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Nano-Lime as a Binder for Injection Grouts and Repair Mortars

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Abstract Lime water, esters of silicic acid and plastics are common materials used for the conservation of historic mortars. Injection grouts containing cement or hydraulic lime are also employed. In recent years, the usage of hydrated lime has increased; however, the mechanical properties of the repaired material are often unsatisfactory. In many cases, due to the large particle sizes of the lime used, only loose connections with the sub-surface are obtained. The availability of materials containing lime \([\text{Ca(OH)}_2]\) nano-particles offers the possibility of creating injection grouts and repair mortars with extremely small particle sizes. All systems suggested in this paper are characterised by solids with particle sizes smaller than 6µm. They can be used to consolidate mortars and to fill voids. An important feature is that the injection grouts are able to migrate into the space between loose particles and to stabilise these areas. The materials developed are aqueous with a high stability. The solids formed by their use are characterised by having a high porosity and demonstrate good capillarity. They are hydrophilic. Typical properties of solids formed from an injection grout are: 36% porosity, 4.3 N/mm² compressive strength after 30 days, 1.1 N/mm² flexural strength, 23 wt.% water uptake and 0.4% shrinkage. This paper summarises the design and development of injection grouts and repair mortars and presents results from initial applications. The concept developed allows the adjustment of the properties of the injection grouts and repair mortars to the properties of the mortars that have to be consolidated.

1 Introduction

Lime based mortars, plasters and stuccoes have been used for centuries. They are amongst the most common binding materials and are found at archaeological sites as well as in historical buildings. Their conservation and restoration is carried
out progressively, requiring different types of materials and different techniques. One main requirement is that the materials used are compatible to those originally used. During pre-consolidation, loose particles and surfaces that exhibit “sanding” have to be fixed. Consolidants must, therefore, be able to penetrate deep into the damaged zones. If necessary, this process can be followed by the removal of soluble salts by for example, poultices. Injection grouts with free flowing properties are required to fill voids and fissures. A porous transition zone allowing capillary transport from intact masonry through the mortar to the surface should be formed.

Repair mortars are used for the replacement of lost parts but also for the filling of open voids and cracks in mortars, plasters and frescoes. In many cases, the use of repair mortars is also necessary as a first step to stabilise historic mortars and plasters before the fundamental conservation process can begin. For that purpose, materials which can be varied in composition and concentration are necessary.

Until recently, the following materials were available [1, 2]:

- Lime suspensions,
- Lime water,
- Injection grouts and repair mortars based on lime hydrate and / or cement,
- Lime or cement based filling pastes and slurries,
- Hydraulic lime mortars, plaster and injection grouts,
- Silica sols, water glass solutions,
- Esters of silicic acid and
- Organic resins.

The application of lime mortars and lime water is well known [3, 4]. However, difficulties may arise when lime particles with a large size are present. Similarly, the application of lime water as a pre-consolidant can result in the full saturation of the treated material with water, which may cause additional and/or new deterioration. The use of cement based materials can often result in structures which are too hard and the use of silicon-based organic consolidants and binders are unsatisfactory due to the formation of hydrophobic surfaces [5].

A main consideration for successful conservation is that the materials used in the different working stages are fully compatible among themselves. It is the aim of this paper, to demonstrate that a set of fully compatible conservation materials can be prepared using nano-lime and natural fillers.
2 Materials

2.1 Materials for pre-consolidation

Strength profiles of weathered historical mortars and plasters have shown that the weathered zone often extends to a depth of several centimetres; peeling, flaking and detachment of murals can commonly be observed. Before using injection masses or repair mortars, a pre-consolidation of loose particles and deteriorated zones is therefore often necessary. For this, a material that can migrate into the space between the sand grains and the mortar constituents is required.

The investigations summarised in Drdáký et al. [6] and Maryniak-Piaszczynski et al. [7] have indicated that the nano-lime product CaLoSiL can be used as a pre-consolidant. It contains synthetic calcium hydroxide particles with sizes between 50 and 250 nm which are stable when dispersed in ethanol, n-propanol or isopropanol. The sols formed have a shelf life of three to five months and typical concentrations are between 10 and 50 g/L. CaLoSiL is a product of IBZ-Salzchemie GmbH&Co.KG, Germany.

The nano-sol is able to migrate deeply into the mortar and fine nano-particles of calcium hydroxide are deposited in the treated areas after evaporation of the alcohol. Subsequent carbonation by reaction with atmospheric carbon dioxide results in strengthening and consolidation. In most cases the moisture present in porous systems is more than sufficient to allow complete carbonation, even at depths of several centimetres. XRD investigations (fig. 1) have demonstrated that the two calcium carbonate modifications, calcite and vaterite, are formed. These components also form in conventional lime based mortars.

The use of a water free consolidant is of great importance, especially in situations in which the presence of water can cause additional deterioration, for example during the consolidation of frescos or vaults.
2.2 Injection grouts

Highly concentrated, paste-like suspensions of nano-lime were prepared using the paste-like CaLoSiL. This is a special material containing nano-lime in concentrations up to 350 g/L. The average particle size is a little higher than for the standard materials but is still in the nano-meter range (fig. 2). CaLoSiL was used in combination with natural fillers.

The injection grouts are characterised by a good stability in combination with a high flowability. After hardening, porous masses are formed which demonstrate a high capillarity. All masses are hydrophilic and are able to act as capillary-active,
zone-bridging mortar surfaces, mortar structures and masonry. Another important property is the good adhesion to historic mortar components. The injection grouts are able to adhere to single mortar pieces. Selected physio-chemical properties are shown in Table 1. Typical compositions are given in Table 2.

Table 1 Selected physio-chemical properties of injection grout number 1

<table>
<thead>
<tr>
<th>Properties</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>water absorption (wt.% H₂O)</td>
<td>23.2</td>
</tr>
<tr>
<td>porosity (vol.%)</td>
<td>36.2</td>
</tr>
<tr>
<td>capillary suction up to 5 cm [min.]</td>
<td>225</td>
</tr>
<tr>
<td>coefficient of water absorption kg/(m²h⁻¹⁵)</td>
<td>4.0</td>
</tr>
<tr>
<td>Compressive strength [N/mm²] after 14 days</td>
<td>2.1</td>
</tr>
<tr>
<td>Compressive strength after 24 h water [N/mm²]</td>
<td>1.8</td>
</tr>
<tr>
<td>Compressive strength [N/mm²] after 30 days (temp.20°C, 60% rel. humidity)</td>
<td>4.3</td>
</tr>
<tr>
<td>Bending strength [N/mm²]</td>
<td>1.1</td>
</tr>
<tr>
<td>Dynamic E-Modulus [N/mm²]</td>
<td>4100</td>
</tr>
<tr>
<td>Adhesive tensile bending strength [N/mm²] after 30 days</td>
<td>0.1</td>
</tr>
<tr>
<td>Shrinkage [%]</td>
<td>0.4</td>
</tr>
<tr>
<td>Hygric expansion [mm]</td>
<td>0.01</td>
</tr>
<tr>
<td>Freeze-thaw cyclic test, weight loss [%] after 25 cycles</td>
<td>20</td>
</tr>
<tr>
<td>Crystallization test, weight loss [%] after 10 cycles</td>
<td>42</td>
</tr>
</tbody>
</table>

Table 2 Examples of injection grouts based on CaLoSiL nano-lime as a binder

<table>
<thead>
<tr>
<th>Grout number:</th>
<th>Composition</th>
<th>Mass ratio Binder : aggregates</th>
<th>Stability after storage at 50 °C for one week</th>
</tr>
</thead>
</table>
| 1             | 10g CaLoSiL - paste  
20g limestone powder, mpd¹: 0.8 µm  
20g limestone powder, mpd: 1.7 µm  
10g limestone powder, mpd: 2.4 µm  
14g water  
0.598g Lopon 890 (0.8%) | 1:5 | Stable |
| 2             | 10g CaLoSiL-paste  
25g limestone powder, mpd: 0.8 µm  
10g limestone powder, mpd: 1.7 µm  
15g limestone powder, mpd: 2.4 µm  
15g water  
0.58 g Lopon 890 (0.8%)  
1% meta-kaolinite | 1:5 | Stable |
3 10g CaLoSiL-paste 1:4.5 Stable
20g limestone powder, mpd:0.8 µm
10g limestone powder, mpd:1.7 µm
15g limestone powder, mpd:2.4 µm
13.75g water
0.55 g Lopon 890 (0.8%)
1% meta-kaolinite (0.69g)

1) mpd: mean particle diameter

2.3 Repair mortars

The use of a paste-like nano-lime as a binder allows the creation of materials with variable properties. Changing the ratios between the components and directed selection of the fillers and their particle size distribution allows the adjustment physio-chemical properties of the mortars to the historic materials. A typical recipe is described in Table 3. Characteristic data are given in Table 4. The high capillarity and water suction capacity are typical properties. Water uptake and release takes place rapidly and the mortars can take the role of a protection layer. The mechanical properties of the repair mortars developed are sufficient to protect the historic materials. The amount of water in the mortar, due to the use of ethanolic suspensions of nano-lime as a binder, is low and can be varied on demand.

The colour as well as the surface texture of the mortars can be adjusted by the addition of pigments and it is possible to imitate weathered and discoloured mortar surfaces.

Table 3 Repair mortar

<table>
<thead>
<tr>
<th>Composition</th>
<th>Amount (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>marl powder (0-250μm)</td>
<td>1000</td>
</tr>
<tr>
<td>CaLoSiL-paste</td>
<td>300</td>
</tr>
<tr>
<td>mixture of ethanol and water</td>
<td>as necessary</td>
</tr>
<tr>
<td>1:1 Vol.</td>
<td></td>
</tr>
<tr>
<td>meta-kaolinite</td>
<td>3% of the whole mass</td>
</tr>
<tr>
<td>lime paint umber and ochre</td>
<td>as necessary</td>
</tr>
</tbody>
</table>

Table 4 Properties of the developed repair mortar (the data are the result of duplicated measurements)

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density [g/ cm³]</td>
<td>1.89</td>
</tr>
<tr>
<td>Specific surface [m²/g]</td>
<td>2.9</td>
</tr>
<tr>
<td>Water absorption [wt.% H₂O]</td>
<td>16</td>
</tr>
</tbody>
</table>
Porosity [vol.\%] & 24-29 \\
Capillary suction up to 5 cm [min.] & 20 \\
Coefficient of water absorption in kg/(m²h¹/₂) & 4.85 \\
Compressive strength [N/mm²] after 21 days & 3 \\
Dynamic E-Modulus [N/mm²] & 4000 \\
Bending strength [N/mm²] & 0.23 \\
Shrinkage [%] & 0.2 \\
Hygric expansion [mm] & 0.04 \\
Thermal expansion \(10^{-6}/K\) \(\Delta x\times10^{-6}/K\) & 11.2 \\
Freeze-thaw cyclic test, weight loss [%] after 25 cycles & 20 \\
Crystallisation test, weight loss [%] after 10 cycles & 60 \\

### 3 Application examples

#### 3.1 Conservation of the facade of the rectory St. Peter in Aachen

The gable of the rectory of St. Peter in Aachen-Orsbach (1764) (fig. 3) was built of marl stones. Pointing was carried out using a mortar consisting of lime and extremely fine marl. During a previous restoration, some stones were replaced and the facade was partially re-pointed with cement based mortars which has contributed to the destruction of the remaining original materials (fig. 4). Conservation work performed in 2009 was based on the following steps: At first the mortar was structurally consolidated with CaLoSiL E-25 (fig. 5); after which flakes and shells were adhered to the surface by an injection mass based on a CaLoSiL paste. In the final conservation step, voids were filled with a mortar containing CaLoSiL paste as the binder.

![Fig. 3 Rectory of St. Peter in Aachen - gable before the conservation](image1)

![Fig. 4 St. Peter’s in Aachen-Orsbach - original mortar underneath the flaking cement mortar](image2)
3.2 Conservation of wall paintings in Mersch (Luxemburg)

The conservation of the wall paintings in Mersch was realised in several stages. First, unstable mortar underneath the paintings was stabilised through the injection of the nano-lime CaLoSiL E-25 (fig. 7); defects were then filled with a nano-lime-based repair mortar. Following this, voids, fissures and cracks were filled with an injection grout based on a CaLoSiL paste (fig. 8) and coloured lime was applied in the final retouching. Thus, the conservation was achieved with lime based materials which were fully compatible to each other.

4 Conclusions

Nano-lime can be used as a pre-consolidant as well as a binder in injection grouts and repair mortars. Thus, a conservation concept can be realised in which
fully compatible materials are used in all stages. The advantages of this concept include the reversibility of the product as well as its great flexibility in respect to the physio-mechanical and aesthetic properties required.

5 Acknowledgement

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6 References