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Tests on sustainability of consolidation treatments with CaLoSil® nanosuspensions on plaster reference samples

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I hereby declare that all information in this document has been obtained and presented in accordance with academic rules and ethical conduct. I also declare that, as required by these rules and conduct, I have fully cited and referenced all material and results that are not original to this work.

Name, Last name:

Signature:

I thank my supervisor Ing. Renata Tišlová, PhD. for her highly professional approach, numerous advices, valuable help and great patience.

Annotation:

The main task of this study was to evaluate novel group of materials based on nanosuspension of calcium hydroxide and calcium hydroxide combined with calcium sulphate which should be used for consolidation of calcerous materials. This research has focused on assessment of consolidation on highly corroded pure lime and gypsum plaster. The evaluation was made through comparison of selected physical, mechanical and microstruce properties. The main task was to assess resistance of consolidated substrates to conditions following the external environment, especially the freeze-thaw cycles, resistance to the salts and humid-air conditions.

Keywords:

calcium hydroxide, calcium sulphate, nanosuspensions, plaster, consolidation, testing

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1. Introduction

The consolidation of lime based materials, such as historic plaster, frescoes, sgraffito, as well as lime containing stones are critical steps in conservation treatments. Inorganic consolidants, calcium hydroxide, esters of silica acid, are commonly used within the restoration and conservation treatment. Calcium hydroxide would be the most suitable materials which match the compatibility with the calcareous substrates as much as possible. However, the low solubility of calcium hydroxide in water (1.7 $g.l^{-1}$) and the low stability of lime dispersions in water make these consolidants little effective. Recently, the innovative materials - nanosuspensions of calcium hydroxide in alcoholic medium which can fulfill the material compatibility with the calcareous materials fully have been produced and investigated. The research presented in this thesis proves the useful suggestions for the treatment of the different types of plaster by using the lime and gypsum/lime nanosols in conservation practice. Within this thesis the laboratory research was performed to test the durability and resistance of the laboratory prepared specimens imitating highly corroded lime and gypsum mortars which were consolidated by the new recently developed consolidants based on calcium hydroxide and calcium sulphate/hydroxide nanoparticles dispersed in alcohols. The consolidation effect was verified by measuring several physical, mechanical and microstructure characteristics as well as by resistance tests which imitate the harming external conditions (freeze-thaw test, salt crystallization and sorption isotherm test).

2. Theoretical part

2.1. Nanomaterials

Nanomaterials are nowadays already used as components in hundreds of various products and have great potential to improve the quality of life. They are the chemical substances or materials that are manufactured and used at a very small scale (usual nanosize is down to 10,000 times smaller than the diameter of a human hair). Nano innovations reflect in many sectors including industry, environment, medical care, energy, transport, space etc. The development of nanotechnology is growing fast and becomes the significant aspect for industrial competitiveness, market growth and standard of living. [27]

2.1.1. Definition of nanomaterials

Nanomaterials were developed to provide better properties (such as increased strength, chemical reactivity or conductivity) compared to the same material without nano scale features. An important aspect of nanotechnology is the vastly increased ratio of surface area to volume present in many nanoscale materials, which makes possible new quantum mechanical effects. [25] *Nanomaterials are characterized by scale lengths below 100 nm in one or more dimensions. The conventional granular materials are made up of grains whose dimensions range from microns to a few millimetres, each grain containing billions of atoms. Nanostructures represent a state of matter in between molecules and bulk structures, and are usually characterized by a large surface area that affects their physico-chemical properties. The innovative applications of nanostructures are based on at least two types of unique properties associated with nanostructures: 1) novel optical properties due to quantum confinement effects; 2) changes in reactivity and mechanical properties due to the small physical dimensions and large surface area. In addition to opto-electronic and surface properties, the small particle size results in improved mechanical properties, important for a variety of applications.*[1]

[1]Baglioni P., Giorgi R., Soft and hard nanomaterials for restoration and conservation of cultural heritage, REVIEW Soft Matter, 293–303, The Royal Society of Chemistry, 2006, www.rsc.org/softmatter, page 293 [2]

2.1.2. Nanomaterials in the cultural heritage conservation

Apparent extensive research in the area of nanomaterials development is evident also in the cultural heritage conservation field. Since the second decade of the ´90s there is apparent investigation in nanotechnology considering the calcium hydroxide for its important rule in conservation calcareous materials. Nowadays nanomaterials have huge potential for future conservation of monuments, sculptures, paintings, wood, paper relicts and other artefacts. Nanomaterials, mostly we speak about nanosuspensions, are for example tested and/or used for paper de-acidification, surface cleaning of monuments, as biocides and mostly for consolidation of porous materials (mainly calcareous materials).

In the past acrylic resins were used for conservation (especially consolidation, stabilization and protection) of precious wall paintings. Due to the alternation of polymers the painting were degraded in many ways and degrees. The great endeavour to restore the essential properties of such treated paintings resulted in development of microheterogeneous nanostructurated dispersed systems (as oil water microemulsions) and aqueous micellar solutions with suitable co-solvent for wall paintings cleaning intervention. For example in the year 2006 such nanotechnological cleaning systems were tested and used to remove naturally aged polymeric acrylic layers from the surface of the wall paintings in the Old Sacristy of Santa Maria della Scala in Siena (15th century). [11]

Lately innovative formulations of nansuspensions were prepared and employed also for deacidification treatments of paper and canvases. Nonaqueous dispersions of calcium hydroxide nanoparticles were tested and this new method granted interesting features competitive to others commonly used agents for paper deacidification. [10]

Speaking about the consolidation in general, it should be stated that the structure and characteristics of the original material set criteria for the optimum formulation and application of the consolidation materials used in the restoration process. The consolidation should provide compatible interventions with good effectivity and durability. Consolidation of calcareous materials (e.g. limestone or lime mortars) has been complicated in particular. Recently it has been almost universally done by using silica based consolidants, polymers or others, which are not fully compatible with calcareous substrates. For many years only lime water met the criteria of compatibility with carbonated material, however its consolidation

effect is uncertain. Many conservator´s and scientist´s efforts have been focused on establishing a better technology for consolidation of calcareous materials that would fulfil and satisfy important features such as material compatibility, durability and strengthening effect. Accordingly nonaqueous dispersions of calcium, barium or magnesium hydroxide nanoparticles started to be tested/used and the utilization of calcium hydroxide nano-lime combined with the silicic acid esters as new possible consolidants for calcareous material.

2.1.3. History of nanosuspensions

Calcium hydroxide is one of mankind's oldest and most significant art and building materials. It is used for several applications (i.e. industrial, environmental, and chemical) and is extensively studied by many scientists. Colloidal dispersion of calcium hydroxide stabilized in hydrocarbon medium was firstly synthesized already in the France in the year 1997 by the hydrolysis of calcium hydride under specific experimental conditions. The cores were found to be shaped like thin discs, with diameters ranging from 120 to 300 Å and a thickness of 30 Å. [7] In the year 1998 the same scientists group patented a production of colloidal products containing calcium hydroxide in the centre of micelle which are stabilized in an organic medium by shell of surfactant, in reversed micelle. These products were obtained by reacting calcium oxide CaO or calcium hydride CaH_2 with water in an organic medium in the present of surfactant. [3]

In 2000 a group of scientists from Italy studied and compared the utilization of dispersions containing slaked lime or lime hydrate in water or in alcohol for the consolidation of prepared laboratory specimens and wall paintings. Although the particle sizes of used slaked lime and lime hydrate were not in the range of the nanometres it was revealed that the water dispersions were unstable, while the dispersions in alcohol possessed quite a good stability and consolidation effects. [5] This important finding was a significant impulse for next investigation so further experiments were performed in 2001. A research was performed at the University of Florence. During this research nanoparticles of $Ca(OH)_2$ were produced from solutions of NaOH (sodium hydroxide) and $CaCl_2$ (calcium chloride). Nanoparticles obtained by this way were more stable than commercial $Ca(OH)_2$

microparticles. These nanoparticles were further examinated in the form of colloidal solutions dispersed in water and in propanol. Propanol´s dispersions possessed good consolidation properties and subsequently these products were first used with positive results during the restoration of wall paintings in the cathedral of Santa Maria del Fiore in Florence. [6]

Although the above mentioned researches were successfully done, no common technology for the production of these products in large scale was established. This situation has been changed in 2006 when new commercial products CaLoSiL®(IBZ Freiberg, Germany) based on nanodispersions of lime dispersed in organic solvents have been introduced on the market. In 2009 the EU project Stonecore was created with the goal to study CaLoSil® products properties and introduce or implement this new agent into the real conservation practice.[2]

Still similar research continues in Italy where the scientists follow their previous investigation and examine further possibilities and options of nanodispersion utilization for consolidation of calcareous materials, deacidification of paper as well as surface cleaning by microemulsions and micellas solution. This recent endeavor resulted in establishing another EU project called Nanoforart dealing with the nanomaterials used in culture heritage conservation.[3]

2.1.4. Composition of nanosuspensions

Nanosuspensions used for consolidation of calcareous materials are sols of calcium and magnesium hydroxide and nanoparticles dispersed in short-chain aliphatic alcohols. They differ in concentration and content of alcohols- ethanol, isopropanol and n-propanol. The concentration can vary according to the need of every individual treatment from range 5 till 50 g/l, but there is possibility to dilute each concentration simply by adding more solvent followed by proper mixing. The additions of other solvents (aceton, heptan) are also known. *According to the features of the porous materials, the dispersing solvent can be selected as*

[2] More information about Stonecore project see in the chapter 2.6.1.

[3] More information about Nanoforart project see in the chapter 2.6.2. or on the web pages http://www.nanoforart.eu/ [24]

pure or in a mixture to achieve the ideal penetration inside the artefact and the ideal rheological properties for the application purposes. The features of the solvent make the methodology very simple and available to everybody. Nanodispersions of calcium hydroxide have been applied by using several simple techniques as brushing or spraying, and have been successfully tested over several porous materials.[4] Also the water as one of the compounds in some types of nanosuspensionsis presented. The water content can influence the products stability and particle size of dispersed nanograins. Alcohols evaporate after conservation treatment from treated surface without leaving any residues. Nanosuspensions are clean without any additives or compounds, there are no stabilization agents or tensides so the stability of such consolidants is lower compared to the usual dispersions.

2.1.5. Production process and technology

For many years only lime water met the criteria of compatibility with carbonated materials. However, its consolidation effect is very small due to its very low solubility in water. In addition its application is connected with repeated extensive moistening of consolidated material. Thus, the use of inadequate or low effective restoration materials has also resulted in emerging science for cultural heritage conservation. In last year's many options on how to prepare nanoparticles for conservation usage were examined. Nano-compounds are synthesized via homogeneous and heterogeneous phase. *The main targets of production included the synthesis of crystalline rather than amorphous products (...), lower size heterogeneity, and improved purity and stability of the final product. Successful synthetic procedure should limit particle growth to the nanometer range while maintaining desirable traits such as low sample heterogeneity of size and shape.*[5] *Reactions* can take place in water and also in nonaqueous solvents. Until now the nanoparticles were possible to obtain either by the hydrolysis of calcium hydride under specific experimental conditions or by reacting calcium oxide CaO or calcium hydride CaH_2 with water in an organic medium in the present

[4] Baglioni P., Giorgi R., Soft and hard nanomaterials for restoration and conservation of cultural heritage, REVIEW Soft Matter, 293–303, The Royal Society of Chemistry, 2006, www.rsc.org/softmatter, page 298 [2]
[5]Baglioni P., Giorgi R., Soft and hard nanomaterials for restoration and conservation of cultural heritage, REVIEW Soft Matter, 293–303, The Royal Society of Chemistry, 2006, www.rsc.org/softmatter, page 293 [2]

of surfactant. [3, 7] Other possibility to synthesise particles of $Ca(OH)_2$ can be maintained from solutions NaOH (sodium hydroxide) and $CaCl_2$ (calcium chloride). [6] Another known production process involves reaction of Ca (calcium) with water, in alcoholic medium. [21] The variations in concentration are achieved by evaporation of solvent during the production. It is obviously a quite difficult task to produce the exact required concentration. It was observed, when the smaller size of particles, lower stability of suspension is obtained. So it seems to be necessary to consider the importance of smaller size of particles in one hand and the influence of such feature for the stability of consolidant on other hand. The individual approach to get the best results is an essential task when producing the nanosuspension.

2.1.6. Nanosuspensions properties

The nanosuspensions are dispersed in nonaqueous solvents with the optimal properties for application to cultural heritage conservation. Kinetically stable dispersions can be obtained in short-chain aliphatic alcohols. Alcohols are environmentally friendly, volatile, and, compared to other solvents, have a low toxicity. Surface tension is small enough to ensure optimal wetting that is responsible for high penetration of the dispersions within the porous structure of the wall paintings.[6] One of the main disadvantages for lime water utilization within consolidation treatment is the very low solubility of calcium hydroxide in water. The saturated solution contains only 0,160g/100ml (20 °C). Nanosuspensions of $Ca(OH)_2$ particles dispersed in alcoholic medium are very close to lime water medium, except the production process of nanoparticles can provide a much higher concentration. This suggests a more efficient treatment in less time and on the top of this, during the treatment, no water is introduced into the strengthening material. Also due to the higher surface area of the particles, the carbonisation process should be carried out faster and create a consistent consolidation of the treated surfaces.

Nanomaterials are characterized by scale lengths below 100 nm in one or more dimensions. A medium particle size of calcium hydroxide in nanosuspension called CaLoSil®

[6] Baglioni P., Carretti E., Chelazzi D., Dei L., Giorgi R., Grassi S., Macherelli A., Salvadori B., Colloidal Science and Nanotechnology for Cultural Heritage Conservation [1]

(IBZ Freiberg) is about 150 nm while a medium particle size of usual lime suspensions in water is more than 1 μm. This fact suggests improved mechanical properties and mainly a better penetration into the treated surface. The viscosity and colour of the agent differs from concentration. More concentrated nanosol, more viscose and white appearance is obvious. Nanosuspensions are sensitive to water. It is assumed that a certain amount of water can cause a rise of $Ca(OH)_2$ agglomerates and sedimentation and thus also decrease the penetration abilities. The stability of dispersions is limited and depends on the production process. When the expiration time pass, the sol became not stable, the nanoparticles start to separate and sediment or to create agglomerates. This can again results in changed sol´s properties as it is in the case of water effect mentioned above. The same phenomenon occurs when there is salt content in treated material. Nanosols are not able to penetrate well into such kind of material and they stay on the surface. [2, 21, 15]

There is a possible risk of white haze formation on the consolidated surface. It was observed, when there is low sol´s stability or water and salt effect, the white haze can arise easier. Although the improved properties and the material compatibility of nanosols with carbonated materials suggest a great advantage for future conservation, these negative facts are still complicating the conservation treatment

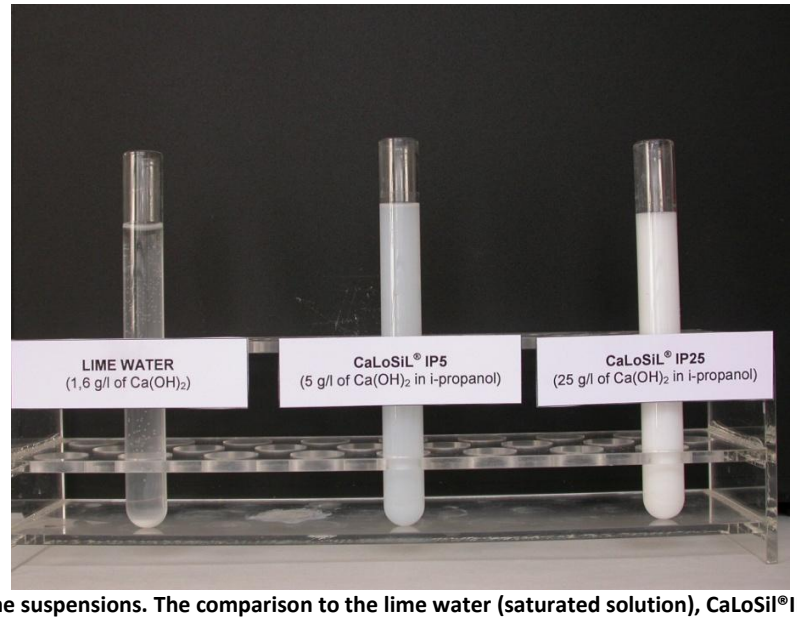

Figure 1. The lime suspensions. The comparison to the lime water (saturated solution), CaLoSil®IP5 and CaLoSil® IP25 nanodispersion appearance.

2.1.7. The consolidaton effect of $Ca(OH)_2$ nanosuspensions

The consolidation effect should be described as a two-step process comprising the evaporation of the solvent and the chemical conversion of calcium hydroxide into calcium carbonate (Figure xx). The latter one brings the hardening of the substrate. It is nearly the same process as in the case of any lime mortar, lime water, or other lime-based material, except no water but alcohol will evaporate during the hardening although the final chemical product is always the same except its mineralogical properties.

$$Ca(OH)_2 + CO_2 = CaCO_3 + H_2O$$

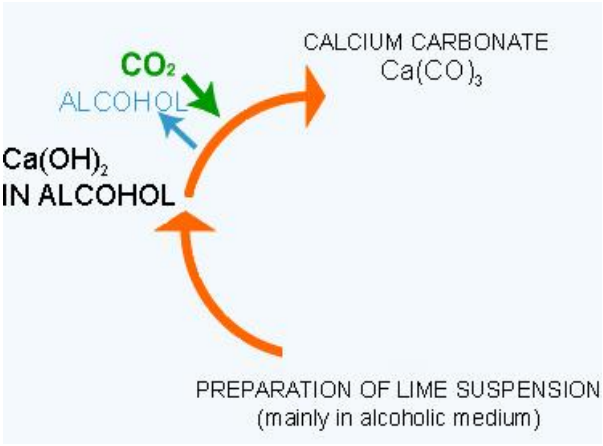

Figure 2. The lime suspensions - the hardening process.

The initial shape and the distribution of the particles and its concentration together with the evaporation speed of alcoholic medium can influence the final strengthening effect. Due to the higher surface area of the particles a carbonisation process should be carried out faster and create the consistent consolidation of the treated surfaces. The carbonisation speed, final structure and shapes of the created calcium carbonate depend on the volume (evaporation ability) of the treated material and the condition to which the consolidated materials are exposed to. The lower evaporation speed of solvent can create a stronger assembling of calcium carbonate and thus a higher strengthening effect can be achieved.

2.2. Possible application field of nanosuspensions

The appropriate substance to be treated by nanosuspensions of calcium hydroxide should be definitely built by at least some amount of calcareous composition. There were trials for consolidadion of sandstone (with very low content of cemented calcite) and brick performed[7] also but the material compatibility does not match the substance of such artefacts fully. Therefore the main advantages of lime suspensions was not taken. The consolidation by nanosuspension is suitable for strengthening the porous materials - mainly lime, lime/gypsum or slightly hydraulic lime plaster and mortar, limestone, marble and other material containing calcium carbonate. Also the consolidation of lime based painting, such as the *frescoes*, *fresco-secco* and the lime *secco* paintings is greatly convenient.

2.2.1. Mortars and plasters

Mortars and plasters with different types of binder have been used since ancient times for different usages and applications such as joining mortars between bricks or stones, wall finishing materials, internal plasters or external renders, foundations for flooring, decoration mortars, supporting materials for pavements, mosaics and frescoes, etc. *"The compositional variation in historic mortars is surprisingly large with great differences both geographically and during different time periods. Mud, gypsum and lime had traditionally been the free most common binder types during the construction history of mankind until about two centuries ago, when their use was replaced gradually by different natural cement types and later by Portland cement, which is nowadays the dominant binder type in the construction industry. Mud is probably the oldest binder type in mortars, the use of clay has been identified for example in Catal Hüyük in Turkey, 6000 BC. The use of lime as a binder dates back to the 6th millennium BC..... Although mud and gypsum have been used in Europe*

[7]Żerkowice sandstone, Gotland sandstone (Restauro, Torun, Poland), Cretaceous sedimentary stone (Institute of Theoretical and Applied Mechanics, Prague, Czech Republic

during certain time periods and in certain regions, the majority of ancient mortars in Europe are lime-based and most of this review will therefore handle historic lime mortars. Gypsum was used for most applications in Pharaonic Egypt and in other countries in the Middle East, but also in medieval times for masonry mortars in the region around Lübeck in Northern Germany and in the Paris region."[8]

"Historic mortars are composite materials, comprised of hydraulic or aerial binding material, or a mixture of binding materials, aggregates – not always in crystalline form – and additives, passive or active, which react with the binding material and are modified during their setting, hardening and ageing, according to processes as yet not well known. Historic composites concern 'disturbed' systems, as in 'service' for tens of centuries under severe mechanical and environmental loadings."[9]

Lime

Lime is one of the most important chemicals as it is the most abundant low-cost alkali and an important compound as binder for plaster, mortars and renderings production. Its high quality is significant for all users and producers. There are two major types - the high-calcium lime and dolomitic lime. They are produced through heating or calcinations of limestone or dolomite in various kilns. Carbon dioxide is driven off, and calcium and magnesium oxides, a product called quicklime (CaO, MgO) that reacts slowly with CO_2 to revert to a carbonate but quickly with water to form hydrated lime ($Ca(OH)_2$), are left. Quicklime needs to be protected from air and moisture to prevent "air slaking". Much quicklime, however, is deliberately hydrated because hydrated lime is much more stable. [19]

[8]Elsen J., Microscopy of historic mortars - a review, Katholieke Universiteit Leuven, Celestijnenlaan 200E, B-3001 Heverlee, Belgium, Abstract, 2005, page 1 [9]

[9]Moropoulou A., Bakolas A., Bisbikou K., Department of Chemical Engineering, Materials Science and Engineering Sector, National Technical University of Athens, Iroon Polytechniou 9, Athens, Greece, page 1 [17]

Gypsum

Gypsum is, as lime, another important component that was/is used as binder alone or together with lime for the production of plaster and mortars. Because of it character, gypsum was/is used especially for building´s interiors. The basic process how to made from gypsum (calcium sulphate hemihydrate $CaSO_4 \cdot ½H_2O$) the hardened gypsum (calcium sulphate dihydrate $CaSO_4 \cdot 2H_2O$) is hydration. Hydration is a typical effect for hydraulic binders. During this process, hydration heat is generated and the volume increases. The volume increasing leads to the expansion of hardened gypsum. Hydration is set off after mixing water with gypsum. The material characteristics of hardened gypsum and the process of hydration and setting are influenced by multiple factors, mainly by the water-gypsum ratio. "*The theoretical water-gypsum ratio necessary for the hydration of calcium sulphate hemihydrate into calcium sulphate dihydrate is 0.187. Additional water, in a so-called over-stoicheiometric quantity, is necessary for the processing of the hardening gypsum paste.*"[10] For many centuries gypsum pieces have been made using water/hemihydrate ratios close to 1.0, which produce low-viscosity water-plaster suspensions that help the conformation of gypsum. The density, mechanical strength and water resistance of such gypsum parts is lower. [18, 4]

2.3. Degradation of plasters and mortars

Degradation, and its causes, ratio and speed are important items when speaking about consolidation. Degradation of plasters and mortars is a huge aesthetic and economic problem for historical buildings. The nature of degradation can vary from decreasing mechanical properties, simple discolouration of the surface to the development of micro-scale weathering forms through to potentially structurally-damaging changes until a total destruction of materials. Degradation can be viewed as a general term covering both the weathering of material and the removal of weathering products arising from the erosion processes. Natural ageing originates the "chemical corrosion" of the binder, calcium

[10] Padevět P., Tesárek P., Plachý T., Evolution of mechanical properties of gypsum in time, INTERNATIONAL JOURNAL OF MECHANICS, Issue 1, Volume 5, 2011, Page 1 [18]

carbonate, with a loss of cohesion between the binder and the substrate. Often in the scientific literature, weathering and erosion are used interchangeably.

"*Degradation can be described by the following equation:*

$$D = (f(s, t (MPE)))$$

Where D is degradation, s and t are space and time respectively, M is material, P is process and E is environment. Any degradation of artwork, both its nature and rate, is the outcome of the variations in space and time of these three interrelated factors, material, process and environment. Degradation at one stage influences the nature and rate of degradation at another stage and so, although general patterns of change may be identified, there is no guarantee as to the precise degradation pathway any particular building or building surface will go through. Each of these factors is looked at separately below, but it is the interaction of the three that produces the complicated nature of degradation as the example of limestone weathering in an urban environment illustrates."[11]

The processes of weathering have traditionally been divided into chemical, physical and biological weathering. Usually, a range of terms such as the salt weathering, the ice-induced weathering and thermal stress are used to distinguish different types of physical or chemical weathering. The environment within which degradation occurs is significant for determining both the nature of that degradation and its rate.

Most of all corrosive processes that occur in our climatic area can run only in the presence of water. Without water, weathering is slow or do not take place at all. The physical degradation rises as a consequence of temperature, moisture changes, ice and salt crystallization process that induce stress, or directly by mechanical stress as rubbing, strike or burden is. The chemical degradation is caused mainly by air pollution from the environment (mostly it is sulphur or nitride oxides). The gaseous and particulate atmospheric pollutants are incorporated into water droplets, falling as rain. Increasing pollution through time together with the physical weathering impact accelerates the weathering rates and therefore the degradation rates rise above a 'natural baseline' level.

[11]May E., Jones M., Conservation Science Heritage Materials, The Royal Society of Chemistry 2006, chapter 9, page 213 [16]

The biological degradation is induced by microorganisms, fungi, algae, mosses, lichens or by the corrosive impact of living organisms or by mechanical damages of plants growth. Microorganisms play a crucial role in mineral transformation in the natural environment, notably in the formation of soils from rocks and the cycling of elements such as nitrogen and sulphur. Microorganisms can be found on the surface or inside materials, as endolithic communities. In some circumstances their long-term surface growth establishes a coloured, varied patina. Although the patina could be considered as a protective layer on the surface, some types of patina growth leads to damage caused by erosion, biopitting and exfoliation. Degradation of mortars and plasters can be also caused by human actions like vandalism, inappropriate construction works or repairs and conservation and restoration treatments. [16, 8]

2.3.1. The physical effect of weathering

The physical effects induce stress inside the material. When the stress exceeds the capacity of the pores, the deformation as fractures formation occurs. This type of behaviour occurs at every scale. The stress results in irreversible changes in the dimensions of the mortar. For degradation, an important consideration is what is the source of the stress and where in the material it occurs. Ice and salt weathering, for example, both operate to induce stresses within the porous structure and these stresses produce the same effects whatever agent induces them. The fracture opens the surface to harmful agents and thus accelerates the degradation process. "*Variations may exist as to where and how agents operate and so, in consequence, when and where the cracks occur. The mechanism, by which the fracture occurs, however, is the same – induced stress."*[12]

Water can enter the material by various ways. With the water inside the pores other substances as soluble salts (chlorides, sulphates, nitrates and others) are brought. As a consequence of crystal growth or volume increase by hydration of crystals, a serious deterioration of material is caused. Formation of crystals just below the surface is called subflorescence, the crystal growth on the surface is called efflorescence.

[12] May E., Jones M., Conservation Science Heritage Materials, The Royal Society of Chemistry 2006, chapter 9, page 215 [16]

The cooperation of water and temperature can cause frost damage. The conditions of ice-induced stresses that can produce damaging strain do not just depend upon it being present. It is the combination of material conditions and processes under particular environmental conditions that produces degradation. As a consequence of crystal growth during the freezing process (volume increase by 9%) the strong pressure arises inside the pores and cracks. When the stress reaches the strength limit of the material, the cracking occurs as a result. The most serious damage is reflected when the temperature fluctuates around 0°C.

2.4. Consolidation

In the chapter dealing with the degradation of mortars it was already mentioned that the deterioration of mortars and plaster goes along with physical and mechanical changes in properties or with total disintegration and decay of material on the surface or in the mass. There are many forms of degradation that can be seen, for example cracking, deformation, detachment, discoloration, creating cavities inside the matrix, blistering, peeling, powdering or crusts and efflorescence development on the surface and much more. Once the mechanical properties of the material worsen, the degradation process takes less time and the decay accelerates.

Consolidation means both the material´s surface and whole mass strengthening process. The crucial task is mechanical properties improvement and original condition reversion (to supply or recover the original binder) and therefore the consolidation of the deteriorated substance. The consolidant should supply deteriorated substance or recover lost material by a new binder. Open porous system of treated material to penetrate the liquid agent inside is necessary. The consoliation treatment is carried out most commonly by brushing or spraying, sometimes by immersion or under vacuum. The spraying method is quite handy and safe, but it is not easy to treat an exact given area of surface without affecting the surroundings. The brushing method can be more precise although the surface abrasion can cause losses.

2.4.1. Required consolidant´s properties

The main task of the treatment is an adequate strengthening effect. Strength should not be too overstated or poor. The optimal shape should be close to the condition of the same but not degraded material. The good agent is stable and resist (in humid condition, in pollution, to chemical agents, in light and UV luminescence impact, immune to microbiological attack), well penetrate into the strengthening substance structure, do not alter the material appearance (shine, colour, the structure) and also the thermal dilatation ratio after consolidation should be close to original. Good consolidant should be non toxic, easy to apply and its price should be acceptable. On top of this, the agent should not change the physical properties of the original treated substance like the porosity, the elasticity (modulus of elasticity), the thermal and humid expansion and water vapour permeability. That means the agent should be physically and chemically compatible with the original strengthened material. Durability and resistance to the ageing of both - the used consolidant and the treated substance - should be sufficient and high. The agent should penetrate sufficiently into the deep matrix and the diffusion of consolidant should be homogenous. If there is a big difference in strength properties in the consolidated and not consolidate interface, the stress, tension and detachment in between both layers can occur. Required reversibility of consolidation treatment can be fulfilled only theoretically. It does not match well with durability demand, because the high durability naturally contradicts to reversibility abilities. Moreover even if the consolidant is still easy to solve and is not fully polymerised or insoluble it is practically impossible to remove the agent from the treated material porous system completely. Speaking about consolidation, the retreat ability is considered more important lately. This means a high importance is given to using such an agent that does not overfill or block off the material´s porous system and that allows the new consolidation treatment in future to be carried out again without any harmful consequences.

Often the most of strengthening agents do not fill fully all required properties mentioned above, so the selection of the right consolidant has to be considered thoroughly according to the real conditions and relations.

2.5. CaLoSiL® product family

The company IBZ-Freiberg (Chemical and Geochemical Consultancy Dr. Ziegenbalg) from Germany was founded in 2003 and is providing extensive chemical and environmental consulting services. It is the first company that introduced the commercial production of the lime nanosuspension for usage in the field of the cultural heritage conservation. This company introduced several products based on calcium hydroxide nanosuspension with the CaLoSiL® trade mark. These products were developed for consolidation and injection treatments mainly of calcareous materials. Thus, the products from CaLoSiL® family include various consolidant agents and injection grouts. [26]

CaLoSiL®

CaLoSiL® products are the first accessible commercial consolidants based on nanoparticles of calcium hydroxide. They comprise several types of nanosols of calcium hydroxide dispersed in alcohols - ethanol, isopropanol and n-propanol. These alcohols will evaporate after the treatment is done without leaving any residues.

The production process involves the reaction of Ca (calcium) with water, in an alcoholic medium.

Production:

Reaction of Ca with water in alcohol medium

$$Ca + 2H_2O \rightarrow Ca(OH)_2 + H_2$$

Several types of CaLoSiL® standard products are available:

CaLoSiL® E-5, E-25 and E-50

CaLoSiL® IP-5, IP-15 and IP-25

CaLoSiL® NP-5, NP15 and NP-50

The letters behind the name "CaLoSiL®" indicate the solvent. The numbers give the total calcium hydroxide concentration in g/l; e.g. E –stands for ethanol, IP for iso-propanol and NP for n-propanol, E-25 means, 25 g/l calcium hydroxide dispersed in ethanol. [21]

2.5.2. Comparison of lime water and CaLoSiL® properties

For many years only lime water met the criteria of compatibility with carbonated materials. However, its consolidation effect is very small due to its very low solubility in water. The concentration of saturated solution of $Ca(OH)_2$ in water is 1,6 g/l and in comparison with the CaLoSil® that is produced in the much higher concentrations 5, 15, 25 and 50 g/l is revealed to be very small ratio. To achieve a sufficient amount of $Ca(OH)_2$ which should be introduced into the material by the lime water many application cycles (at least 50) have to be done. Such application is connected with repeated extensive moistening of the consolidated material, which can be destructive and there is also a possible rising of the white haze on the surface. CaLoSiL® is sol of solid calcium hydroxide nanoparticles which are dispersed in the alcoholic medium and as its concentration is higher compared with the lime water the sufficient consolidation effect can be achieved in less application cycles. Smaller particle size contained in CaLoSil® (a medium particle size of calcium hydroxide in CaLoSil® agent is about 150 nm while a medium particle size of usual lime suspensions in water is more than 1µm) suggests an improved penetration into the substrate. Also the fact that no water comes into the material and alcoholic medium evaporate quickly is a significant task for the consolidation treatment.

The disadvantages of the CaLoSiL® are especially the high sensitivity to water which causes the rising of $Ca(OH)_2$ agglomerates and sedimentation. Another disadvantage is a short stability of dispersions, which is established from the producer for three months. There is also possible risk of the white haze formation on the consolidated substrate due to the back migration of the lime particles which are transported during the evaporation of the solvent. [21]

2.6. Existing projects

The extensive interest in nanomaterials useful in cultural heritage conservation resulted in several researches/projects supported by the European Union. Projects help out to develop new materials, to share and provide new knowledge and to enlarge the possible options in a relatively traditional conservation area and thus synthesize the new science with conventional restoration and conservation. The profits for cultural heritage preservation are essential. There are two projects dealing with the use of nanotechnology within the heritage conservation and preservation supported by the European Union. The Stonecore project already passed, new, 3-years project, Nanoforart have been raised from the beginning of 2012.

2.6.1. STONECORE Project

This diploma thesis was carried out within STONECORE (*Stone conservation for the refurbishment of buildings*), 7th Frame work EU Programme, Theme 4, Nanosciences, Nanotechnologies, Materials and new Production Technologies, Project Number 213651. The main idea of the project was to develop, test, examine and finally implement nano-materials in the field of conservation of cultural heritage, especially as a consolidation material of lime-based materials such as limestone, lime mortars and stucco. The project started in 2009 and was ended in September 2011. Twelve partners from Europe were participating together in this research. [23]

Stonecore project at the Faculty of Restoration

As one of the partner of the project, the Faculty of Restoration was involved in the testing of properties of nanomaterials. The series of tests comprised the evaluation of the nano-lime colloidal dispersions CaLoSiL® which were applied on highly corroded substrates - biodetritic limestone from Kutná Hora and historic and laboratory prepared highly corroded lime mortars. The first stage of the three years project period was focused on the testing of nanomaterials in laboratory scale. Further experiments were carried out on-site on reference historic objects.

Laboratory testing included the investigation of nanosols properties such as consolidation effectiveness, penetration ability, colour changes and others. The relation of soluble salt and water content in prepared substrates to nanosuspension properties was studied and evaluated. [15] During laboratory testing in cooperation with project partners it has been used the most recent advanced testing methods in order to determine and evaluate the consolidation capability and impact of nanosols on treated materials properties.

The CaLoSil® was tested and subsequently used with positive results for the conservation of the statue - *The angel with the child* from Kutná Hora. Nanosuspension was used for stone consolidation and grouting of this sculpture made from biodetritic coarse-grained limestone. An essential problem during the usage of nanosols for the sculpture consolidation was the white haze formation on the surface after the consolidation treatment. The tests of white haze removal were performed and so the white haze was finally removed by water vapour and abrasive cleaning methods. The final evaluation of consolidation effect was performed by means of drilling resistance and ultrasound velocity measurement. [13]

Figure 3. The statue The angel with the child. On the left picture there is the sculpture before the conservation treatment, on the right side the sculpture after the conservation treatment. Foto Dana Macounová.

The CaLoSil® was also tested and successfully used for the consolidation of historic lime mortar in the former monastery of *Rosa Coeli* in the Czech Republic. The consolidation of two different coarse mortars was performed with the aim of preventing further deterioration of the mortar and to preserve its present visual appearance. [22]

Another consolidation trial was carried out within the conservation and restoration treatment of the medieval wall paintings in the *St. Vitus church* in Zahrádka, Ledeč nad Sázavou, The Czech Republic. The nanosuspension CaLoSil® was tested for the consolidation of the exposed plaster and powdered paint layer. The different concentration and amount of cycles was carried to compare the nanosuspension properties. Although the trials were evaluated only by the naked eye and by mechanical abrasion in situ the consolidation effect was obvious. The suspension was applied on the painting by stippling with a very soft brush, on the exposed plaster by brush and spraying. A slight white haze was observed after the evaporating of solvent on the surface of painting, but it was easy to remove mechanically the same way as a cleaning of a wall painting is carried out. In the case of the black areas of painting, the cleaning together with the white haze removal was impossible to carry out due to the extremely sensitive and thin layer of black colour used. Any mechanical stress produced on the black areas cause abrasion and thus the exposure of the layers being under. Although the consolidation effect of CaLoSil®E25 on other colour areas was successful, it was decided to use a different consolidant for the full area painting consolidation treatment. However the overall consolidation of the exposed plaster was carried out by two application cycles of CaLoSil®E25 with positive results.

Practical evaluation

The results of the entire investigation performed in the Faculty of Restoration in Litomyšl within the project Stonecore have led to the evaluation of basic useful information important for practical conservation treatment. The nanosuspensions obviously provided better features and they appeared to be more suitable for consolidation of calcareous materials than any other consolidation materials which are nowadays used, especially the lime water or silica based consolidants.

In the practical fieldwork tests, there were some problems with porous materials regarding penetration depth and the creation of white haze on the surface. The agent penetrates very well into “open” surfaces. The penetration depth obviously depends on the

surface´s layer properties and conditions during penetration and curing of consolidation substrates. In case of calcareous materials the difficulties are caused namely by gypsum crust, which formulate a surface impermeable layer that completely defend consolidant to be penetrated in. Similarly, a tiny protective layer of carbonated surface or dirt is another reason for an insufficient penetration depth. It was revealed thet also the soluble salt and water content in treated material have essential impact on the consolidation treatment effectiveness by means of decreasing the penetration abilities and white haze appearance on the surface.

The way of application has also a significant impact on the penetration. Better penetration was achieved by spraying while application of the nanosol with a brush was less efficient. The slow solvent evaporation ratio has proved to be the crucial task regarding to penetration depth and calcium carbonate formation and its distribution. It was found that the quick evaporation of solvent cause nanoparticles to migrate back to the surface of treated material. As the evaporation ratio is influenced by atmospheric condition it is clear, the nanosuspension in alcohols should not be applied on the surface under the direct sun as long as high temperature, a treated area must be sheltered from the direct sun for all the time of evaporation of solvent.

The white haze formation is caused by no or low penetration and a back migration of the nanosol. However, it is possible to remove it by mechanical cleaning. Apparently the mechanical cleaning can´t be carried out on every type of consolidated materials and surfaces without losses of material. This fact suggests the necessity to consider individually whenever consolidation treatment by nanosuspensions can be done or not.

It was confirmed that using a lower concentration in more application cycles provide a more sufficient consolidation effect. With the consolidant CaLoSil® E25 in most cases we obtained good consolidation effect after three application cycles. Nevertheless the proper concentration and amount of application cycles differ according to the treated material and its properties.

2.6.2. NanoForArt project

The ongoing EU project called NanoForArt *"Nano-materials for the conservation and preservation of movable and immovable artworks",* 7th Frame work Programme, Project Number 282816, started on the beginning of the year 2012 and will cover a three years period. The main objective of the NANOFORART proposal is the development and experimentation of new nano-materials and responsive systems for the conservation and preservation of movable and immovable artworks. The main effort of NANOFORART is the implementation of progress in material science such as the sophisticated nanostructured materials are into the restoration and preventive conservation of cultural heritage. The international consortium of partners comprises universities, laboratory research institutions and museums. In addition SME´S from restoration institution are involved in practical assessment of the scientific research of the project.

The research activity is focused on the development of manageable methodologies, based on nanosized structures and with a low environmental impact. The main tasks include the production of dispersions of nanoparticles, micellar solutions, microemulsions and gels, in order to offer the new reliable pathways to restore and preserve works of art.

In the second part of the project great importance will be given to technology transfer to SMEs and in commercialization of technology and evaluation of the eco-toxicity of nano-materials. A fundamental part of the project is also related to the role of end-users. Important museums will validate the technology and the methods developed in the first part of the project, and provide training activities and dissemination of the developed techniques. [24]

3. Experimental part

3.1. Aim of the study

This study was developed to test the consolidation of heavily corroded substrates (plaster, mortars) which are exposed to atmospheric conditions such as water soluble salts, freeze-thaw and varying humid conditions. For the consolidation of such deteriorated substrates a new group of consolidation materials based on calcium hydroxide nanoparticles called CaLoSil® was tested. The main aim was to simulate, describe and determine the influence of different negative climate conditions on prepared consolidated plaster substrates. The aim was to get broaden knowledge about nanosuspensions properties as essential information important for consolidation treatments. The measurement was based on previous testing carried within the European Project STONECORE by the Faculty of Restoration, University of Pardubice and its partners. Durability and resistance characteristics were studied on samples imitating the aerial lime mortars as well as on combined gypsum mortars with the rather low gypsum content. Both substrates simulate traditional historic materials commonly used in middle Europe.

3.2. Materials

3.2.1. Materials used

Silica sand (Běstovice, CZ)

Silica sand (Kremer Pigmente GmbH & Co. KG, DE)

Crushed limestone (St. Margareten, 0-2 mm; Osliper Betonwerk und Baustoffhandel, AT)

CaLoSil® E25 (IBZ Freiberg, DE)

Sol $CaSO_4$-$Ca(OH)_2$ (IBZ Freiberg, DE)

Na_2SO_4 (14 wt.% solution, Penta, CZ)

Demineralized water

KNO_3, KCl, NaCl, LiCl $CaCl_2$, Ca $(NO_3)_2$- saturated salt solutions (Penta, CZ)

3.2.2. Laboratory Substrates

3.2.2.1. Preparation of substrates

Two types of plaster substrates were prepared for testing. The first type of substrates is imitating highly corroded lime mortar[13] and has a darker colour in the mass. It was prepared by mixing crushed limestone (St. Margaretten, size max. 2 mm), sand type 1[14] and demineralised water in 2:4:1 volume ratio (Fig.1). To achieve a good simulation of corroded lime mortar and to distinguish the difference between the lime binder contained in prepared samples and influence of consolidant used during our treatment the crushed limestone worked only as a binder in the composition of the prepared specimens. The second type of substrate is gypsum substrate imitating highly corroded gypsum mortar which has a lighter colour in the mass. It was composed of crushed gypsum mortar (obtained from Dahlen castle-Germany, size max. 0.5 mm), sand type 2[15] and demineralised water in volume ration 1:8:1. These mixtures were filled into cube shaped moulds of dimension 4x4x4 cm^3. Prepared specimens were stored in laboratory conditions for 7 days to get dry (Figure 3). After the drying process and removing the substrates from moulds, both types of prepared samples were considered as very weak and able to disintegrate easily. Some amount of prepared specimens was then cut to small cubes of 2x2x2 cm^3 for sorption isotherm testing.

[13] These substrates were already used in the previous research within Stonecore project at FR, UPCE. See more in References - e.g. Dunajská J., Zhodnocení současných možností konsolidace vápenných omítek konsolidanty na bázi hydroxidu vápenatého, Bakalářská práce, Univerzita Pardubice, Fakulta restaurování. Litomyšl, 2009. []

[14] More in the Chapter 3.2.3.2.

[15] More in the Chapter 3.2.3.2.

The substrates can be characterized as follows:

NCLS - *Specimens imitating highly corroded lime mortar (4x4x4 cm^3)*

- mixture of crushed limestone (size max. 2 mm, St. Margaretten), sand type 1 (size max. 2 mm) and demineralised water (2:4:1 by volume)

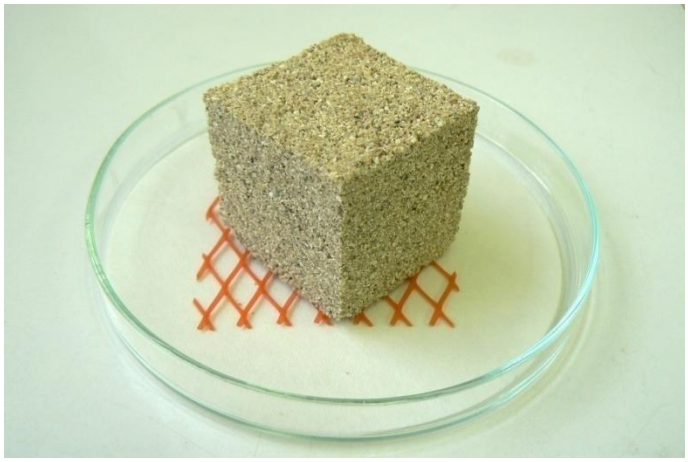

Figure 4. NCLS - specimen imitating highly corroded lime mortar.

NCGS - *Specimens imitating highly corroded gypsum mortar (4x4x4 cm^3)*

- mixture of crushed gypsum mortar (obtained from Dahlen castle-Germany size max. 0,5 mm), sand type 2 and demineralised water (1:8:1 by volume)

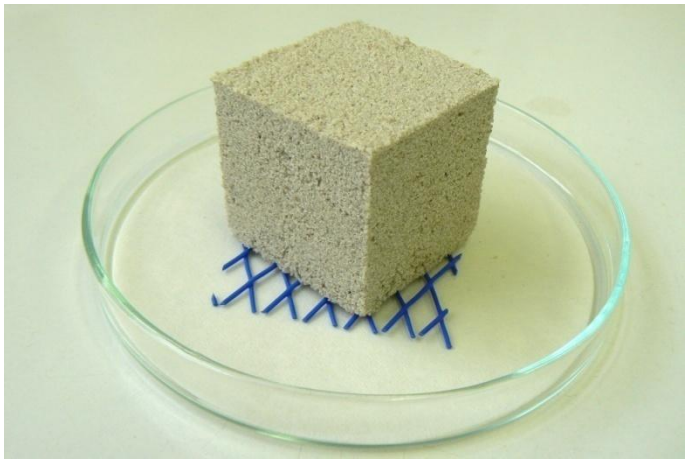

Figure 5. NCGS - specimen imitating highly corroded gypsum mortar.

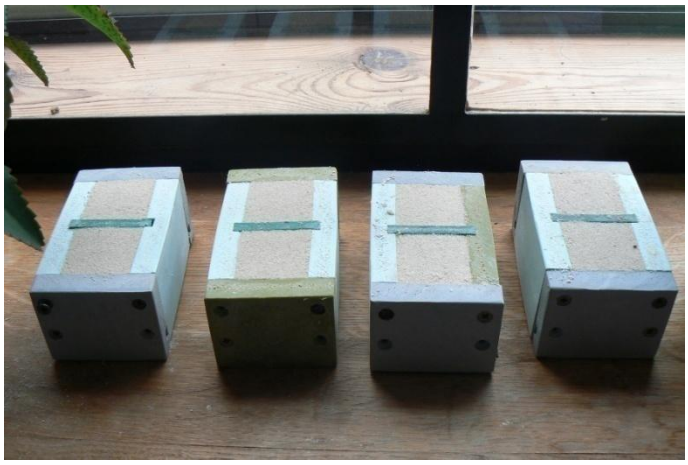

Figure 6. Prepared samples were drying in the moulds.

The composition of specimens imitating highly corroded gypsum mortar have been proposed and recommended by colleges from Hochschule für Bildende Künste, Dresden, DE. To get comparable results and to broaden knowledge about the behaviour of such substrates after consolidation, we followed their recommendations to maintain the same way of preparation and the exact same content and composition of substrates as they used during their scientific research within the Stonecore project. The composition of sands and plaster used and proposed by colleges from Hochschule für Bildende Künste is reported in Appendices 9.4., 9.5. The grain size distribution of the aggregates-sands used for preparation of this plaster was set up according to Fuller curve[16]. The gypsum binder in prepared specimens (NCGS) comes from gypsum plaster only (Dahlen Castle plaster), no more gypsum or other binding medium such as calcium carbonate was used during their preparation[17]. More detailed information about the Dahlen Castle historic mortar composition is given in the Chapter 3.4.4.

The University Hochschule für Bildende Künste Dresden was one of the partners of the STONECORE project. They focused on material testing of CaLoSil® products in laboratory and also on real objects. In East German territory the gypsum lime mortars are quite commonly found as a historic building material and so they were naturally interested in the new possibilities of consolidation gypsum mortars by nanosols containing the gypsum. For their research on laboratory prepared samples and on the real objects the original plaster from

[16] Ref. Fuller and Thompson (1907)

[17] Dahlen Castle (2011, May 9). In Wikipedia, The Free Encyclopedia. Retrieved 17:09, March 3, 2012, from http://en.wikipedia.org/w/index.php?title=Dahlen_Castle&oldid=428174058

Dahlen Castle has been used. The Dahlen Castle was built between 1744 and 1751 in the late Baroque style in the small town of Dahlen, located in Saxony. The castle featured over 30 rooms with the rich wall paintings decoration. On 20 March 1973, a fire caused by a defective chimney burnt the castle to an empty shell [33]. Today there is great endeavour for the restoration of the castle, but the castle is still in ruins. The gypsum plaster and stucco from Dahlen castle were investigated during the STONECORE project in Hochschule für Bildende Künste Dresden: "*Laboratory specimens (prisms, 10x2x2 cm³) were made from weak gypsum mortar. Subsequently, they were impregnated (3 times) with calcium sulphate nanosol. Also original material from the object was treated in the same way. Three-point bending strength of the laboratory made mortars was significantly increased to multiple by treatment with nanosol. The original samples, initially of a much higher strength as the laboratory specimens, did not show a clear consolidation effect after treatment.*"[18]

Figure 7. Dahlen castle mortar.

3.2.2.2. Consolidation of substrates

Consolidants

- CaLoSiL® E25 – nanosuspension of $Ca(OH)_2$ dispersed in Ethanol
- Sol $CaSO_4$-$Ca(OH)_2$, dispersed in isopropanol (30g/l $Ca(OH)_2$+ 15g/l Ca SO_4)

[18] Dähne A., Köberle T., Consolidation of mortars and stucco with calcium hydroxide and calcium sulphate nanosols – results and questions. The University of Fine Arts in Dresden.

Each type of mortar substrates was treated by two different consolidants. For consolidation of specimens imitating highly corroded lime mortar the consolidant CaLoSil® E25 was used. When the specimens imitating highly corroded gypsum mortar were consolidated the Sol $CaSO_4$-$Ca(OH)_2$ was applied. This gypsum sol contains 30 g/l of $Ca(OH)_2$ and 15 g/l of $CaSO_4$). Consolidants and its composition are given in Table 1, Figure 5.

Figure 8. Consolidants.

Type of specimen	**Consolidant and its composition**	**Solvent**
Specimens imitating highly corroded lime mortar (NCLS)	CaLoSiL® E25 – nanosuspension of $Ca(OH)_2$, (25g/l)	ethanol
Specimens imitating highly corroded gypsum mortar (NCGS)	Sol $CaSO_4$-$Ca(OH)_2$, (30g/l $Ca(OH)_2$+ 15g/l Ca SO_4)	isopropanol

Table 1. Consolidants used. Each type of mortar substrates was treated by different consolidants.

Application of consolidants

The application of both types of consolidant was carried out by immersion. In the case of CaLoSiL® E25 its application on lime mortar specimens (NCLS) was made in **5** cycles for

each specimen. The Sol $CaSO_4$-$Ca(OH)_2$ was applied on gypsum mortar specimens (NCGS) in **3** cycles. This sol is more viscous and when the specimens were removed from the bath container after each consolidation cycle to get dry all the samples were covered by thick layer of liquid consolidant which did not drain from the surface completely (Fig.6, 7). After the each cycle the all samples were covered for one day by a slightly opened cover to avoid quick evaporation of ethanol. Next day the cover was removed and the specimens were exposed to laboratory conditions to get dry. The following application cycle was done when the specimens became completely dry. After drying the gypsum specimens were obviously covered by white layer of created crystals as the result of the viscous consolidant´s residues trapped on the surface after the immersion process. All samples were weighted before and after each application.

Figure 9. The gypsum substrates during consolidation by immersion in Sol $CaSO_4$-$Ca(OH)_2$.

Figure 10. The gypsum substrate after removing from the consolidation bath.

Although there is a discrepancy in the number of application cycles between both types of substrates, the amount of consolidant introduced into each substrate is nearly equal. In the case of lime substrates 125 g/l of calcium hydroxide was introduced during 5 cycles of application. In case of gypsum specimens 135 g/l of consolidant during 3 cycles was introduced (90 g/l of $Ca(OH)_2$, 45 g/l of $CaSO_4$).

Curing conditions

After the last consolidation cycle all specimens were stored for one month in the laboratory under the average condition of 50-65% RH and temperature 21-25°C.

3.2.3. Material characteristics

3.2.3.1. Consolidants characteristics[19]

Three general characteristics of both types of consolidants are presented in Table 2. For comparison, the similar characteristics of pure solvent are labelled in the same table. These characteristics were obtained within the Stonecore project. Both consolidaton systems are milky white liquids with low density around 0.8 $g.cm^{-3}$ and with high surface tension very close to pure solvent. (Figure 11, Table 2)

[19] Properties of consolidant CaLoSil E25 and Sol $CaSO_4$-Ca $(OH)_2$ were performed within the Stonecore project.

Figure 11. Nanosuspension CaLoSil® E25 (1) and Sol $CaSO_4$-$Ca(OH)_2$ (2)

The particle size distribution of lime nanosol is shown on Figure 8 and 9. It has the plate like structure with submicrons particle size. It can be characterized by unimodal distribution of particle size with only one maximum of 150 μm. This means that in the sol there is only one type of $Ca(OH)_2$ particles with diameter of some 150 μm.

Consolidant	**Concentration [g/l]**	**Surface tension (σ) 20 °C [N.m^{-1}]**	**Density[20] (ρ) 20 °C [g/cm^{-3}]**
CaLoSiL®E25	25 ($Ca(OH)_2$	24.92±00.12	0.8360
Sol $CaSO_4$-$Ca(OH)_2$	15 ($CaSO_4$) 30 ($Ca(OH)_2$	-	0.8071
Ethanol	-	22.55	0.789
Isopropanol	-	21.7	0.786

Table 2. The consolidants characteristic.

[20] Measured by ITAM, Prague

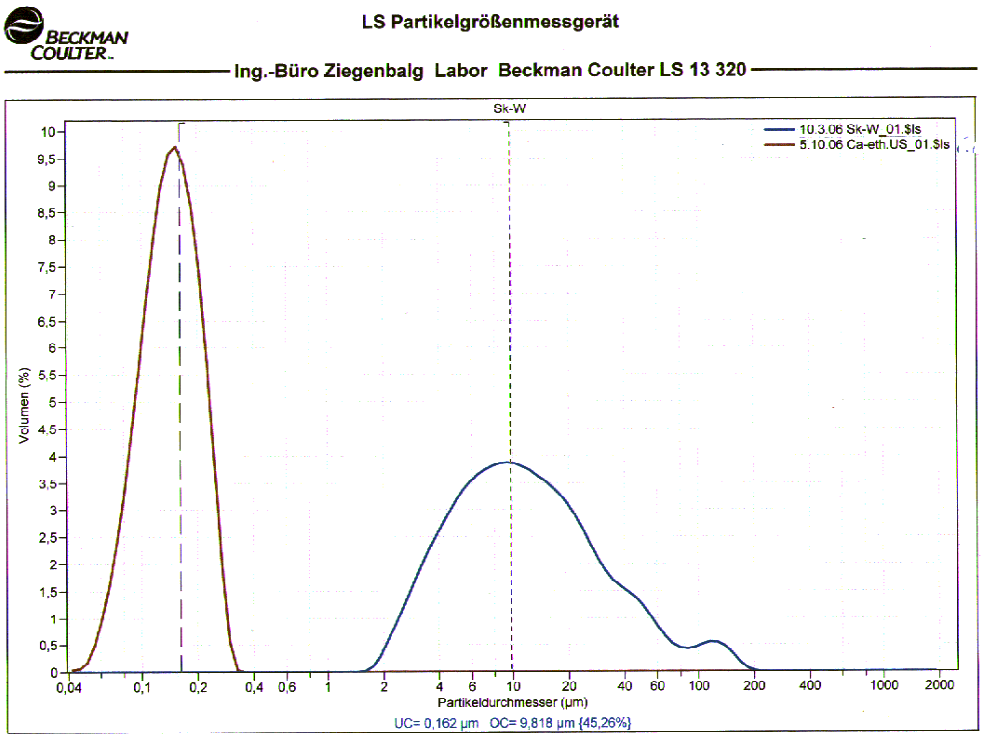

Figure 12. Particle size of CaLoSil® nanosuspension (the left curve) and lime wash (the right curve). The measurement was taken by IBZ Freiberg (D).

Sol $CaSO_4$-$Ca(OH)_2$ has bimodal distribution characterized by two maxima: first, with values around 150 □ m is probably due to $Ca(OH)_2$ particles, the second, much bigger particles with diameter of 8 □ m, is a result of presence of $CaSO_4$. The shape of crystals can be described as regular much smaller particles of $Ca(OH)_2$ dispersed between the fibbers of $CaSO_4$ (Figs. 10, 11).

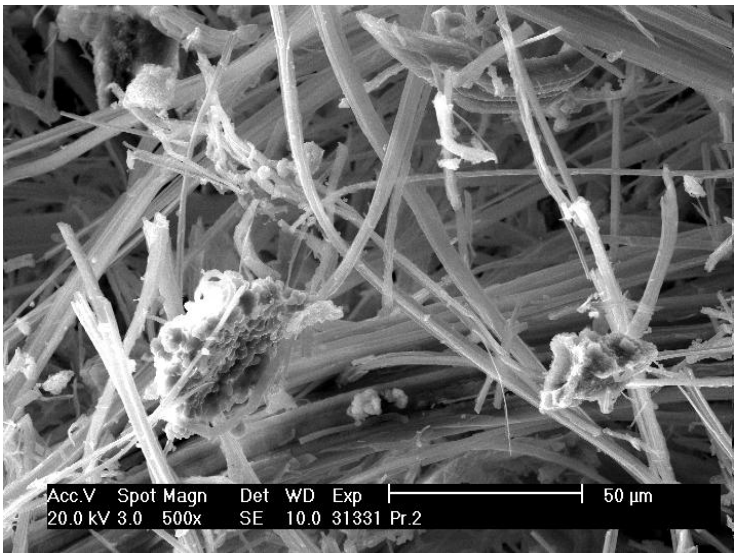

Figure 13. Distribution of pores and particles of Sol $CaSO_4$-$Ca(OH)_2$. Picture was taken by IBZ Freiberg (D).

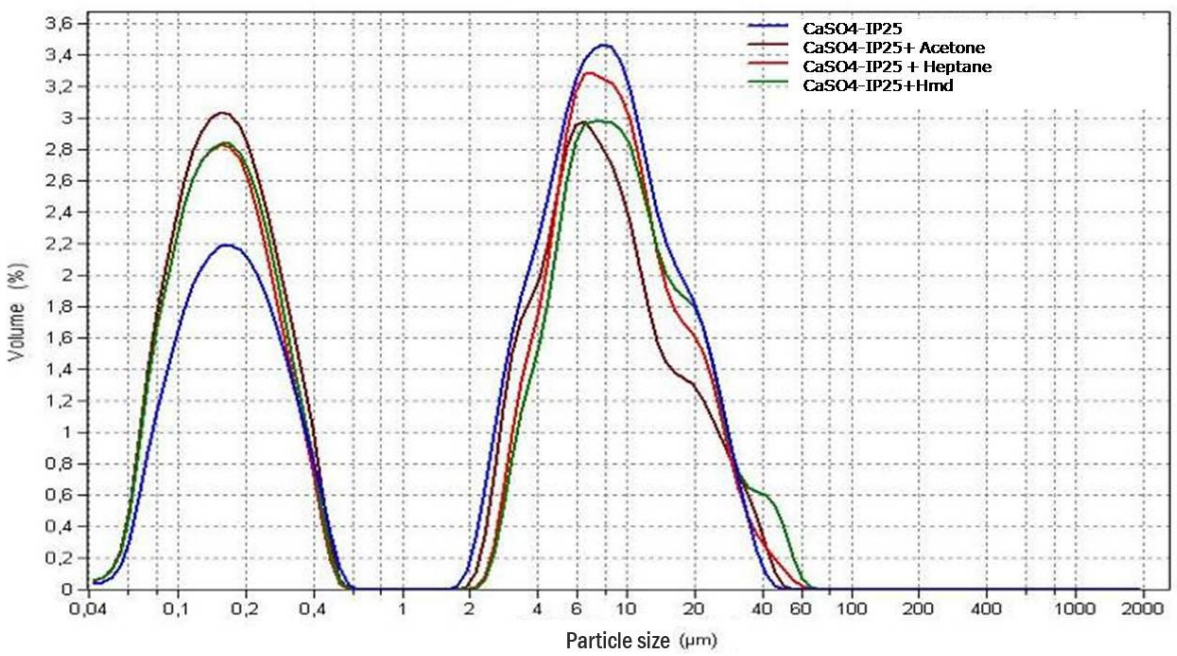

Figure 14. The particle size distribution of different $CaSO_4$-$Ca(OH)_2$ sols. The blue line present pure isopropanol system used within this research. Measurement was taken by IBZ Freiberg (D).

3.2.3.2. Substrates characteristic

Particle size distribution of aggregates

Two types of aggregates and crushed limestone (St. Margaretten) were used for this research. The sand type 1 and the crushed limestone were used for the preparation of compacted specimens imitating lime mortar. Particle size distribution of sand and crushed limestone was achieved by sieve analysis and is given in Table 3 and Figure 10. The sand can be characterized by the distribution of grains between (<0.063 mm and 2 mm) with highest content of grains with 0.25 mm. Crushed limestone has almost a similar range of particles and distribution very close to the analysed sand type 1 with a maximum content of grains with a size around 0.5 and 0.25 mm.

Grain size d [mm]	Sand type 1 [hm. %]	Crushed limestone [hm. %]
2	11.35	0
1	8.73	8.15
0.5	18.17	39.50
0.25	45.57	33.58
0.125	14.31	12.33
0.063	1.18	6.17
less than 0.063	0.43	0.43
Σ	100	100

Table 3. Particle size distribution of silica sand type 1 and crushed limestone.

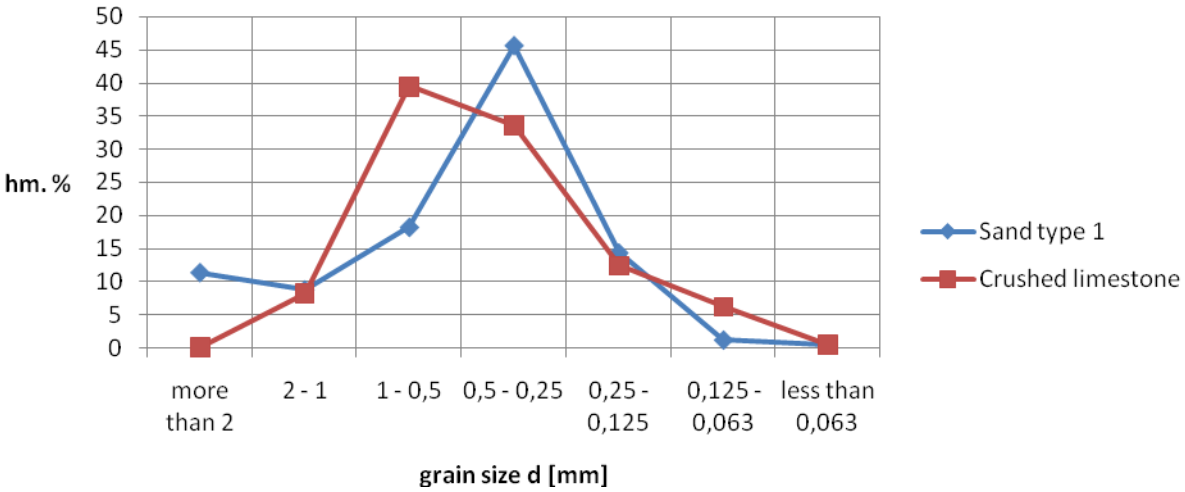

Figure 15. Particle size distributions of sand type 1 and crushed limestone.

Particle size range of sand type 2 used for preparation of gypsum specimens has been proposed by colleges from Hochschule für Bildende Künste, Dresden. To get comparable results, we followed the same composition of substrates as they used during their scientific research within the Stonecore project. The aggregates were bought in a commercial store and their particle sizes were defined by the producer. The grain size distribution of this used sand was set up according to the Fuller curve.[21]

Particle size distribution of sand type 2 is given in Table 3 and Figure 11, more detailed information about aggregate analysis is given in Appendices 9.4., 9.5.

[21] Ref. Fuller and Thompson (1907)

Grain size d [mm]	Sand type 2 [hm. %]
1 – 0.5	28.24
0.5 – 0.4	8.23
0.4 - 0.25	21.50
0.25 - 0.1	18.81
0.15 – 0.04	23.22
Σ	100

Table 4. Particle size distribution of silica sand type 2 (Sand used for preparation of samples imitating highly corroded gypsum mortar).

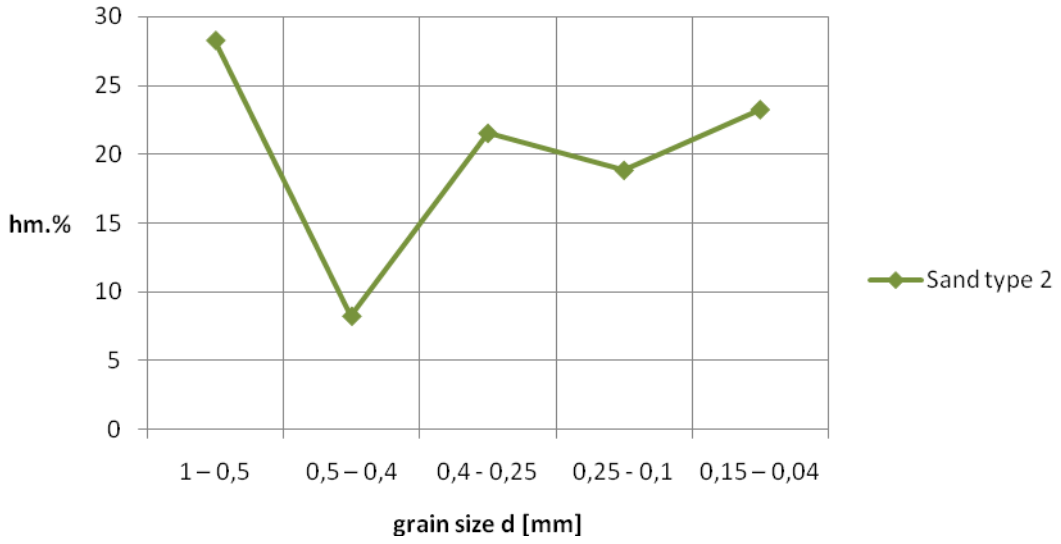

Figure 16. Particle size distribution of sand type 2.

3.3. Methods

The following characteristics were measured on standard samples before consolidation (NCLS, NCGS) and subsequently on consolidated lime and gypsum substrates (CLS, CGS).

3.3.1. Properties determination

3.3.1.1. Physical characteristics

Water absorption coefficient

Water absorption is an extremely important characteristic of mortars, as they are usually exposed to environmental conditions (rain, snow) or they can be in contact with construction elements that could be wet (bricks, soil). As a consequence, the untreated mortar could become damaged and cause water movement inside the building structure, thus affecting or damaging other materials such as stones or plaster [35]. Water absorption test through capillarity at atmospheric pressure has been performed to study water transport behaviour of specimens and to characterise the parameters associated with fluid uptake and transport inside the pores. When a porous material is put in contact with water, the capillary tension allows the fluid to penetrate inside the pores of this material. This phenomenon can be followed by the change in weight, which is directly linked to the volume of water absorbed. [36]

Water absorption test through capillarity was performed according to procedure given by EN 1015-18. Water absorption test through capillarity was measured by weighting the specimen (m) in time (t). Capillarity coefficients C were calculated by determining the slope of the curves in the linear segment of the graph. Then absorbed water was calculated according to the following equation ($kg.m^{-2}$).

$$W = \frac{m}{S.\sqrt{t}}$$

W	water absorption coefficient [$kg.m^{-2}.h^{-0,5}$]
m	amount of absorbed liquid [kg]
S	surface [m^{-2}]
t	time [hod]

Three specimens of cube shape (4x4x4 cm^3) of each type of substrate were used for measurement. Before testing, all samples were dried up to constant weight at 80 °C in a drying chamber for 24 hours. After the drying process the substrates were left to get cold for two hours in a dessicator and their weigh was measured. Samples were placed into the water container with the plastic grille at the bottom. The water level was 5-10 mm from the bottom. To ensure perfect contact of substrate with water and to avoid creation of air bubbles, specimens were put at the bottom of container in sloping position. However, due to quick water absorption of all substrates the testing procedure was adapted, time interval between each weighting was shorten in comparison with the recommendations given by standard. Not consolidated substrates disintegrated in contact with water immediately. Due to the water absorption test was carried only on consolidated specimens (CLS, CGS).

The water absorption test by immersion was not performed. Not consolidated specimens (NCLS, NCGS) disintegrated completely after immersion into the water. Although the consolidated substrates (CLS, CGLS) when immersed into the tank filled with water did not disintegrated, they were fully saturated in few seconds due to their high porosity and “corroded” state, therefore the measurement of water absorption coefficient by immersion was impracticable.

Bulk density

Bulk density is an important concept regarding the material properties. The mass density or density of a material is defined as its mass per unit volume. The density of the material including the air spaces is the bulk density, which differs significantly from the density of an individual grain of sand with no air included - the real density. It is defined as the ratio of the dry specimen mass to the volume of its solid part. [36, 37]

The bulk density was calculated according to the following equation:

$$\rho_v = \frac{m}{V}$$

$\boldsymbol{\rho_v}$ the bulk density of the sample [g.cm^{-3}]

$\boldsymbol{m}$ the weight of the sample [g]

$\boldsymbol{V}$ volume of the sample [cm^3]

Mass gain

All samples were weighted before and after each application of the consolidant and finally let to dry in laboratory conditions (20-22°C; 60-70% RH) for 2 months. The consumption of used agent was calculated and increase of weight during and after treatment was determined. The weight changes after evaporation of alcohol and proper period of curing should correspond to $CaCO_3$ formation in the matrix of the sample.

The mass gain was calculated according to the following equation:

$$\Delta m = \frac{m_i - m_o}{m_o} * 100$$

$\boldsymbol{\Delta m}$ mass gain [wt. %]

$\boldsymbol{m_i}$ weight of the sample after consolidation treatment and curing [g]

$\boldsymbol{m_o}$ initial weight of the sample [g]

3.3.1.2. Microstructure characteristic

Porosity measurement by means of Mercury intrustion porosimetry (MIP)

Mercury intrusion porosimetry (MIP) has been widely used in the study of porosity and pore structure characteristics. Knowledge of porosity and pore size distribution allows better understanding of many physical and mechanical properties such as strength, permeability or durability of materials. Therefore, porosity and pore structure can be considered as one of the major criterias of compatibility between the original mortar before and after the restoration treatment.

This method was used to characterize pore structure of substrates before and after the consolidation by pore size distribution measurements. Other parameters measured were surface area, total porosity and bulk density.

The measurements were performed at The Institute of Theoretical and Applied Mechanics AS CR, v. v. i in Prague. The data was collected by the Quantachrome porosimeter, model Poremaster PM-60-13 within pressure range of 0.005-413 MPa [36]. (Appendice 6.3)

Optical and Scanning electron microscopy (SEM)

Optical and Scanning electron microscopy research was performed to investigate microstructure characteristic of the specimens. Special attention was paid to the effectiveness of consolidation treatment observable namely in the pores and cracks. It is mostly the size of pore openings and the chemical/ mineralogical nature of the pore walls which are of relevance to the treatment by consolidant.

Polished sections were coated with carbon and observed in the scanning electron microscope (SEM) using back-scattered electron mode (BSE) and eventually employing energy dispersive X-ray analysis (EDX). The Philips 515 apparatus was used (high vacuum, accelerated voltage of 20 kV). Representative micrographs obtained either through PL or SEM were selected for pseudo colour editing. The images were then digitally calculated for total porosity (as percentage by area). Regarding the porosity values, it has to be noted that the calculated amounts are always lower than those obtained by other methods such as e.g.

mercury intrusion porosimetry, caused by the limit of resolution of the range of approx. 10 μm [22].

The analysis has been performed at the IATCS - Division of Conservation Sciences at the Institute of Art and Technology, University of Applied Arts Vienna (Austria).

3.3.1.3. Strength determination

Compressive strength and bending strength

To determine the effectiveness of the consolidation compressive and three point bending strength tests were carried out. Both types of consolidated and not consolidated substrates were tested. The destructive methods were used for these tests and the measurements were performed at The Institute of Theoretical and Applied Mechanics AS CR, v. v. i in Prague. Specimens were tested in electromechanical and servohydraulic testing frames and loaded with constant crosshead velocity. Compression strength was calculated from measured ultimate loads and real cross section areas given by measured actual dimensions of individual specimen. Three point bending was calculated from measured ultimate loading force and deflection in the middle of span. The results were evaluated according to the standart ČSN 12372 (721145) and ČSN 1926 (721142). Measurements were performed on three samples of each kind of specimens and final strength was calculated as their average value.

However, due to the non standard character of samples, standard testing procedure of mechanical characteristics was modified. Testing of non-standard materials, such as historic mortars and fragmental pieces of other historic materials, was developed at the Institute of Theoretical and Applied Mechanics AS CR, v. v. i in Prague (ITAM). The correction coefficients applicable for assessment of equivalent standard compression strength from the tests on non-standard specimens were determined. The method was developed at ITAM in 1998 and has been used for analysing various types of historic mortars [36, 39].

[22] Ghaffari E., Weber J., *Petrographic key characteristics of samples to be treated*, Institute of Art and Technology – Conservation Sciences, University of Applied Arts Vienna (Austria), Contribution to Deliverable 5.1 of the STONECORE-project, 2009, page 23

Figure 17. The compression strength testing device. The picture was made by ITAM AS CR v.v. i Prague.

Ultrasound velocity measurement

Ultrasonic is a non-destructive versatile testing that can be applied to a wide variety of inorganic materials to assess its physical and mechanical state. Ultrasonic material analysis is based on a simple principle of physics: the motion of any wave will be affected by the medium through which it travels. Thus, changes in one or more of four easily measurable parameters associated with the passage of a high frequency sound wave through a material-transit time, attenuation, scattering, and frequency content-can often be correlated with changes in physical properties such as hardness, elastic modulus, density, homogeneity, or grain structure. The ultrasonic velocity depends on physical and mechanical properties of the substrate such as porosity and bulky density, mineralogical composition, intercristalline connection and water content. [40]

This means the speed of ultrasound waves passing through the more massive and better united and homogenous structure is faster than the wave speed coming through the more porous and less cohesive material. It is also possible to distinguish corroded and not corroded material by this way of measurement, as in damaged and corroded material the ultrasound wave speed is lower than in the same structure of good shape and better condition. In some cases the structure composition, deformation or corrosion of material can cause the ultrasound wave to not be able to pass through it at all. [41, 42]

In this study transit time or velocity respectively of ultrasonic longitudinal waves as a ratio of the distance between a transmitter and a receiver to the transition time was measured on dry substrates before and after consolidation. Measurement was carried by USME-C (fa. Krompholz,BRD) device with a 250 kHz frequency. For transmission of wave into and out of moving materials by transmitter and receiver (pulse/echo mode) the permanently plastic sealant based on silicone rubber (without the addition of plasticizers) was used for the direct contact with measured material.

The ultrasonic velocity was calculated according to the following equation:

$$v = \frac{d}{t}$$

v	ultrasound velocity [m/s]
d	diameter of measuring (distance between transmitter and receiver) [m]
t	time of wave passing the diameter [s]

Transmission of wave was led trough the specimen by three lines/direction *x, y, z*. In the case of not consolidated specimens (NCLS, NCGS) each direction was measured two times - in the middle and on the edge of specimens. The consolidated substrates (CLS, CGS) were measured three times in one direction, (in the middle and in upper and lower part of the specimen). These measurements should confirm homogenous consolidation through whole sample mass. The full data can be seen in Appendices 9.7.

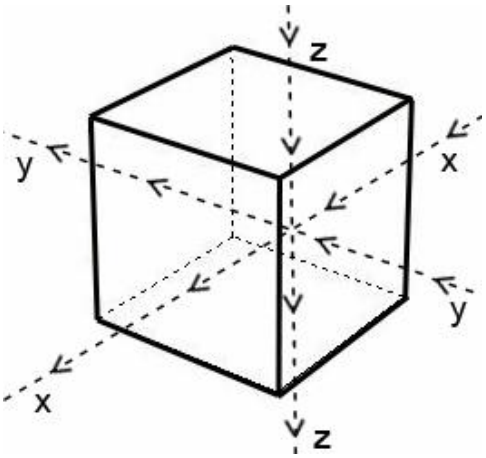

Figure 18. The lines/directions of UZ measurements on cube specimens (4x4x4 cm^3).

3.3.1.4. Thermal analysis

Thermal analysis is defined as a group of techniques in which a property of the sample is monitored against time or temperature while the temperature of the sample, in specific atmosphere, is programmed. The programme may involve heating or cooling at a fixed rate of temperature change, or holding the temperature constant, or any sequences of these. The graphical results obtained are called the thermal analysis curve, or by specific name of the method [43].

Thermal analysis is a useful technique in the determination of historic mortar composition. It comprises differential thermal analysis (DTA), thermogravimetry (TG) a differential thermogravimetry (DTG). The TG method is based on the detection of weight loss due to the decomposition of phases presented in mortar when fired up to 1000°C. DTA locates the ranges of temperature corresponding to the thermal decomposition of different phases in the mortar. [36]

Within this study, thermal analysis was carried out to determine the content of gyspum in a gypsum substrates before and after treatment by the consolidant - sol $CaSO_4$-$Ca(OH)_2$ The samples were heated in a nitrogen atmosphere up to a temperature of 1000°C at a heating rate of 10°C/min to obtain simultaneously the TGA (thermogravimetric analysis) and DSC (differential scanning calorimetry) traces [36].

Measurement was performed by *TA SDT Q600* instrument at The Institute of Theoretical and Applied Mechanics AS CR, v. v. i in Prague (ITAM). Full original report of thermal analysis measurement is given in the chapter Appendices 9.2.

3.3.2. Durability determination

One of the essential properties of a proper consolidant is the ability to provide a long term stable strengthening effect. The durability and resistance is an important element when speaking about consolidation treatment effectiveness and when these features are not sufficiently filled, the consolidation treatment can be considered as unsatisfactory.

The aim of the durability tests were to observe and determine the influence of different environmental conditions on substrates which were simulated in laboratory conditions. To evaluate resistance, stability and the effectiveness of the consolidation treatment the consolidated and not consolidated specimens were exposed to freeze/thaw cycles, salt crystallization tests and test of water vapour sorption (sorption isotherm). However, in the case of the freeze-thaw and salt crystallization test, the data were collected only for substrates after the consolidation treatment (CLS, CGS) because not consolidated samples (NCLS, NCGS) disintegrated in contact with water or salt solution immediately.

3.3.2.1. Freeze-thaw test

Freeze-thaw test - determination of frost resistance

Freeze-thaw cycles were performed according to the procedure given by RILEM MS-B.1.

Testing procedure

The principle of the test is as follows. The specimen is immersed into the water, then frozen and melted down at ambient temperature. This cycle is performed until the disintegration of the samples but maximum of 25 cycles. The percentage of weight change is then measured.

Three not consolidated and three consolidated substrates of each type of mortar have been tested. Before testing all samples were dried at 80°C degrees in the drying chamber for 24 hours. The freeze-thaw cycle was set up as follows: The specimens were immersed under the water for 8 hours and weighed[23]. They were then stored for 8 hours at a temperature of -25°C and after this melted 8 hours at ambient temperature. Specimens were weighed after each cycle and loss of mass in relation of initial mass of the specimen was plotted.

$$\Delta m_i = \frac{m_0 - m_i}{m_0} * 100$$

Δm_i weight change of the sample after the each cycle of freeze-thaw test [wt.%]

m_i weight of the sample after each cycle [g]

m_0 weight of the dry sample [g]

Damage has been also monitored visually and photographically. Cycles have been repeated until the destruction of specimens.

Adaptation of the procedure:

The testing procedure was adapted to the actual conditions in the laboratory. The temperature of freezing was set up instead of -15 to -25 °C and the immersion time of specimens in the water was increased from 4h to 8h per cycle.

[23] Not consolidated substrates (NCGS, NCLS) disintegrated in contact with water immediately. Due to this fact the testing was carried only on consolidated specimens (CLS, CGS)

3.3.2.2. Salt crystallization tests

Salt crystallization test by immersion

The salt crystallization test by immersion (the determination of resistance ability to salt crystallisation process) were performed according to the procedure given by ČSN EN 12370. This European norm was approved by CEN 1999-02-12.

The principle of the test is as follows. The specimen is after drying to constant weight immersed into the sodium sulphate solution, then dried and cooled down to ambient temperature. This cycle is performed until disintegration of samples but maximum 15 times and the percentage of weight change is measured.

Testing procedure

For this experiment three not consolidated three consolidated and substrates of each type of mortar were used. Before testing all samples were dried up to constant mass at 80°C degrees in the drying chamber for 24 hours. After the drying process, the substrates were left to get cold for two hours in the dessicator and then weighted. The substrates were placed into the container with a solution of Na_2SO_4 (14 wt.%) till 8±2 mm above the top level of specimens.[24] The free space between each individual specimen stored in the container was 10 mm. The free space between the container´s wall and the specimens was 20 mm. During the immersion the container was covered to avoid the evaporation of salt solution. After two hours of absorption under ambient temperature samples were moved to the drying chamber and dried for 12 hours at the temperature of 80°C. Initial drying phase was carried under a high relative humidity. This was arranged by placing several shallow water containers into cold drying chamber for half of an hour. After half an hour, when the chamber was hot enough and initial humidity was sufficient, the water containers were moved out and all specimens were placed into the chamber for the drying procedure. After drying, the substrates were left to get cold for two hours in the dessicator and then weighted. Specimens were weighed after each cycle and loss of mass in relation of initial mass of the specimen was plotted.

[24] Not consolidated substrates (NCLS, NCGS) disintegrated in contact with soluble salt solution immediately. Due to the testing was carried only on consolidated specimens (CLS, CGS).

$$\Delta m_i = \frac{m_0 - m_i}{m_0} * 100$$

Δm_i weight change of the sample after the each salt crystallization cycle [wt.%]

m_i weight of the sample after each cycle [g]

m_0 weight of the dry sample [g]

Cycles have been repeated until the destruction of specimens. Damage has been monitored visually and photographically.

The salt crystallisation test by capillarity action

In real conditions the deterioration of plasters and mortars is very often caused by capillary action. Therefore, the salt crystallisation test was also performed by capillarity action. The test was carried out to bring the laboratory testing procedure closer to real practice and to compare the differences in degree and ratio of decay caused by immersion on one hand and by capillary action on the other hand.

The testing procedure

The salt crystallization test by capillary action was fully following the salt crystallization test by immersion described above, except the level of the salt solution in the container which was only 8±2mm above the bottom of the specimens. This allowed the salt solution to penetrate by capillary action into the all specimens.

3.3.2.3. Sorption isotherm test

"Building materials like cement mortar are qualified as porous highly hygroscopic media. Being dry, they soak moisture from humid air, and conversely, being moist, they give the moisture back to dry air. The moisture transfer consists of three stages: The adsorption/desorption at the solid/gas interface, the moisture diffusion inside the pores, and the convective exchange of vapour between the porous material and the ambient air. The rate of this process varies in time, even if the external conditions provoking it are stable. This means that the diffusion rate changes accordingly to the moisture content in the material." [25]

The objective of water vapour adsorption isotherm testing is to assess the behaviour of the substrates in variable humid conditions and provide a comparison of moisture adsorption before and after consolidation treatment [29]. The adsorption isotherms show dependence of moisture content adsorbed by sample until equilibrium expressed in per cent on relative pressure of water vapour (given by saturated solutions of salts). The change of the moisture on-site should lead in some interactions, especially in case of gypsum substrates. These are expected to be more sensitive after consolidation.

The testing procedure

The consolidated and not consolidated substrates were cut to small cubes of more or less 2x2x2 cm^3 (Figure 15)[26]. Each cut specimen was placed on a plastic grille in a Petri dish to enable the humidity to flow from all sides during the testing. Before the testing all samples were dried until the constant weight at 80 °C degrees in the drying chamber for 24 hours. After the drying process, the substrates were left to get cold for one hour in dessicator and their weigh was measured. As following, the specimens were stored in the containers with the saturated water soluble salt solutions: KNO_3 (φ = 93%); KCl (φ = 85%); NaCl (φ = 75%), $Ca(NO_3)_2$ (φ = 50%); $CaCl_2$ (φ = 30%); LiCl (φ = 12%).

The specimens were weighed continuously during the time of testing until constant weight was achieved (app. 3 months). Three specimens of each specimen type have been tested.

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[25] Garbalińska H., Kowalski S. J., Staszak M., *Linear and non-linear analysis of desorption processes in cement mortar,* Cement and Concrete Research 40 (2010), (752-762), journal homepage: http://ees.elsevier.com/CEMCON/default.asp, page 1

[26] Specimens were cut up from prepared substrates (4x4x4 cm) by small saw. The exact shape of these small cubes is not precise and regular. See on the Figure 15.

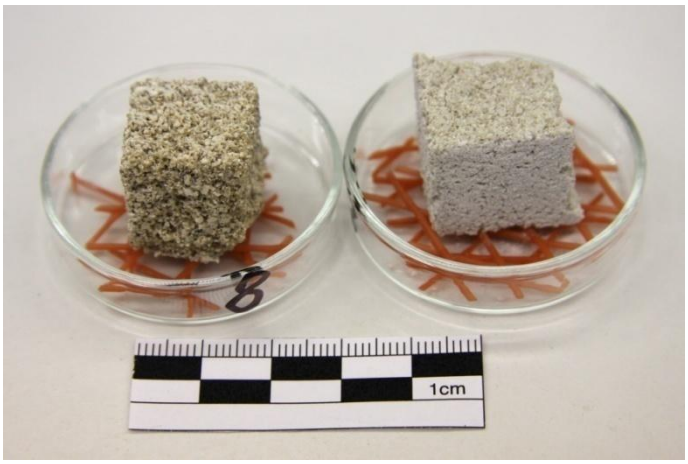

Figure 19. Specimens (cubes 2x2x2 cm^3) for water vapour adsorption test.

3.4. Results and discussion

3.4.1. Physical characteristics

Water absorption by capillary action

Water absorption is an extremely important property for mortars, as they are usually exposed to environmental phenomena such as rain or in contact with elements that could be wet (soil). Table 6 shows water absorption coefficients of both types of specimens. Measurements were performed before and after the consolidation. During testing, not consolidated substrates (NCGS, NCLS) disintegrated immediately after contact with water and no values of water adsorption coefficient could be measured. This proved an extremely low resistance and a weak condition of not consolidated specimens simulating well a highly corroded plaster on-site. Thus, measurements were carried out only on consolidated specimens (CLS, CGS).

Samples		Bulk density [$g.cm^{-3}$]	Water adsorption coefficient w [$kg.m^{-2}.h^{-0,5}$]
Lime specimens	***NCLS***	1.39	
	CLS	1.44	337.3
Gypsum specimens	***NGLS***	1.34	
	GLS	1.42	94.9

Table 5. Properties of laboratory samples before and after consolidation.

After the consolidation treatment and curing, the consolidated samples stayed unchanged and the testing of absorption through capillarity was able to proceed. However, both values of water adsorption coefficient were extremely high, especially the one obtained for CLS. The results are consistent with data obtained by mercury intrusion porosimetry which show high total porosity values and presence of macro pores in both types of samples. The different behavior of both types of sample should be partly caused by their different

composition. However, as it was described previously, on the surface of gypsum samples an impermeable crust was formulated which can preclude or slow down the penetration of water into to the substrate. Full report of this measurement is given in the Appendices 9.1.

Bulk density

The bulk density of both treated and not treated specimens of both types of plaster samples were calculated and are presented in Table 5. Data demonstrates the increase of bulk density which are connected with the decrease of volume mass of the samples and thus proves the capillary pores were filled by the new consolidant. Measured values correspond with other measurements -water adsorption by capillarity, strength and ultrasound velocity.

Mass gain

Lime specimens were consolidated by lime nanosol CaLoSiL® E25 and gypsum specimens by Sol $CaSO_4$-$Ca(OH)_2$. After the treatment, the total amount of introduced calcium hydroxide and mass gain of specimens after their consolidation and curing was calculated and the results are labelled in Table 6.

Samples	**Consolidant**	**Number of cycles**	**Consolidant consumption [ml/cm^3]**	**Mass gain Δm [wt. %]**
Lime specimens	CaLoSiL® E25	5	93	4.3
Gypsum specimens	Sol $CaSO_4$-$Ca(OH)_2$	3	69.9	6.3

Table 6. The mass gain and consumption of nanosols after the consolidation treatment.

CaLoSil®E25 was applied in five application cycles to compare gypsum specimens consolidated only 3 times. Though, based on theoretical calculations which comprise much higher concentration of gypsum nanosuspension the amount of introduced consolidant should be the same in the case of both types of substrate.

However, real results show some discrepancy. Mass gain of CGS samples showed higher values of consolidant content (6.3 wt.%) to compare values of lime substrates (CLS) which show 4.3 wt.% increase of mass. This occurred probably due to the higher viscosity of $CaSO_4$-$Ca(OH)_2$) nanosuspension which is cumulating on a surface as a liquid cover during the

application. When this viscous layer got dry it turns into the solid state and this could artificially increase the mass gain of sample.

3.4.2. Microstructure characteristic

3.4.2.1. Pore structure measured by means of Mercury intrusion porosimetry

Table 7 shows the results of bulk density, total porosity and surface area of both types of studied specimens obtained by Mercury instursion porosimetry before and after consolidation. In addition, Figure 20 and 21 shows pore size distribution of pore diameters of both types of substrate and present the change in pore diameter distribution after consolidation treatments. On x axis there is pore diameter intruded by the mercury, y axis shows values of volume of the pores which are intruded by the mercury.

Samples		**Bulk density [g.cm^{-3}]**	**Total porosity [%]**	**Surface area [m^2/g]**
Lime specimens	***NCLS 1***	1.737	39.6	1.8
	NCLS 2	1.648	39.0	2.7
	CLS 1	1.714	37.4	2.9
	CLS 2	1.862	35.1	4.0
Gypsum specimens	***NGLS 1***	1.488	45.9	0.4
	NGLS 2	1.422	47.9	1.4
	GLS 1	1.524	47.8	4.5
	GLS 2	1.504	44.7	1.6

Table 7. Properties of laboratory samples before and after consolidation measured by mercury intrusion porosimetry.

Original untreated substrates are highly porous with high total porosity about 40 % for lime (NCLS) samples and even higher (46-48 %) for gypsum (NGLS) substrates. After the consolidation, an only marginal decrease in the total porosity values was measured. Especially for NGLS samples the values stayed almost unchanged indicating a bad penetration of consolidant into the bulk of the specimens and confirm the precipitation

effect of the consolidant on the surface. Better results were obtained by bulk density and surface area measurements which gives direct information about the evolution of the pore space of the substrates. The values of mercury surface area are very low, however it exhibits a nearly double increase after the consolidation treatment with both types of substrates. This fact points to the development of pore space due to the consolidant´s precipitation.

Additional information on dimension and distribution of pores were obtained by pore size distribution measurement. Both types of untreated reference mortar samples (NCLS, NCGS) exhibit unimodal distribution of the pore dimensions characterized with sharp and well defined peak. In case of NCLS substrates the unimodal peak at 200 □m was observed and 100 □m for NCGS respectively. These pores can be defined as macro pores and are usually obtained in severally deteriorated substrates as a result of secondary weathering. After consolidation (light and dark blue lines), only marginal effect in pore size distribution can be observed. There is no change in pore size (similar peak position) but the slight decrease of the pore volume intruded can be observed. This is the result of the filling the pores by consolidant.

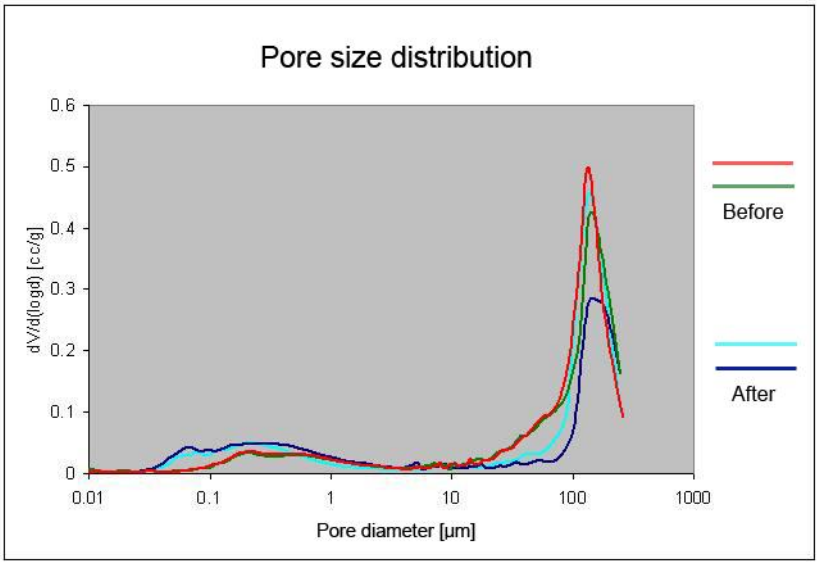

Figure 20. Differential volume of intruded mercury vs pore diameter for the lime specimens before (red and green lines) and after consolidation (light and dark blue lines).

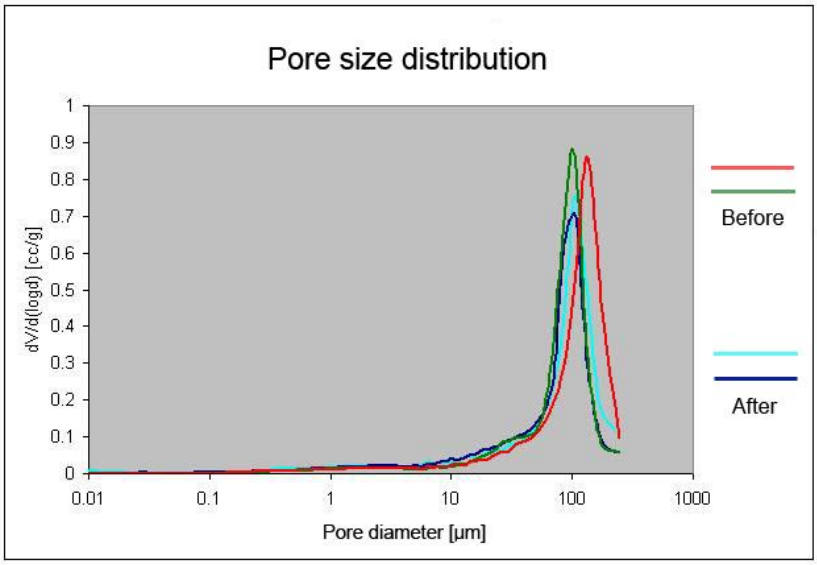

Figure 21. Differential volume of intruded mercury vs pore diameter for the gypsum specimens before (red and green lines) and after consolidation (light and dark blue lines).

However, better consolidation effect was seen for lime substrates (CLS). The consolidation of bulk gypsum specimen is less effective, as it was demonstrated by only a low change in the total porosity values.

The measurements of porosity, bulk density and surface area were performed by the Institute of Theoretical and Applied Mechanics AS CR, v. v. i in Prague. Full original report of this measurement is given in the chapter Appendices 9.3.

3.4.2.2. Electron microscopy

The structure of the substrates was studied by means of ESEM technique. ESEM was made on a broken section (Figures 22-35) of both untreated and treated samples. Moreover, CGS samples were undergone EDX mapping to give the clear information about the consolidant distribution. ESEM of both untreated reference samples shows a very weak and highly porous structure with no connection of aggregate particles (Figure 22-24, 28-30). Only NCGS show some local binder in between the aggregates (Figure 28, 30, 32), which comes from one of the component used for the preparation of the substrates – (historic gypsum mortar). After consolidation only the local connections between particles was formed by the consolidant precipitation (Figure 25-27, 31, 33-34). It is very weak and strictly localised in smaller pores and intergrain spaces.

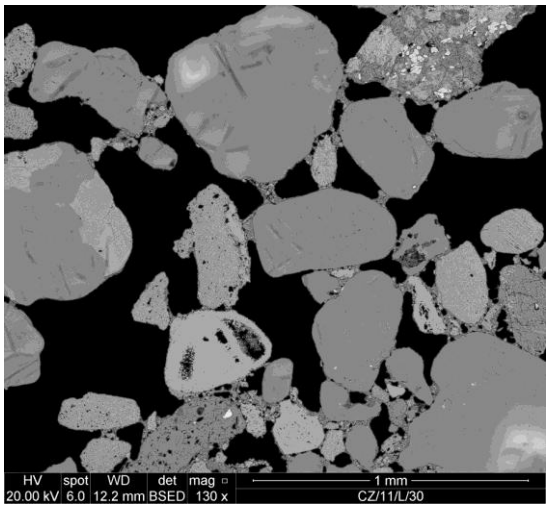

Figure 22. NCLS – the matrix of the substrate, overwiev.

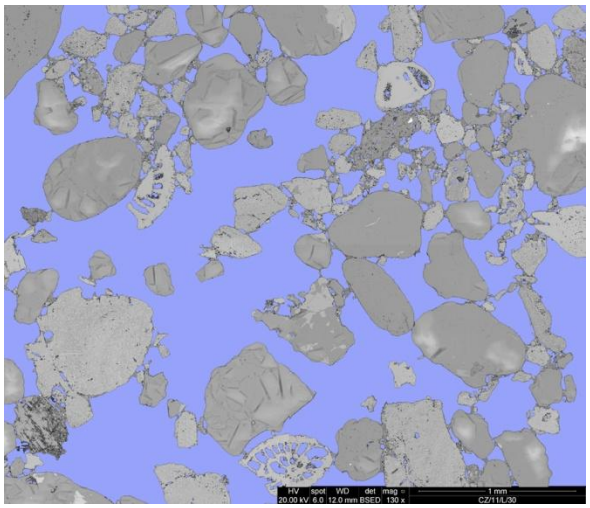

Figure 23. NCLS – the matrix of the substrate (for digital analysis).

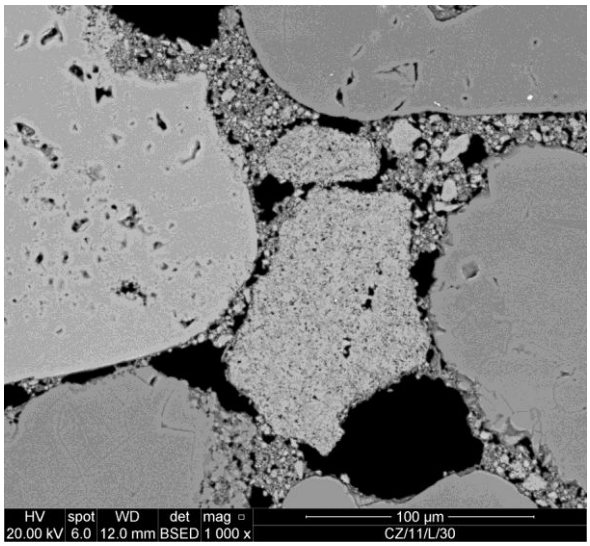

Figure 24. NCLS – the binder detail.

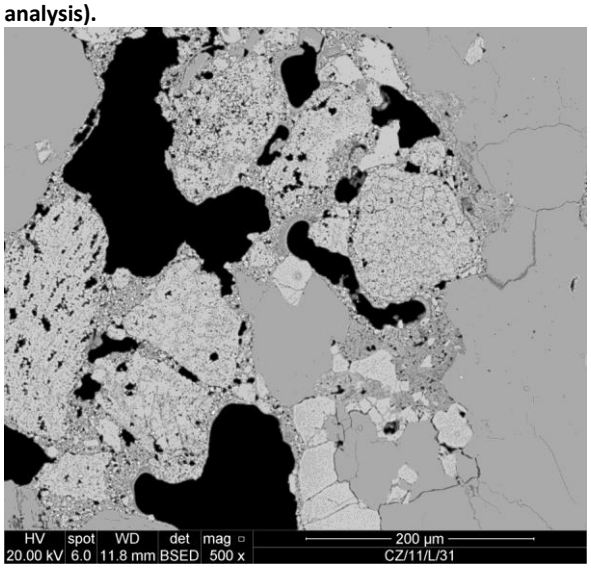

Figure 25. CLS - the consolidant precipitation in the pore space.

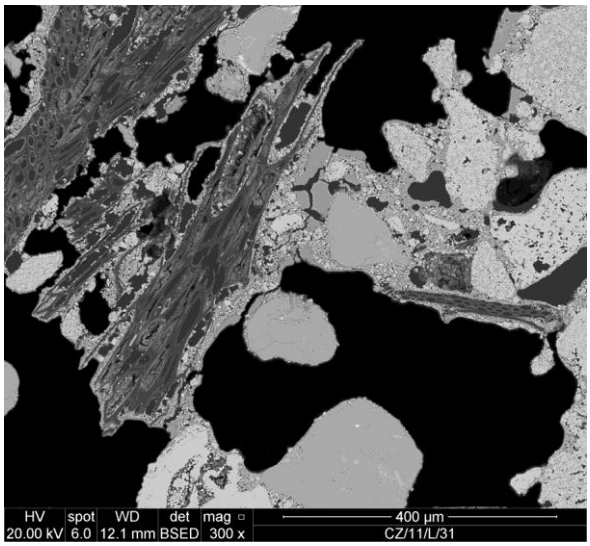

Figure 26. CLS – the consolidation precipitation - detail.

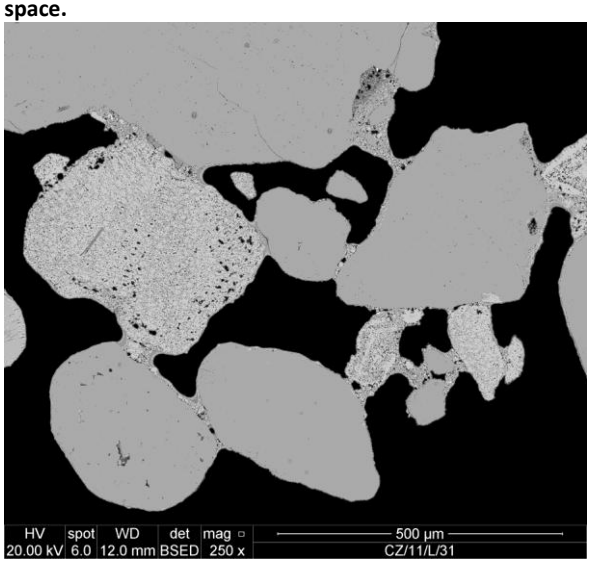

Figure 27. CLS – the formation of the bridges between the grains.

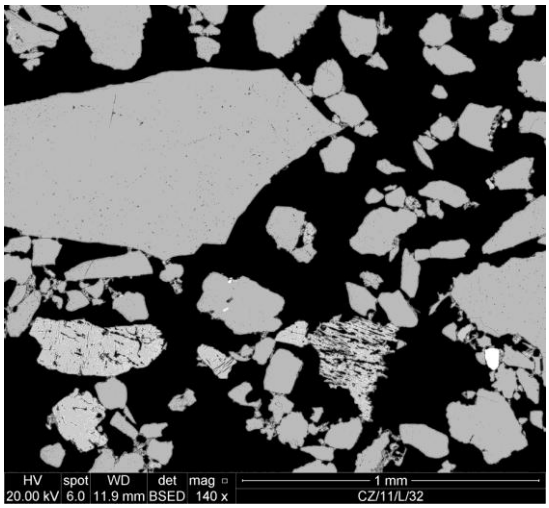

Figure 28. NCGS – the matrix overview, highly disintegrated matrix.

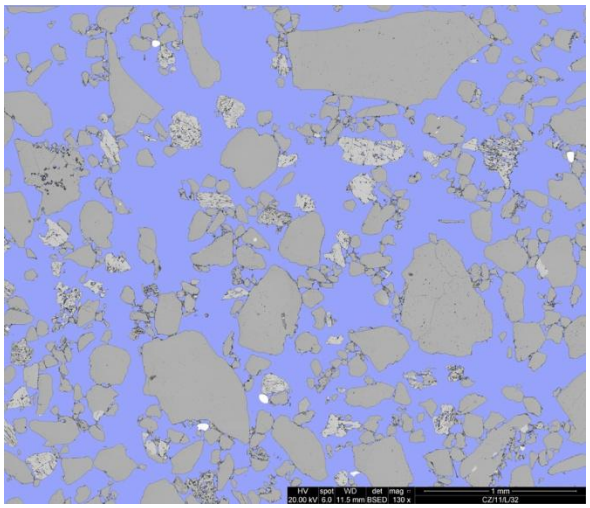

Figure 29. NCGS - the matrix overview (for digital analyses).

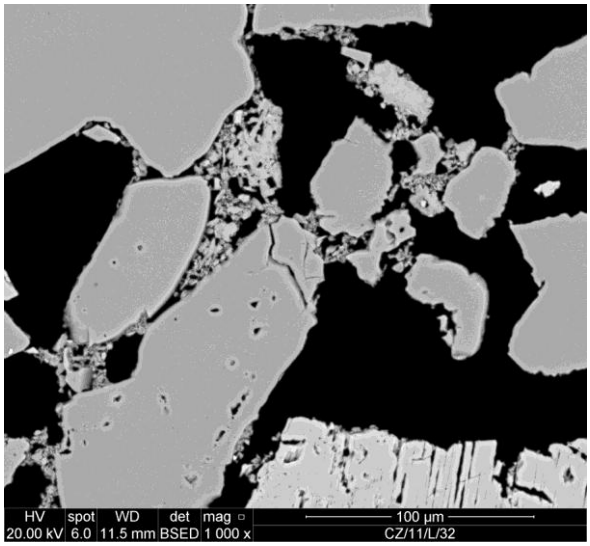

Figure 30. NCGS- detail of binder

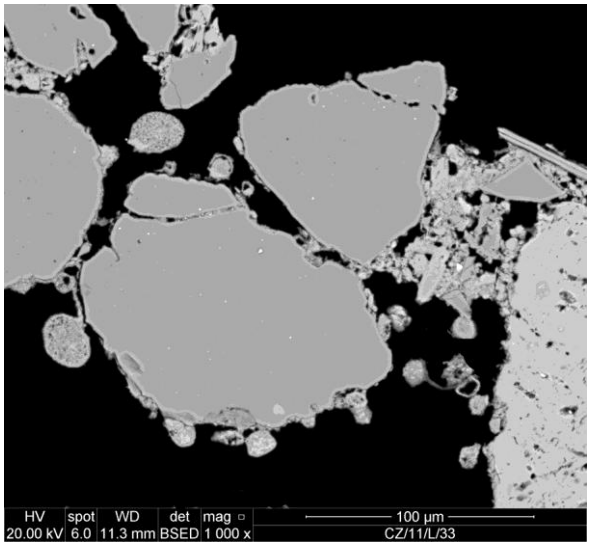

Figure 31. CGS – precipitation of consolidant (spherical structures = consolidant?)

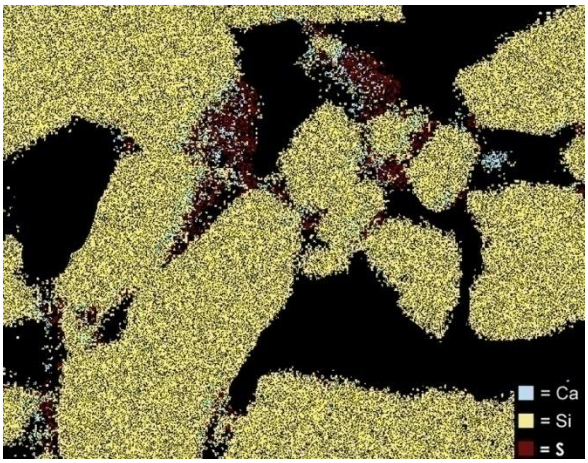

Figure 32: NCGS - EDX mapping of Ca, Si and S. The overlapping indicates the presence of $CaSO_4$.

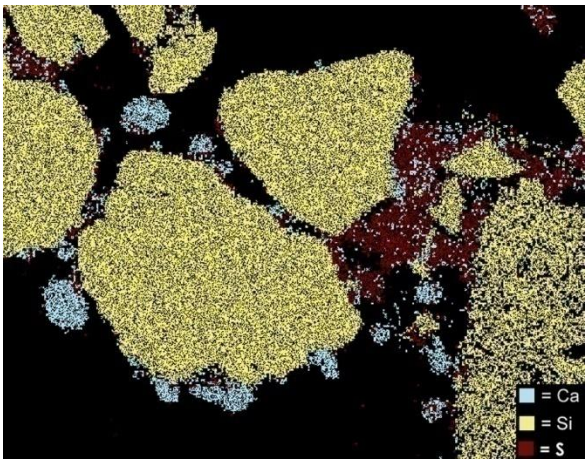

Figure 33. CGS- EDX mapping of Ca, S, Si. The overlapping indicates the presence of $CaSO_4$.

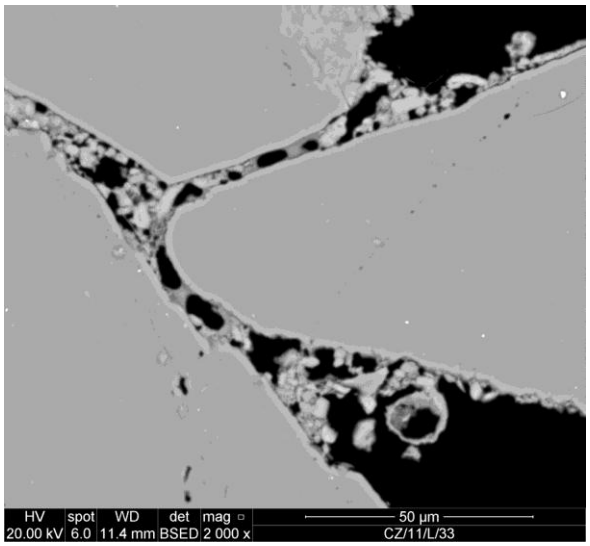

Figure 34. CGS - precipitation of the consolidant, predominantly in pore space.

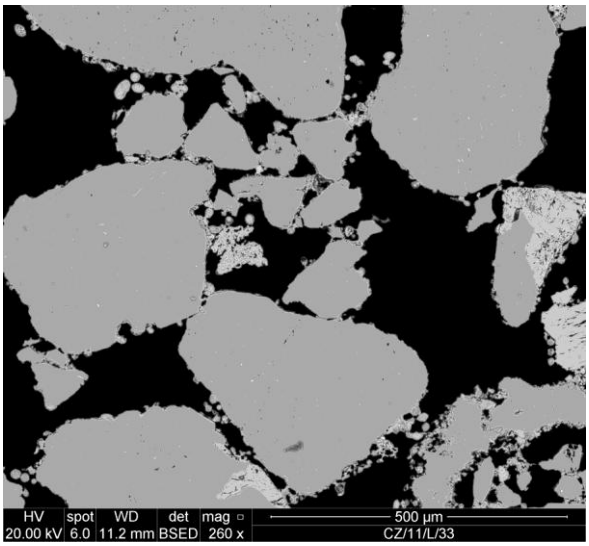

Figure 35. CGS - the structure overview after the consolidation, the characteristic content of spherical structures (in lower third of the image).

Figures 28-35: ESEM photomicrographs and EDX mapping of NCGS and CGS samples.

In case of CGS EDX mapping of Ca, Si and S was made to show the distribution of consolidant within the sample. It was revealed that gypsum consolidant is precipitated in globular structures around aggregate particles. Some of them contain only Ca, some are combined with S. Such overlapping indicates the presence of gypsum (Fig. 33).

One phenomenon occurs during the ESEM analysis which was not visualized. The consolidant distribution varies throughout the sample, especially in case of CGS; the content of consolidant is increasing from the middle part of the specimen to the top which confirms inhomogeneous consolidant content and surface crust formation.

3.4.3. Strength determination

3.4.3.1. Compressive and bending strength

The consolidation effect was very well seen on the strength values. Both substrates increase their compressive and bending strength confirming an effective consolidation. However, it was more evident in the case of the lime substrates whose values of compressive strength increased from 0.06 MPa to 1.6 MPa and from 0.01 MPa to 0.38 MPa when we consider the bending strength values (Table 8).

	Lime specimens		*Gypsum specimens*	
	NCLS	***CLS***	***NCGS***	***CGS***
Compressive strength R [MPa]	**0.06** ± 0.02	**1.61** ± 0.21	**0.04** ± 0.00	**0.11** ± 0.13
Bending strength R^{tf} [MPa]	**0.01** ± 0.00	**0.38** ± 0.05	-	**0.11** ± 0.11

Table 8. Compressive and bending strength results.

The consolidation efficiency is much lower for gypsum substrates. Even though the consolidation effect was obvious, the consolidated gypsum substrates were attaining lower strength values and were still very poor. Moreover, due to their weakness, they disintegrate during manipulation and their surface was easily broken so the strength measurement values varied significantly. The crust enriched by gypsum was detected on the surface of consolidated gypsum (CGLS) specimens which could be also one of the reasons for not equal strength measurements. The bending strength values of NCGS should be also labelled in the Table 8, however it was not possible to obtain them due to the weak cohesion of samples. Substrates disintegrated already before placing them on the measurement machine. Full report of compressive and bending strength measurements is given in the Appendices 9.6.

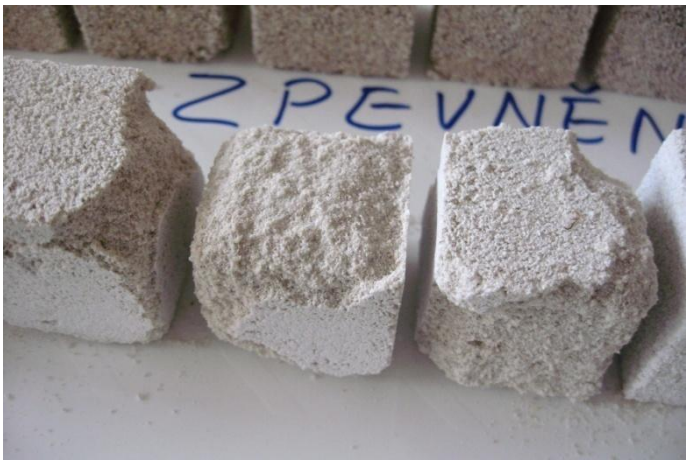

Figure 36. The crust on the consolidate gypsum (CGLS) specimens.

3.4.3.2. Ultrasound velocity measurement

The values of the ultrasound velocity could indirectly determine the strengthening effect based on the increase of its values due to the filling of pore space by the consolidant. However, it does not provide information about the homogeneity and distribution of the consolidant within the mass of the sample.

Therefore, several values are placed in the Table 9. These values were either obtained as an average data from measurements made on whole sample or they were obtained as the average values measured on different sample´s position – on the upper part, the lower part and the middle of the sample. Such values are more useful to determine the consolidant´s distribution.

Both not consolidated substrates (NCLS, NCGS) are homogenous; there is nearly no difference in measured data in the middle or on the side of the samples. Slightly lower total average values of gypsum substrates (NCGS) can be explained by different composition of the materials used for their preparation or lower compaction of the substrate. The consolidation effect is obvious. The two times higher measured values in the case of lime substrate (CLS) and a bit lower but still high measured values of the gypsum substrates (CGS) demonstrate pretty well that the pores were filled by the new consolidant sufficiently (the particles in the substrate were connected by the consolidant).

The average values measured from upper and lower parts of both types of consolidated specimens (CLS, CGS) differ from their total average value. These data demonstrate the differences in consolidant distribution. The highest values were attained on the upper part of sample which suggests there is a possible presence of a more compact layer enriched by consolidant (crust). The crust can speed up the transmission wave passing through the specimen because of its higher homogeneity.

The crust appeared either because of the way the sample preparation or as a consequence of the penetration and evaporation of the consolidant. For the preparation of samples, stress was used when composing the material into the moulds and this treatment can distribute the material unequally. Nevertheless if this happened it should be reflected also in the values measured for the not consolidated substrates (NCLS, NCGS) and such situation was not observed. The evaporation can play an important role and can cause the possible back migration of $Ca(OH)_2$ particles to the surface of the sample and thus the crust

formation can appear as a result. Also the penetration of the consolidant can be accompanied by the "filtering effect" during the substrate´s impregnation and thus the different distribution of calcium hydroxide or sulphate particles within the sample can occur.

The full data information about the ultrasound measurement is given in the chapter Appendices 9.7.

Samples		Average value total v [km.s^{-1}]	Average value of the middle v [km.s^{-1}]	Average value of the upper part v [km.s^{-1}]	Average value of the lower part [km.s^{-1}]
Lime specimens	***NCLS***	1.15	1.14	1.16	-
	CLS	2.11	1.99	2.28	2.05
Gypsum specimens	***NGLS***	0.99	0.98	1.00	-
	GLS	1.74	1.70	1.83	1.70

Table 9. Ultrasound velocity measurement results.

3.4.4. Thermal analysis

Thermal analysis was used for the precise determination of composition of gypsum specimens before and after the consolidation treatment. NCGS reference samples were prepared using the historic Dahlen Castle stucco mortar which originally contained gypsum. However, precise analysis of Dahlen Castle mortar composition was missing and thus the gypsum content was not defined.

From thermal analysis of both reference (NCGS) and consolidated (CGS) samples two major phases were detected – gypsum and calcium carbonate. NCGS mortars contains about 3 wt.% of gypsum (related to binder) and no calcium carbonate. After the consolidation the gypsum content increased to approximately 5 % and calcium carbonate´s content to 1 % which is obviously the effect of consolidation by gypsum nanosol (Sol $CaSO_4$-$Ca(OH)_2$).

	NCGS [wt. %]	CGS [wt. %]
Gypsum	2.8	4.9
Calcium carbonate	none	0.9

Table 10. Phase detected and its content in gypsum samples.

Thermal analysis shows, that Dahlen castle mortar, which was used for preparation of lime-gypsum substrates in ratio plaster : sand (1:8) is pure gypsum plaster with no content of calcium carbonate inside, because any calcium carbonate was during the thermal analysis detected (Table 10). However there is only a small amount of gypsum in the not consolidated gypsum lime substrates determined (2.8 wt.%) and the increase of its amount after the consolidation treatment to 4.9 wt.% is significant.

The theoretical calculations of calcium carbonate and calcium sulphate in CGS samples which take into account the composition of sol $CaSO_4$-$Ca(OH)_2$, and its concentration (the producer says that the content of calcium hydroxide in consolidant is 30 g/l and calcium sulphate is 15 g/l) do not correspond with the amount of consumed consolidant. There is a lower formation of calcium carbonate (0.9 %) than gypsum formation (2.1 %). But according to the theoretical calculations the opposite results were expected.

A possible explanation can be the heterogenous distribution of consolidant within CGS samples; the formation of the crust on the CGS closed the pores on the surface and thus prevented the calcium hydroxide to penetrate sufficiently into the mass of the substrate. However, this effect should be happening with calcium sulphate´s penetration into the substrate and should be reflected in the ratio of gypsum formation as well, but such phenomenon is not reflected in the thermal analysis results. Another possible explanation for this not corresponding data is the size of the sample which is needed for the thermal analysis. Only small amount (30 mg) of the specimen was used. It is obvious that the heterogeneous distribution of the consolidant inside the matrix can play an important role in data evaluation. If there is no heterogeneous dispersion of consolidant inside the sample and the distribution of calcium carbonate and calcium sulphate inside the mass vary the measured values can be blurred or incorrect especially if there is the small amount of the sample measured. Full report of thermal analysis is given in the Appendice 9.2.

3.4.5. Durability determination

3.4.5.1. Freeze-thaw test

Filling of the capillaries by consolidant and improvement of the pore structure enhance significantly the resistance of samples to freezing and thawing. (Figures 37, 38) represents the freezing and thawing resistance of reference untreated mortars and consolidated substrates.

Visual observations (Figures 39-41) and weight changes measurements were able to demonstrate the effectiveness of the consolidation treatments towards freezing and thawing. Untreated samples (NCLS, NCGS) disintegrated immediately in contact with water during the first cycle. This proved the low resistance and weak condition of not consolidated specimens (Figure 39).

The tested specimens kept their shape more or less stable until the third cycle and they were completely disintegrated after 7 cycle. The lime specimens (CLS) were cracking and rupturing and they kept their shape more compact for longer time while the gypsum specimens (CGS) were losing the volume consistently by washing the weakened surface off. Although the lime specimens kept their shape longer, when the rupturing of mass achieved certain level, the decay ran out rapidly. After this moment the acceleration of lime specimens decay was faster than the gypsum specimens therefore the final disintegration of both specimen types was almost equal. This phenomenon is confirmed also on Figures 37, 38.However durability and resistance of the consolidated substrates is still very low and not so satisfactory.

The pore size distribution in samples dictate the range of damage formed during the freeze–thaw cycles. Mainly the amount of freezable water present in the capillary pores is important. All the tested mortars are very similar in their sizes of capillary pores, however the consolidated samples have a slightly lower content of these pores. As a consequence they have lower water content at the beginning of the freezing and thawing cycles and thus they can resist better then the pure not consolidated substrates.

Samples		The weight change of substrates [wt.%]						
		Number of cycles						
		1	**2**	**3**	**4**	**5**	**6**	**7**
Lime substrates (CLS)	***NCLS***	**-100**						
	CLS 7	-0.22	0.80	1.19	1.22	-51.50	-71.55	-90.64
	CLS 18	-0.38	0.69	0.88	1.25	1.47	-91.19	-92.58
	CLS 34	0.38	-0.56	-28.55	-55.94	-89.16	**-100.00**	
Gypsum substrates (CGS)	***NCGS***	**-100**						
	CGS 3	-6.31	-31.43	-41.06	-54.97	-77.89	-96.98	**-100.00**
	CGS 14	-5.28	-12.09	-22.05	-33.93	-76.13	**-100.00**	
	CGS 7	-5.63	-12.84	-21.63	-31.81	-47.65	-83.15	-87.29

Table 11. Weight change of specimens during freeze-thaw cycles.

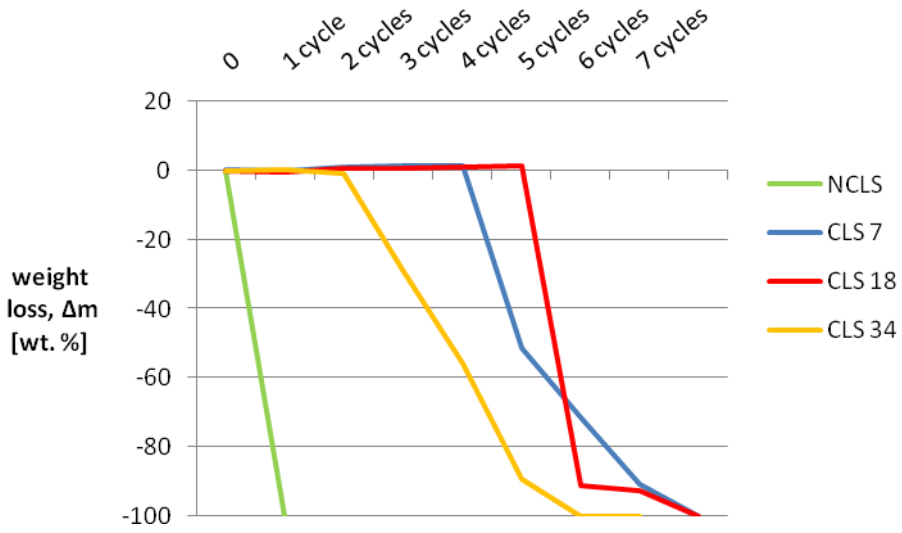

Figure 37. The weight change of not consolidated (NCLS) and consolidated lime substrates (CLS) during the freeze-thaw test.

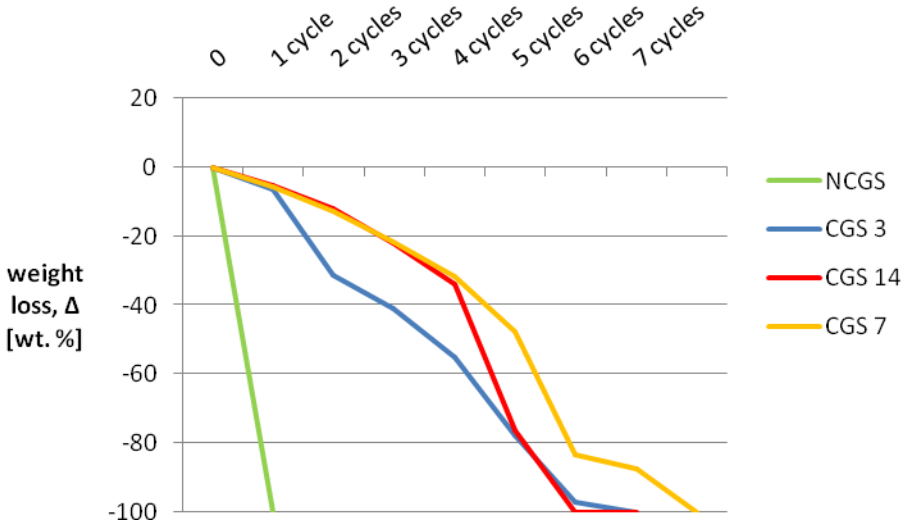

Figure 38. The weight change of not consolidated (NCGS) and consolidated (CGS) gypsum substrates during the freeze-thaw test.

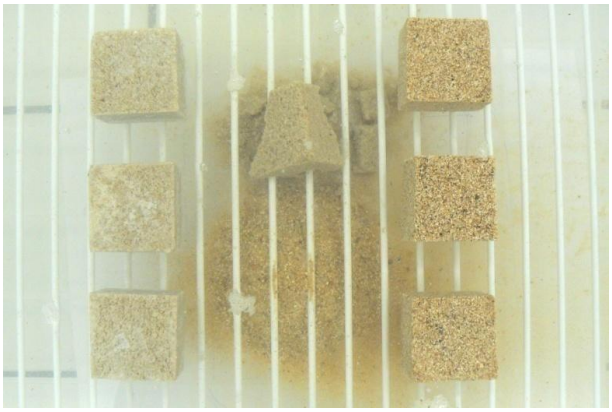

Figure 39. Specimens during 1st cycle of freeze-thaw test. Not consolidated substrates (in the middle) disintegrated immediately after immersion into the water container.

Figure 40. Specimens after 5th cycle of freeze-thaw test.

Figure 41. Cracking and rupturing of CLS specimen after 6th cycle of freeze-thaw test.

3.4.5.2. Salt crystallization test

The properties of the substrates are also of crucial importance for salt transport and for damage due to salt crystallization.

The salt crystallization tests were performed by two different methods which were set up as it can be observed in real-world conditions. Both generally follow standard procedure given in Chapter 3.3.2.2. Figures 42, 43 and 46-49 and Table 12 presents the salt crystallization resistance of not consolidated substrates and consolidated ones tested by immersion procedure, Figures 44, 45 and 50-52, Table 13 presents the salt crystallization resistance to capillary action procedure.

The consolidation process enhanced the resistance to salt crystals formation and confirmed the improved pore structure and filling of the capillaries. Visual observations and weight changes measurements were able to follow the effects of the consolidation treatments towards salt crystallization. Not consolidated substrates (NCGS, NCLS) disintegrated immediately in contact with soluble salt solution when first cycle started (Figure 46, 50). This proved the low resistance and weak condition of not consolidated specimens.

The immersion test

In general, both types of samples are very weak and resist to salt crystallization only for 3 or 4 cycles. Moreover, there is slightly better resistance of CLS samples which is in correlation with the general higher strength of these samples (Chapter 3.4.3.) and their lower porosity as measured by means of mercury intrusion porosimetry (Chapter 3.4.2.1.). The deterioration of samples can be described as follows. After the first immersion cycle no differences in the shape and condition have been observed. This means that the capacity of pores was not yet overfilled. After second cycle, when the samples got dry in the drying chamber, the creation of rich salt crystals mainly on the top of gypsum lime substrates occurred (Figures 48, 49). The disintegration ratio and shape of each gypsum lime specimens was quite balanced; each specimen was covered by salt crystals and retained in analogous dimensions. No crystals creation was observed on the lime substrates surface and their disintegration ran over the whole sample not as well balanced and regularly as it happened in the case of gypsum samples (Figure 37).

The capillary action test

After the first cycle of salt crystallization, the creation of a salt crystals layer on the surface of gypsum specimens was observed, though the specimens kept their original shape and volume (Figure 50). This salt layer differs from crystals created on specimens tested by immersion. Crystals are smaller and cover all specimens equally as a white haze. Since the second cycle, deterioration was obvious and accelerating. After the 3rd cycle, when one of the lime substrates broke down, it was revealed that there was crust created on the sample surface (Figure 40). It was found that salt appeared not only on the surface but penetrate 1-2 mm and formed a rigid and resistant crust on the weak matrix. Such crust had appeared also when the gypsum specimens were broken during the testing, but the gypsum samples have resisted in more compact shape. While the lime specimens were rupturing and breaking in whole mass, the gypsum specimens were losing the material gradually from the bottom and kept a compact shape which was held by a crust of salt for a longer time. Although the decay ran over both specimen types differently they were destroyed within more or less the same amount of cycles. However, the gypsum specimens were considered slightly more resistant.

For samples which were salt loaded by capillary action there is a slight improvement of salt crystallization resistance, especially for CGS samples. These samples are less capillary active and are characterized by the consolidant´s enriched surface layer which prevents the salt solution to penetrate.

Samples		**The weight change of specimen [wt.%]**			
		Number of cycles			
		1	**2**	**3**	**4**
Lime substrates (CLS)	***NCLS***	**-100**			
	CLS A	3.59	-40.65	**-100.00**	
	CLS B	3.83	-72.81	-75.52	**-100.00**
	CLS C	3.59	-83.19	-88.14	**-100.00**
Gypsum substrates (CGS)	***NCGS***	-100			
	CGS 2	1.64	-30.52	**-100.00**	
	CGS 8	1.91	-33.33	**-100.00**	
	CGS11	2.39	-20.37	**-100.00**	

Table 12. The weight change of lime and gypsum specimens during the salt crystallization test by immersion.

Samples		The weight change of substrates [wt. %]					
		Number of cycles					
		1	**2**	**3**	**4**	**5**	**6**
Lime substrate (CLS)	***NCLS***	**-100**					
	CLS 6	3.93	-29.26	-68.19	-69.44	-77.16	**- 100**
	CLS 14	3.73	-4.10	-15.40	-19.15	-37.77	-74.62
	CLS 35	4.13	-59.54	-62.40	-72.25	-92.45	**- 100**
Gypsum substrate (CGS)	***NCGS***	**-100**					
	CGS 4	1.94	-2.57	-5.42	-27.81	-61.95	**- 100**
	CGS 5	4.62	2.55	0.06	-18.17	-41.35	-77.92
	CGS 12	1.77	-1.19	-4.04	-34.42	-71.73	**- 100**

Table 13. The weight change of lime and gypsum specimens during salt crystallization test by capillary action.

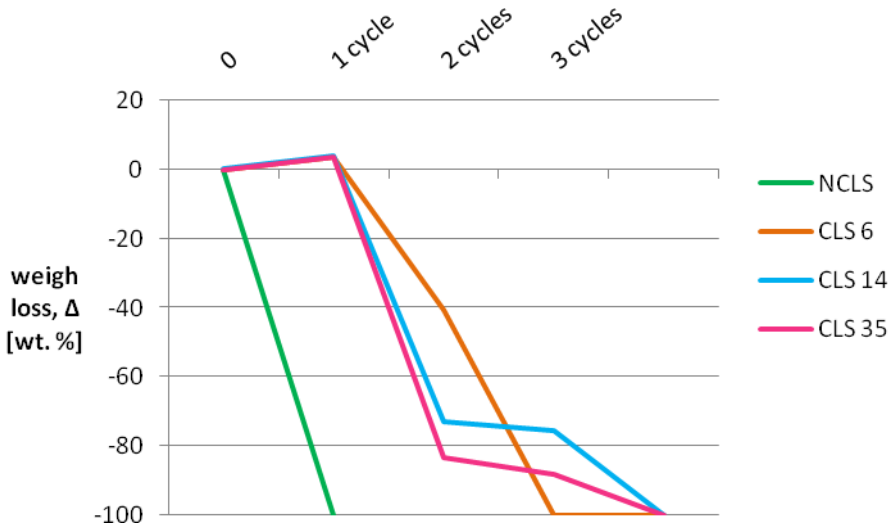

Figure 42. The weight change of not consolidated (NCLS) and consolidated lime substrates (CLS) during the salt crystallization test by immersion.

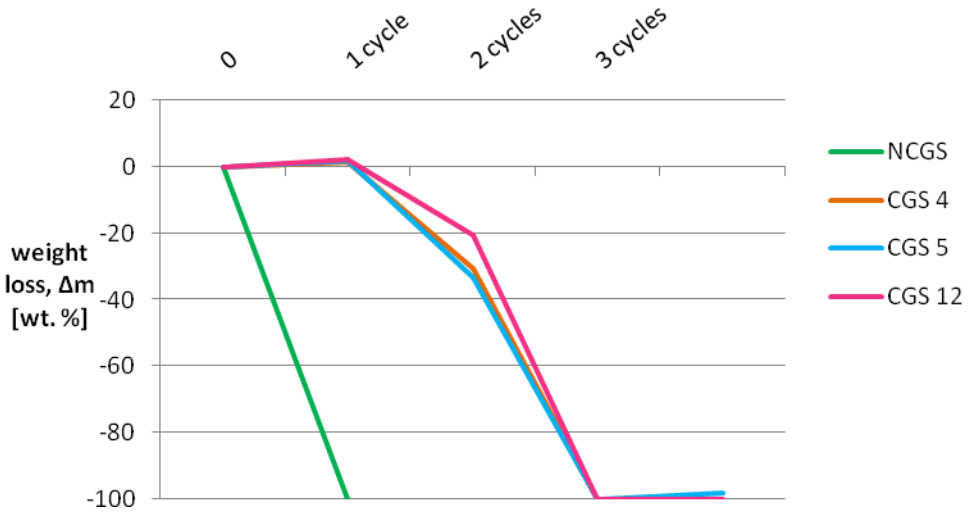

Figure 43. The weight change of not consolidated (NCGS) and consolidated (CGS) gypsum substrates during the salt crystallization test by immersion.

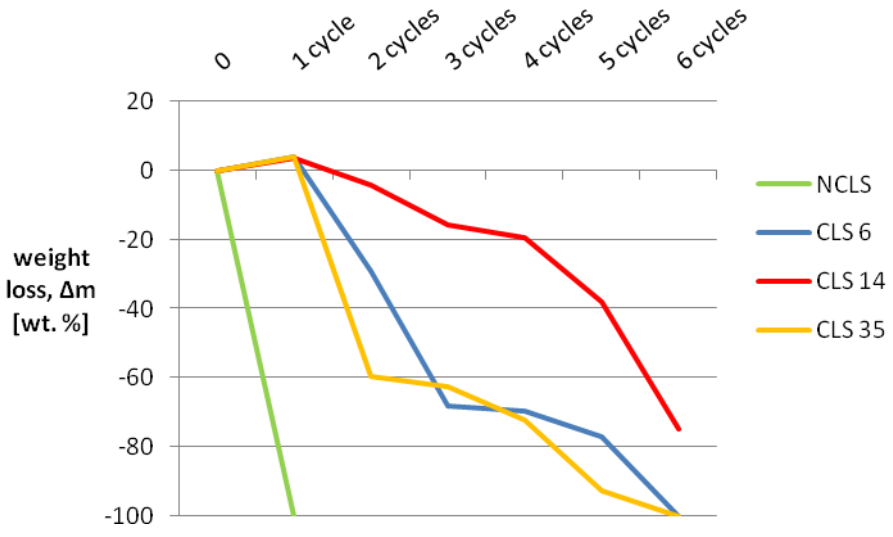

Figure 44. The weight change of not consolidated (NCLS) and consolidated lime substrates (CLS) during the salt crystallization test by capillary action.

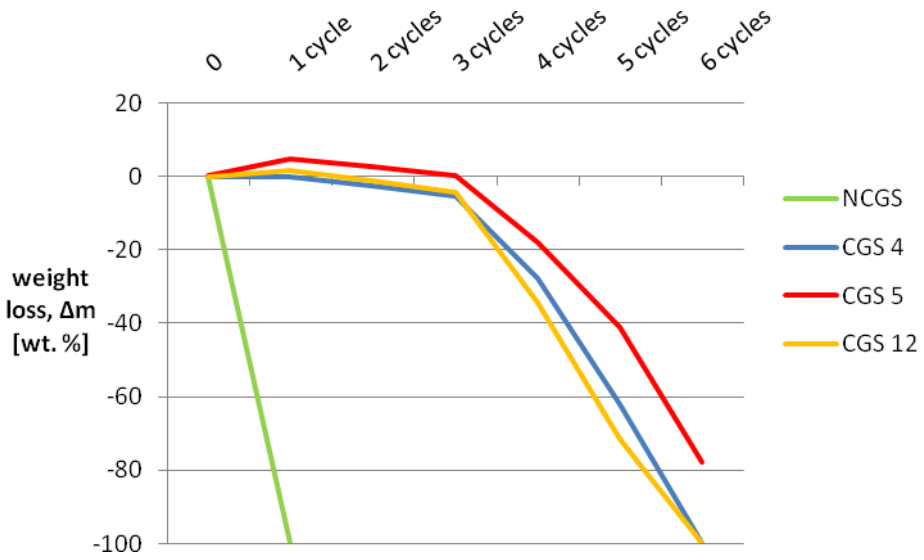

Figure 45. The weight change of not consolidated (NCGS) and consolidated (CGS) gypsum substrates during the salt crystallization test by capillary action.

Figure 46. Specimens during 1st by capillary action. Not consolidated substrates (in the middle) disintegrated immediately in contact with salt solution.

Figure 47. Salt crystallization test by immersion. The substrates after 1st cycle.

Figure 48. Salt crystallization test by immersion. The substrates after 2st cycle.

Figure 49. The formation of salt crystals on the top of the gypsum specimen. The substrate after 2st cycle of immersion.

Figure 50. Salt crystallization test by capillary action. The substrates after 1st cycle. The white colour of gypsum specimens is caused due to the presence of small crystals layer on the surface.

Figure 51. The crust created on the lime specimen. Salt crystallization test by capillary action. The substrate after 3th cycle.

Figure 52. Salt crystallization test by capillary action. The substrates after 4th cycle.

In general, although the consolidation effect can be considered as efficient when we compare it to salt crystallization resistance of untreated substrates (NCGS, NCLS) and consolidated ones (CLS,CGS), the durability and resistance of the consolidated samples is still quite poor. In both cases of testing, the decay of consolidated specimens (CLS, CGS) ran over quickly. The open porous system of specimens allowed good penetration of salt solution inside the pores and when the capacity of pores was filled, the stress caused by salt crystal formation disintegrated the samples.

3.4.5.3. Sorption isotherm test

Water adsorption test was performed to investigate moisture behaviour of samples before and after the consolidation. The test was divided into two parts: one set of samples were stored outside at atmospheric humid conditions (the samples were hidden from rain but exposed to the change of RH). The next set of samples were stored under the different RH conditions which were arranged by storing the samples in dessicators filled with different saturated salt solutions (in the range of 11-93 % RH).

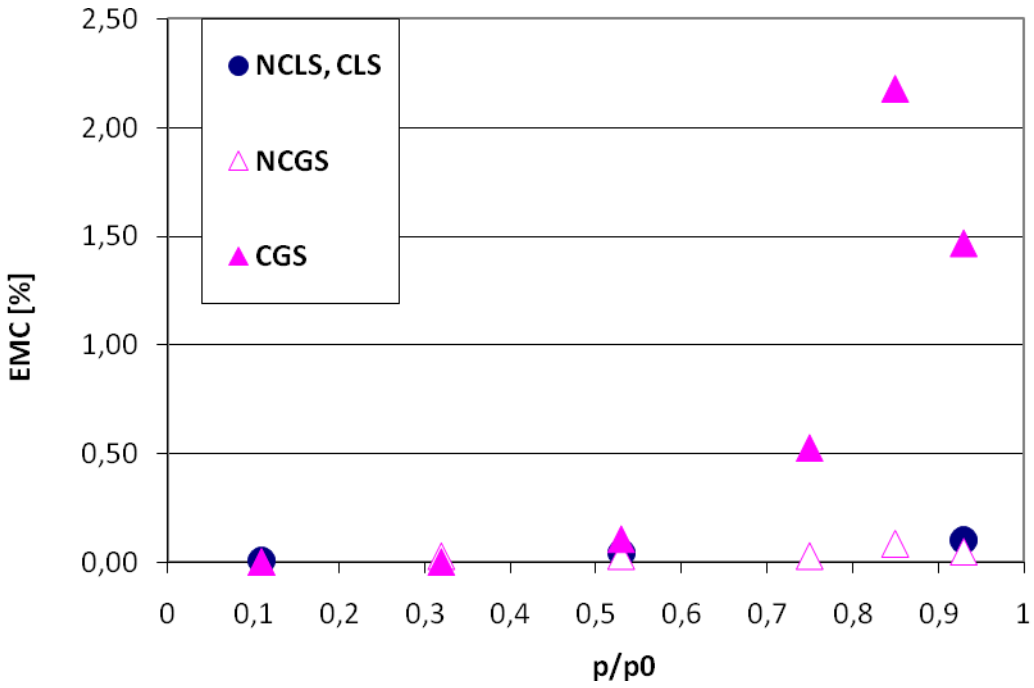

Figure 53. Equilibrium moisture content (EMC) of treated and untreated samples at different RH values (p/p_o).

On the Figure xx, one of the CGS sample is presented. After one week of exposure to external humid condition it revealed as weak crumbling from the bottom of the sample. The harder crust on the surface covered the poorly compacted material inside (Figure 42). Although the consolidation should enhance the specimen´s properties, the specimens were found as extremely sensitive to atmospheric humidity and its fluctuation.

It was also confirmed by second measurements. The equilibrium moisture content (EMC) was measured at each RH, the results can be seen in Figure 57. As expected, gypsum substrates are much more sensitive to higher humid conditions (above 75% RH), because of

hygroscopicity of gypsum component presented in the substrates. It is even more evident when samples after consolidation treatment (CGS) are studied due to their increased content of gypsum. The amount of absorbed water in gypsum consolidated samples (CGS) at 75% of RH is 0.5% and the maximum of water is absorbed 2.5% which is attained at RH around 90%. These findings limit the possible usage of tested gypsum consolidant on monuments exposed to external humid conditions. Such environment increases humid conditions in the substrate as well and can cause a migration of gypsum components to the surface and the formation of a rigid, more compact and less permeable layer.

Figure 54. The substrate (CGS) after one week of the outside exposition.

4. Conclusion

The structural consolidation of the highly corroded mortars is a very important task within the conservation treatment. In most cases, the monuments need an urgent consolidation to survive, keep their good shape and preserve their cultural and historical values for the future. Although for many years the structural consolidation of lime based plasters have been studied and investigated a lot, there are not many agents nowadays who can fulfil the material compatibility with the calcium carbonate binder in the lime plasters and mortars.

Lately the development of nanosuspensions of calcium hydroxide suitable for consolidation of lime based materials appeared and is being investigated. Two of such products were tested within this diploma thesis, namely the consolidant CaLoSil® E25 and Sol $CaSO_4$-$Ca(OH)_2$. The resistance and durability of laboratory plasters imitating highly corroded lime and gypsum mortars before and after the consolidation by these new consolidants was studied. The properties of prepared consolidated and not consolidated plasters were investigated and the consolidation effect was verified by measurement of several physical, mechanical and microstructure characteristics as well as resistance test which imitate the harming external conditions (salt crystallization test, freeze-thaw cycles and sorption isotherm test)

Laboratory testing demonstrated the durability and resistance properties increased after the consolidation treatment significantly. The open pores and (the contact “points” between the particles) of prepared plasters were filled by the new consolidant and thanks to this the consolidated substrates (CLS, CGS) were able to resist longer to the harming environment. Although the decay ran over both consolidated specimen types differently they were destroyed within more or less the same amount of cycles when both the salt crystallization tests and freeze-thaw cycle test were carried out. However, the gypsum specimens were considered slightly more resistant when the salt crystallization tests were performed.

On the other hand, although the sample´s durability increased evidently after the consolidation treatment, even so all substrates disintegrated in a quite short time. This can be solved by using a slightly higher concentration of consolidant or by enhancing the number of consolidation cycles. It should be mentioned that to consolidate such highly corroded

material in a real situation, the extremely increase of strength and durability is either impossible or undesirable and can bring many harming side effects.

In general the tested consolidant CaLoSil® E25 possesses the good features for structural consolidation of calcareous materials. While the consolidation of lime substrates by CaLoSil® E25 was satisfying (homogenous) and brought the positive results, the crust appeared on the consolidated samples imitating highly corroded gypsum mortar suggesting that the consolidant´s (Sol $CaSO_4$-$Ca(OH)_2$) distribution in the sample was not sufficient. When this consolidated specimen was broken it was revealed that the hard crust on the surface covered the poorly compacted material inside, which was disintegrating easily. These facts together with the high sensitiveness to the humid environment which even increased after the consolidaton by gypsum nanosol and together with the high viscosity of gypsum/lime consolidatns points to the limited usage of this gypsum/lime Sol $CaSO_4$-$Ca(OH)_2$ in real conservation field.

5. References

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6. List of figures

7. List of tables

8. List of abbreviation

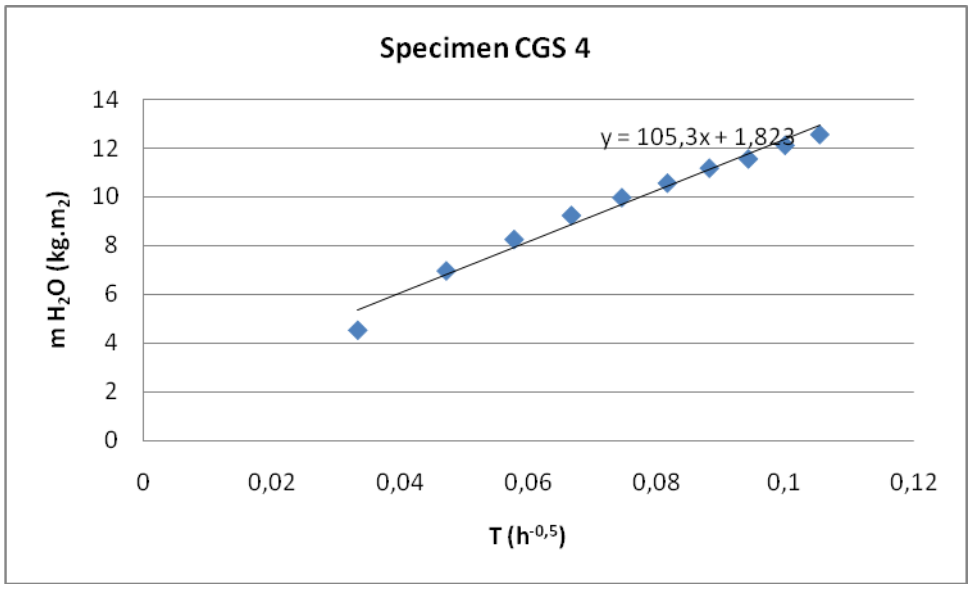
CaLoSiL®	colloidal dispersion $Ca(OH)_2$ in alcohol solvents
CaLoSil®E25	colloidal dispersion $Ca(OH)_2$ dispersed in Ethanol, amount of $Ca(OH)_2$ is 25g/l
Sol CaSO4-$Ca(OH)_2$	colloidal dispersion of $CaSO_4$ and $Ca(OH)_2$ dispersed in Ethanol (30g/l of $Ca(OH)_2$, 15g/l of $CaSO_4$
NANOFORART	EU project, full title: "Nano-materials for the conservation and preservation of movable and immovable artworks ", 7. Framework Programme of the European Commission, Grant agreement no: 282816
CLS	consolidated lime substrate
NCLS	not consolidated lime substrate
CGS	consolidated gypsum substrate
NCGS	not consolidated gypsum substrate
ITAM	The Institute of Theoretical and Applied Mechanics AS CR, v. v. i
STONECORE	Stone Conservation for the Refurbishment of Buildings, Project funded in the 7. Framework Programme of the European Commission, Grant Agreement No: NMP-SE-2008-213651

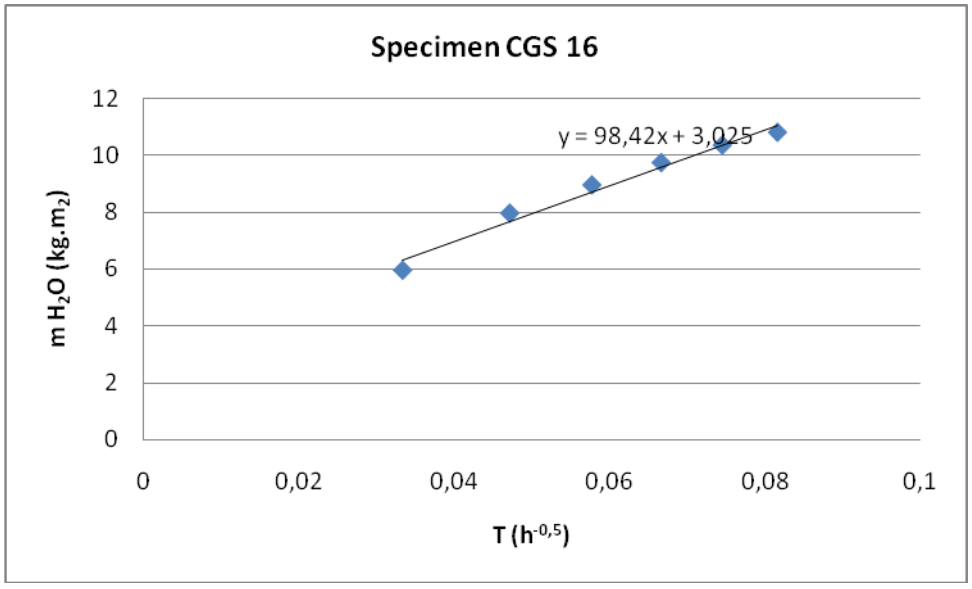
9. Appendices

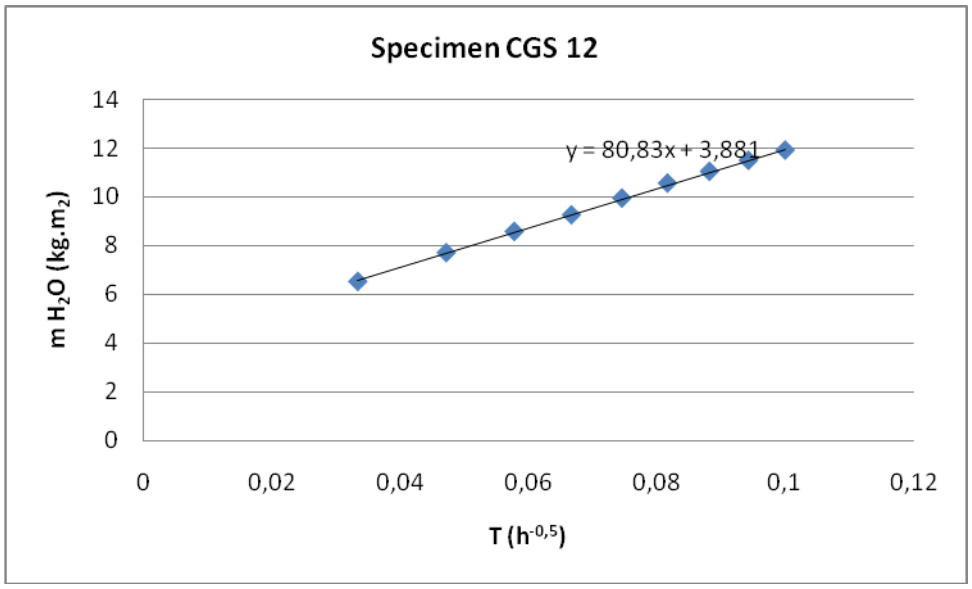
9.1. Water absorption by capillarity

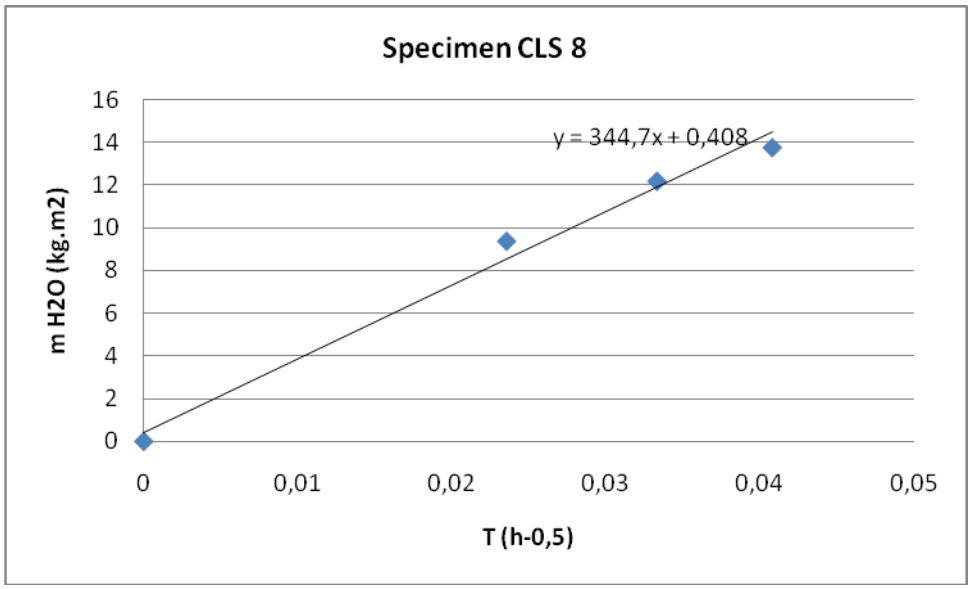
gypsum substrate		w [kg.m^{-2}.h$^{-0,5}$]
CGS 4		105.4
CGS 12		80.83
CGS 16		98.42
average		94.88

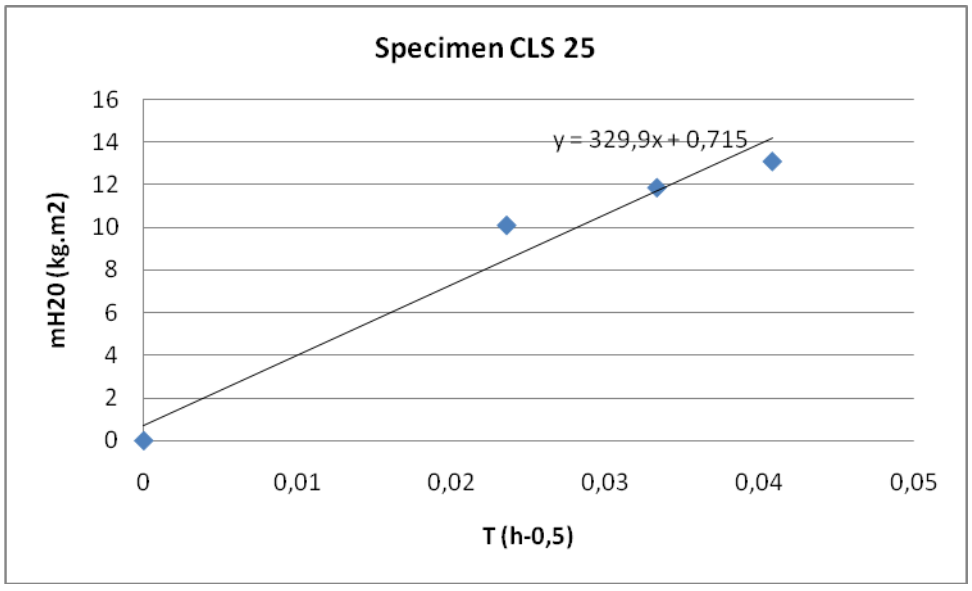
lime plaster substrate		w [kg.m^{-2}.h$^{-0,5}$]
CLS 8		344.7
CLS 25		329.9
CLS 33		314.4
average		337.3

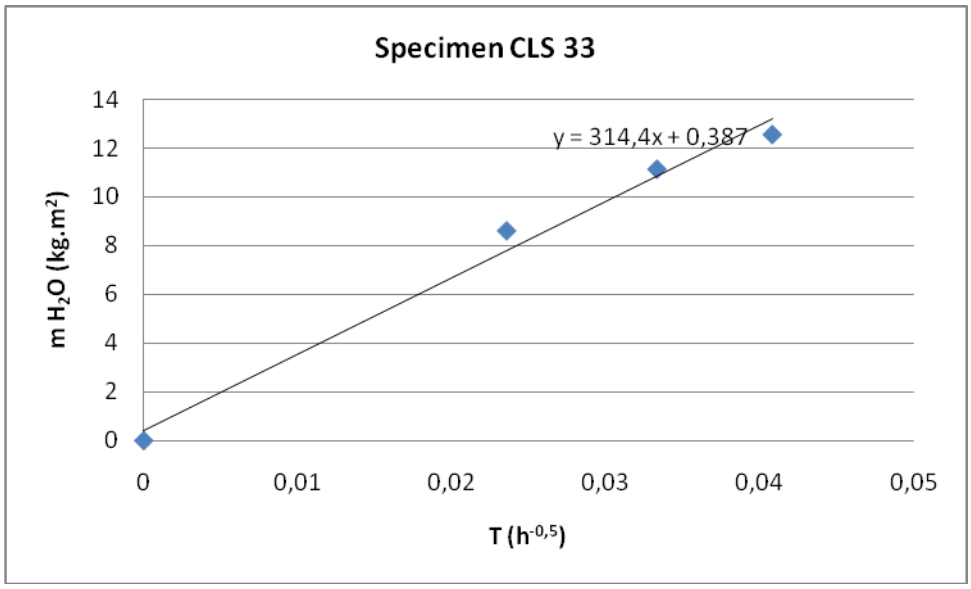





Specimen CGS 12
y = 80,83x + 3,881
m H_2O ($kg.m_2$)
T ($h^{-0,5}$)
0
2
4
6
8
10
12
14
0
0,02
0,04
0,06
0,08
0,1
0,12


Specimen CLS 8
y = 344,7x + 0,408
m H2O (kg.m2)
T (h-0,5)
0
2
4
6
8
10
12
14
16
0
0,01
0,02
0,03
0,04
0,05


Specimen CLS 25
y = 329,9x + 0,715
mH2O (kg.m2)
T (h-0,5)
0
2
4
6
8
10
12
14
16
0
0,01
0,02
0,03
0,04
0,05


Specimen CLS 33
y = 314,4x + 0,387
m H2O (kg.m2)
T (h-0,5)
0
2
4
6
8
10
12
14
0
0,01
0,02
0,03
0,04
0,05

9.2. Thermal analysis

Akademie věd ČR

Ústav teoretické a aplikované mechaniky AV ČR, v. v. i.

Evropské centrum excelence ARCCHIP

Oddělení partikulárních látek

Prosecká 76 190 00 Praha 9

Tel. 222363074 Fax. 286884634 frankeova@itam.cas.cz

Posouzení chemického složení vzorku termickou analýzou

Objednatel	*UPCE FR Litomyšl*
Objednávka číslo	
Požadované analýzy	*Stanovení obsahu sádry ve vzorcích*

Typ přístroje	*TA Instruments SDT Q600* *simultánní záznam signálu TG (úbytek hmotnosti), DTG (derivace úbytku hmotnosti) a DSC(tepelný tok)během ohřevu vzorku*
Podmínky měření	*Proplachovací plyn N2* *rychlost ohřevu 20°C/min* *teplotní rozsah 30 – 1000°C* *keramické kelímky*
Datum měření	*4.8.2011*
Příprava vzorku	*rozetření v porcelánové misce (přibl.1/4 krychle)*
Množství vzorku	*Přibl. 30 mg*

Posuzované vzorky:

Sádrová malta

Vzorek B1 – nezpevněná

Výsledky rozboru

TG analýza

Vzorek	Hmot. úbytek 90-150°C %	Hmot. úbytek 600-800°C %	Celkový úbytek 50-1000°C %
B1 nezpevněná	0,58	0	0,98
B2 zpevněná	1,04	0,40	2,12

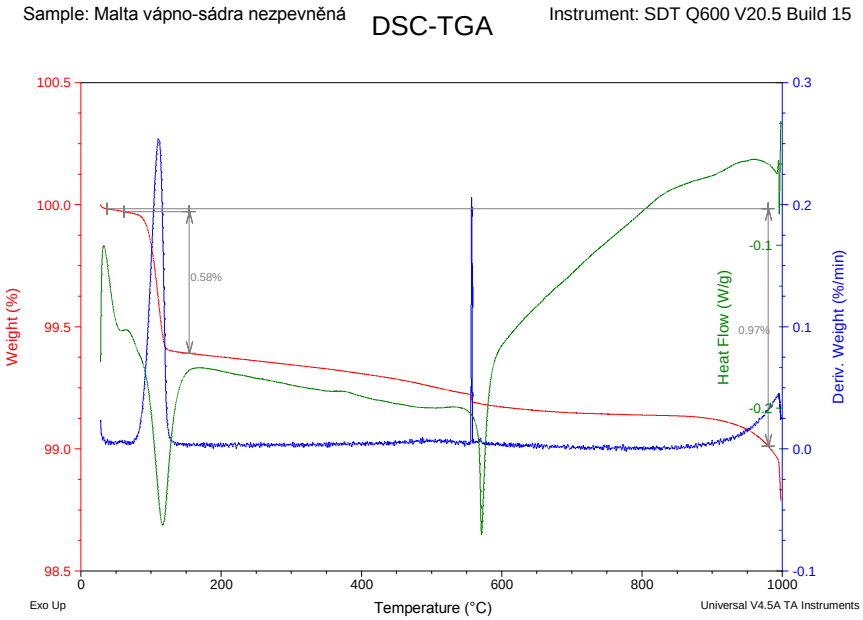
Vyhodnocení záznamu:

TG (červená) a DTG (modrá) křivky jsou znázorněny na obr. 1 a 2.

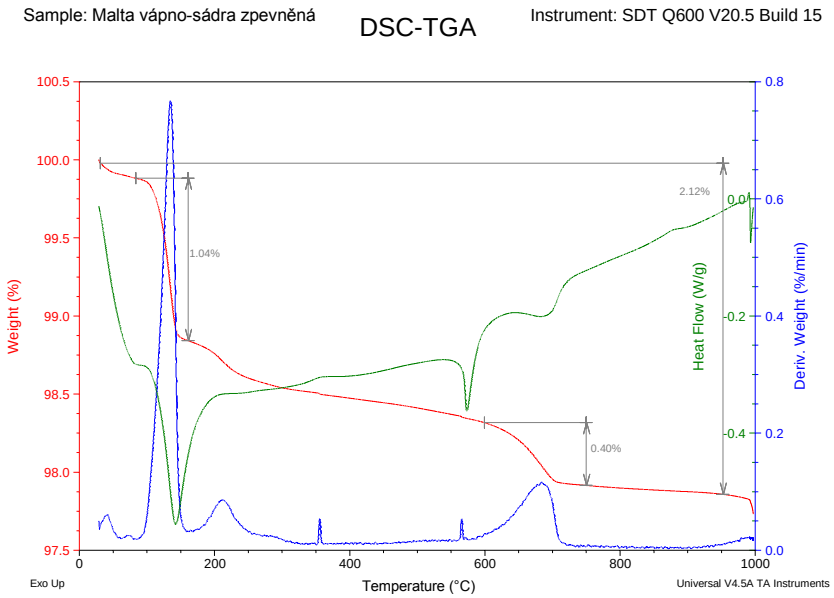
Hlavním dějem probíhajícím v rozmezí teplot 90 až 150°C je dehydratace sádry, s hmotnostním úbytkem 0,58 (B1) a 1,04 % (B2). Toto množství uvolněné vody odpovídá obsahu sádry 2,8 % a 4,9 % hm. U vzorku B2 probíhá ještě rozklad CaCO3 v teplotním intervalu 600 – 800 °C, projevující se hmotnostním úbytkem 0,40 % na křivce TG. Tento úbytek odpovídá množství 0,9 % hm. CaCO3.

DSC analýza		
Teplota v °C	Efekt	Reakce
90-150	Endotermní	Dehydratace sádry
550-600	Endotermní	Přeměna alfa-beta křemen
600-800	Endotermní	Rozklad CaCO3

Obr.1. vzorek B1



Obr. 2. vzorek B2



Závěr:

Nezpevněný vzorek obsahuje 2,8% sádry, zpevněný kromě 4,9 % sádry také 0,9 % uhličitanu vápenatého.

V Praze 4.8.2011 Analýzu a vyhodnocení provedla Mgr. Dita Frankeová

9.3. Porosimetry

Ústav teoretické a aplikované mechaniky AV ČR, v. v. i.

Akademie věd ČR

Evropské centrum excelence ARCCHIP

Prosecká 76 190 00 Praha 9

Posouzení

pórovitosti vzorků modelových malt

Požadovaná zkouška	*Pórovitost, objemová hmotnost a distribuce velikosti pórů metodou rtut˘ové porozimetrie*

Typ přístroje	*Porozimetr: Poremaster PM-60-13*
	Výrobce: Quantachrome
Parametry měření	*Povrchové napětí rtuti: 480 erg/cm^2*
	Smáčecí úhel: 140°
	Hustota rtuti: 13.5487g/cm^3
	Tlak: 0,0055 – 413 MPa
	Odpovidající průměr porů: 258 µm – 3,6 nm
Datum měření	*27.7.2011*

Posuzované malty a jejich značení

A – vzorky imitující korodovanou vápennou omítku

B - vzorky imitující korodovanou vápenosádrovou omítku (extrémně křehké)

V každé skupině byly nezpevněné (N) a zpevněné(Z) vzorky. Každý typ vzorku byl měřen dvakrát (1. a 2. měření). Příklad značení: AZ1 – vzorek A zpevněný, první měření.

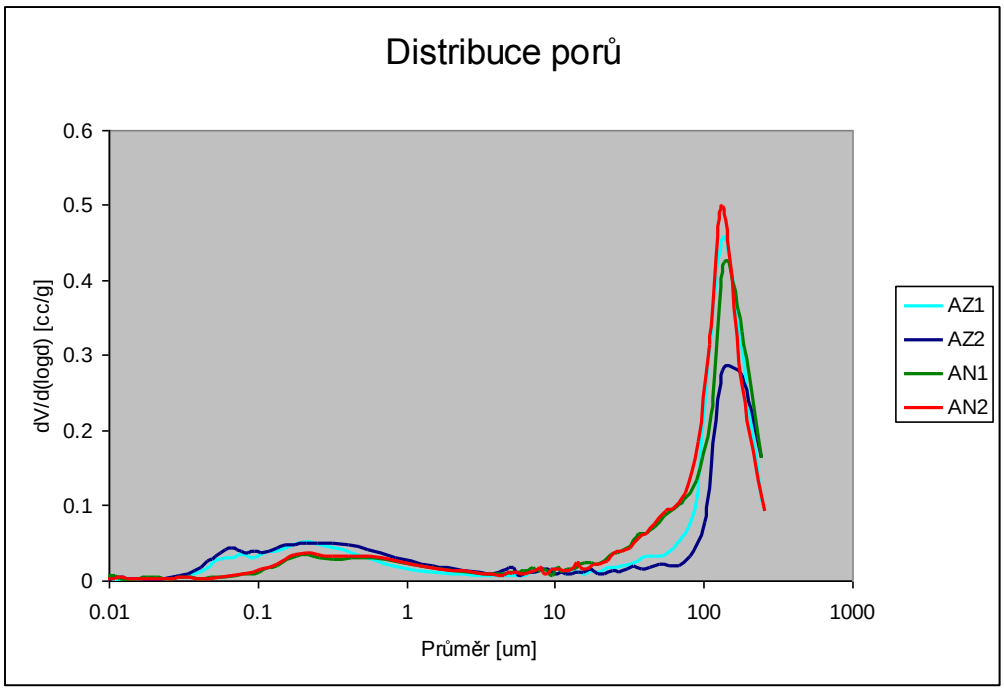
Výsledky

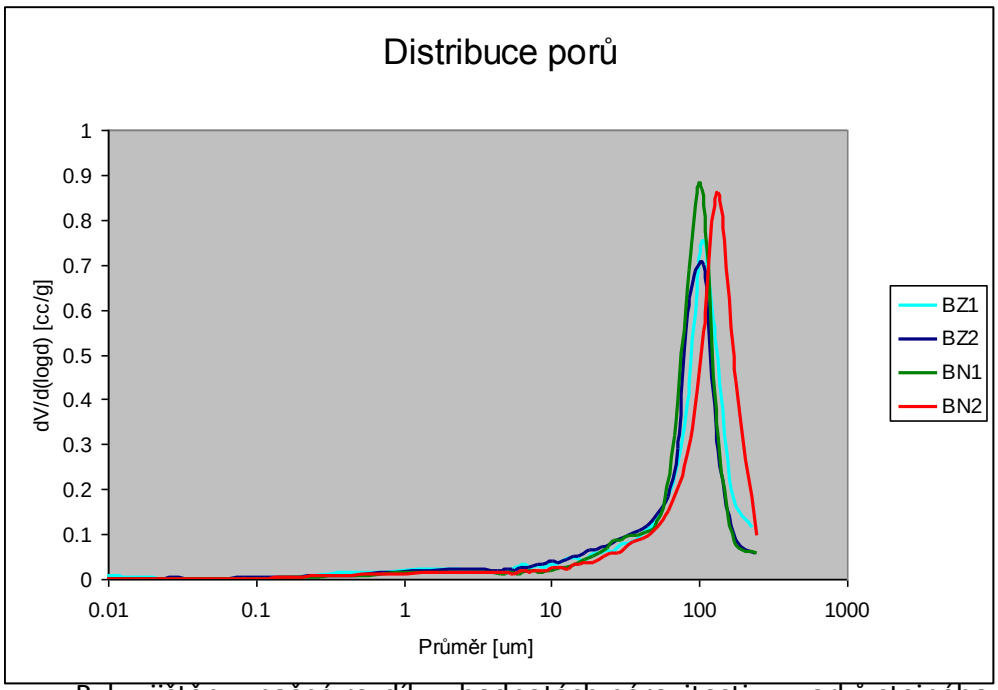
sample	porosity [%]	bulk density [g/cm^3]	solid density [g/cm^3]	surface area [m^2/g]
BZ1	47.95	1.524	2.928	4.4709
BZ2	44.68	1.504	2.718	1.5862
BN1	45.87	1.488	2.748	0.3892
BN2	47.90	1.422	2.730	1.4028

1. vápenná omítka

sample	porosity [%]	bulk density [g/cm^3]	solid density [g/cm^3]	surface area [m^2/g]
AZ1	37.38	1.714	2.738	2.897
AZ2	35.08	1.862	2.868	4.0475
AN1	39.63	1.737	2.878	1.8379
AN2	39.03	1.648	2.702	2.6508

2.vápenosádrová omítka





Byly zjištěny značné rozdíly v hodnotách pórovitosti u vzorků stejného typu (maximální rozdíl je 3,27%), což je pravděpodobně způsobeno nehomogenitou materiálu. U vzorků skupiny B může být zdrojem chyby také velká křehkost a nesoudržnost materiálu. Vzhledem ke značnému rozptylu hodnot zejména u vápenosádrové malty je obtížné přesně interpretovat vliv zpevnění na pórovitost materiálu. U vápenné malty (A) byl zjištěn pokles otevřené pórovitosti o několik málo %. U vápenosádrové malty se nepodařilo metodou rtuťové porozimetrie pokles pórovitosti jednoznačně prokázat.

Z grafů je možné usoudit na tendenci snížení objemu pórů o velikosti kolem 100 µm v důsledku konsolidace malty a zejména u malty A je patrný mírný nárůst plochy pod distribuční křivkou v oblasti 0,04 – 0,7 µm, která pravděpodobně odpovídá velikosti pórů konsolidantu.

V Praze 2.8.2011

Mgr. Krzystof Niedoba, Ing. Zuzana Slížková, Ph.D.

9.4. The composition of sands (Hochschule für Bildende Künste in Dresden)

STONECORE

BERICHT

SANDMISCHUNG NACH DER FULLERKURVE M2

Nr. STONECORE 10/03/04 Sande nach der Fullerkurve

Bearbeiter Thomas Köberle

Datum des Berichts 25.06.09

Fragestellung

- Mischen von unterschiedlichen Sanden zu einer annähernd optimalen Siebline nach Fuller

Material

fünf unterschiedliche Sande von:

Kremer Pigmente GmbH & Co. KG
Hauptstr. 41 – 47
DE 88317 Aichstetten

Tel. 0049 75 65 911 20
Fax 0049 75 65 16 06
E-Mail: info@kremer-pigmente.de

Sand 1	Quarzsand hellgrau feiner Sand 0,5 - 1 mm Artikelnummer: 58678
Sand 2	Quarzmehl gesiebt 0,4 - 0,5 mm Artikelnummer: 58660
Sand 3	Quarzmehl gesiebt 0,25 - 0,4 mm Artikelnummer: 58650
Sand 4	Quarzmehl gesiebt 0,1 - 0,25 mm Artikelnummer: 58640
Sand 5	Quarzmehl gesiebt 0,04 - 0,15 mm Artikelnummer: 58630

Vorgehen

Von den einzelnen Grenzkörnungen wird der Anteil durch Einsetzen in die Fullerformel[1] berechnet.

Formel: $A = 100\ \% * (d / D)^n$

A: Anteil einer Korngruppe [Vol %]
d: ein beliebiger Korndurchmesser zwischen 0 und D [mm]
D: Größtkorndurchmesser der Siebline [mm]
n: Korrekturwert (für gerundete Körner = 0,4)

Ergebnisse

Korngröße [mm]	Siebdurchgang [Vol %]	Anteil [Vol %]		Werte mit Korrekturfaktor 1,186 multipliziert[2]	
1	100	24,22		28,72	
0,5	75,78		6,47		7,67
0,4	69,31	16,78		19,9	
0,2	52,53				
0,25	57,43	17,63		20,91	
0,1	39,8				
0,15	46,8	19,21		22,78	
0,04	27,59				
Summe		**84,31**		**99,98**	

Aus den Werten in den letzten beiden Spalten werden 100 ml Sand gemischt.

[1] aus GRÜBL, WEIGLER UND KARL (2001): Beton - Verlag Ernst & Sohn; 2. Aufl. S. 137
[2] Korrekturfaktor: 100 : 84,31 (Summe der Anteile) = 1,186

Tabellarische Ansicht der Verteilung

Korngröße	Summe 100 ml	Summe 300 ml	Summe 600 ml	Summe 600 ml in g	Summe 1200 ml	Summe 1200 ml in g
0,5 - 1	28,72 ml	86,16	172	224,1	344	448
0,5 - 0,4	7,67 ml	23,01	46	65,3	92	130
0,4 - 0,25	19,9 ml	59,7	118	170,6	236	340
0,25 - 0,1	20,91 ml	62,73	124	149,28	248	289
0,15 - 0,04	22,78 ml	68,34	136	184,24	272	386

9.5. The composition of plaster (Hochschule für Bildende Künste in Dresden)

STONECORE

BERICHT

MÖRTELPRISMEN AUS GIPSMÖRTEL GM3

Nr. STONECORE 10/03/29 Mörtelprismen (2*2*10) mit Gips

Bearbeiter Thomas Köberle

Datum des Berichts 29.03.2010

Fragestellung

- Herstellen von Mörtelprismen mit den Mischungsverhältnissen 1:8 (Volumenverhältnis!!) in einer neu entwickelten Form. Als Bindemittel wird aufgemahlenes und gesiebter (< 0,5 mm) Originalmörtel aus Dahlen verwendet (D_015)

Material

als Prismenformen wird eine selbst entworfene Form aus Plexiglas und Multiplexplatten verwendet. Die Form enthält 2 mal 10 Einzelformen.

Jede Prismenform hat die Abmessungen: 2 * 2 * 10 cm

Sandmischung	Sandmischung M2 (Fuller - Sand) siehe Bericht: STONECORE 09/06/25 Sande nach der Fullerkurve Schüttdichte[1]: 1,71 Kg / l
Bindemittel	aufgemahlener Gipsmörtel aus Dahlen (D_015). Der Mörtel besteht aus Gips als Bindemittel und Sandzuschlag, die genaue Zusammensetzung ist nicht bekannt. Schüttdichte: 1,1 Kg / l

Vorgehen

Die Mischung wird nach Gewichtsanteilen zusammengestellt. Anschließend wird der Mörtel in die Prismen gestrichen und in der Form einige Tage im Labor gelagert.

[1] die Schüttdichte wurde an fünf Proben ermittelt siehe Bericht:
STONECORE 09/05/13 Mörtelprismen mit dolomithaltigem Mörtel

Mörteldaten

Proben-nummer	Mischungs-verhältnis	Volumen Sand-mischung [ml]	Masse Sand-mischung [g]	Volumen D_015 [ml]	Masse D_015 [g]	Masse Wasser-zugabe [g]
GM3	1:8	1200	1732	150	172	100
GM3	1:8	800	1196,5	100	113	100

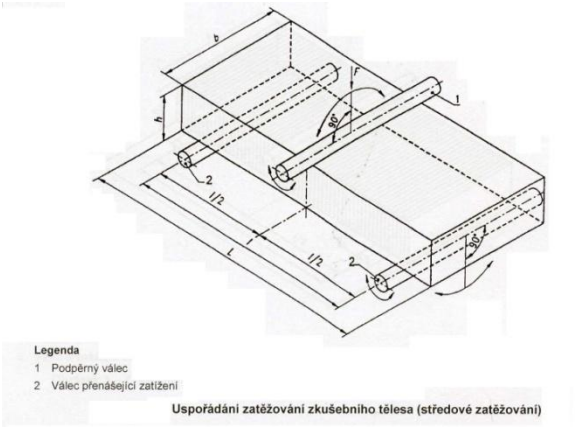
Ergebnisse

Die zweite Mischung mit 800g Sand ist für die Form ausreichend. Es bleibt ein kleiner Rest über.

9.6. Compressive strength and bending strength

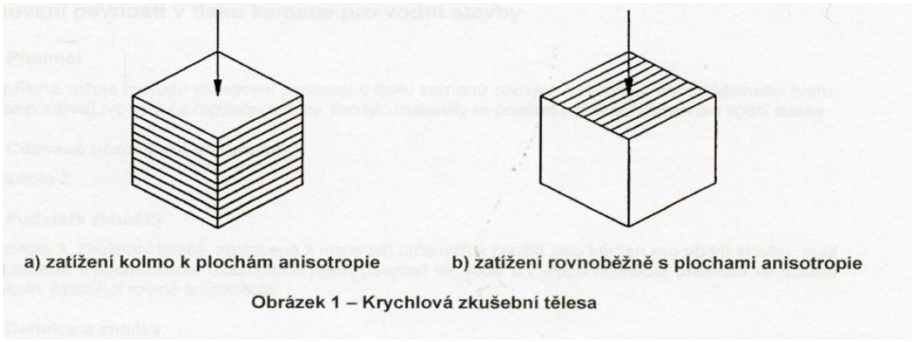
Datum	17.8.20 11
Účastníci	Hodrmen ,Koleš
RH	%
T	25°C

Schéma Stanovení pevnosti za ohybu při soustředěném zatížení

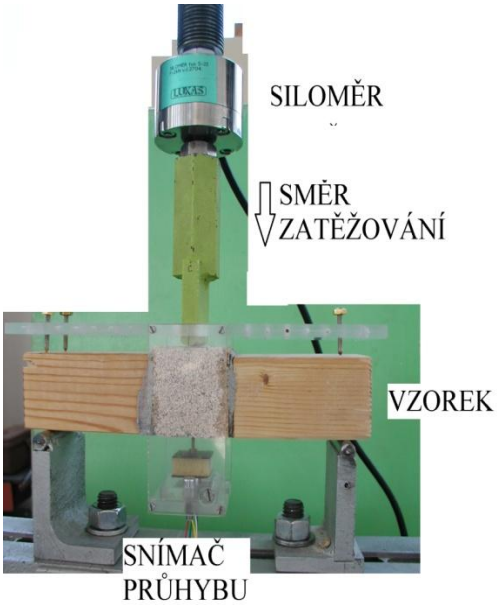


Uspořádání zatěžování zkušebního tělesa (středové zatěžování)

Schéma Stanovení pevnosti v prostém tlaku


a) zatížení kolmo k plochám anisotropie b) zatížení rovnoběžně s plochami anisotropie

Obrázek 1 – Krychlová zkušební tělesa



Vyhodnocení podle ČSN 12372 (721145) Stanovení pevnosti za ohybu při soustředěném zatížení

$$R_{tf} = \frac{3.F.l}{2.b.h^2}$$

R_{tf}	pevnost v ohybu, v megapascalech
F, F_{max}	zatížení při porušení, v newtonech
l	vzdálenost mezi podpěrnými válečky, v milimetrech
b	šířka průřezu zkušebního tělesa v blízkosti lomové plochy, v milimetrech
h	(tloušťka) výška průřezu zkušebního tělesa v blízkosti lomové plochy, v milimetrech

Vyhodnocení podle ČSN 1926 (721142) Stanovení pevnosti v prostém tlaku

$$R = \frac{F}{A}$$

R	pevnost v tlaku zkušebního tělesa v prostém tlaku, v megapascalech
F	zatížení při porušení, v newtonech
A	plocha příčného průřezu zkušebního tělesa před zkouškou, ve čtverečních milimetrech

Statistické vyhodnocení měření

Výsledná pevnost R byla vypočtena jako vážený průměr všech vzorků

$$\bar{x} = \frac{1}{n}\sum_i x_i$$

$$s = \pm\sqrt{\frac{\sum (x_i - \bar{x})^2}{n-1}}$$

$$v = \frac{s}{\bar{x}}$$

x	aritmetický průměr z měřených hodnot
x	měřené hodnoty
n	počet měření
s	směrodatná odchylka
v	variační součinitel

Výsledky

Tlak, *CSN 1926*

Pevnost v Tlaku [MP

Název vzorku	F_{max} [N]	Výška h [mm]	Šířka b [mm]	Hloubka [mm]	Název obr	Název záznamu	Pevnost R [MPa]
NA 1	137	40,2	41,5	39,7	na1.jpg	na1.xls	0,08
NA 3	85	39,4	40,9	40,04	na3.jpg	na3.xls	0,05
NA 6	88	37,5	40,4	39,9	na6.jpg	na6.xls	0,05
					R =		**0,06**
					Směrodatná odchylka		0,02
					Variační součinitel		0,27

Název vzorku	F_{max} [N]	Výška h [mm]	Šířka b [mm]	Hloubka [mm]	Název obr	Název záznamu	Pevnost R [MPa]
NB 1	77	40,2	40,7	39,9	nb1.jpg	nb1.xls	0,05
NB 2	70	38,7	41,3	39,5	nb2.jpg	nb2.xls	0,04
NB 5	67	40,1	40,7	40	nb6.jpg	nb6.xls	0,04
					R =		**0,04**
					Směrodatná odchylka		0,00
					Variační součinitel		0,07

Zpevněné

Název vzorku	F_{max} [N]	Výška h [mm]	Šířka b [mm]	Hloubka [mm]	Název obr	Název záznamu	Pevnost R_{tf} [MPa]	
ZA 2	2433	41,1	40,2	40,5	za2.jpg	za2.xls	1,49	*
ZA 4	2934	40,4	39,9	39,7	za4.jpg	za4.xls	1,85	
ZA 6	2413	41,1	40,2	40,1	za6.jpg	za6.xls	1,50	
					R =		**1,61**	
					R =		**1,67**	bez vzorku za2
					Směrodatná odchylka		0,21	
					Variační součinitel		0,13	
					Směrodatná odchylka		0,25	bez vzorku za2
					Variační součinitel		0,15	bez vzorku za2

ZA2 měřeno 2x po změně siloměru z 2kN na 10kN

Název vzorku	F_{max} [N]	Výška h [mm]	Šířka b [mm]	Hloubka [mm]	Název obr	Název záznamu	Pevnost R [MPa]
ZB 1	506	40,8	40,7	40,7	zb1.jpg	zb1.xls	0,31
ZB 3	43	40,3	37,9	36	zb3.jpg	zb3.xls	0,03
ZB 4	51	41	38	38,6	zb4.jpg	zb4.xls	0,03
ZB 6	69	36,7	38,5	36,7	zb6.jpg	zb6.xls	0,05
					R =		**0,11**
					R =		**0,04**
					Směrodatná odchylka		0,13
					Variační součinitel		1,27
					Směrodatná odchylka		0,01

Variační součinitel	0,24

ZB3 zatěžovaná plocha byla značně nerovná, proto došlo k nerovnoměrnému zatížení
ZB6 zatěžovaná plocha byla značně nerovná, proto došlo k nerovnoměrnému zatížení

Siloměr	Lucas2kN a Lucas 10kN
Snímač průhybu	hbm lvdt
rychlost zatěžování	0,15 mm x min-1

Ohyb

CSN 12372

Pevnost v Ohybu [MPa]

Název vzorku	F_{max} [N]	Výška h [mm]	Šířka b [mm]	Podpory l [mm]	Hmotnost m [g]	Název záznamu	Název obr	délka [mm]	Pevnost R_{tf} [MPa]
AZ_1	92	41,3	39,4	160		AZ_1.xls	AZ_1.jpg		0,33
AZ_3	105	40,5	40,1	160		AZ_3.xls	AZ_3.jpg		0,38
AZ_5	115	40,1	40,3	160		AZ_5.xls	AZ_5.jpg		0,43
							Průměr =		**0,38**
							Směrodatná odchylka		0,05
							Variační součinitel		0,13

Název vzorku	F_{max} [N]	Výška h [mm]	Šířka b [mm]	Podpory l [mm]	Hmotnost m [g]	Název záznamu	Název obr	délka [mm]	Pevnost R_{tf} [MPa]
AN_2	3	39,7	37,3	160		AN_2.xls	AN_2.jpg		0,01
AN_4	3,7	37,7	39,7	160		AN_4.xls	AN_4.jpg		0,02
AN_6	3,8	37,4	40,4	160		AN_6.xls	AN_6.jpg		0,02
							Průměr =		**0,01**
							Směrodatná odchylka		0,00
							Variační součinitel		0,15

Název vzorku	F_{max} [N]	Výška h [mm]	Šířka b [mm]	Podpory l [mm]	Hmotnost m [g]	Název záznamu	Název obr	délka [mm]	Pevnost R_{tf} [MPa]
BZ_2	7	39	38,9	160		BZ_2.xls	BZ_2.jpg		0,03
BZ_5	47,8	39,5	40,1	160		BZ_5.xls	BZ_5.jpg		0,18
							Průměr =		**0,11**
							Směrodatná odchylka		0,11
							Variační součinitel		1,03

BZ_5 oproti vzorku BZ_2 vykazoval značné tvarové nerovnosti

Siloměr	Lucas2kN		
Snímač průhybu	hbm lvdt	rychlost zatěžování	0,15 mm x min-1

9.7. Ultrasound velocity measurement

UZ *Before consolidation, lime substrates (NCLS)*

č.m.		*směr*	t (μs)	t_{korr} (μs)	*d (cm)*	v (km/s)	Average
1	nezpevněný vápenný 1	*x*	32.6	31.2	*4*	1.28	
2	nezpevněný vápenný 1	*y*	34.3	32.9	*4*	1.22	1.21
3	nezpevněný vápenný 1	*z*	36.5	35.1	*4*	1.14	
4	nezpevněný vápenný 1 - edge	*x*	32.9	31.5	*4*	1.27	
5	nezpevněný vápenný 1 - edge	*y*	35.8	34.4	*4*	1.16	1.19
6	nezpevněný vápenný 1 - edge	*z*	36.4	35	*4*	1.14	
7	nezpevněný vápenný 2	*x*	36.3	34.9	*4*	1.15	
8	nezpevněný vápenný 2	*y*	37.2	35.8	*4*	1.12	1.13
9	nezpevněný vápenný 2	*z*	37.1	35.7	*4*	1.12	
10	nezpevněný vápenný 2 - edge	*x*	36.4	35	*4*	1.14	
11	nezpevněný vápenný 2 - edge	*y*	33.3	31.9	*4*	1.25	1.17
12	nezpevněný vápenný 2 - edge	*z*	36.9	35.5	*4*	1.13	
13	nezpevněný vápenný 3	*x*	38.7	37.3	*4*	1.07	
14	nezpevněný vápenný 3	*y*	38.5	37.1	*4*	1.08	1.08
15	nezpevněný vápenný 3	*z*	38	36.6	*4*	1.09	
16	nezpevněný vápenný 3 - edge	*x*	36.5	35.1	*4*	1.14	
17	nezpevněný vápenný 3 - edge	*y*	37.1	35.7	*4*	1.12	1.13
18	nezpevněný vápenný 3 - edge	*z*	37	35.6	*4*	1.12	
	Average					**1.14**	
	Min					**1.07**	
	Max					**1.27**	

UZ *Before consolidation, gypsum substrates (NCGS)*

č.m.		*směr*	t (μs)	*t_{korr} (μs)*	d (cm)	v (km/s)	Average
1	nezpevněný sádrový 1	*x*	40.6	39.2	*4*	1.02	
2	nezpevněný sádrový 1	*y*	40.8	39.4	*4*	1.02	1.03
3	nezpevněný sádrový 1	*z*	39.1	37.7	*4*	1.06	
4	nezpevněný sádrový 1 - edge	*x*	41.9	40.5	*4*	0.99	
5	nezpevněný sádrový 1 - edge	*y*	39.5	38.1	*4*	1.05	1.02
6	nezpevněný sádrový 1 - edge	*z*	40.3	38.9	*4*	1.03	
7	nezpevněný sádrový 2	*x*	40.2	38.8	*4*	1.03	
8	nezpevněný sádrový 2	*y*	40.1	38.7	*4*	1.03	1.04
9	nezpevněný sádrový 2	*z*	39.2	37.8	*4*	1.06	
10	nezpevněný sádrový 2 - edge	*x*	40.2	38.8	*4*	1.03	
11	nezpevněný sádrový 2 - edge	*y*	37.3	35.9	*4*	1.11	1.07
12	nezpevněný sádrový 2 - edge	*z*	38.5	*37.1*	4	1.08	
13	nezpevněný sádrový 3	*x*	48.1	*46.7*	4	0.86	
14	nezpevněný sádrový 3	*y*	48.1	*46.7*	4	0.86	0.87
15	nezpevněný sádrový 3	*z*	46.5	45.1	*4*	0.89	
16	nezpevněný sádrový 3 - edge	*x*	48.6	47.2	*4*	0.85	
17	nezpevněný sádrový 3 - edge	*y*	43.1	41.7	*4*	0.96	0.90
18	nezpevněný sádrový 3 - edge	*z*	46.1	44.7	*4*	0.89	
	Average					**0.99**	
	Min					**0.85**	
	Max					**1.11**	

UZ ***After consolidation, lime substrates (CLS)***

č.m.		*směr*	t (µs)	t_{korr} (µs)	*d (cm)*	v (km/s)	Average
1	zpevněný vápenný NE 25 14 - center	*x střed*	20.4	19	*4*	2.11	average x,y,z center
2	zpevněný vápenný NE 25 14 - on high	*x horní*	18.9	17.5	*4*	2.29	2.02
3	zpevněný vápenný NE 25 14 - beneath	*x dolní*	20.8	19.4	*4*	2.06	
4	zpevněný vápenný NE 25 14 - center	*y střed*	21.8	20.4	*4*	1.96	average x,y,z on high
5	zpevněný vápenný NE 25 14 - on high	*y horní*	18.4	17	*4*	2.35	2.25
6	zpevněný vápenný NE 25 14 - beneath	*y dolní*	21.1	19.7	*4*	2.03	
7	zpevněný vápenný NE 25 14 - center	*z střed*	21.5	20.1	*4*	1.99	average x,y,z beneath
8	zpevněný vápenný NE 25 14 - on high	*z horní*	20.3	18.9	*4*	2.12	2.07
9	zpevněný vápenný NE 25 14 - beneath	*z dolní*	20.4	19	*4*	2.11	
10	zpevněný vápenný NE 25 29 - center	*x střed*	21.1	19.7	*4*	2.03	average x,y,z center
11	zpevněný vápenný NE 25 29 - on high	*x horní*	17.5	16.1	*4*	2.48	2.00
12	zpevněný vápenný NE 25 29 - beneath	*x dolní*	21.5	20.1	*4*	1.99	
13	zpevněný vápenný NE 25 29 - center	*y střed*	21.2	19.8	*4*	2.02	average x,y,z on high
14	zpevněný vápenný NE 25 29 - on high	*y horní*	17.7	16.3	*4*	2.45	2.37
15	zpevněný vápenný NE 25 29 - beneath	*y dolní*	20.5	19.1	*4*	2.09	
16	zpevněný vápenný NE 25 29 - center	*z střed*	21.9	20.5	*4*	1.95	average x,y,z beneath
17	zpevněný vápenný NE 25 29 - on high	*z horní*	19.7	18.3	*4*	2.19	2.08
18	zpevněný vápenný NE 25 29 - beneath	*z dolní*	19.8	18.4	*4*	2.17	
19	zpevněný vápenný NE 25 27 - center	*x střed*	21.3	19.9	*4*	2.01	average x,y,z center
20	zpevněný vápenný NE 25 27 - on high	*x horní*	18.8	17.4	*4*	2.3	1.94
21	zpevněný vápenný NE 25 27 - beneath	*x dolní*	21.7	20.3	*4*	1.97	
22	zpevněný vápenný NE 25 27 - center	*y střed*	21.5	20.1	*4*	1.99	average x,y,z on high
23	zpevněný vápenný NE 25 27 - on high	*y horní*	18.5	17.1	*4*	2.34	2.22
24	zpevněný vápenný NE 25 27 - beneath	*y dolní*	21.9	20.5	*4*	1.95	
25	zpevněný vápenný NE 25 27 - center	*z střed*	23.2	21.8	*4*	1.83	average x,y,z beneath
26	zpevněný vápenný NE 25 27 - on high	*z horní*	21.1	19.7	*4*	2.03	2.00
27	zpevněný vápenný NE 25 27 - beneath	*z dolní*	20.6	19.2	*4*	2.08	
	Average					**2.11**	
	Min					**1.83**	
	Max					**2.48**	

UZ *After consolidation, gypsum substrates (CGS)*

č.m.		*směr*	t (µs)	t_{korr} (µs)	*d (cm)*	v (km/s)	Average
1	zpevněný sádrový NS 4 - center	*x střed*	24.3	22.9	*4*	1.75	average x,y,z center
2	zpevněný sádrový NS 4 - on high	*x horní*	22.5	21.1	*4*	1.9	1.76
3	zpevněný sádrový NS 4 - beneath	*x dolní*	24.6	23.2	*4*	1.72	
4	zpevněný sádrový NS 4 - center	*y střed*	24.1	22.7	*4*	1.76	average x,y,z on high
5	zpevněný sádrový NS 4 - on high	*y horní*	22.7	21.3	*4*	1.88	1.87
6	zpevněný sádrový NS 4 - beneath	*y dolní*	24.5	23.1	*4*	1.73	
7	zpevněný sádrový NS 4 - center	*z střed*	24.1	22.7	*4*	1.76	average x,y,z beneath
8	zpevněný sádrový NS 4 - on high	*z horní*	23.1	21.7	*4*	1.84	1.74
9	zpevněný sádrový NS 4 - beneath	*z dolní*	24	22.6	*4*	1.77	
10	zpevněný sádrový NS 16 - center	*x střed*	24	22.6	*4*	1.77	average x,y,z center
11	zpevněný sádrový NS 16 - on high	*x horní*	22.2	20.8	*4*	1.92	1.76
12	zpevněný sádrový NS 16 - beneath	*x dolní*	23.7	22.3	*4*	1.79	
13	zpevněný sádrový NS 16 - center	*y střed*	24.1	22.7	*4*	1.76	average x,y,z on high
14	zpevněný sádrový NS 16 - on high	*y horní*	21.5	20.1	*4*	1.99	1.92
15	zpevněný sádrový NS 16 - beneath	*y dolní*	23.7	22.3	*4*	1.79	
16	zpevněný sádrový NS 16 - center	*z střed*	24.3	22.9	*4*	1.75	average x,y,z beneath
17	zpevněný sádrový NS 16 - on high	*z horní*	22.9	21.5	*4*	1.86	1.79
18	zpevněný sádrový NS 16 - beneath	*z dolní*	23.9	22.5	*4*	1.78	
19	zpevněný sádrový NS 11 - center	*x střed*	26.6	25.2	*4*	1.59	average x,y,z center
20	zpevněný sádrový NS 11 - on high	*x horní*	23.7	22.3	*4*	1.79	1.57
21	zpevněný sádrový NS 11 - beneath	*x dolní*	27.5	26.1	*4*	1.53	
22	zpevněný sádrový NS 11 - center	*y střed*	26.8	25.4	*4*	1.57	average x,y,z on high
23	zpevněný sádrový NS 11 - on high	*y horní*	24.9	23.5	*4*	1.7	1.69
24	zpevněný sádrový NS 11 - beneath	*y dolní*	27.8	26.4	*4*	1.52	
25	zpevněný sádrový NS 11 - center	*z střed*	27.1	25.7	*4*	1.56	average x,y,z beneath
26	zpevněný sádrový NS 11 - on high	*z horní*	26.7	25.3	*4*	1.58	1.55
27	zpevněný sádrový NS 11 - beneath	*z dolní*	26.3	24.9	*4*	1.61	
	Average					**1.74**	
	Min					**1.52**	
	Max					**1.99**	

9.8. Mass gain measurement

MASS GAIN, gypsum substrates NS1- S16, immersion by sol CaCO3-Ca SO4,

Name of sample	1. application date 21.3.		2. application date 13.4.		3. application date 19.4.		m date 24.4.	m date 26.4.	m date 28.4.	m date 1.5.	m date 3.5.	m date 5.5.	comments
	mo	mp	mo	mp	mo	mp	mo	mo	mo	mo	mo	mo	
NS1	85.82	108.76	87.38	109.72	89.18	110.98	90.91	90.98	90.98	90.95	90.9503	90.941	po 1.aplikaci odpadl kousek spodního rohu-váha bude odlišná
NS2	92.75	113.79	94.54	113.95	96.14	111.59	97.41	97.46	97.45	97.44	97.438	97.4311	
NS3	85.75	109.08	87.45	110.18	89.32	112.05	91.18	91.23	91.24	91.2	91.2088	91.2009	
NS4	89.87	111.9	91.76	112.39	93.48	113.94	95.14	95.19	95.19	95.17	95.1731	95.1663	
NS5	79.1	102.53	81.02	103.56	82.85	106.3	84.74	84.8	84.8	94.78	84.7784	84.7682	
NS6	87.19	109.43	89.05	110.17	90.78	110.7	92.42	92.48	92.47	92.47	92.4558	92.4443	
NS7	83.71	107.34	85.71	108.44	87.63	110.73	89.45	89.5	89.51	89.48	89.4906	89.48	
NS8	92.36	113.7	94.19	113.5	95.81	113.36	97.22	97.28	97.28	97.26	97.2614	97.2532	
NS9	87.75	110.78	89.71	111.12	91.5	110.74	93.05	93.09	93.11	93.08	93.0921	93.0842	
NS10	81.31	105.38	83.33	106.78	85.27	107.25	87.09	87.14	87.14	87.12	87.1212	87.1079	
NS11	83.05	106.93	85.06	108.43	86.95	108.54	88.75	88.8	88.77	88.76	88.7532	88.742	26.4. seškrábán vzorek výkvětu na rozbor
NS12	93.15	114.42	94.94	113.84	96.52	109.91	97.62	97.67	97.67	97.65	97.6648	97.6568	
NS13	89.3	111.74	91.26	111.61	92.99	105.67	94.02	94.07	94.07	94.05	94.0499	94.0433	
NS14	80.06	104.16	82.09	106.24	84.09	107.4	86.02	86.07	86.07	86.5	86.0448	86.0334	
NS15	85.16	108.18	87.05	110.1	88.97	108.97	90.65	90.7	90.7	90.68	90.6793	90.671	
NS16	87.01	109.18	88.54	110.79		109.44	92.37	92.42	92.41	92.4	92.3948	92.3876	

mo - before application of consolidant (g) mp - after application of consolidant (g)

MASS GAIN, gypsum specimens NS17-NS24, immersion by sol $CaCO_3$ - Ca SO_4,

Name of sample	1. application date 20.5.2011	2. application date 27.5.2011		3. application date 6.6.2011 (RH 62%)		m date 11.6.2011 (RH 49%, 27°C)		m date 13.6.2011 (25°C, 57% RH)	m date 15.6.1011	m date 21.6. 2011 (65%RH)	m date 23.6.2011 (57%RH)	m date 30.6.2011 (59%RH, 24,5°C)	m date 4.7.2011 (64%RH, 21,5°C)
	mo	**mp**	**mo**	**mp**	**mo**	**mp**	**mo**	**mo**	**mo**	**mo**	**mo**	**mo**	**mo**
NS17	84.7597	107.4890	86.4963	108.3650	88.0789	107.7109	89.4065	89.3651	89.3543	89.3853	89.3427	89.3202	89.3135
NS18	82.1605	107.4890	83.8791	104.6287	85.3678	104.4949	86.7668	86.7036	86.6975	86.7151	86.6771	86.6675	86.686
NS19	89.2300	112.0846	91.0051	112.6849	92.5488	112.4023	94.1312	93.9589	93.9802	93.9802	93.9435	93.9355	93.9499
NS20	85.4499	107.9879	87.0649	108.7433	88.6935	107.8205	90.0315	90.0137	90.0430	90.043	90.0114	90.0061	90.0286
NS21	85.2050	107.4262	86.9823	108.5542	88.4782	107.3134	89.6182	89.5937	89.5871	89.6188	89.5889	89.5868	89.5996
NS22	82.2117	103.8132	83.6176	105.5706	85.3440	104.3312	86.6618	86.652	86.6454	86.6614	86.633	86.6309	86.641
NS23	83.0071	104.1414	84.5472	105.5130	86.1142	104.1743	87.2355	87.2114	87.1973	87.209	87.1492	87.1393	87.1491
NS24	82.7125	103.9668	84.3744	105.2691	85.9379	104.0634	87.0145	86.9736	86.9421	86.9467	86.8927	86.8739	86.8742

mo - before application of consolidant (g) mp - after application of consolidant (g)

MASS GAIN, lime specimens NE1-NE28, immersion by CaLoSil®E25

Name of sample	1. application date 15.3.2011		2. application date 22.3.		3. application date 12.4.		4. application date 18.4.		5. application date 24.4.		m date 28.4.	m date 1.5.	m date 3.5.	m date 5.5.	m date 7.5.	m date 19.5.
	mo	**mp**	**mo**	**mp**	**mo**	**mp**	**mo**	**mp**	**mo**	**mp**	**mo**	**mo**	**mo**	**mo**	**mo**	**mo**
NE1	89.31	109.96	89.71	110.5	90.56	110.57	91.36	111.12	92.13	111.66	92.98	93.04	93.0373	93.0341	93.0482	93.091
NE2	89.7	109.59	90.24	110.03	91.03	110.25	91.77	110.38	92.5	111.1	93.31	93.3546	93.3461	93.3425	93.3548	93.3909
NE3	85.65	105.3	85.41	105.24	86.25	105.82	87.01	106.5	87.8	106.61	88.62	88.6658	88.6638	88.6609	88.6733	88.7036
NE4	89.83	109.34	90.43	109.91	91.28	110.15	92.03	110.35	92.78	110.81	93.56	93.6097	93.6072	93.6026	93.6146	93.65
NE5	88.16	108.15	88.64	108.6	89.54	108.8	90.19	109.45	90.96	109.94	91.78	91.8406	91.8371	91.8338	91.8457	91.8776
NE6	87.76	107.86	88.02	108.18	88.8	108.2	89.56	108.81	90.35	109.46	91.17	91.2229	91.2178	91.2141	91.2265	91.2655
NE7	87.56	107.36	88.15	107.9	89.02	108.17	89.78	108.76	90.55	109.03	91.34	91.3998	91.3961	91.3926	91.4039	91.4451
NE8	88.11	108.76	88.61	109.57	89.53	109.69	90.33	110.54	91.15	111.08	92.01	92.0765	92.0761	92.0729	92.0837	92.1232
NE9	90.39	109.7	89.44	109.1	90.3	109.45	91.01	110.06	91.73	110.18	92.53	92.5692	92.567	92.5612	92.5733	92.6157
NE10	90.24	110.22	90.93	110.77	91.86	111.22	92.62	111.74	93.39	112.01	94.21	94.2442	94.8411	94.2365	odesláno na testy	odesláno na testy
NE11	88.9	108.58	89.12	108.94	89.86	109.15	90.6	109.15	91.34	109.99	92.16	92.1995	92.1982	92.1943	92.207	92.2469
NE12	86.08	106.2	86.17	106.47	87.1	107.15	87.86	107.65	88.65	108.09	89.5	89.5368	89.5372	89.5307	89.5382	89.5727
NE13	90.3	111.4	90.95		91.87	112.4	92.68	113.12	93.49	113.28	94.34	94.4022	94.4016	94.3986	94.4122	94.4518
NE14	90.57	110.62	91.12	110.96	90.07	111.59	92.84	112.22	93.62	112.55	94.45	94.4968	94.4969	94.4919	94.5092	94.5437
NE15	86.45	106.54	86.87	106.75	87.78	107.4	88.49	107.82	89.28	107.94	90.08	90.1401	90.138	90.1329	90.1436	90.1673
NE16	91.15	110.98	91.86	111.67	92.79	112.37	93.56	112.99	94.34	113.17	95.17	95.2183	95.2183	95.2141	95.2248	95.2633
NE17	88.51	108.28	89.12	108.7	90.01	109.34	90.77	109.82	91.53	109.97	92.32	92.3782	92.3713	92.3655	92.3791	92.421
NE18	90.08	111.19	90.63	111.26	91.62	112.09	92.43	112.28	93.23	112.84	94.07	94.132	94.1248	94.1203	94.1328	94.1717
NE19	89.06	109.08	89.67	109.51	90.59	109.95	91.36	110.59	92.14	110.77	92.94	93.0074	93.0003	92.9965	93.0101	93.0499
NE20	88.79	109.58	89.43	110.06	90.4	110.66	91.21	110.97	92	111.69	92.85	92.9197	92.9136	92.909	92.9227	92.9618
NE21	89.87	109.79	90.55	110.21	91.48	110.77	92.25	110.94	92.99	111.64	93.79	93.86	93.8536	93.8474	93.8612	93.9023
NE22	89.82	109.63	90.47	110	91.38	110.42	92.16	111.17	92.92	111.16	93.71	993.7809	93.7755	93.7711	93.7844	93.8232
NE23	87.53	107.33	88.2	107.7	89.09	108.25	89.87	108.56	90.61	108.97	91.41	991.4716	91.4648	91.46	91.4736	91.5132

MASS GAIN, lime specimens NE23-NE35, immersion by CaLoSil®E25

Name of sample	1. application date 15.3.2011		2. application date 22.3.		3. application date 12.4.		4. application date 18.4.		5. application date 24.4.		m date 28.4.	m date 1.5.	m date 3.5.	m date 5.5.	m date 7.5.	m date 19.5.
	mo	**mp**	**mo**	**mp**	**mo**	**mp**	**mo**	**mp**	**mo**	**mp**	**mo**	**mo**	**mo**	**mo**	**mo**	**mo**
NE23	87.53	107.33	88.2	107.7	89.09	108.25	89.87	108.56	90.61	108.97	91.41	991.4716	91.4648	91.46	91.4736	91.5132
NE24	88.72	108.68	89.19	109.15	90.12	109.78	90.91	110.25	91.69	110.49	92.51	92.576	92.5681	92.564	92.5778	92.6167
NE25	89.48	108.72	90.08	109.74	91.02	109.88	91.74	110.58	92.51	110.75	93.3	93.3585	93.9515	93.3449	93.9575	93.3989
NE26	88.3	107.95	88.93	108.73	89.82	108.99	90.56	109.57	91.34	109.77	92.14	92.211	92.2042	92.2002	92.2134	92.2522
NE27	89.99	106.99	87.57	107.8	88.51	708.07	89.3	108.76	90.06	109.62	90.9	90.96	90.9529	90.9481	90.9611	91.0007
NE28	87.85	107.74	88.54	108.33	89.4	108.59	90.17	109.26	90.93	109.62	91.79	91.8306	91.8241	91.8177	91.8289	91.8538
NE29	92.32	112.11	92.97	112.87	93.94	113.3	94.7	113.3	95.44	114.1	96.26	96.3117	96.302	96.2967	96.3099	96.3571
NE30	87.87	107.28	88.41	108.27	89.27	108.32	90.02	109.2	90.79	109.27	91.6	91.6639	91.6568	91.6523	91.6656	91.7047
NE31	87.8	105.73	88.37	106.52	89.28	106.89	89.96	107.38	90.66	107.81	91.41	91.4702	91.4599	91.4547	91.4663	91.5144
NE32	88.68	107.64	89.28	109.68	90.2	109.2	90.95	110.09	91.74	110.63	92.54	92.6048	92.5981	92.5938	92.6049	92.6438
NE33	89.12	109.4	89.69	109.68	90.56	109.88	91.31	110.43	92.09	110.59	92.93	92.969	92.9608	92.9559	92.9655	92.9894
NE34	87.93	107.4	88.55	107.64	89.41	107.95	90.15	85.08	90.86	108.64	91.69	91.7225	91.7157	91.7089	91.7173	91.74
NE35	83.18	104.02	83.41	103.7	84.31	103.83	85.08	104.61	85.87	105.11	86.73	86.7739	86.7672	86.7628	86.7709	86.794
NE29	92.32	112.11	92.97	112.87	93.94	113.3	94.7	113.3	95.44	114.1	96.26	96.3117	96.302	96.2967	96.3099	96.3571
NE30	87.87	107.28	88.41	108.27	89.27	108.32	90.02	109.2	90.79	109.27	91.6	91.6639	91.6568	91.6523	91.6656	91.7047
NE31	87.8	105.73	88.37	106.52	89.28	106.89	89.96	107.38	90.66	107.81	91.41	91.4702	91.4599	91.4547	91.4663	91.5144
NE32	88.68	107.64	89.28	109.68	90.2	109.2	90.95	110.09	91.74	110.63	92.54	92.6048	92.5981	92.5938	92.6049	92.6438
NE33	89.12	109.4	89.69	109.68	90.56	109.88	91.31	110.43	92.09	110.59	92.93	92.969	92.9608	92.9559	92.9655	92.9894
NE34	87.93	107.4	88.55	107.64	89.41	107.95	90.15	85.08	90.86	108.64	91.69	91.7225	91.7157	91.7089	91.7173	91.74
NE35	83.18	104.02	83.41	103.7	84.31	103.83	85.08	104.61	85.87	105.11	86.73	86.7739	86.7672	86.7628	86.7709	86.794