Mechanical activation of frozen lime putties

D Michoinová 1 and R Nečas 2

1 Czech National Heritage Institute, Valdštejnské nám. 162/3, Prague 118 01
2 Research Institute for Building Materials, Hněvkovského 30/65, Brno 617 00
Email: michoinova.dagmar@npu.cz, necas@vustah.cz

Abstract. The lime putty used for mortar preparation loses its desired properties, especially the plasticity and other rheological parameters, when it freezes. Two kinds of lime putty with 30 wt. % of solid content underwent 5 freeze/thaw cycles and their properties were investigated. Their consistency worsened dramatically after freezing. Mechanical activation was carried out by high-speed mixing of lime putty. This procedure led to a significant improvement in the lime putty plasticity and viscosity. The rheological parameters reached the original values that were determined before freezing. Rheological tests of lime putties were determined by rotational rheometer with the solids characterized by laser particle size analyzer.

1. Introduction
Lime based mortars have been used in building construction for thousands of years. The non-hydraulic lime, in the form of lime putty, was one of the most common form of this binder. The characteristics of both historic and new mortars are known to be affected by the properties of the lime putty in addition to other factors [1].

After the development of Portland cement, it rapidly became the binder component of choice in mortar for new masonry works and, unfortunately, for use in conservation and rehabilitation of architectonic heritage, too. However, the rapid hardening and high mechanical strengths of cement mortars are incompatible with old building materials [2]. With the increased use of Portland cement, and other binders, in mortars, the use of air lime-based mortars fell into gradual disuse and, along with this, the knowledge and skills of craftsmen almost disappeared. Over time, it became apparent that the replacement of non-hydraulic lime mortars in the conservation and restoration of historic buildings and structures was a serious error. Subsequently, a new phase in the use of air lime, along with new research into the understanding of the properties of air lime and their mortars commenced [3, 4].

The aged, wet slaked, air lime (in the form of lime putty) is preferred for lime mortars preparation in certain situations. An alternative method, sometimes employed in the preparation of lime putty, is the mixing of powdered hydrated lime with water and aging the putty formed.

There is a great deal of skill and expertise required in good putty preparation and storing (optimal slaking temperature, water/quicklime ratio, aging of lime putty, avoidance of drying and inhibiting contact with air) and, last but not least, the knowledge gained by practitioners that lime putty cannot be allowed to freeze [5, 6]. The need to protect lime putties from frost is also highlighted by commercial suppliers in their instructions for use [7, 8] as lime putties lose the properties for which they are known to impart to mortars, such as plasticity, workability, cohesion, etc. when frozen. This has also led to the discarding of quantities of lime putty affected by frost, both in storage and on sites, and, therefore,
any procedure that would permit the continued use of frost affected materials would be of significant value.

A satisfactory objective explanation of the risk of damage due to frost is still unknown. A possible explanation is (as in the cases of polymeric dispersions) that the freezing of the system causes a certain coagulation of slightly dispersed particles thereby resulting in the deterioration of its rheological properties [9].

Rheological properties of lime putties are very important, if the putty is used in mortar mix design. Lime putty is a non-Newtonian fluid, usually a Bingham type of fluid, i.e. in absence of external forces, it behaves as a solid. If the external forces are present, the putty starts to change its form and behaves as a liquid and starts to flow. The minimal stress necessary for putty to start to flow is called its yield stress. This parameter together with its plasticity is important for mortar applications. Other properties, called “time-dependent properties” i.e. thixotropy and rheopexy, are significant for the non-Newtonian fluids, too. When thixotropic fluid is sheared, its apparent viscosity decreases, whereas a shear of the rheoplectic fluid results in an increase in its apparent viscosity. In order to determine the general flow behaviour of a material, a graph of the shear stress against the shear rate is plotted. This graph is called its flow curve. For fluids with time-dependency, the flow curve for increasing and decreasing shear rate are not identical and the curve forms a hysteresis loop. The area of the loop determines thixotropy value (the “falling” curve lies under the “rising” curve) or rheopexy value (the “falling” curve lies above the “rising” curve).

In the past, experiments were made to improve putty properties damaged by frost using the mechanical activation of lime putty [9, 10]. The aim of our study was to compare the time dependent behaviors of two aged putties, before and after freezing and after mechanical activation.

2. Experimental Procedure

2.1. The lime putty preparation

Two types of lime putty were prepared from the same high calcium quicklime (Hydrated lime EN 459-1 CL 90-Q, producer Vápenka Čertovy schody a. s., Czech Republic):

- Lime putty prepared from technical dry slaking calcium hydrate by mixing the powder with water and aged for 3 years in plastic container (sample LP-D).
- Lime putty prepared by wet slaking of quicklime and aged for 3 years in a lime pit (sample LP-W).

The samples of lime putty (~ 2 kg) were homogenized for short time by employing a helical stirrer, fitted to a hand-operated electrically powered drill before freezing. Prior to use, the content of dry matter was determined gravimetrically. To allow comparison of rheological properties of the lime putties, the content of dry matter was corrected to 30 wt. % by adding a calculated quantity of demineralized water. Initial and corrected values are given in Table 1. Adjusted samples were used in the experiments and analyzes.

|         | Solid content (original samples) | Solid content (adjusted samples) |
|---------|---------------------------------|---------------------------------|
| LP-D    | 48.10                           | 29.43                           |
| LP-W    | 45.15                           | 29.55                           |

2.2. Frost treatment of samples

Approximately 1 kg of lime putty, in plastic vessels, were placed in a temperature controlled environmental cabinet KD20 and the samples exposed to 5 freeze/thaw cycles according to the following schedule:

- Freezing from ambient temperature to -10°C (linear temperature decrease, 6 hours),
- Maintained at a constant temperature -10°C (6 hours),
• Thawing to ambient temperature (linear temperature increase, 6 hours),
• Maintained at a constant ambient temperature (6 hours).

The freezing device (environmental cabinet) was operated under fully automatic control for 5 days. After the freeze/thaw cycling treatment, samples were aged for 1 month, at ambient temperature (lab temperature ~24°C). After aging, the mechanical activation was applied by using a laboratory stirrer, model IKA RW 20, which has a digital display; this permitted all samples to be activated under the same conditions. The stirrer was fitted with a helical paddle. Each putty was reactivated by using the stirrer at speeds of 450 rpm for 10, 20, 30 and 40 minutes.

2.3. Measurement methods
Particle size distribution was determined by laser particle size analyzer CILAS 920L in range 0.3 to 400 μm in isopropyl alcohol medium. The measurements of particle size of the putty samples was determined before freezing, after freezing, after 1 month aging and following each of the mechanical activation (stirring) periods. Particles coarser than 0.315 mm were removed by sieve to prevent clogging of apparatus measuring cell.

Rheometer TA Instruments DRH-1 was used to obtain flow curves measurement. Geometry of coaxial cylinders according to DIN/ISO 3219 was used in the measurement, and the range from 0 to 150 s⁻¹ for shear rate was investigated. Data was evaluated by firmware TRIOS and the yield stress and time-dependent rheological properties determined.

3. Results and Discussion
The experiments have confirmed the crucial role of frost on the rheological properties of lime putty. Frozen putty loses the properties necessary for mortar preparation – plasticity (that corresponds with yield stress value) and optimal particle size distribution. The putties following freeze/thaw cycling were liquid coagulate solids and their rheological parameters were non-measurable by the rheometer employed (out of measurement range). An increase in the number of coarser particles was also found after freezing. Both these effects most likely cause the loss of plasticity and the rapid sedimentation of particles in suspension. This is probably related to changes in surface charge (analogous effect is known for organic material dispersions) along with the aggregation of portlandite crystals [12, 14, 15, 16].

The increase in the proportion of larger particles after 1 month of aging can be explained by portlandite crystals growth and recrystallization (see Figure 2 and 3 for LP-D and 6 and 7 for LP-W).

It was confirmed that the properties of frozen lime putties were improved by intensive remixing, by using the laboratory stirrer at 450 rpm for 10, 20, 30 and 40 minutes. Mechanical activation by external forces appears to have caused the breakage of crystal aggregates in the suspension. The quantity of larger particles, after activation, became lower, as is shown by the particle size analyses. The particle size distribution returned to approximately original values after activation (see Figure 1–8 and Table 2). The medians of the particle sizes determined after activation are practically identical to those of the original putties, before treatment.

In general, colloidal suspensions show a variety of nonlinear rheological properties (yield stress, shear thinning, shear thickening, thixotropy, and/or rheopexy) that depend on interparticle forces, Brownian motion of the particles, and hydrodynamic interactions as well as on the shape, size, and volume fraction of particles, on the degree of aggregation, and on the fraction of fluid immobilized by the particles [11].

For the suspension of particles below 1 μm in size, the influence of Brownian motion is important. In this case, the probability of sedimentation can be predicted from the gravitational and Brown strength ratios using equation (1) [13]:

\[ p = \frac{a^4 \Delta \rho g}{k_B T} \]  

where
\( a \) radius of particle (m)
\( \Delta \rho \) difference between particle and liquid density (kg.m⁻³)
\[ g \quad \text{gravitational acceleration (m.s}^{-2}\text{)} \]
\[ k_B \quad \text{Boltzmann constant } 1.38064852 \times 10^{-23} \text{ (m}^2\text{.kg s}^{-2}\text{.K}^{-1}) \]
\[ T \quad \text{absolute temperature (K)} \]

If this ratio is greater than one, a degree of sedimentation can be expected, while a ratio of less than one is likely to indicate a stable system. However, this equation does not take into account the potential interactions between particles. Due to Brown's motion, the particles will continually collide with each other, and as a result, the particles can collapse due to Van der Waals's attractive forces. This may lead to the formation of much larger particles, or secondary particles (flakes) and, therefore, experience a larger contribution of gravity than that indicated in equation (1).

Using the equation (1), \( \Delta \rho \) difference between calcium hydrate and water density = (2240 – 1000) kg.m\(^{-3}\), \( g = 9.81 \text{ m.s}^{-2} \) and \( T = 295 \text{ K} \) the critical value \( (p = 1) \) of particle radius is about 0.75 \( \mu \text{m} \) (i.e. diameter 1.5\( \mu \text{m} \)). The higher content of larger particles is the reason for the rapid particle sedimentation in freeze/thaw lime putties. Results of tests are shown in Figure 1 to 8, with the changes of median particle size, during test, shown in Table 2.

**Figure 1.** LP-D before freezing.

**Figure 2.** LP-D after freezing.

**Figure 3.** LP-D after freezing + 1 month of spontaneous aging.

**Figure 4.** LP-D after 40 min of activation.
Figure 5. LP-W before freezing.

Figure 6. LP-W after freezing.

Figure 7. LP-W after freezing + 1 month of spontaneous aging.

Figure 8. LP-W after 40 min of activation.

|                  | Before freezing | After freezing | Frozen putty + 10 min | 20 min | 30 min | 40 min | 1 month aging | mixing | mixing | mixing | mixing |
|------------------|-----------------|----------------|-----------------------|--------|--------|--------|---------------|--------|--------|--------|--------|
| LP-D             | 6.44            | 24.20          | 44.93                 | 13.29  | 8.99   | 7.69   | 6.40          |        |        |        |        |
| LP-W             | 3.36            | 5.89           | 35.67                 | 4.51   | 3.05   | 3.06   | 3.27          |        |        |        |        |

For better clarity, the overlay curves of particle size distribution are shown in Figures 9–12.
Figure 9. Overlay curves of particle size distribution of LP-D sample:
+ before freeze/thaw cycling; × after freeze/thaw cycling; □ after 1 month of aging.

Figure 10. Overlay curves of particle size distribution of LP-D sample:
+ 10 min. of activation; × 20 min. of activation; □ 30 min. of activation; o 40 min. of activation.
Figure 11. Overlay curves of particle size distribution of LP-W sample:
+ before freeze/thaw cycling; × after freeze/thaw cycling; □ after 1 month of aging.

Figure 12. Overlay curves of particle size distribution of LP-W sample:
+ 10 min. of activation; × 20 min. of activation; □ 30 min. of activation; o 40 min. of activation.

4. Rheological properties
The rheological properties of putty samples before freezing and after 40 min of activation were measured only, as the samples after freezing, and after 1 month of aging, were not measurable by means of the rheometer. More precisely, the samples had the appearance and properties of a water suspension, and were very runny, displaying extremely fast sedimentation of solid matter, and this made the measurement impossible.

Based on the rheological measurements made, LP-D after reactivation showed a larger yield stress after 40 minutes activation, compared to the putty before freezing. Activation of LP-W sample was
stopped after 40 minutes, because median of particles size didn’t decrease in last twenty minutes of mixing. However, a lower yield stress was found in the case of LP-W. All measured samples of lime putty exhibited rheopectic behavior. At high shear rates, hydrodynamic stresses can act upon the lose clusters and fragment them. These stresses are manifested as velocity differences across the structure of the aggregates that produce several fragments of similar size and fluid drag forces that strip primary particles or small flocules from the surface of the original aggregates. As a consequence, both smaller aggregates and individual Ca(OH)$_2$ nanoparticles are released from the original clusters. This caused an increase in the viscosity of the suspension upon relaxation of the flowing system. This behavior may also help to explain the results by Vávrová and Kotlík [9] who indicate that, after prolonged shearing, fresh lime putties showed much higher values of viscosity then nonsheared pastes [11].

Values of rheopexy are lower (approximately half the value) after treatment by frost and activation. The flow properties of the lime putties are shown in Figures 13–16 and in Table 3.

**Figure 13.** LP-D before freezing.

**Figure 14.** LP-D after freezing and 40 min of activation.

**Figure 15.** LP-W before freezing and activation.

**Figure 16.** LP-W after freezing and 40 min of activation.
Table 3. Rheological properties of lime putties.

| Sample                  | Yield stress (Pa) | Thixotropy (+) or rheopexy (-) (Pa.s⁻¹) |
|-------------------------|-------------------|-----------------------------------------|
| LP-D (before freezing)  | 35.3              | -1021                                   |
| LP-D (mixing 40 min)    | 65.6              | -661                                    |
| LP-W (before freezing)  | 59.7              | -622                                    |
| LP-W (mixing 40 min)    | 48.5              | -347                                    |

5. Conclusion
There are minor differences in the behavior of lime putties prepared by wet slaking quicklime and by mixing of dry slaked calcium hydroxide with water, even when the original quicklime was the same for both putties, and the storage condition were comparable.

The action of frost had a negative effect on the rheological properties of both lime putties.

Frozen putties lose their plasticity due to significant changes in their particle size distribution. Decrease of plasticity and sedimentation of coagulated particles is related to changes in surface charge and aggregation of portlandite crystals.

The content of larger particles increased spontaneously after 1 month of aging, this is considered to be due to growth and recrystallization of portlandite crystals.

Properties of frozen lime putties can be improved by intensive mixing. The reactivation of lime putties can be achieved by mechanical operation, by applying external forces that cause the deagglomeration of aggregates in the suspension, and it has been shown that the particle size distributions can reach almost original values, after intensive activation.

Based on the results of these experiments, it can be said that the behavior of lime putties damaged by frost can be re-established by intensive mixing – by mechanical activation – to approximately the same condition, as before freezing.

Acknowledgements
The Czech Ministry of Culture and The National Heritage Institute financed the research under “Long-term Conceptual Development of Research Organizations” project (99H30PP110).

References
[1] Elert K, Rodriguez-Navarro C, Pardo E S, Hansen E and Cazalla O 2002 Lime mortars for the conservation of historic Buildings Studies in Conservation 47 pp 62–75
[2] Klemm A J and Wiggins D E 2015 Microstructural Characteristics of Modern Repair Materials vs. The Performance Requirements of Historic Lime Mortar In International Symposium on Brittle Matrix Composites RILEM pp 33–42
[3] Torraca G 1982 Porous Building Matrials Materials Science for Architectural Conservation ICCROM
[4] Wiggins D 2017 Traditional lime mortars and masonry preservation The Journal of the Building Limes Forum 24 pp 28–37
[5] Gibbons P 1995 Preparation and Use of Lime Mortars, An Introduction to the principles of using lime mortars 2nd ed. (Edinburg: Historic Scotland)
[6] Holmes S and Wintage M 2002 Building with lime 3rd ed. (London: ITDG Publishing)
[7] Superfine lime putty 2017 (Online http://www.roseofjericho.co.uk/product/superfine-lime-putty)
[8] Heritage Restoration - Slaked Lime Putty 2017 (Online http://www.stratacote.co.nz/heritage-restoration-slaked-lime-mortar/)
[9] Vávrová P and Kotlík P 2016 Rheological properties of lime putty (Online http://www.schleibinger.com/k2004/vavrova04/Prezentace_Regensburg.pdf)
[10] What Happens When Lime Putty Freezes? 2017 (Online http://www.preservationscience.com/materials/lime/FL.html)
[11] Vávrová P and Kotlík P 2005 Rheological properties of lime putty Conference paper of 36th
International Conference on Coatings Technology CCT’ Seč, Czech Republic

[12] Ruiz-Agudo E and Rodriguez-Navarro C 2010 Microstructure and rheology of lime putty Langmuir 26 pp 3868–3877
[13] Barnes H A 2000 A Handbook of Elementary Rheology University of Wales, Institute of Non-Newtonian Fluid Mechanics
[14] Atzeni C, Farci A, Floris D and Meloni P 2004 Effect of aging on rheological properties of lime putty J. Am. Ceram. Soc. 87 pp 1764–1766
[15] Boháč M and Nečas R 2016 The role of aging on rheological properties of lime putty Procedia Engineering ICEBMP 2016
[16] Lopes M G and Margalha B 2013 Microstructural Changes of Lime Putty during Aging Journal of Materials in Civil Engineering 25(10) pp 1524–1532