

# COMPARISON OF SELECTED PHYSICAL PROPERTIES OF TESTED NANOSUSPENSIONS – THE RESULTS OF THE EXPERIMENTAL RESEARCH OF THE DEGREE OF SEDIMENTATION AND THE DEPTH OF PENETRATION IN REFERENCE MATERIALS IN LABORATORY CONDITIONS

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## ABSTRACT

Between used and already verified technologies for the reinforcement of plasters mainly include nanosuspension containing nanoparticles of calcium hydroxide and nanomaterials based on magnesium hydroxide and barium carbonate [1]. Individual lime nanosuspension, which consists of nanoparticles of calcium hydroxide, are dispersed in an alcoholic environment and they differ from each concentration and type of alcohol. When the material is cured, carbonatation occurs, as well as in the case of fresh plaster, where the calcium hydroxide reacts with atmospheric carbon dioxide to produce calcium carbonate. Due to the deposition of calcium carbonate in the damaged material, occurs re-strengthened ties and its hardening. The undoubted advantage of the consolidation of plaster using nanolime is the low number of impregnation cycles, where after a few applications nanosuspension occurs to the reinforcement of degraded material.

## KEYWORDS

Nanolime, nanosuspension, plaster, consolidation, sedimentation, depth of penetration

## INTRODUCTION

The success of the consolidation process using the "nanolime" is influenced by the mineralogical and chemical composition of the treated material, characteristics of the porous system, the structure of the surface, degree of reinforcement before treatment, the properties of the active substance of the strengthening agent (the size of the ions and particles, chemical composition, concentration, rate of drying and hardening, etc.) and last but not least, also the temperature-humidity conditions during application. At sufficiently low surface tension of the lime nanosuspension is to ensure optimum wetting, which is responsible for the depth of penetration of the dispersions in the porous structure of the plaster [2].

Until the recent past, it was possible nanoparticles of calcium hydroxide obtained either by the hydrolysis of calcium hydride ( $\text{CaH}_2$ ) under specific experimental conditions or by reactions of the calcium oxide  $\text{CaO}$ , or of calcium hydride  $\text{CaH}_2$ , with water in an organic environment, in the presence of surfactants [3]. A newer option, how to synthesize crystalline nanoparticles of calcium hydroxide, is the reaction of sodium hydroxide  $\text{NaOH}$  and calcium chloride  $\text{CaCl}_2$ . Calcium chloride  $\text{CaCl}_2$  is dropwise added to an aqueous solution at a temperature of 90 °C and the reaction creates

calcium hydroxide  $\text{Ca}(\text{OH})_2$  and sodium chloride  $\text{NaCl}$ , which is from the suspension subsequently removed. In the last stage of production are particles of lime broken in the ball mill to a particle size of several  $\mu\text{m}$  to  $\text{nm}$  and the resulting clusters of particles are scattered using the ultrasound [4]. Another known manufacturing process involves the reaction of the metal calcium with water in an alcoholic medium [5].

The stability of the produced nanosuspension is directly proportional to the particle size – the smaller the particles, the lower stability and vice versa. Kinetically stable dispersions can be obtained with aliphatic alcohols with short chain. The advantage of these alcohols is that it quickly evaporates (the possibility of rapid repeat cycles) and in comparison with other solvents have low toxicity.

The size of the nanoparticles is in the lime nanosuspension usually varies in the range of 150 – 300 nm, which creates restrictions in relation to the size of the pores of the treated material. In the suspension there are also larger particles, which most often arise from accidental cluster of primary particles during the manufacture or subsequent storage. The viscosity and color of the suspension varies according to the concentration – the more concentrated the mixture is more viscous and usually whiter (or may have a pale ochre or grey, depending on the source material and method of production).

## TESTED NANOSUSPENSIONS

In the framework of the research project NAKI nanosuspensions of  $\text{Ca}(\text{OH})_2$  were produced from different precursors, which were subsequently modified and enriched by other components that were expected to have a positive potential for use in conservation. Production of nanosuspensions took place in close cooperation with the Center of Polymer System UTB in Zlín.

For the purposes of experimental tests were made 4 lime nanosuspensions [6]. Three samples were prepared by NaOH precipitation method (mark. CA3, CA5 and CA-Mg) and one sample (mark. CA4) by alkoxide hydrolysis, where

- a sample of CA3 was made from a portion of the  $\text{CaCl}_2$  solution (the value of content of dry solid is 1,66 g),
- a sample of CA4 was made from a portion of the methoxide calcium  $\text{Ca}(\text{OCH}_3)_2$  (the value of content of dry solid is 1,39 g),
- a sample CA5 was made from a portion of the acetate phosphate  $\text{Ca}(\text{OCOCH}_3)_2 \cdot \text{H}_2\text{O}$  (the value of content of dry solid is 1,52 g),
- a sample of the CA-Mg was made from a portion of the acetate phosphate  $\text{Ca}(\text{OCOCH}_3)_2 \cdot \text{H}_2\text{O}$  and acetate magnesium oxide,  $\text{Mg}(\text{OCOCH}_3)_2 \cdot 4\text{H}_2\text{O}$  (the value of content of dry solid is 1,46 g).

Individual nanolime suspensions were prepared by dispersing 0.75 g of the products (CA3, CA4, CA5 and Ca-Mg) in 250 ml of isopropyl alcohol. To increase the homogeneity of the resulting dispersion was each suspension placed for 1 hour in an ultrasonic bath.

In order to compare the individual results of the tests and the effectiveness of the newly prepared nanosuspension was also prepared whitewash (mark. CA, the value of content of dry solid is 1,68 g) and used CaLoSiL®E5 (the value of content of dry solid is 0,814 g).

## RATE OF SEDIMENTATION

The rate of sedimentation of dispersed particles is among the important criteria in the evaluation of the functionality nanosuspension. If the suspension is functional, “it must be able to suspend the dispersion phase after the period of the existence of the product and/or easily dispersed, if there was a sedimentation. To the stability of the dispersed phase contributes to a number of factors and these can be thermodynamic or kinetic in origin” [7].

Sedimentation means the movement of dispersed particles of the dispersion system, which in this case is induced by the action of gravitational forces. The gravitational force acts perpendicular to the surface of the earth and leads to the deposition of the particles on the bottom of the container. The rate and character of sedimentation are mainly affected by the size and shape of the particles, the viscosity of the dispersion environment, the ratio of the densities of the particles and the dispersion environment and the other. "Sedimentation occurs to the uneven distribution of concentration, which has resulted in the diffusion of dispersion of the particles. Diffusion the dispersion of particles will seek compensation concentration, will therefore work in the opposite direction than the sedimentation rate, i.e. the direction from the earth's surface. Diffusion and sedimentation operate in the opposite direction and leads to the creation of sedimentation equilibrium, when at any point of the system is the sedimentation rate equal to the rate of diffusion" [8].

For all the above-mentioned funds (nanosuspension CA3, CA4, CA5, CA-Mg, whitewash CA and CaLoSiL®E5) was monitored the rate and speed of settling of the solid ingredients in the mixture in order to determine and compare the degree of stability of the lime mixture.

In the laboratories of the FCE CTU in Prague were prepared lime nanosuspension, whitewash (mark. CA) and CaLoSiL®E5 (mark. CaL) cast into test tubes of a volume of 20 ml. Samples were left in a laboratory environment at a temperature of 24 °C. The sedimentation process was continuously monitored and after a period of 60 days recorded and photographically documented (Figure 1). Sedimentation rate is zobrazena in a bar and a comparative chart (Chart 1, 2).

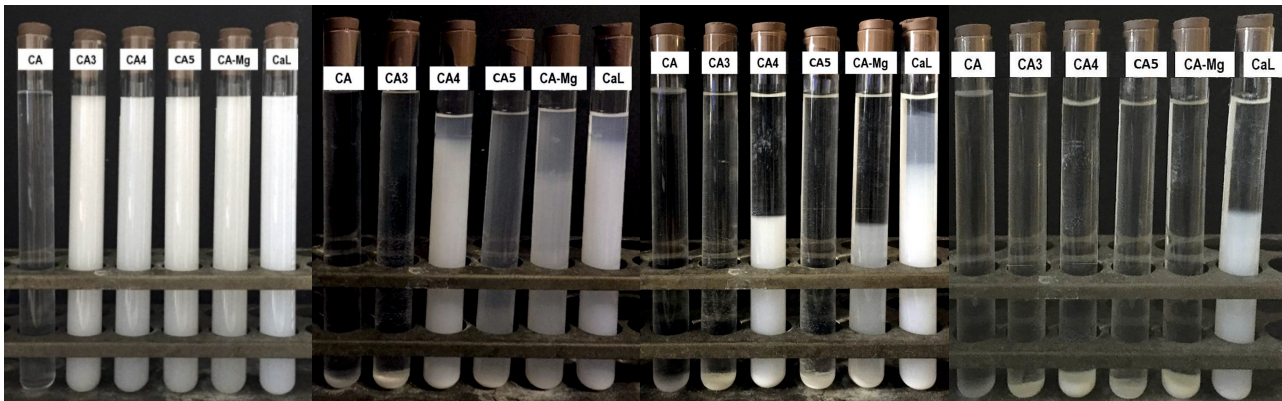


Fig. 1 - Photographic documentation of sedimentation nanosuspensions: the tube containing the studied lime nanosuspension. The documentation captures the sedimentation status: from the left after 24 hours, after 14 days, after 28 days and after 60 days. (Legend: CA =  $\text{Ca}(\text{OH})_2$ , CA3 =  $\text{CaCl}_2$ , CA4 =  $\text{Ca}(\text{OCH}_3)_2$ , CA5 =  $\text{Ca}(\text{OCOCH}_3)_2 \cdot \text{H}_2\text{O}$ , CA-Mg =  $\text{Ca}(\text{OCOCH}_3)_2 \cdot \text{H}_2\text{O}$  a  $\text{Mg}(\text{OCOCH}_3)_2 \cdot 4\text{H}_2\text{O}$  a CaLoSiL®E5)

## RESULTS OF LABORATORY RESEARCH OF THE RATE OF SEDIMENTATION

In the case of samples CA, CA3, CA5 and CA-Mg was possible to observe sedimentation of the particles almost immediately after their casting into tubes. In the case of samples CA4 and CaLoSiL®E5 occurred to the initiation of the deposition of the particles after 5 days of monitoring.

The fastest sedimentation took place in the case of the sample of whitewash, when its termination occurred already after 12 hours. Column of the settled particles reached a height of 5 mm.

The second fastest sedimentation was recorded for a sample of lime nanosuspension CA3, when the column of the settled particles reached after 3 days the height of 4 mm.

With a long interval of time – i.e. for 17 days, was terminated sedimentation of nanosuspension CA5, when the sedimentation column reached a height of 4 mm.

A sample of the CA-Mg ended the sedimentation after 38 days, the height of the sedimentation column reached a height of 5 mm.

The slowest sedimentation rate between the tested nanosuspensions, i.e. 43 days, was recorded for a sample of CA4. In terms of the amount of settled particles the results were the worst, the height of the sedimentation column was 8 mm.

Commercially available nanosuspension CaLoSiL®E5 did not shut the sedimentation even after 60 days, the height of the sedimentation column to 60th day was 4 mm. This positive result is probably influenced both by stabilizers, which suspension contains, and, secondly, the shape of the nanoparticles lime (hexagonal, very thin particles).

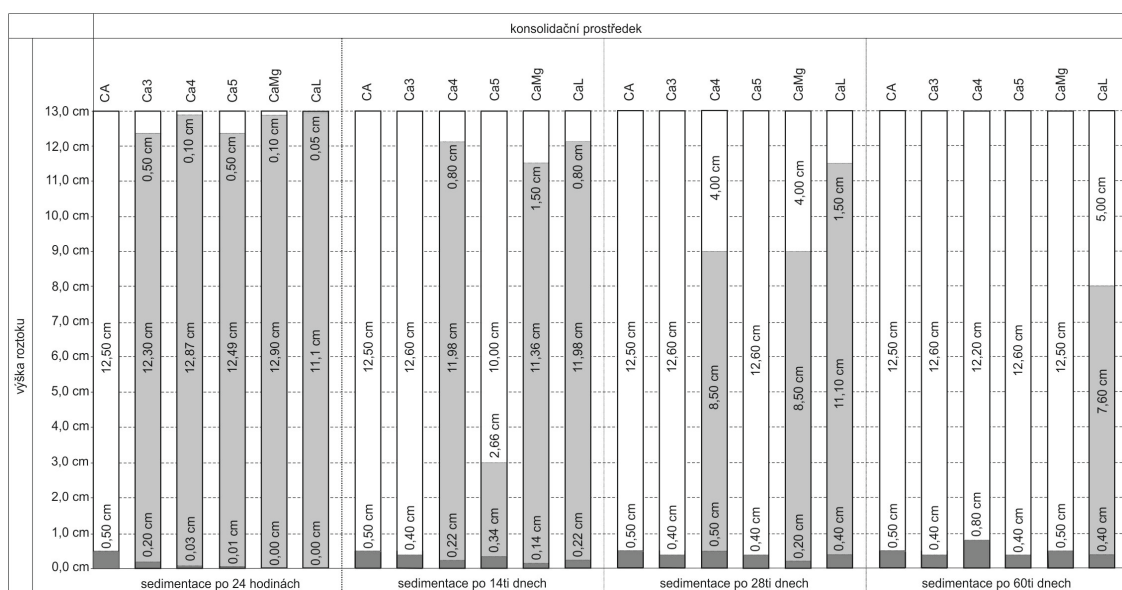


Chart 1 - The course of sedimentation of the samples CA, CA3, CA4, CA-Mg and CaL. The chart shows the progress of sedimentation from the left: after 24 hours after 14 days after 28 days and after 60 days (Legenda: CA =  $\text{Ca}(\text{OH})_2$ , CA3 =  $\text{CaCl}_2$ , CA4 =  $\text{Ca}(\text{OCH}_3)_2$ , CA5 =  $\text{Ca}(\text{OCOCH}_3)_2 \cdot \text{H}_2\text{O}$ , CA-Mg =  $\text{Ca}(\text{OCOCH}_3)_2 \cdot \text{H}_2\text{O}$  a  $\text{Mg}(\text{OCOCH}_3)_2 \cdot 4\text{H}_2\text{O}$  a CaLoSiL®E5)

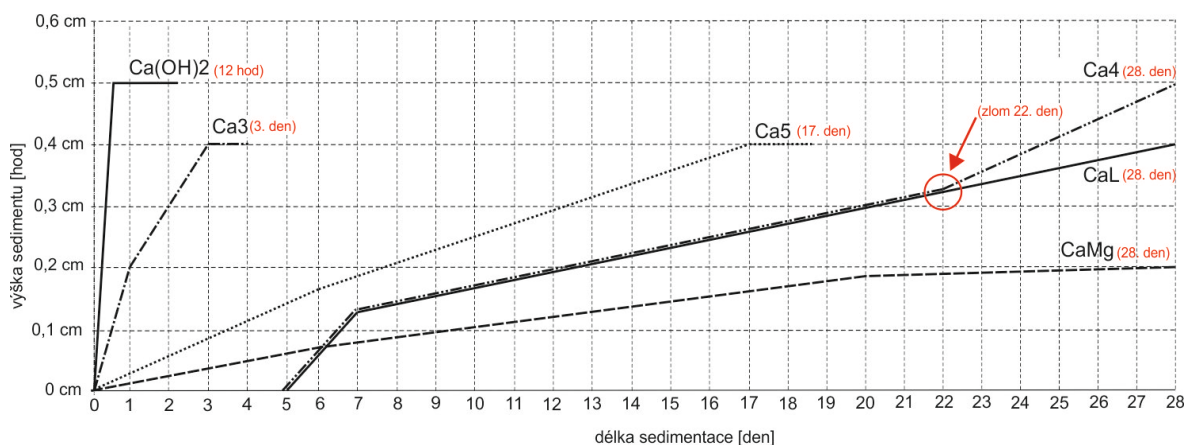


Chart 2 - Comparison of the sedimentation curves of the samples CA, CA3, CA4, CA-Mg and CaL. (Legend: CA =  $\text{Ca}(\text{OH})_2$ , CA3 =  $\text{CaCl}_2$ , CA4 =  $\text{Ca}(\text{OCH}_3)_2$ , CA5 =  $\text{Ca}(\text{OCOCH}_3)_2 \cdot \text{H}_2\text{O}$ , CA-Mg =  $\text{Ca}(\text{OCOCH}_3)_2 \cdot \text{H}_2\text{O}$  a  $\text{Mg}(\text{OCOCH}_3)_2 \cdot 4\text{H}_2\text{O}$  a CaLoSiL®E5)

In the case of nanosuspension CA4 it is necessary to consider the positive postponement of the beginning of sedimentation for 5 days and the same course of sedimentation with commercial nanosuspension CaLoSiL®E5 (up to 22. day), which confirms approximately the same distribution of the particles in the range of 50 – 250 nm.

The best results in terms of the speed of sedimentation of solid particles of nanosuspension was achieved in the case of nanosuspension CA-Mg (38 days) and CA4 (43 days) and in terms of the height of the sedimentation column showed the best result, i.e. 4 mm, nanosuspension CA3 and CA5.

## DEPTH OF PENETRATION OF NANOSUSPENSIONS

The ability of the plaster to absorb the consolidation substance, and the associated depth of its penetration, are among the basic evaluation parameters when assessing the assumption of the consolidation. Average values of penetration of the consolidants range from a few millimeters to several centimeters depending on the size and nature of the porous system and the size of the particles of the reinforcing substance [8].

For the experimental tests of verification of the depth of penetration of the tested device were used test prisms about the size of a 4 x 4 x 9 cm. The test samples were made in the laboratories of the FCE CTU in Prague. The composition of the mortar mixture was determined on the basis of the original recipe, which was detected by analysis of the removed plaster of historic building in-situ: 5 kg of dry hydrated lime, 12.5 kg of river sand (fraction 0 – 2 mm) and 3.5 l of water. Application of consolidation bars was held on the 24-month-old test samples.

The samples were put into Petri's dishes on filter paper and then was on the test samples applied consolidation substance (volume of 20 ml) using a dropper. Application of consolidants was carried out continuously only to the center of the top surface of the sample, when every other application has been made after absorbing the previous, and only to such extent, in order to avoid sagging of the solutions on the walls of the samples. The fastest absorption consolidants was recorded in the application of whitewash (mark. CA), and then the consolidation of suspensions in order CA5, CA3, CA-Mg, CA4 and CaLoSiL®E5 (mark. CAL).

After the application of consolidants were samples along their height resolved and the phenolphthalein indicator (1 % solution in ethanol) was applied on the entire surface of the cut by brush. To determine the depth of penetration was subsequently followed by a section of the sample by the change of the color caused by the phenolphthalein indicator (Figure 2) when the intense red - purple detected the non-carbonated calcium hydroxide, thus the depth of penetration of the consolidation agent.

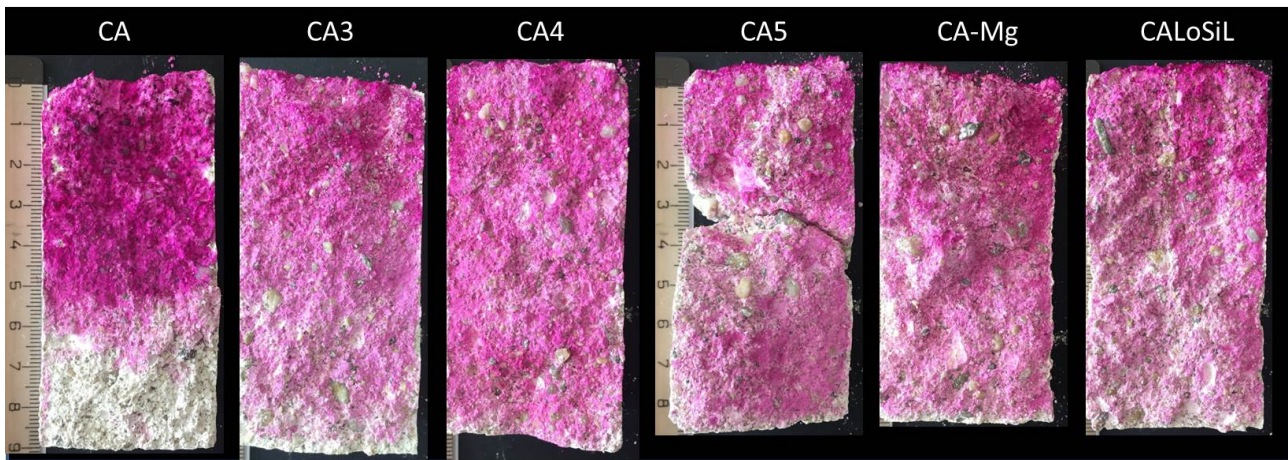


Fig. 2 - Samples of plasters treated with 20 ml of the consolidation agent: the depth of penetration of the consolidation agent was highlighted by phenolphthalein indicator in the section of the sample (Legend: CA =  $\text{Ca}(\text{OH})_2$ , CA3 =  $\text{CaCl}_2$ , CA4 =  $\text{Ca}(\text{OCH}_3)_2$ , CA5 =  $\text{Ca}(\text{OCOCH}_3)_2 \cdot \text{H}_2\text{O}$ , CA-Mg =  $\text{Ca}(\text{OCOCH}_3)_2 \cdot \text{H}_2\text{O}$  a  $\text{Mg}(\text{OCOCH}_3)_2 \cdot 4\text{H}_2\text{O}$  a  $\text{CaLoSiL}^{\text{®E5}}$ )

## RESULTS OF LABORATORY RESEARCH OF THE DEPTH OF PENETRATION

The smallest achieved depth of penetration was measured in the case of whitewash (mark. CA), which was 52 mm. Stained by the phenolphthalein indicator (1 % solution in ethanol) shows a uniform saturation throughout the penetrated area, the boundary between penetrated and non-penetrated material is narrow (width 10 mm) and clearly defines the depth of penetration of the consolidation agent.

The phenolphthalein indicator applied to the sample with nanosuspension CA3 stained the cut to a depth of 75 mm, and the intensity of staining decreases after crossing the border 35 mm. This phenomenon of reducing the intensity of the discoloration in the cut below the boundary of 35 mm can be observed even in the application of nanosuspension CA5, Ca-Mg and CaLoSiL<sup>®E5</sup>. Below the threshold of 35 mm is noticeable a slight brighten of the indicator, which indicates penetration of a smaller amount of lime nanoparticles in greater depth.

The most intense discoloration of the sample in the entire area of the incision after application of the indicator was observed in the case of nanosuspension CA4. Visual evaluation of coloration of the upper surface of the test samples after the application of nanosuspensions indicates the deposition of lime and the unwanted emergence of whitish discoloration of the plaster. The possibility of removing white staining by application of  $\text{H}_2\text{O}$  was not part of the carried out laboratory tests of reason, to avoid affecting the penetration depth of nanosuspensions.

From the above results of the measurement of the depth of penetration is evident in the high rate of penetration of nanosuspensions into the plaster, where the best results were achieved by applying nanosuspension CA4.

## CONCLUSION

The CA4 ( $\text{Ca}(\text{OCH}_3)_2$ ), CA-Mg ( $\text{Ca}(\text{OCOCH}_3)_2$ ,  $\text{H}_2\text{O}$  and  $\text{Mg}(\text{OCOCH}_3)_2$ ,  $4\text{H}_2\text{O}$ ) nanosuspension tests have comparable laboratory results in both sedimentation and penetration depths. In this work, different product properties were observed depending on the calcium precursor used.

The sedimentation results of tested CA4 and CA-Mg nanosuspensions demonstrate good stability and therefore long-term functionality. For these devices, laboratory tests have also proved good penetration of the suspension into sufficient depth of material to be treated.

Compared to a traditional lime-consolidating agent, CA4 and CA-Mg have a longer service life and greater penetration depth, indicating the suitability of these materials for use in reinforcing of historical plaster coats.

## ACKNOWLEDGEMENTS

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