnány s hodnotami neošetřené (referenční) omítky.

Dokumentace výsledků: peeling test

Metodika: Peeling test hodnotí povrchovou soudržnost materiálu a lze jej využít pro posouzení zpevňující účinnosti konsolidačního prostředku aplikovaného na degradovaný materiál. Během testu je na hodnocený povrch posuzovaného materiálu aplikován proužek lepicí pásky, vždy stejným tlakem prstu připevněn lepivou stranou k omítce a následně vždy stejným tlakem od omítky odtržen. Hodnotí se hmotnost omítky uvolněná z povrchu v důsledku odtržení lepicí pásky. Hmotnost se zjistí vážením (gravimetricky).

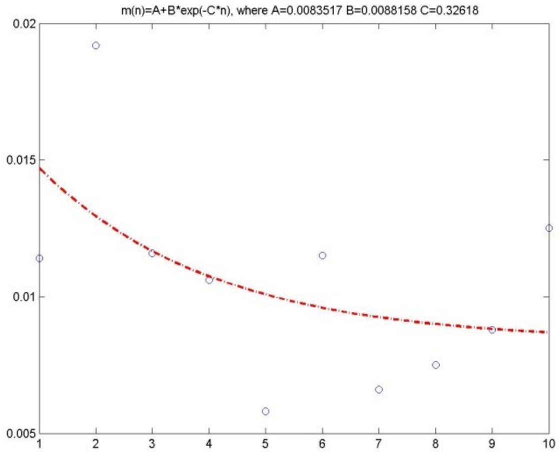
Použitá metodika vychází z hodnocení uvolněného množství omítky po postupném nalepení a odtržení deseti různých adhezních proužků vždy na stejné místo [12]. Ilustračně je celý postup patrný na obr. 3. Při matematickém vyhodnocení testu je nalezena asymptotické hodnota A [g], k níž se blíží křivka (exponenciální funkce) proložená všemi deseti po sobě jdoucími hodnotami, zjištěnými při jednotlivých měřeních, a která představuje množství uvolněného materiálu. Při odtrhu na omítce může dojít k uvolnění větších zrn písku a data zkreslená tímto způsobem jsou při vyhodnocení vyloučena z aproximace. Na grafu 7 jsou tyto vyloučené hodnoty přeškrtnuty.



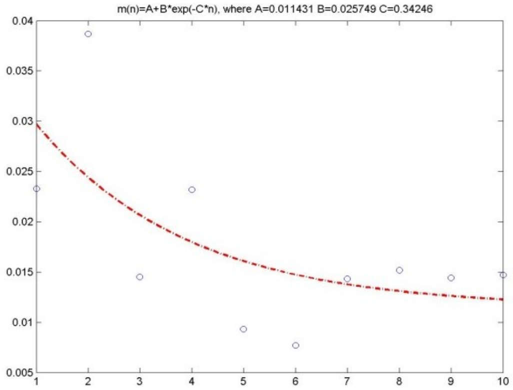
Obr. 3. Hlavní kroky postupu měření – aplikace předem zvážené lepicí pásky, bezpečný transport proužku s odtrženým materiálem k váze a opětovné vážení

Peeling test byl proveden na dvou různých místech v případě referenční neošetřené omítky (REF 1, REF 2) a na jednom místě v případě omítky ošetřené vápennou disperzí (VD). Na sledovaných površích byla vybrána místa dostatečně homogenní a soudržná tak, aby na nich bylo měření uskutečnitelné, viz obr. 4. V tabulce 1 jsou uvedeny všechny naměřené hodnoty, graficky znázorněné v obr. 5-7.

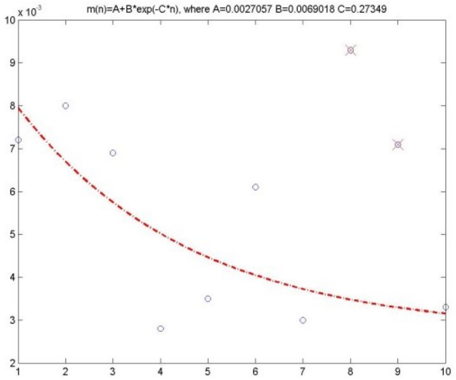
Obr. 4. Aplikace adhezního proužku během in-situ měření na Karlštejně



Obr. 5. Vyhodnocení prvního peeling testu REF 1 pro referenční omítku



Obr. 6. Vyhodnocení druhého peeling testu REF 2 pro referenční omítku



Obr. 7. Vyhodnocení peeling testu pro omítku ošetřenou vápennou disperzí

Tab. 1. Výsledky peeling testu na referenčních neošetřených plochách omítky (REF 1, REF 2) a na ploše omítky ošetřené vápennou disperzí (VD)

odtrh č.	**REF 1**	**REF 2**	**VD**
1	0,0114	0,0233	0,0072
2	0,0192	0,0387	0,008
3	0,0116	0,0145	0,0069
4	0,0106	0,0232	0,0028
5	0,0058	0,0093	0,0035
6	0,0115	0,0077	0,0061
7	0,0066	0,0143	0,003
8	0,0075	0,0152	0,0093
9	0,0088	0,0144	0,0071
10	0,0125	0,0147	0,0033
konst. A	**0,0083**	**0,0114**	**0,0027**

Stanovení absorpce vody omítkou pomocí Karstenovy trubice

Metodika: Karstenova trubice byla upevněna tmelem na omítku a naplněna vodou po rysku, viz obr. 8. Sledoval se úbytek vody penetrující z trubice do omítky plochou 25 mm v závislosti na čase.

Obr. 8. Průběh měření nasákavosti pomocí Karstenovy trubice

Tab. 2. Hodnoty koeficientu absorpce vody vycházející z měření absorpce pomocí Karstenovy trubice.

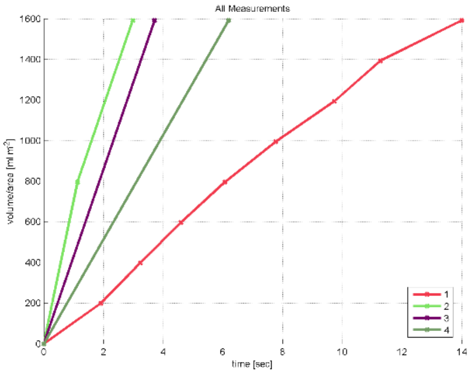
	Čas t [s]	60	120	180	240	**byreta**		**wac [kg.m^{-2}.s$^{-0.5}$]**	**Pokles wac kons./ref.**
	Čas t [min]	**1**	**2**	**3**	**4**	**d [mm]**	**A [m^2]**		
	Čas t^{0,5} [s^{0,5}]	**7,75**	**10,95**	**13,42**	**15,49**				
REF	**Objem vody [ml]**	1,40	2,30	3,10	3,80	25,12	4,96E-04	**0,50**	
	m/A [kg/m^2]	2,8	4,6	6,3	7,7				
	m/A [ml/m^2]	2824,9	4640,9	6255,1	7667,5				
VD	**Objem vody [ml]**	1,2	2,0	2,7	3,3	25,12	4,96E-04	**0,43**	14%
	m/A [kg/m^2]	2,4	4,0	5,4	6,7				
	m/A [ml/m^2]	2421,3	4035,5	5448,0	6658,6				

Stanovení absorpce vody omítkou pomocí mikrotrubice

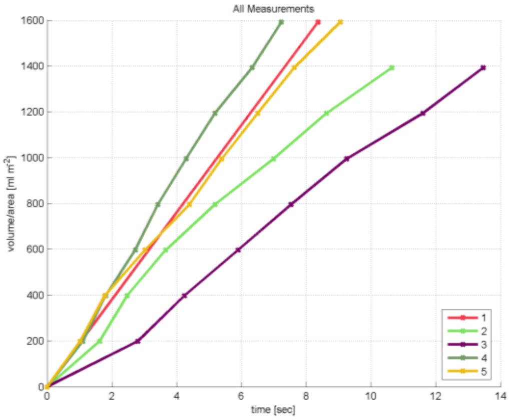
Metodika: Rychlost penetrace vody do omítky byla zjišťována na základě sledování rychlosti posunu vodního sloupce ve skleněné tenké trubici o objemu 0,1 ml, obr. 9. Trubice je uchycena k „pistoli“, která je přiložena na povrch měřeného materiálu středovou výtokovou hubicí, což je kovová trubička vyplněná papírovým filtrem. Voda penetruje do omítky přes papírový filtr, který je měněn po každém měření. Operátor, který drží „pistoli“ přiloženou ke zkoumanému povrchu, zmáčkne spoušť pistole (modifikovanou na spínač) pokaždé, kdy zadní hladina vodního sloupce v mikrotrubici míjí rysku objemového dílu na stupnici trubice (celkem 8x, po 0,01 ml). Příslušný časový údaj zaznamenává paměť, která je součástí zařízení, a grafické vyhodnocení měření (objemové množství vody odcházející z trubice přes definovanou plochu v závislosti na čase) následně provede software.

Měření bylo provedeno na referenční ploše (4krát) a na ploše ošetřené vápennou disperzí (5x), na různých místech. Na obr. 10-11 jsou uvedeny grafické výsledky závislosti objemu vody absorbované definovanou plochou omítky na čase. Grafické vyhodnocení absorpce vody omítkou v hodnocených zkušebních plochách je v Tab. 3 doplněno číselnou hodnotou koeficientu nasákavosti (wac , water absorption coefficient) v [kg.m^{-2}.s$^{-0.5}$] pro snazší vzájemné porovnání.

	
Obr. 9a. Mikrotrubice pro měření nasákavosti	Obr. 9b. Měření absorpce vody ref. omítkou



Obr. 10. Rychlost absorpce vody ref. omítkou. 4 měření na různých místech ref. omítky.



Obr. 11. Rychlost absorpce vody omítkou ošetřenou vápennou disperzí.

Tab. 3. Hodnoty koeficientu absorpce vody vycházející z měření absorpce pomocí mikrotrubice.

typ konsolidantu	wac [kg.m^{-2}.s$^{-0.5}$]	Pořadí rychlosti	Pokles wac kons./ref.
Referenční	0,70	1	
VD	0,50	4	29%

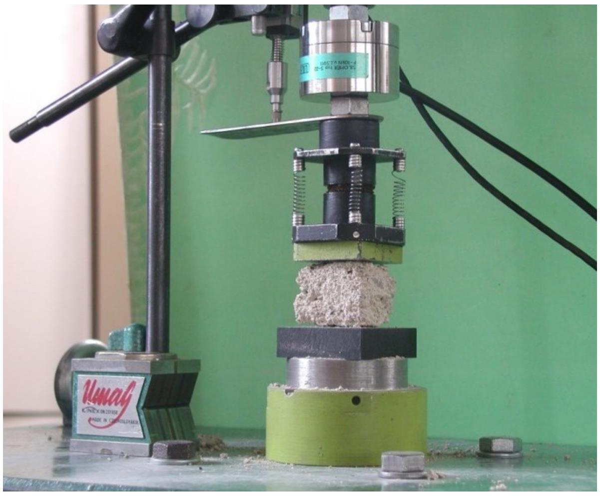
Zkouška pevnosti v tlaku

Metodika: Zkouška byla provedena na plochých hranolech o přibližných rozměrech 30 × 35 × 40 mm, které vznikly vyříznutím z odebraného bloku materiálu, viz. obr.12. Rozměry hranolů byly změřeny s přesností 0,1 mm. Bylo zajištěno, aby tlak působil kolmo na horní plochu vzorku. Rychlost zatěžování byla zvolena v režimu 0,45 mm/min.

Pevnost v tlaku se stanovila výpočtem z mezního zatížení, které odpovídá okamžiku porušení vzorku.

Pro zatěžování se použil elektromechanický zatěžovací stroj TESTATRON o kapacitě 100 kN. Zatěžovací síla byla měřena siloměrem MTS o rozsahu 10 kN a deformace zkušebního vzorku ve směru působící síly byla měřena potenciometrem fy Megatron.

Obr. 12. Odběr vzorků pro pevnostní zkoušky a zjištění pórovitosti omítky



Obr. 13. Zkušební těleso před začátkem zkoušky pevnosti v tlaku

Výsledné hodnoty odečtené při měření byly přepočítány podle vztahu:

$$R_e = \frac{F}{S}$$

kde R_e je experimentálně měřená pevnost omítky v tlaku v MPa,

F je maximální působící síla do porušení v N,

S je plocha tlačeného průřezu v mm^2.

Naměřené hodnoty byly opraveny o vliv štíhlosti podle metodiky druhého autora zprávy tak, aby se získaly hodnoty ekvivalentní krychlené pevnosti R_c [7,8].

Tab. 4. Hodnoty tlakových pevností omítek.

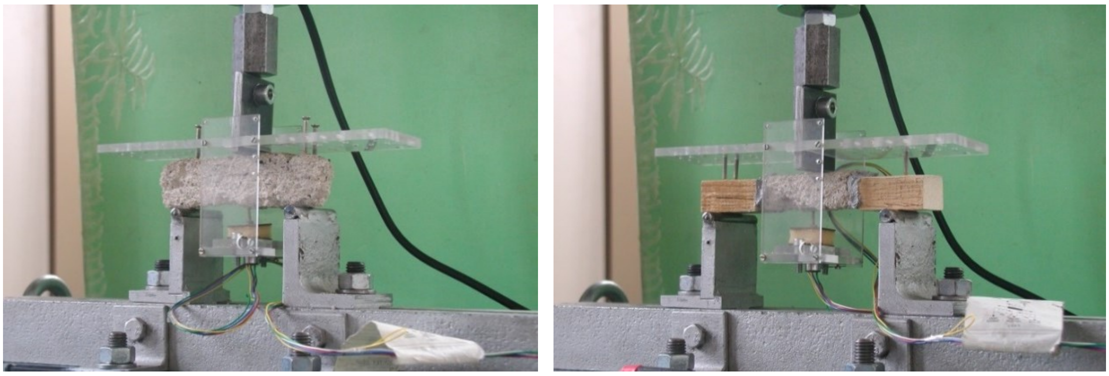
vzorek č.	**hloubka a [mm]**	**šířka b [mm]**	**výška h [mm]**	**maximální síla F [N]**	**tlaková pevnost R_e [MPa]**	**ekvivalentní průměrná krychelná pevnost R_c [MPa]**	**nárůst pevnosti kons./ref.**
K_VD_t1	28.6	36.0	40.4	939.99	0.65	**0,43**	68 %
K_VD_t2	27.0	29.0	33.8	495.07	0.51		
K_VD_t3	30.9	34.3	39.3	702.58	0.52		
K_ref_t1	30.6	40.0	44.2	750.10	0.42	**0,26**	
K_ref_t2	27.0	38.2	41.3	781.36	0.50		

Zkouška pevnosti v tahu za ohybu

Metodika: Zkouška byla provedena na nestandardních trámečcích o rozměrech shrnutých v Tab. 5. Trámečky byly vyřezány z většího bloku odebraného na místě. Jejich rozměry byly změřeny s přesností 0,1 mm. Některé trámečky byly příliš krátké pro ohybovou zkoušku a výsledek by byl ovlivněn smykovým namáháním. Proto byly vzorky prodlouženy přilepenými dřevěnými protézami podle ověřené metodiky [18]. Ohybový moment je vyvozován jednou silou, umístěnou uprostřed trámečku (tříbodový ohyb).

Pevnost v tahu za ohybu se stanovuje výpočtem mezního napětí v tahu za ohybu pomocí měření maximálního ohybového momentu při porušení nestandardního trámečku.

Pro zatěžování se použil elektromechanický zatěžovací stroj TESTATRON o kapacitě 100 kN. Zatěžovací síla byla měřena siloměrem fy LUKAS se jmenovitým rozsahem do 500 N. Průhyb uprostřed trámečku byl měřen snímačem LVDT zavěšeným na přípravku eliminujícím zatlačování podpor do povrchu vzorku. Citlivost snímače byla lepší než 0,00015 mm a rozsah ±1 mm. Signál ze snímače byl měřen ústřednou DAM a registrován pomocí PC. Při zkoušce se zatěžovalo rychlostí posunu příčníku 0,15 mm/min.



Obr. 14. Zkušební tělesa, bez protéz a protézovaná, před začátkem zkoušky pevnosti v tahu za ohybu

Výsledné hodnoty odečtené při měření byly přepočítány podle vztahu:

$$R_t = \frac{1.5Fl}{bh^2}$$

kde R_t je pevnost malty v tahu za ohybu v MPa,
F je maximální působící síla do porušení v N,
l je vzdálenost mezi podporami v mm,
b, h jsou šířka a výška průřezu v místě lomu v mm.

Získané výsledky jsou shrnuty v Tab. 5.

Tab. 5. Hodnoty pevností omítek v tahu za ohybu.

vzorek č.	**výška h [mm]**	**šířka b [mm]**	**podpory l [mm]**	**maximální síla F [N]**	**tahová pevnost R_t [MPa]**	**nárůst pevnosti kons./ref.**
K_VD_1	22.8	33.2	80	40.41	0.28	64 %
K_VD_3	20.1	26.6	120	9.80	0.16	
K_ref_1	32.1	28.6	120	43.70	*0.27*	
K_ref_2	24.6	20.0	120	4.01	0.06	
K_ref_3	27.5	29.2	120	9.88	0.08	

Objemová hmotnost, pórovitost přístupná vodě, nasákavost

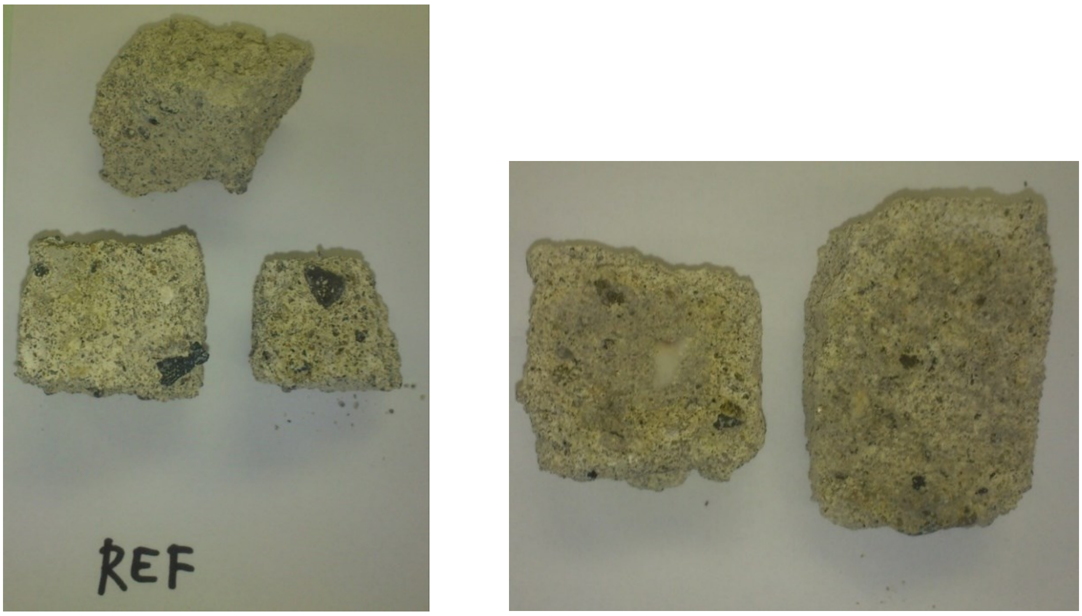
Objemová hmotnost, pórovitost přístupná vodě a nasákavost neošetřeného i ošetřených vzorků omítky byly stanovena dle normy ČSN EN 1015-10 (Zkušební metody malt pro zdivo - Část 10: Stanovení objemové hmotnosti suché zatvrdlé malty). Vzorky byly vystaveny nasakování vodou po dobu 70 h za normálního atmosférického tlaku. Nasákavost je poměr hmotnosti vody přijaté vzorkem $(m_s - m_d)$ k hmotnosti vysušeného vzorku m_d.

$$A_b = \frac{m_s - m_d}{m_d} \cdot 100$$

Fotodokumentace vzorků použitých při zkoušce je na obr. 15, výsledky zkoušek jsou shrnuty v Tab. 6.

Tab. 6. Hodnoty objemové hmotnosti, otevřené pórovitosti a nasákavosti.

vzorek		**objemová hmotnost [kg.m^{-3}]**	**otevřená pórovitost [%]**	**pokles kons./ref.**	**nasákavost [%]**
REF	Průměr	**1622**	**30,1**		**18,6**
	Stdv	29	0,9		0,9
VD	Průměr	**1661**	**26,8**	**11 % rel.**	**16,1**
	Stdv	30	0,6		0,6



Obr. 15. Vzorky pro otevřenou pórovitost – referenční omítka (obrázek vlevo) a omítka ošetřená vápennou disperzí (obrázek vpravo)

Měření pevnostního profilu odporovým vrtáním

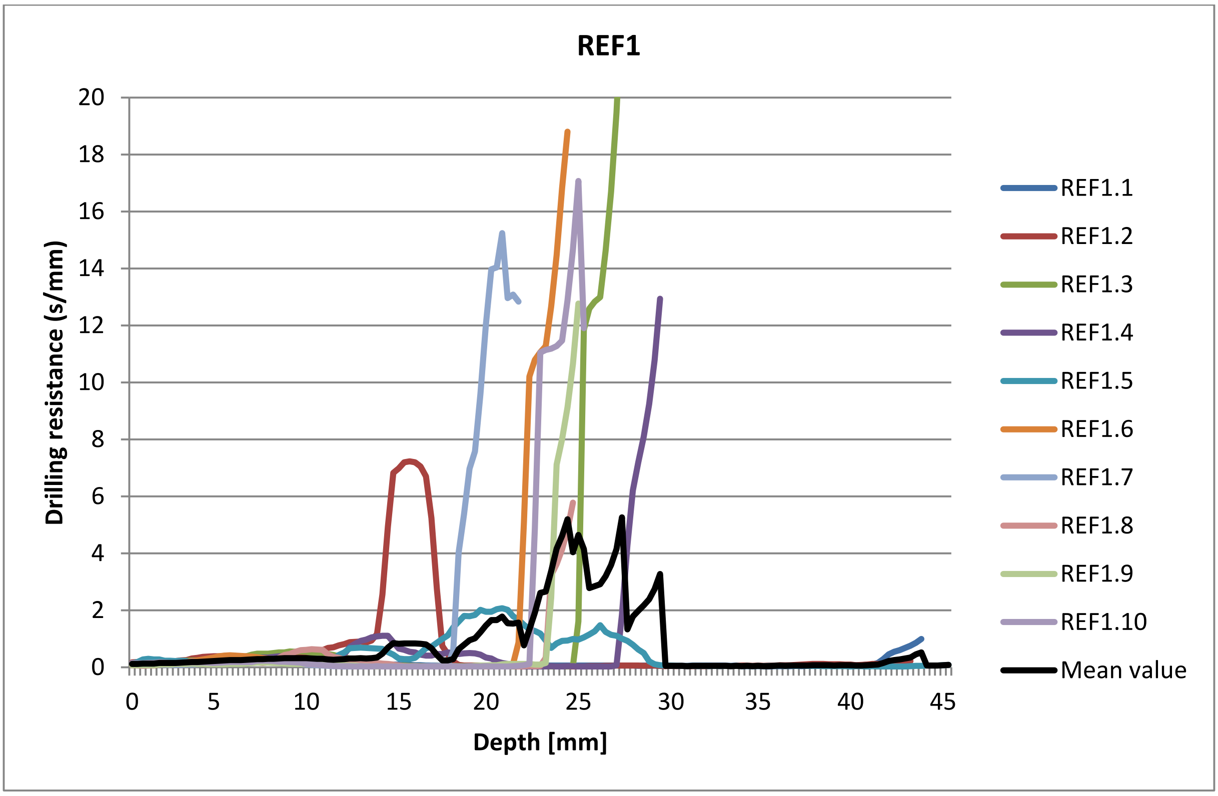
Metodika: Zkouška byla provedena pomocí odporové vrtačky TERSIS T2 od firmy Geotron Elektronik (DE). Pro měření byly použity vrtáky PROFI LINE do betonu a kamene od firmy Vrbovský, o průměru 4 mm, vrták byl vyměňován po 3 vrtech. Stálý tlak pro vrtání byl zajištěn kompresorem Nardi Esprit 3T (tlak pro vrtání je možno nastavit v rozmezí 60 – 397mBar podle odolnosti a tvrdosti zkoušeného materiálu, na Karlštejně byl tlak nastaven na 150 mBar). Vrtání bylo provedeno za podmínek, že přístroj nebyl uchycen ve stativu, ale v rukách technika. Výsledkem měření je graf, který ukazuje čas nutný pro posun vrtáku o 1 mm v sekundách, v určité hloubce pod povrchem omítky (v milimetrech) při stálém přítlaku (150mBar). Vyšší hodnoty času posunu vrtáku odpovídají vyššímu odporu materiálu vůči vrtání. Výsledky jsou uvedeny v Tab. 7 a grafické záznamy na obr. 16 a 17.

Obr. 16 a.
Detail omítky na zkušební ploše REF 1
po 10 vrtech.

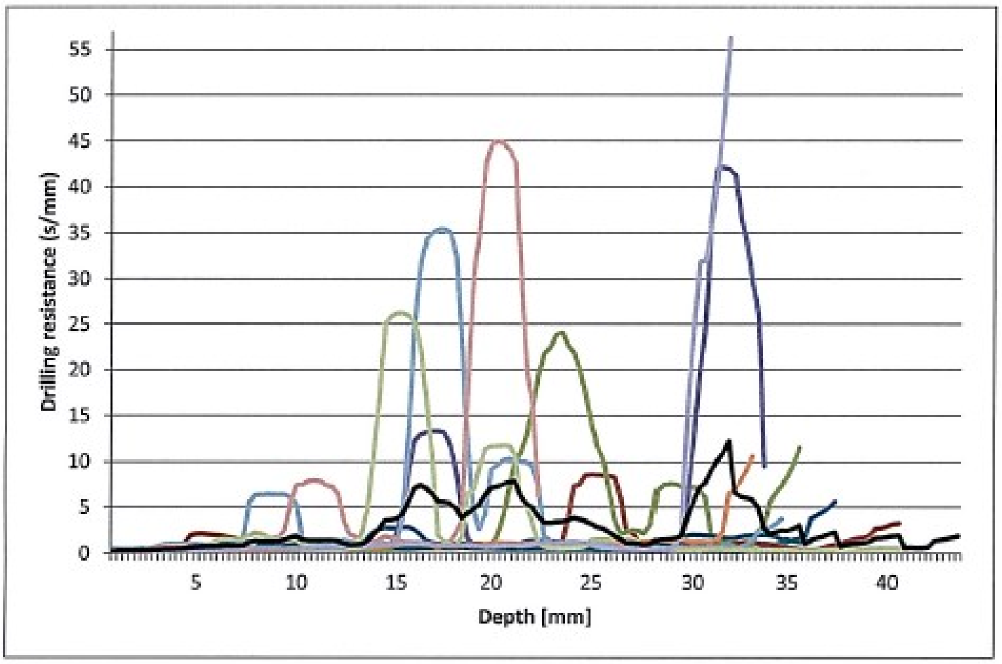
Tab. 7. Hodnoty času posunu vrtáku v omítce v různých hloubkách pro různé zkušební plochy (průměrné hodnoty z 10 vrtů do každé zkušební plochy)

Čas nutný pro posun vrtáku (s/mm) v určité hloubce pod povrchem omítky			
Hloubka pod povrchem	**0-0,5 cm**	**0,5-1,5 cm**	**1,5-3 cm**
REF 1 (za zkušebním polem ZFB)	0,2	0,2	0,05
VD	0,5	0,7	0,9

Ošetřená omítka je odolnější vůči vrtání ve srovnání s referenční plochou. Zkouška odporovým vrtáním není vhodná pro materiály, kde je vysoký rozdíl v tvrdosti a pevnosti jednotlivých složek, jako je tomu v případě omítky na Karlštejně. Velký rozdíl v odporu vůči vrtání mezi pojivem a zrny písku znesnadňuje vyhodnocení zkoušky. Ani opakování zkoušky 10x na stejném materiálu situaci příliš nezlepšilo. Výsledky zkoušky jsou proto v tomto případě orientační.



Obr. 16 b. Výsledky odporového vrtání na referenční (neošetřené) ploše



Obr. 17. Výsledky vrtání na ploše omítky zpevněné vápennou disperzí

Závěr

Tlaková pevnost omítky ošetřené vápennou disperzí je vyšší o 68 % ve srovnání s pevností referenční omítky.

Hodnocení **ohybové pevnosti** je komplikováno velkým rozptylem naměřených hodnot u referenční omítky. Při respektování všech tří zjištěných hodnot u referenčních vzorků omítky a jejich průměrné hodnoty je pevnost omítky ošetřené vápennou disperzí vyšší o 64 % ve srovnání s průměrem referenční omítky.

Výsledky peeling testu, který vypovídá o **soudržnosti povrchu** hodnocených omítek, jsou ve shodě se zjištěnými pevnostmi omítek. Na ošetřené omítce byl zjištěn pokles odloučeného množství materiálu (zlepšení soudržnosti) o 72% ve srovnání s referenční omítkou.

Otevřená pórovitost ošetřené omítky poklesla relativně o 11 %, přiměřeně se snížila také rychlost **absorpce vody do omítky.**

V Praze 16. 6. 2015

Ověřil: Ing. Petr Justa

podpis a razítko

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