CaLoSiL®

Consolidation of stone, plaster and mortar

Imprint

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CaLoSiL®- Application recommendations

The following guideline summarises the most frequently asked questions concerning the properties, uses and handling of CaLoSiL® nanolime dispersions. These have been developed in cooperation with scientists and restorers from many countries. Whereas detailed information about the fundamentals of nanolime dispersions and their reaction mechanism can be found in the book „Nanomaterials in Architecture and Art Conservation" (G. Ziegenbalg, M. Drdacky, C. Dietze, D. Schuch; Pan Stanford Publishing Pte Ltd, 2018. ISBN: 9789814800266), this guideline focuses on practical advice for the successful use of nanolime dispersions in the conservation of stone, mortar and plaster as well as wall paintings.

What are the main applications of CaLoSiL® products?

CaLoSiL® nanolime dispersions are used in the conservation of stone, mortar and plaster as well as for the consolidation of wall paintings and stucco. Carbonatic stones in particular are highly suitable for **structural consolidation** with CaLoSiL®.
It is also possible to fill and close small gaps or cracks or add the products to lime-based mortars and injection grouts.

Apart from their application as a consolidation agent, CaLoSiL® can also be used prophylactically **against microbial contaminations** or to remove fungal and algae growth.

Which CaLoSiL® products are available and what are their properties?

All products contain calcium hydroxide nanoparticles with sizes between 50 nm and 250 nm, which is around 100 times smaller than conventional lime putty. The small particle size and the special synthesis guarantee a storage of at least 6 months without sedimentation (storage conditions: unopened original container at temperatures between 5 – 25 °C). The colloidal dispersion of fine calcium hydroxide particles in several alcohols results in the characteristic white-opal colour of the products.

All of the standard products are summarised in the Table 1.

Table 1: Standard products of CaLoSiL®.

Products	Solvents	$Ca(OH)_2$ concentration
CaLoSiL® E	Ethanol	5 – 50 g/L
CaLoSiL® IP	*iso*-Propanol/Ethanol	5 – 25 g/L
CaLoSiL® NP	*n*-Propanol/Ethanol	5 – 25 g/L
CaLoSiL® grey	Ethanol	5 – 25 g/L
CaLoSiL® paste like	Ethanol	100 g/L
CaLoSiL® micro	Ethanol	120 g/L

The product designation describes the composition and the concentration. The letter after the product name CaLoSiL® stands for the alcohol:

E - Ethanol
IP - *iso*-Propanol
NP - *n*-Propanol

The number following the letters represents the concentration of calcium hydroxide in g/L. CaLoSiL® E50, for example, means 50 g/L calcium hydroxide ($Ca(OH)_2$) dispersed in ethanol. The different solvents result in various physico-chemical properties such as surface tension, viscosity and evaporation behaviour. The slowest evaporation is typical for products dissolved in *n*-propanol.

CaLoSiL® grey is characterised by a light grey colour due to a slightly different synthesis. All of the other properties are the same as CaLoSiL® E25. It is particularly suited to consolidate wall paintings and darker surfaces.

CaLoSiL® micro is a suspension of calcium hydroxide particles with a size of 1 – 3 µm, which is between nanolime and conventional lime. In contrast to the other products, it has a high potential for sedimentation so that it has to be shaken before use. It is especially suited for filling fractures and for the modification of lime mortar or injection grout.

CaLoSiL® paste like is also a product with a high calcium hydroxide content, so that it too has to be shaken before use. Like CaLoSiL® micro, this product is mostly used to fill gaps or cracks and to modify special lime-based mortars and injections grouts.

All CaLoSiL® products can be mixed with each other as well as with ethanol, *iso*-propanol, *n*-propanol and organic solvents such as acetone, hexane or heptane.

Diluting with water will lead to a destabilisation of the nanolime dispersion and is therefore not recommended. The particles will coagulate and a gel may form. The diagram in Figure 1 provides a brief overview of which product is suitable for different problems.

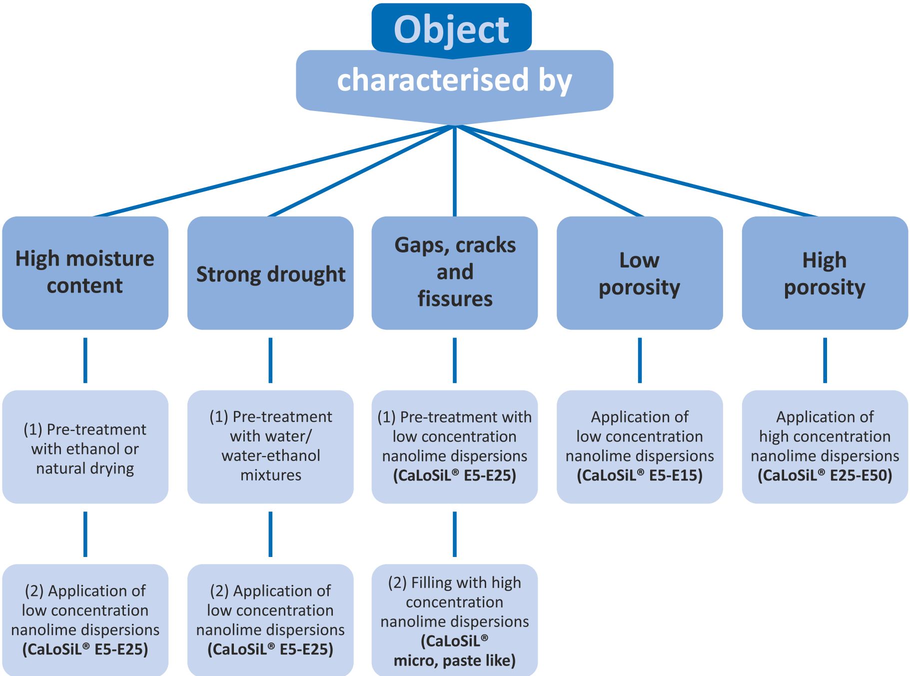

Figure 1: Application of nanolime dispersions depending on objective characteristics.

What is the principle mode of action of CaLoSiL®?

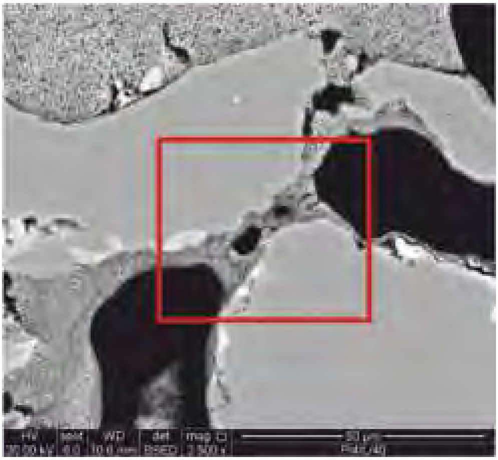

Figure 2: SEM-picture of a porous stone sample treated with CaLoSiL®. Red frame indicates the bond between loose particles with nanolime. (Photo: E. Mascha)

Treatment with CaLoSiL® will result in the precipitation of fine calcium hydroxide particles during the evaporation of the alcohol. These particles will be converted into calcium carbonate, mainly calcite, through a reaction with atmospheric carbon dioxide. Loose particles are reconnected and open pores are partially filled and stabilised. Figure 2 shows a typical, consolidated, porous stone. The nanoparticles are able to penetrate deep into the stone and a consolidation of the surface as well as of deeper layers is possible. The alcohol ultimately evaporates without leaving any residue. Another advantage is the combination of lime and alcohol to produce antimicrobial effect. The alcohol removes the residual moisture and the lime provides an alkaline milieu which removes the basis of any microbial growth. Figure 3 shows the treatment of a stone covered with lichens. CaLoSiL® can also be combined with other consolidation agents. Silicic acid esters in particular are preferred and displayed some very promising results.

Figure 3: Ancient seats at the theatre of Megalopolis (Greek).
Red frame: untreated surface, yellow: cleaned area with CaLoSiL®.

How are the products applied?

All CaLoSiL® products are liquids and can be applied with all standard techniques such as: Spraying • Immersion • Injection (pipette or syringe) • Vacuum suction (see Figure 4)

The most suitable application technology has to be chosen on the basis of the characteristics of the substrates and preliminary tests. **Spraying** is the most favourable way to consolidate powdery surfaces. The penetration depth is often low, but a significant consolidation of surface layers can be achieved. This is ideal for the consolidation of wall paintings. Large surfaces can be treated in reasonable times by using liquid jet pumps. When it comes to filling cracks and detached layers as well as the saturation of small surfaces, nanolime dispersions can be applied to the substrates using **syringes** or **pipettes**. **Infusionkits** may also be used if a slow and continuous saturation into deeper layers is necessary. **Vacuum suction** is always a favourable way to guarantee a complete saturation of porous objects. Application with a brush or roller is in principle possible, but is not recommended. Brushing often entails the risk of blocking surfaces with fine particles such as dust or the results of biological growth. These are mechanically liberated by the action of the brush and may fill voids and pores, thus making the penetration of the nanolime dispersions impossible.

Figure 4: Application possibilities for CaLoSiL®.

Practical tips for a successful application

The application of nanolime dispersions should always be realised at low temperatures (5 – 25 °C) and under conditions that lead to slow evaporation rates. The treated surfaces should be protected against rain and direct sunlight for at least 24 hours. The penetration depth of nanolime depends on several factors:

- Structure and surface properties of the substrate • Porosity and suction capacity
- Presence of salts • Moisture content • Temperature and air humidity

An initial impression of the characteristics of nanolime dispersions can be obtained by determining the penetration behaviour into materials. The suction behaviour of substrates can be determined by tests with the Karsten tube. The penetration depth can be visualised by spraying treated surfaces with an ethanolic, 1 wt.-% phenolphthalein solution (30 vol.-% water, 70 vol.-% ethanol), which acts as pH-sensitive indicator. The solution is colour-less in the pH-range between 0 and 8.2, but turns purple at higher values. It is also possible to pretreat the material (for example mortar prism) with phenolphthalein solutions and to then track the capillary rise by the change in colour caused by the migration of the calcium hydroxide nanoparticles (see Figure 5). If the purple colour disappears, carbonation is complete and all of the calcium hydroxide ($Ca(OH)_2$) particles have been converted to calcium carbonate ($CaCO_3$).

Figure 5: Phenolphthalein indicating the diffusion of CaLoSiL® E25 into a porous mortar sample.

It is always important that only surfaces be treated that are able to absorb the nanosol. Nanolime dispersions cannot diffuse through dense skins such as gypsum layers, biological growth or dust. Loose layers beneath dense skins can be consolidated when the nanolime dispersions are introduced into these zones through micro drills. Penetration is also impossible when the material is wet and water saturated, especially when low porous substrates have to be strengthened. Apart from natural drying, pretreatment with alcohol will result in the rapid removal of water. Nanolime dispersions can be applied after the evaporation of the water-ethanol-mixture.

Transportation is only possible by means of capillary action in small voids, fissures and cracks. In order to guarantee a deep penetration, it is always necessary to prevent a fast blocking of the flow paths. Although the particles are small near-surface blocking is possible, especially when relatively dense materials have to be treated. In most cases, filter cake-like zones form, thus preventing any further transport of the nanosols into deeper zones.

Therefore, it is always advisable to start all treatments with low concentrations of nanosols, for example of only 5 g/L. These can be prepared by means of dilution, for example of CaLoSiL® E25 in ethanol or *iso*-propanol. In a second step, materials with a higher concentration can be used. In most cases, repeated treatments with diluted nanolime dispersions have resulted in higher consolidation effects than single treatments with higher concentrations of sols. All CaLoSiL® products can be fully intermixed. An oversaturation of the substrate must always be avoided. Any excess nanolime should be sponged off immediately. One main problem in many applications is the formation of a white haze after the application of nanolime dispersions. This means that, although a good penetration has been achieved, the treated materials are characterised by the occurrence of a white haze after drying.

General rule: It is always better to use products with a lower concentration several times than a product with a higher concentration only once.

It is always beneficial to prepare test areas or test samples. It also has to be remembered that synthetic test samples are not absolutely identical to natural weathered stone, but they are of course useful to get a basic idea about the general behaviour of the product. If possible, it is always better to use original samples for testing.

Why does a white haze form and how can this be prevented?

The formation of a white haze following the treatment with CaLoSiL® is the most frequently asked question. Figure 6 shows an affected area.

What are the possible reasons for this phenomenon?

- Incomplete penetration of the nanolime dispersion due to a dense surface.
- The concentration that was applied was too high.
- Reverse-migration of the nanolime particles took place during the evaporation of the alcohol.

An oversaturation of the substrate must always be avoided. Any excess nanolime has to be sponged off immediately.

Although a good penetration has been achieved, the treated materials may display a white haze after drying. Apart from overdosing, the main reason for this is a reverse-migration of the nanoparticles during evaporation of the alcohol. In addition, the treatment of humid/wet substrates characterised by a low porosity with relatively high concentrations of nanolime dispersions can cause the formation of white haze.

The following recommendations are given to prevent the formation of white haze:

- Pretreatment with CaLoSiL® E5.
- Nanolime dispersions should always be applied at low temperatures (5 – 25 °C) and under conditions that lead to slow evaporation rates. The treated surfaces should be protected against rain and direct sunlight for at least 24 hours.
- Covering the treated surfaces with a plastic foil or wet cloths are a favourable way to prevent rapid evaporation.

Figure 6: Plaster treated twice with CaLoSiL® E25.

- If allowed by the characteristics of the substrates (pore radii, suction behaviour etc.), small amounts of CaLoSiL® micro or acetone should be added to the nanolime dispersion that is used.[1]
- **Aftertreatment** with:
  - Water (careful spraying to moisturise)
  - Ethanol
  - Ethanol-water mixtures
  - 0.5 wt.-% Hydroxylpropyl cellulose in ethanol/water mixtures (1 : 1 by volume)[1]

The aftertreatment with water has to be discussed from different points of view:

- All nanolime dispersions form $Ca(OH)_2$ agglomerates with significantly larger particles than in the original product after the addition of water. This limits their penetration into narrow structures. On the other hand, when coagulation takes place in the pore space, reverse migration can be safely prevented.
- The capillarity of water is much higher than that of alcohols. If a capillary-active system is treated with nanolime dispersions followed by water, the water forces the nanolime dispersion deeper into the substrate.
- If a system with narrow capillaries is aftertreated with too much water, gel-like calcium hydroxide layers quickly form on the surface. Enhanced white haze formation is possible.

In conclusion, a careful aftertreatment with small volumes of water (or water/ethanol mixtures) significantly reduces the formation of white haze.

[1] "Calcium hydroxide nanosols for the consolidation of porous building materials results from EU-STONECORE project", A. Dähne, C. Herm; Heritage Science, 2013, 1:11.

What are the benefits of combining CaLoSiL® and silicic acid esters?

Silicic acid esters (SAEs), especially tetraethyl orthosilicate (TEOS), have found broad applications in conservation interventions over the past decades. The consolidation effect is caused by silica gels, which form during the hydrolysis of TEOS. Main drawbacks of SAEs are:

- Their use is irreversible, meaning that conservation treatments cannot be undone in the future.
- SAEs are unable to bridge large spaces, making them unsuitable as a consolidant for flaking and scaling stones.
- Problems occur when permanent hydrophobic properties remain after the application, especially where the relative humidity and moisture content conditions in the material are either too low or too high due to sorption.
- It is difficult to apply SAE-based consolidants on objects that have a high concentration of salts and/or are affected by damp.
- The consolidation of carbonatic materials is difficult.

In principle, there are two possibilities for the combination of nanolime and SAEs:

- Preparation of homogeneous mixtures of nanolime dispersions and SAEs.
- Successive application of nanolime dispersions and SAEs.

The combination of both consolidants has the following advantages:

- The alkaline character of nanolime induces enhanced gel formation due to the presence of hydroxide ions. The higher the nanolime content, the faster gelation takes place and the higher the mechanical stability of the formed gels.
- Nanolime contains small amounts of water as a result of the manner of its synthesis. Due to the presence of an excess of ethanol, *iso*-propanol or *n*-propanol, mixing with TEOS is possible in any ratio. Water also accelerates the hydrolysis of TEOS. Additional water can be added to the nanolime-TEOS mixtures to support the mixing ratio and the reaction time if necessary.

If homogenous mixtures are used, weak gels are usually obtained. The gel time decreases with an increasing amount of the nanolime dispersion. Such mixtures have to be applied before the start of any significant hydrolysis and condensation reactions. Otherwise, no or only extremely limited penetration will be achieved. Extensive investigations have shown that the highest mechanical properties are obtained with a **successive treatment**. What is important is that the treatment with nanolime dispersions take place in the first step. The aftertreatment of areas which have first been treated with SAEs has no positive effects. The nanolime dispersions are unable to penetrate into treated zones. They are also unable to convert surfaces that have hydrophobic properties into ones with hydrophilic properties after SAE has been applied.

The following recommendations are given for the successive application of nanolime dispersions and SAE:

- In a first step, the substrate has to be saturated with CaLoSiL®. Depending on the suction behaviour and the overall conditions, single or repeated treatments are possible. In the latter case, the second and all further treatment steps can be realised after the alcohol in the nanolime dispersion has evaporated. In the majority of cases, however, a single pretreatment with the nanolime dispersion is sufficient. The standard product is CaLoSiL® E25, through dispersions with a lower nanolime contents may also be favourable.
- The SAE treatment should be carried out 24 hours after the last application of the nanolime dispersion. It could be shown that both earlier and later applications are connected with a lower final strength of the treated material.

General rule:
1. Application of CaLoSiL® E5 – E25; 24 h Dwell time; 2. Application of SAE

The nanolime dispersions form a layer of fine calcium hydroxide particles on treated surfaces. These can act as anchor for the SAEs. This makes it possible to treat materials that are normally difficult to strengthen with SAEs, mainly calcareous materials. Finally, the alkaline character of nanolime dispersions results in the accelerated hydrolysis of the SAE and hydrophilic surfaces are obtained much faster than by a simple SAE treatment.

Are there any safety instructions which must be observed?

All CaLoSiL® products are **highly flammable** and **alkaline**. Highly flammable aerosols are formed which must not be inhaled, especially if the products are applied by spraying. Avoid all sources of ignition. The wearing of **protective gloves** and **safety glasses** is recommended, along suitable clothing. Ensure adequate ventilation! Please pay attentions to the safety data sheets. All products are stable for at least six months. Storage for longer than 12 month is not recommended. If the fine calcium hydroxide particles have settled in a sediment, they can be dispersed again by shaking the closed bottle. The applicability will be not affected.

Potentially health-damaging effects of nanoparticles are currently an extremely controversially question. It has to be emphasized that the potential risk generally concerns particles smaller than 10 nm. All CaLoSiL® products have particle sizes above 50 nm. A comprehensive study was recently published on this topic. It could be confirmed that nanolime dispersions do not have any cytotoxicity.[2]

[2] „Cytotoxicity and antibacterial activity of a new generation of nanoparticle-based consolidants for restoration and contribution to the safe-by-design implementation",Tedesco, E. and Micetic, I. and Ciappellano, G. S. and Micheletti, C. and Venturini, M. and Benetti, F., Toxicology in Vitro, 29, 1736-1744.

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