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Nano-Lime - a New Material for the Consolidation and Conservation of Historic Mortars

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Abstract The consolidation and conservation of historic mortars requires materials which are compatible with the components originally used. The application of nano-lime offers such a possibility. Lime nano-particles are stable when dispersed in different alcohols. The particles have sizes ranging between 50 and 250nm. Typical concentrations in such dispersions are between 5 and 50g/L. Ethanol, n-propanol and iso-propanol are used as solvents. Treatment of mortar with nano-lime results, after evaporation of the alcohol, in the formation of solid calcium hydroxide. This converts into $CaCO_3$ in a way similar to traditional lime mortars by reaction with atmospheric carbon dioxide. The solvent evaporates without leaving any unwanted residues. Another possibility to consolidate mortar is the combined treatment with esters of silicic acid. The calcium carbonate nano-particles formed after the nano-lime treatment catalyse the gel formation resulting in improved mechanical properties. This paper gives an overview of the typical properties of calcium hydroxide nano-sols and summarises a number of laboratory tests on them.

1 Introduction

Historic mortars and plasters are of manifold composition. Typical binders are lime, hydraulic lime and calcium sulphate. Deterioration by either erosion or weathering can result in damage of various kinds which can require different conservation and strengthening approaches. The main challenge is the consolidation of surfaces in which the particles comprising the mortar are no longer bound as well as the structural consolidation of loose zones, for example behind crusts and shells [1-2].

At present, esters of silicic acid are the most favourable material for the consolidation of mortars and plasters. Their application, however, is not without problems. One aspect that has to be considered is the formation of hydrophobic surfaces after the application. Conversion back to hydrophilic surfaces requires days to weeks to occur and is dependent on the product used, its concentration and the climatic conditions [3].

The use of lime water as a consolidant has been discussed for many years, however, lime water contains not more than 1.6 g/L $Ca(OH)_2$ and the resulting consolidation effect is low. Additionally, large volumes of water are added to the treated areas which may result in new damage [4-5]. Barium hydroxide ($Ba(OH)_2$) has a much higher solubility (80 g/L) and reacts in a similar manner to $Ca(OH)_2$ with atmospheric carbon dioxide resulting in the formation of insoluble carbonates [6]. Deep penetration into mortar may be difficult to achieve due to its high reactivity with even traces of sulphate ions being spontaneously converted into $BaSO_4$. Alkali silicate solutions (water glass solutions), which form insoluble, amorphous silicates in contact with calcium or magnesium ions or silicic acid after mixing with acids, are strongly alkaline. The formation of silicic acid can also be caused by reactions with carbon dioxide. The penetration depth of water glass solutions is low. In addition, the formation of soluble salts is, along with the high alkalinity, the main disadvantage that prevents their use for the consolidation of mortar and stone [7].

One potential alternative for the consolidation and conservation of mortars and plasters is the use of suspensions of nano-sized lime particles, termed nano-lime. Products based on nano-lime are commercially available under the trade name "CaLoSiL" (producer: IBZ-Salzchemie GmbH & Co.KG, Germany). The letters behind the name indicate the used solvent; numbers associated with the product code give the total calcium hydroxide concentration in g/L. For example, E-25 means, 25 g/L calcium hydroxide dispersed in ethanol. This article will summarise typical properties of CaLoSiL and gives an overview about possible applications.

2 Experimental

The following methods and tests were used to characterise the properties of sols containing nano-lime:

- *Particle size distribution*: All measurements were performed using a Beckman Coulter Laser Diffraction Particle Size Analyser LS 13 320. Ethanol served as the solvent.
- *Density*: Conventional density determination by pycnometer was used.
- *Viscosity*: The viscosity was determined with the Brookfield DV-II viscometer at 25°C.
- *Zeta-potential*: The surface charge of the nano-lime particles in ethanol was determined by using the Field ESA system from PA Partikel-Analytik-Messgeräte GmbH.

The following tests were used to characterise the consolidation effect of calcium hydroxide nano-particles:

- *Consolidation of loose sea sand*: Plastic O-rings having a height of 1 cm were placed on a glass plate and filled with sea sand. Either CaLoSiL and / or the silicic acid ester were then introduced by applying them drop-wise onto the surface of the sand until the sand was fully saturated (Fig. 1).
- *Consolidation of mortar samples*: Mortar prisms with the dimensions 4 x 4 x 16 cm were prepared using sand and lime hydrate mixtures. Conventional concrete sand with a particle size < 2 mm served as the aggregate. The tests to characterise the achievable consolidation by nano-lime were carried out on prisms prepared using a volume ratio of sand to lime hydrate of 5:1. A volume ratio of 2.5:1 was selected for the tests of the combined treatment with nano-lime and silicic acid esters. All samples were stored for three months at atmospheric conditions and room temperature. The process of carbonation was followed by the periodic testing of samples that had been fractured by treatment with phenolphthalein. All treatments with esters of silicic acid were performed four weeks after the application of CaLoSiL. Funcosil 300 (producer: Remmers, Germany) and SILRES® BS-100 OH (producer: Wacker, Germany) were selected for the tests. Both the nano-lime suspension and the esters of silicic acid were applied as droplets onto the surface of the prisms until saturation was achieved. The consolidant uptake as well as the amount of calcium hydroxide / silicic acid ester precipitated was determined by the change in weight.

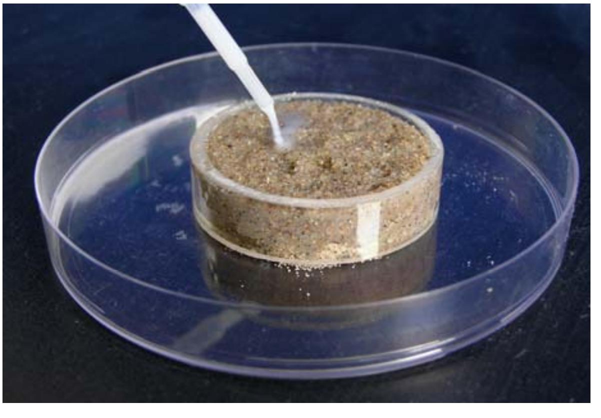

Fig. 1 Application of CaLoSiL onto the surface of an O-ring filled with sea sand

3 Results

3.1 Characteristics of nano-lime suspensions

Nano-lime suspensions are white to opal solutions containing stable dispersed calcium hydroxide nano-particles. A typical particle size distribution of nano-lime is given, in comparison to a conventional lime slurry, in Fig. 2. The extremely fine size of synthetic nano-lime results from its preparation, which is based on chemical synthesis. The particles are stable when suspended in ethanol, iso-propanol or n-propanol. Typical concentrations are in the range between 5 and 50 g/L.

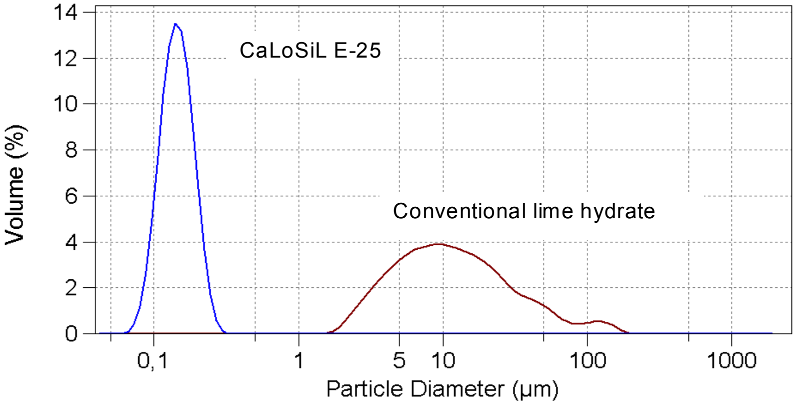

Fig. 2 Particle size distribution of nano-lime and conventional lime hydrate

Due to the small particle size stable sols are formed, meaning that the solids do not settle for a long time. Zeta-potential measurements have shown that calcium hydroxide particles have a positive surface charge in alcoholic solvents. The stability of the nano-lime suspensions is due to electrostatic repulsion. As long as these remain stable, the sols do not settle and a shelf life of between three and five months is possible.

Typical properties of different calcium hydroxide nano-sols are given in Figs. 3 and 4. As one would expect, the density (Fig. 3) of the sols increases with increasing solids content. The same is the case for the dynamic viscosity, whereas the absolute values remain low. This means, the flowing behaviour is only slightly impacted by the nano-particles.

After evaporation of the alcohol, nano-lime particles remain in treated materials. These react with atmospheric carbon dioxide in the same manner as conventional lime resulting in the formation of calcium carbonate.

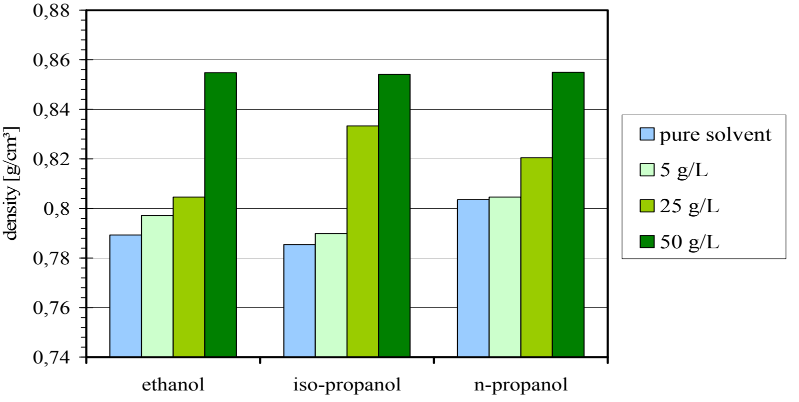

Fig. 3 Density of lime nano-sols depending on the concentration and the solvent

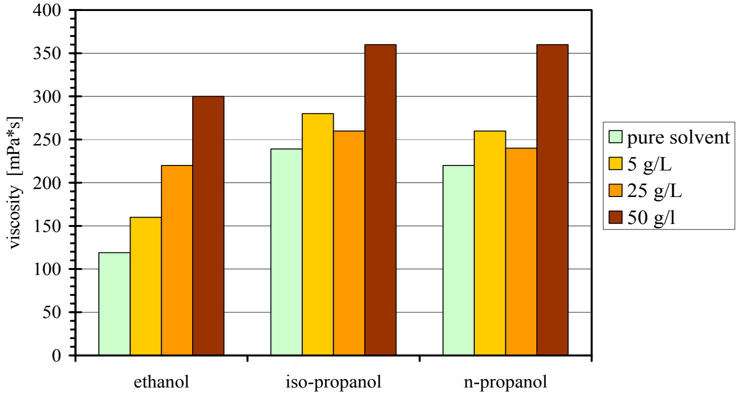

Fig. 4 Viscosity of lime nano-sols depending on the concentration and the solvent

3.2 Consolidation by carbonation

Due to the small particle sizes of the suspended lime the sols were able to fully penetrate the mortar samples. The change in compressive and bending strength as a result of the treatment with different types of CaLoSiL is summarised in Table 1. As expected, the consolidation effect increases with the increasing calcium hydroxide content of the sols, although the total relative increase in compressive and bending strength was low. However, this needs to be considered in respect to the total amount of binder brought by the sol into the prisms. The average absorption of the prisms was between 35 and 40 mL nano-lime sol. At a concentration of 25 g/L a total mass of calcium hydroxide of between 0.8 and 1.0 gram was introduced into the mortar samples following one treatment. It is clear that such low amounts produce only a small increase both in compressive and bending strength.

Table 1 Mechanical properties of mortar prisms after the treatment with nano-lime sols.

Treatment process:	Compressive strength [N/mm²]	Bending strength [N/mm²]
Reference sample	1.1 ± 0.1	0.26 ± 0.05
Two treatments with CaLoSiL E-25	1.4 ± 0.05	0.54 ± 0.05
Two treatments with CaLoSiL E-25 and storage under elevated CO_2-atmosphere (1 vol.-% in air)	1.35 ± 0.05	0.52 ± 0.05
Two treatments with CaLoSiL IP-12.5	1.25 ± 0.1	0.55 ± 0.05

3.3 Consolidation by combined application of CaLoSiL and silicic acid esters

The use of calcium hydroxide offers the possibility of the alkaline hydrolysis of silicic acid esters. This reaction should be much faster than hydrolysis by moisture. The question is: Will the silicic acid gel formed by this reaction produce a consolidation effect? To test such a conservation strategy, sand treated with a first application of nano-lime suspensions (CaLoSiL), was then treated using different commercially available silicic acid ester-based products. The consolidation effect as well as the surface characteristics was assessed visually.

The treatment with CaLoSiL produced a first consolidation. Loose sand particles were bridged together and a solid, non powdering surface was formed. The penetration behaviour of all of the silicic acid esters tested was not disturbed by the pre-treatment with CaLoSiL. The sand was fully penetrated, both by Funcosil 300 and Wacker Silres BS-100 OH. As Fig. 5 shows, the loose sand particles were converted into a solid mass.

Fig. 5 Sea sand consolidated by CaLoSiL E-25 and the silicic acid ester Funcosil 300 from Remmers

SEM investigations have shown a morphology of the formed silicic acid similar to that achieved by conventional hydrolysis with moisture (Fig. 6). EDX-Analyses of the amorphous material between the sand particles have indicated that the calcium containing phases are fully incorporated into the silicic acid structure.

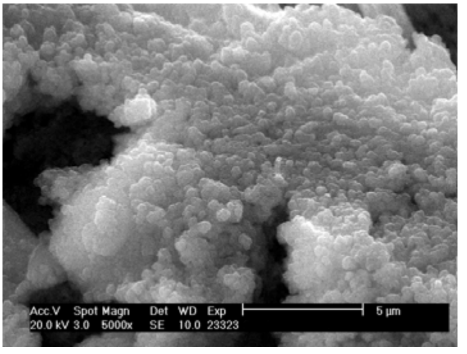

Fig. 6 SEM micrograph of sand particles fully covered by amorphous silicic acid resulting from the combined treatment with CaLoSiL E-25 and Funcosil 300.

Table 2 Mechanical properties of mortar prisms after treatment with nano-lime sols and esters of silicic acid (all data are the mean values of 3 different samples).

Test-No.	1. treatment	2. treatment	E-modulus untreated [kN/mm²]	E-modulus [kN/mm²]	Comp. strength [N/mm²]	Bending strength [N/mm²]
0	reference sample		7.98	-	4.3 ± 0.3	1.3 ± 0.1
1	CaLoSiL IP 12.5	CaLoSiL IP 12.5	7.13	8.54	3.6 ± 0.3	1.4 ± 0.1
2	CaLoSiL IP 12.5	Wacker BS OH 100	6.66	11.88	8.2 ± 0.15	1.9 ± 0.1
3	CaLoSiL IP 12.5	Funcosil 300	7.17	12.47	6.7 ± 0.4	2.7 ± 0.15
4	CaLoSiL E 25	CaLoSiL E 25	7.52	8.26	4.3 ± 0.4	1.2 ±0.1
5	CaLoSiL E 25	Wacker BS OH 100	7.61	11.81	8.8 ± 0.15	2.9 ± 0.3
6	CaLoSiL E 25	Funcosil 300	7.48	11.11	8.4 ± 0.3	2.7 ± 0.1
7	Funcosil 300	Funcosil 300	7.83	13.51	10.6 ± 0.15	2.6 ± 0.2

The lime – sand prisms used for the characterisation of the effect of a combined treatment with CaLoSiL and silicic acid esters were characterised by a compressive strength of 4.3 N/mm² and a bending strength of 1.3N/mm².

Two pre-treatments with either CaLoSiL E-25 or CaLoSiL IP-12.5 did not produce an increase in the compressive and bending strength (tests 1 and 4, Table. 2). In the mortar prisms treated initially with CaLoSiL E-25 followed by the application of Funcosil 300 and Silres BS-100-OH, respectively, a significant consolidation effect was observed. The increase in compressive and bending strength correlates very well with the dynamic elasticity modulus determined by ultrasonic measurements.

It is notable that the combined treatment with calcium hydroxide nano-sol and the esters of silicic acid produce strengths only slightly lower than those obtained by a double treatment with Funcosil 300 (test No. 7). It is considered likely that the calcium carbonate nano-particles formed after the nano-lime treatment catalysed gel formation resulting in improved mechanical properties. This is supported by the fact that the pre-treatment with the lower concentrated nano-lime (CaLoSiL IP-12.5) produced a lower compressive strength than when the 25 g/L $Ca(OH)_2$ containing CaLoSiL E-25 was employed.

4 Summary

Nano-lime suspensions containing up to 50 g/L colloidal calcium hydroxide stable dispersed in ethanol, n-propanol or iso-propanol offer new possibilities for the consolidation of historic mortars. Deep penetration into damaged zones is possible due to the small size of the lime particles. There are two possibilities to achieve consolidation: the carbonation by reaction with atmospheric carbon dioxide and the formation of colloidal silica obtained by the combined application of nano-lime suspensions and esters of the silicic acid. Apart from structural consolidation, nano-lime suspensions can be used to stabilise powdering and unstable surfaces.

5 Acknowledgements

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6 References

1. Stein, Zerfall, Konservierung (2005) editors: Siegismund S, Auras S, Snethlage, R Edition Leipzig
2. Snethlage R (2005) Leitfaden Steinkonservierung, Fraunhofer IRB Verlag
3. Wheeler G (2008) Alkoxysilanes and the consolidation of stone; Where we are now; in: in; Procceedings of the International Symposium "Stone consolidation in cultural heritage" editors: Rodrigues JD, Mimoso JM, Lisbon: 41-52
4. Peterson S (1982) Lime water consolidation. Proc. Mortars, Cements and Grouts Used in the Conservation of Historic Buildings. ICCROM, Rome: 53-61
5. Quayale NJT (1996) The Case Against Lime Water (or, the futility of consolidating stone with calcium hydroxide) Conservation News, Issue 59: 68-71
6. Drádácký M, Sliźková Z (2008) Calcium hydroxide based consolidation of lime mortars and stone in: Procceedings of the International Symposium "Stone consolidation in cultural heritage" editors: Rodrigues JD, Mimoso JM, Lisbon: 229-308
7. Weber H (1985) Steinkonservierung, expert verlag, Sindelfingen