
MECHANISM OF EFFICIENCY OF SELECTED NANOSYSTEMS INTENDED FOR CONSOLIDATION OF POROUS MATERIALS

Klára Kroftová[1] and David Škoda[2]

1. *Czech Technical University of Prague, Faculty of Civil Engineering, Department of Architecture, Prague, Thákurova 7, Czech Republic; Klara.Kroftova@fsv.cvut.cz*
2. *Centre of Polymer Systems, Tomas Bata University in Zlin, Tr. Tomase Bati 5678, Zlin, CZ-76001, Czech Republic; dskoda@utb.cz*

ABSTRACT

Over the past 20 years, the possible usage of disperse and colloid systems of organic consolidation agents as well as mineral systems with particle size in nanodimensions in the context of cultural heritage care has been examined. Nanomaterials, with particle size of up to 1μm whose properties are at a certain intersection between properties at the level of molecules and mass are the subject-matter of extensive scientific research for their positive physical and mechanical properties such as high chemical efficiency, excellent plastic, consolidation and diffusion properties, low sintering temperature, cleaning capabilities and others. Nanomaterials whose consolidation efficiency has been tested by experimental research, include, in particular, hydroxide nanodispersions. The article summarises basic conditions for application and principles of efficiency of selected nanosystems for consolidation of historic lime-based porous materials, i.e. in particular lime-based plasters that form integral part of historic buildings

KEYWORDS

Nanomaterials, Calcium Hydroxide, Consolidation, Plaster, Cultural Heritage

INTRODUCTION

Consolidation – improving physical and mechanical properties and stabilising or, alternatively, slowing down or completely stopping degradation – is one of the fundamental objectives of restoration of historic plasters. The plaster consolidation principle is based on returning the binding material into their structure, filling up any cavities that arise and joining up cracks or increasing the adhesion of the plaster to the base and reducing salt content in the plaster porous system. Plaster layers can be strengthened and stabilised by a sequence of individual interventions and the specific procedure and scope of care cannot be universal and generally applicable. It is always an *ad hoc* process, affected by a number of factors, different for different buildings, conditions and properties of preserved historic materials. The general requirement is that renovation of historic buildings and cultural heritage should not damage the original preserved surface finishes and the original method and that the selected material for renovation should respect the preserved condition and follow the original composition of the plaster. After a conservation intervention is completed, the appearance, colour as well as structure of the new supplements and renovated parts should be as close to the original material as possible.

In recent decades, nanotechnologies have started to appear in restoration of surface finishes of historic buildings; these technologies introduce new ways of protection of building structures using specific, functionalised properties of materials caused by increasing the proportion of the area of the surface of the particles to the volume of the particles in nanomaterials. Nanomaterials, when compared to macro-materials, excel in extremely high “performance” in contrast to a very low consumption of material. By achieving sufficient depth of penetration into the porous system and preserving the original mass, nanomaterials can facilitate the cleaning of surfaces degraded by vandalism (graffiti), they can provide temporary strengthening of the surface to be plastered, increase protection of material against UV radiation, provide biocide protection, and so on. Application of nanomaterials has been documented, inter alia, for deacidification of movable artworks (paper, textile or, for example, leather) [1] - [4], cleaning of surfaces of historic monuments (for example, using nanosuspension from titanium hydroxide, nanoemulsion of organic solvents in water, etc.) [5] - [7] or in consolidation of frescoes or mural paintings [8] - [9]. Preparations for protection and sterilisation of wood and walls against harmful and degrading agents are a specific area of application of materials doped with nanoparticles, for example. In certain justified cases, nanosuspensions can be applied to the surface of historic material independently or as carriers of nanoparticles (for example, silver or diamond) that lend them the capability to, for example, strengthen locally the damaged historic materials, to provide resistance against harmful effects of aggressive exterior environment, etc.

Probably the most widespread application of nanomaterials in care for historic buildings is the use of nanosuspensions based on calcium hydroxide, in particular to strengthen lime construction materials (plasters, limestones, etc.) [10] - [12]. The lime nanosuspension consists of nanoparticles of calcium hydroxide dispersed in alcohol, with individual types displaying different concentrations and type of alcohol. In terms of stabilisation and conservation of these materials, the main advantage is the chemical composition of the resulting product, i.e. calcium carbonate that forms the main binding element in lime materials. The calcium carbonate is deposed in the damaged material; hence, the ligations are strengthened again and the material is hardened. At the same time, calcium carbonate is highly compatible with the original lime-based material and it does not bring irreversible deposits into the consolidated material [13]. The size of nanoparticles usually ranges between 150 to 300 nm for lime nanosuspensions (for example, in the commercially available CaLoSiL® nanosuspension, the size of a particle of calcium hydroxide ranges between 50 and 200 nm) and this does not create any major limitations in relation to the size of pores of the treated material. The suspension contains also larger particles which, however, are produced most frequently by undesired agglomeration of primary particles during manufacture or subsequent storage [14]. The viscosity and colour of the suspension differs depending on its concentration – a more concentrated compound displays higher viscosity and is usually whiter (or it can have a light ochre or grey colour, depending on the source material and the production method used).

An undeniable advantage of consolidation of plasters using calcium hydroxide nanosuspension is a dramatic reduction of the number of impregnation cycles – already several applications of $CA(OH)_2$ nanosuspension will result in strengthening in the case of corrupt finishes; if limewater is used, such strengthening is achieved only after dozens of cycles (for example, 100 to 120 application cycles are required on average for strengthening with limewater while 5 to 10 applications are sufficient to achieve equivalent strengthening if lime nanosuspensions are applied). Dispersion of active agents in alcohols is also beneficial from technological perspective; first, no repeated wetting of surfaces by water, development of migration and re-crystallisation of salts occurs; second, their applicability in relation to the risk of freezing is not restricted. The success of the consolidation process using nanomaterials is affected by mineralogical and chemical composition of the treated material, properties of the porous system, surface structure, extent of erosion and degradation of material before treatment, properties of the active agent in the strengthening product (size of ions and particles, chemical composition, concentration, speed of drying and hardening, etc.) and, last but not least, temperature and moisture conditions upon application. If the lime nanosuspension displays sufficiently low surface tension, optimal wetting is safeguarded and this is responsible for deep penetration of dispersions in the porous plaster structure.

METHODS

In the NAKI research project, extensive research focusing on possible usage of nanomaterials in restoration of historic materials (in particular, plaster and stone) has been conducted. The research is carried out in co-operation with the Faculty of Civil Engineering of the Czech Technical University in Prague and the Centre of Polymer Systems of the Tomáš Baťa University in Zlín.

Consolidation materials and their properties

After the basic steps in restoration of lime-based surfaces of historic buildings are carried out (i.e. mainly cleaning, removing the causes of damping and reduction of salt content), the surface can be consolidated. The strengthening product should penetrate through the entire degraded layer, recover its structure and adhesion to the "healthy" base and not to create surface crust. The important properties of the consolidation product include:

- stability (against moisture, alkaloids and acids, light, air and microbiological attack);
- UV radiation resistance;
- display high penetration capability;
- it should not affect the appearance of the treated material (lustre, colour, surface structure, etc.);
- the coefficient of thermal expansion close to the coefficient of expansion of the original material;
- health-related fitness, easy application and affordability.

At the same time, the consolidation agent must be compatible with the original material, i.e. it must not change or affect materially the physical properties of original materials, e.g. porosity, vapour-permeability, thermal or moisture expansion, elasticity (modulus of elasticity). High durability and resistance against aging of the strengthening product and the consolidated material is also very important. The requirement of removability (reversibility) is among basically unrealizable requirements for products and procedures used in treatment of historic materials; it is tempered by the requirement of possible retreatability so as not to prevent subsequent care in later years. From this perspective, materials on inorganic basis, compatible with the treated material and, at the same time, stable with high efficiency following application, seem as most suitable consolidation products.

Great focus is placed primarily on penetration capabilities of the consolidation agent; the material is strengthened only when it penetrates into sufficient depth from the surface and spreads evenly in the mass of the substance to be strengthened (a sharp transition between non-strengthened and heavily strengthened material leads to development of tension between layers and subsequent mutual separation). The rate of penetration of the consolidation agent depends mainly on the properties of the strengthened material (in particular, its porosity, moisture and pH value), properties of the solution (size of solved molecules, viscosity) and the consolidation method. The higher surface tension, the lower viscosity, density and contact angle at the interface between a solid and a liquid the consolidation liquid displays, the better its penetration. When disperse consolidation products are used, the size of particles and possibility of their penetration into the porous system is important.

Possibilities of production of nanosuspensions

Until recently, nanoparticles of calcium hydroxide have been obtained either through hydrolysis of calcium hydride (CaH_2) under specific experimental conditions or through reaction of calcium oxide or calcium hydride CaH_2 with water in organic environment in the presence of surfactants [15].

A more modern possibility of synthesising crystallised nanoparticles of calcium hydroxide is the reaction of sodium hydroxide (NaOH) and calcium chloride ($CaCl_2$) that is added (drop by drop) into water solution at 90 °C and the reaction produces calcium hydroxide $Ca(OH)_2$ and sodium chloride (NaCl) that is removed from the suspension subsequently. In the last stage of production, the lime particles are broken in a ball mill to particles of several μm to nm in size; the resulting clusters of particles are subsequently separated using ultrasound [16].

Another known production method involves the reaction of metallic calcium with water in alcohol medium [17] to [18]. The reaction occurs pursuant to this equation:

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

Yet another alternative is a method based on ion exchange between resin (anion) and water solution of calcium chloride at 20 to 25°C. Clean suspension containing nanoparticles of $Ca(OH)_2$ can be obtained quickly after separation of the resin from the suspension without any need for cleaning. Exhausted resins can be regenerated and re-used for repeated production of nanolime [19].

When manufacturing nanosuspension, it is relatively difficult to create accurately the required concentration; different concentrations are achieved by evaporating the solvent during manufacture. Stability of suspension is proportionate to the particle size – the smaller the particle, the lower stability. Kinetically stable dispersions can be obtained with short-chain aliphatic alcohols. The benefit of these alcohols is that they evaporate fast (the cycles can be repeated quickly) and, when compared to other solvents, they have low toxicity.

Verifying the efficiency of selected nanosuspensions

In the NAKI research project, lime nanosuspensions were designed and manufactured by the most frequent procedure of synthesis of $Ca(OH)_2$; these nanosuspensions were subsequently modified and enriched by other components that had been assumed to display positive potential for use in cultural heritage care. The nanosuspensions have been manufactured in close co-operation with the Centre of Polymer Systems of the Tomáš Baťa University in Zlín. Based on the results of preceding research, 3 various lime nanosuspensions have been prepared and tested [20] - [21]:

Ca4: Ca(OMe)2 dispersed in isopropyl alcohol;

Ca4O: calcium oxide dispersed in ethanol;

CaMg1: Ca and Mg pre-cursors have been dissolved in distilled water; subsequently, NaOH solution was added.

(Each nanosuspension was prepared in concentration of 5 g / l.)

In order to determine the crystalline structure of products, XRD powder analysis on the Rigaku MiniFlex 600 diffractometer was used. Each diffractogram was compared to the JCPDS Ca(OH)2 (JCPDS 01-076-0571) (Figure 1) card.

The basic parameters in assessment of potential success of strengthening include the capability of the plaster to absorb the consolidation agent and the depth of its penetration associated therewith. The average values of the depth of penetration of consolidation products range between several millimetres and several centimetres, depending on the size and character of the porous system and the size of particles of the strengthening agent. The laboratory research verified the depth of penetration of the tested nanosuspensions on plaster beams using phenolphthalein (Figure 2). The research demonstrated sufficient depth of penetration and equal distribution of the consolidation product.

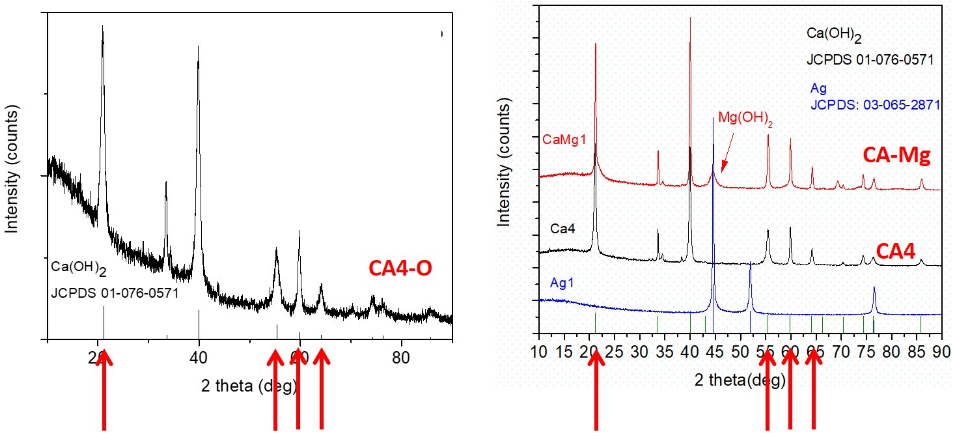

Fig. 1 - The XRD powder diffraction patterns of prepared products (Ca4-O, Ca4 and Ca-Mg) showing the peaks corresponding with the library diffractogram of $Ca(OH)_2$

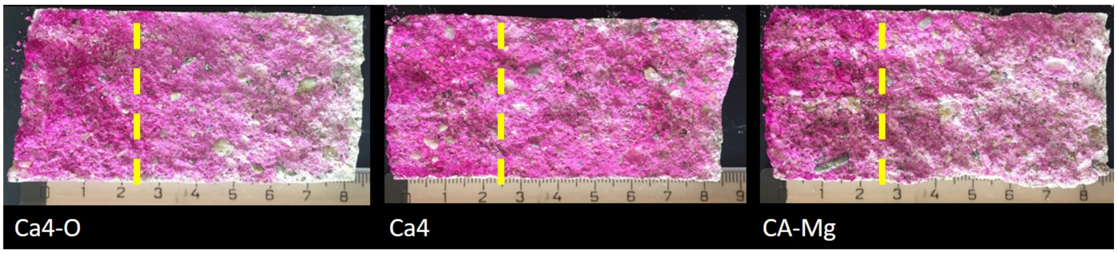

Fig. 2 - Verifying the rate of penetration of selected nanosuspensions: a) Ca4-O; b) Ca4; c) Ca-Mg. The photographs of sections of historic plaster samples showing the depth of penetration of consolidation product using colouring caused by application of phenolphthalein indicator (the yellow dotted line shows the border of 25 mm)

Another important characteristic is provided by assessment of sub-surface cohesion of the plaster (cohesion, ultimate tensile strength) that represents the condition of the historic material before and after consolidation, in terms of efficiency and quality of consolidation intervention to the degraded plaster surface. The efficiency of consolidation products can be verified in the case of plaster-coated surfaces using, for example, the “Scotch tape test” that can be accompanied by scanning electron microscopic examination. This will provide information about the deposit of the strengthening agents (i.e. lime) in the porous system of the degraded plaster. The scratch “Scotch Tape” test provides a reliable estimate of surface and shallow sub-surface strengthening after application of consolidation products and it provides a clear presentation of the differences between individual types of treatment or agents. However, the measuring of the cohesion is without any link to correlations to solidity characteristics; the result of the test is a “strengthened – not strengthened" statement (Figure 3).

RESULTS

Nanosuspensions of calcium hydroxide in alcohols represent an alternative of almost water-free restoration of lime-based historic surface finishes. Clear advantages of lime nanosuspensions prepared in alcohol include their material compatibility with the original structural binding agent (i.e. lime), small size of lime particles (this should have positive impact upon the depth of penetration), low number of application cycles which does not support mobilisation of water-soluble salts in the material.

The success of the strengthening process is influenced by a number of factors. The basic properties and parameters that need to be taken into consideration when designing the strengthening technology include: chemical and mineralogical composition of the material to be strengthened, hardness of the material before strengthening, size and shape of open pores, porosity, size of ions, molecules or particles of the active strengthening agent in the strengthening product, chemical composition and concentration of the active agent, speed of drying and hardening of the active agent in the strengthened substrate at specific temperature and moisture conditions of material and ambient air. The knowledge of the above parameters is a good basis when designing the strengthening technology - the type of the strengthening product, concentration of the active agent, method of application of the consolidation agents, number of repeated applications within one consolidation cycle, method of verification of substrate after impregnation.

a) b) c)

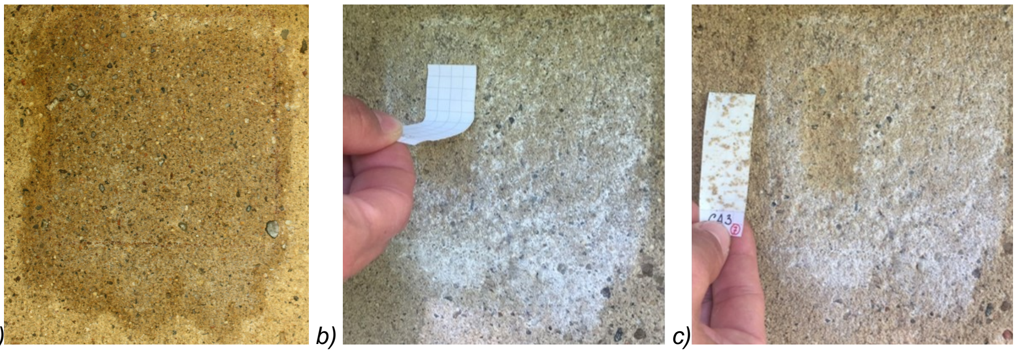

Fig. 3 - The Scotch tape test carried out in situ on the plaster of the historic building of the Voršilky Monastery: a) Test field after application of nanosuspension Ca4; b) after 28 days: pressing down of an adhesion tape during the Scotch tape test (third measuring out of ten); c) after the test tape was torn away.

CONCLUSION

At the moment, nanomaterials are applied in historic and cultural heritage structures in the Czech Republic occasionally and sufficient know-how and experience for their reliable and permanent application are not available. However, if these new materials should be applied, e.g., to surfaces or to below-surface layers of materials, verified know-how about long-term behaviour of these materials (i.e. verifying the stability in light of attack of outside environment, influence of radiation, interaction with the ambient environment, transparency, diffuse transmittance, resilience against chemical and biochemical degradation, etc.) would be required so as to avoid gradual and irrecoverable damage of valuable historic structures such as paintings, plaster, wooden, stone elements, etc. The tested nanosuspensions comply with the assumptions of their future use to consolidate porous lime-based materials.

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