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The role of aging on rheological properties of lime putty

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Abstract

The role of aging on rheological properties of lime putties was investigated by rotational rheometry, scanning electron microscopy and particle size distribution analyzes. Disaggregation of large clusters during aging and resulting microstructural enrichment of micron-sized particles was found to be one of the possible reasons for the continuous increment of plasticity and yield stress of lime putties during long-term aging. The extent of thixotropic and rheopectic behavior is affected by both calcination process and microstructure development during aging.

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Keywords: Lime putty; aging; rheology; time-dependent properties

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1. Introduction

Rheology is the study of flow and deformation of materials under applied forces. All liquids can be characterized by flow curve. This curve shows the relation between the shear stress (*Pa*) and shear rate (s^{-1}). If the relation is linear, this liquid is called “Newtonian”. Typical Newtonian liquids are water, oils, concentrated solutions of sugar i.e. syrups, honey etc. Many commonly used materials exhibit complex rheological properties, whose viscosity and viscoelasticity can vary depending on the external conditions, such as applied stress, strain, timescale, and temperature. These liquids are called non-Newtonian. Typical examples are proteins in water, polymers, toothpaste, creams, yogurts, cement suspensions, plasters, slaked lime etc.

Various kinds of rheometers allow the measurement of rheological properties of all materials – from fluids such as dilute solutions of polymers and surfactants through to concentrated protein suspensions to semi-solids such as

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pastes and creams, to molten or solid polymers as well as asphalt. Rheological properties can be measured from bulk sample deformation using a rotational rheometer. The type of rheometer required for measuring these properties is often dependent on the relevant shear rates and timescales as well as sample size and viscosity.

Rheological properties can be divided into two big parts – time-dependent properties and time-independent ones. Time-independent properties comprise shear-thickening (viscosity increases with increasing shear rate), shear-thinning (viscosity decreases with increasing shear rate), Bingham behavior (if the shear rate is low, the liquid shows elastic deformation only, if the determinate shear stress is exceeded, the sample flows as liquid) etc.

Time-dependent properties are thixotropy and rheopexy. Thixotropy behavior is characterized by different “viscosity” in a calm state and after mixing. “Viscosity” after mixing is lower than “viscosity” before mixing. The rheopectic behavior is the opposite of the thixotropy behavior (therefore, rheopexy is sometimes called “negative thixotropy”). Thixotropy or rheopexy can be revealed from flow curve. Flow curves of shear stress for increasing or decreasing shear rate are not identical and, therefore, they show hysteresis loop. If the curve which corresponding with decreasing shear rate lies under the curve of increasing one, the sample is thixotropic. In opposite case, the rheopexy is found. Time-dependent rheological properties are explained in Fig. 1. The area that is bordered by both flow curves is proportional to the quantity of thixotropy or rheopexy.

Nomenclature

CH	portlandite, $Ca(OH)_2$
DHP	dry hydrate putty
PSD	particle size distribution determined by laser diffraction method
SEM	scanning electron microscopy
SQP	slaked quicklime putty

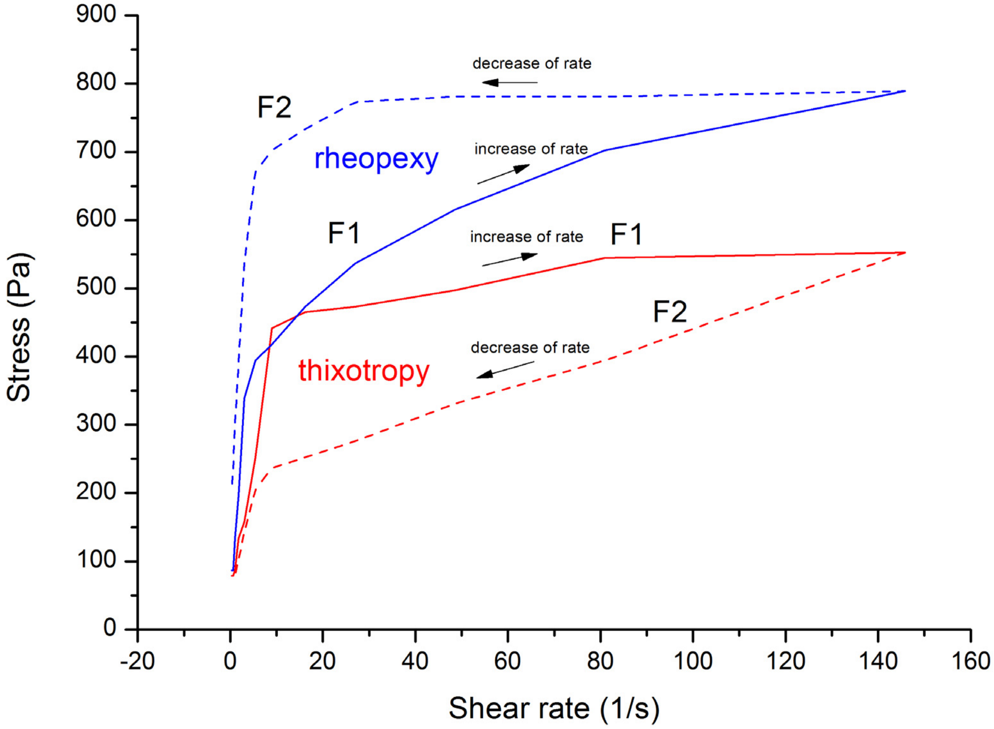


Fig. 1. Time-dependent rheological properties determination on flow curves

Calculation and units of thixotropy or rheopexy

Exactly, the thixotropy or rheopexy can be determined as an area between flow curves, Eq. (1):

$$\int_{\min}^{\max}(F_1 - F_2)dy \tag{1}$$

where F1, F2 are flow curves for increasing ad decreasing shear rate γ [2].

According to Eq. (1), the units of thixotropy/rheopexy are Pa/s [1]. The normalized thixotropy is defined by the area of the hysteresis loop divided by the maximum rate, the maximum stress and the step time which is characterized as alternated increasing and decreasing shear stress dependency on shear rate (s^{-1}). It is used to compare results obtained from different test conditions [2].

In practice, time-dependent properties quantification and standard model fitting can be carried out using software which is provided with the rheometer. The thixotropy/rheopexy model calculates the parametres from the stress in up and down stress or rate ramps. The thixotropy analysis uses the area under the curve model to compute the thixotropic index. The integration can be replaced with a numeric calculation of square. The area is calculated using the trapezoidal rule [2] (or Simpson rule) to interpolate the points on the curve. Positive value indicates the thixotropy, negative value indicates the rheopexy.

Processing parameters such as calcination, slaking and aging have an important role on the microstructure of quicklime (CaO) and slaked lime. The microstructure of slaked lime rules the rheology and thus the workability, performance and use of lime-based materials. The paper deals with the role of aging of two different lime putties on their rheological parameters.

2. Experimental

Two kinds of lime putties were tested: The first one was made by slaking of very soft burnt quicklime (from VUSTAH experimental pilot rotary kiln) and the second one was prepared from common dry calcium hydrate. Putties were stored in plastic containers at ambient temperature. Properties of both putties were tested after 6, 12 and 24 months after preparation.

The putties were diluted in distilled water before testing to obtain “putty of normal consistency” (by ASTM C110-76 „Standard methods of physical testing of quicklime, hydrated lime, and limestone“). Normal consistency was determined by Vicat apparatus for testing lime putties. The principle of this method is monitoring the depth of indentation of the Vicat needle. If the depth is small, the putty must be diluted by mixing with water. The putty has a normal consistency when the indentation depth of the needle is 20 ± 5 mm. Content of solids in the putties of normal consistency was determined gravimetrically by drying the putty at 105 °C. Content of solids is shown in Tab. 1.

Table 1. Solid content in lime putties of normal consistency.

Time before testing	6 months	12 months	24 months
	wt. %		
Putty prepared from quicklime VUSTAH	22.93	25.01	42.67
Putty prepared from dry calcium hydrate	38.85	40.49	43.89

The rheological measurements were realized by rotational rheometer DHR1, using the measuring geometry of coaxial cylinders. Lime putties were tested in flow-sweep regime in the range of shear rate of 1-150 and 150-1 (1/s), at the temperature of 25 °C. Duration of the test was 150 s. Samples were pre-sheared for 10 s with the angular velocity of 1 rad/s. The obtained data was evaluated by software TRIOS.

PSD was measured on CILAS 920L. Samples of lime putties were sieved to get fraction below 0.315 mm. Free water was removed from samples by repeated (4 times) decantation in isopropyl alcohol. Each sample was measured repeatedly 4 times to avoid the role of continuous ultrasonic deagglomeration of clusters in various structures.

Micrographs of lime putties were taken in secondary electrons mode at 10000 x magnification, EHT 10 kV and 100 µA on SEM Zeiss EVO LS 10.

3. Results and discussion

3.1. Characterization of particles – PSD and SEM

PSD, a shape of particles, and degree of aggregation and the change of these physical parameters in time can help to understand and interpret rheological parameters. It has been suggested [3] that aging of slaked lime putties results in the formation of submicrometer platelike crystals out of large prismatic portlandite crystals and secondary nucleation of nano-sized platelike crystals. PSD of DHP show decrease up to 12 months and then increase at 24 months of aging in the size of particles with size 10 – 25 µm. The increase after 24 months is at the expense of the largest agglomerates and the decrease up to 12 months is compensated by the increase of particles with the size 1 – 5 µm. PSD of SQP during aging show reduction in the size of relatively large aggregates from 10 to 20 µm and the increase in the amount of particles with size ~ 1 µm.

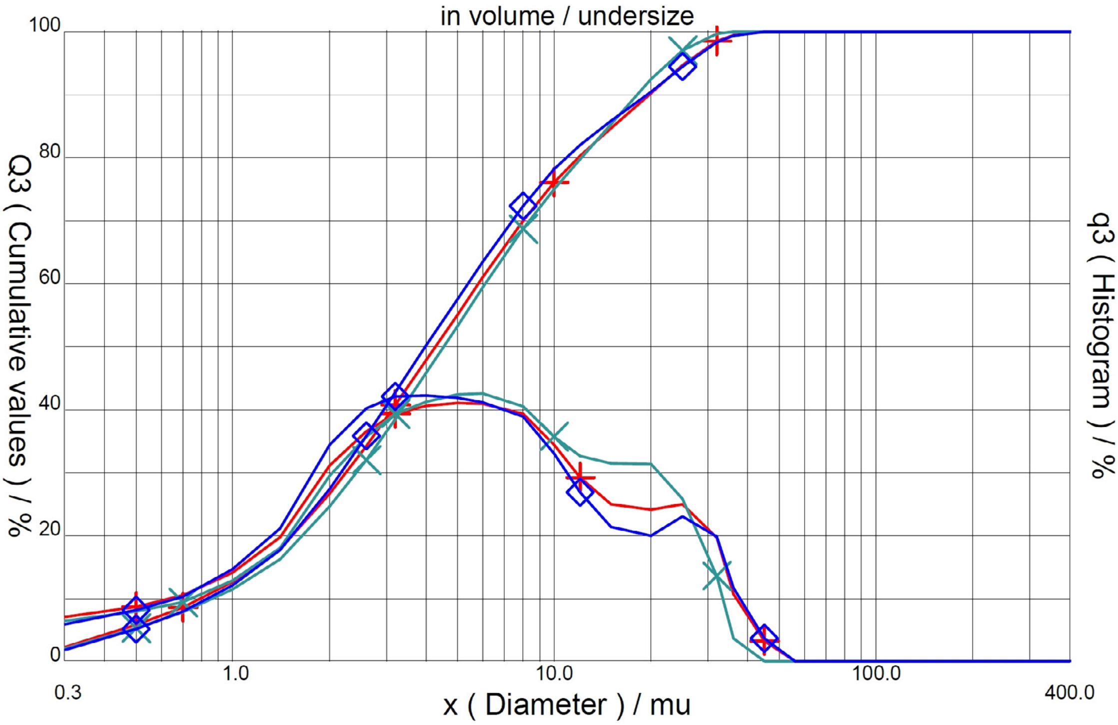


Fig. 2. The role of aging on particle size distribution of DHP, 6 months – red, 12 months – green, 24 months – blue (mu means µm).

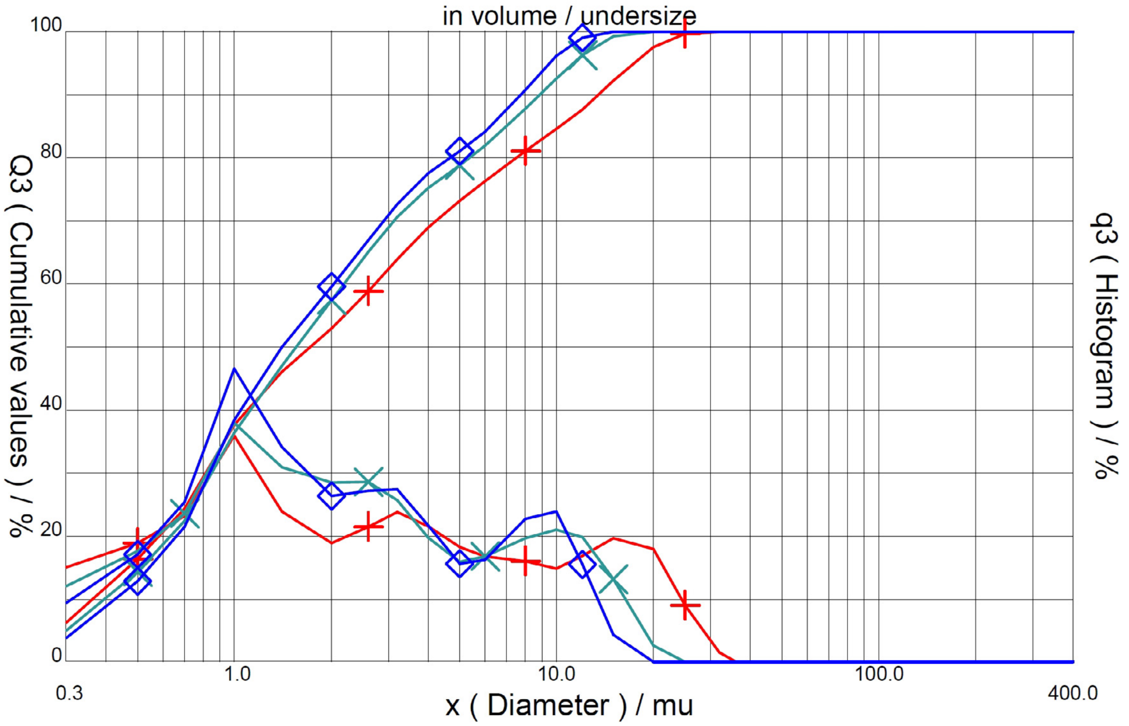
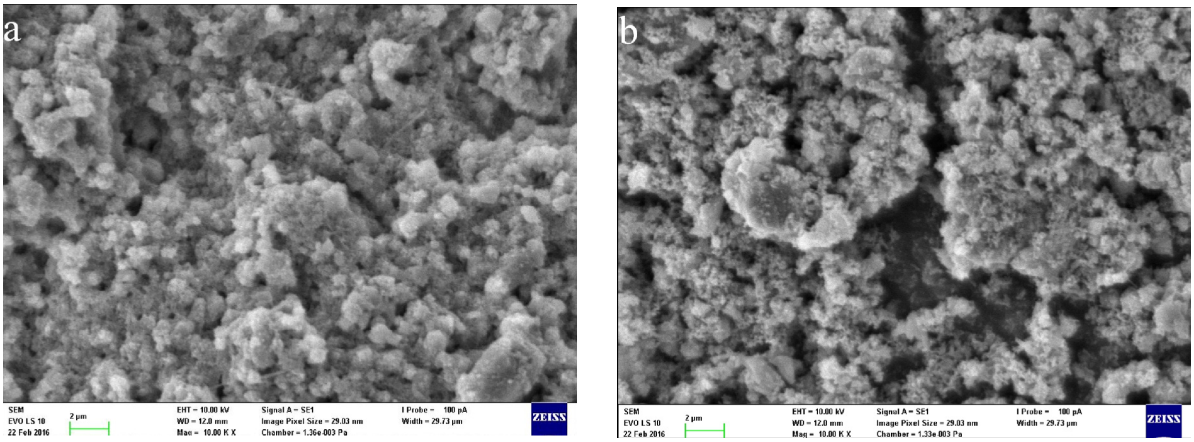


Fig. 3. The role of aging on particle size distribution of SQP, 6 months – red, 12 months – green, 24 months – blue (mu means µm).

SEM micrographs show microstructure of DHP and SQP after 12 and 24 months of aging. Samples of putties were spread on filter paper and dried at ambient temperature.

The microstructure of DHP and SQP differed considerably in size and shape of the particles. DHP consisted of round-shape clusters with micron size and no preferable orientation after 12 months while after 24 months the structure was more developed with increased amount of nano-sized particles attached to large clusters. Highly porous clusters with variable size and shape but definitely finer compared to DHP was found in the microstructure of SQP. During aging this microstructure became less porous and larger clusters were less abundant (see Fig. 4).



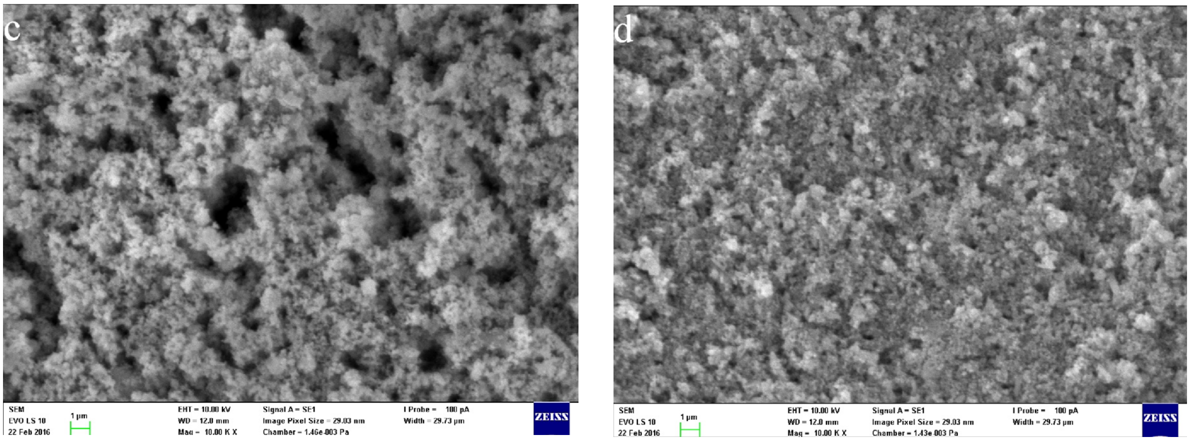


Fig. 4. SEM-SE micrographs DHP (a, b) and SQP (c, d) after 12 and 24 months of hydration, mag. 10000×.

3.2. Rheology

Lime putty as a colloidal suspension shows a variety of nonlinear rheological properties (thixotropy/rheopexy, shear thinning/shear-thickening, yield stress) [4]. These properties depend on Brownian motion of the particles, hydrodynamic interactions and on the shape, size, and on the volume fraction of particles, on the degree of aggregation and on the fraction of fluid immobilized by the particles [5,6]. Two tested lime putties differed considerably in rheological behavior (Fig. 5 and 6).

DHP shows shear-thickening especially after 6 months of aging. Furthermore, strong rheopexy can be revealed on flow curves. The rheopectic behavior (Table 1), and the plasticity of DHP decreases between 6 and 12 months and then considerably increases between 12 and 24 months. The yield stress increases between 12 and 24 months.

SQP shows shear-thinning and slight thixotropy. The thixotropic behavior of SQP increases with time (Table 2). The plasticity of SQP decreases between 6 and 12 months and then increases between 12 and 24 months. Yield stress increases between 12 and 24 months. A similar trend for plasticity and yield stress was found for DHP.

Possible explanation of increase of plasticity between 12 and 24 months is decrease in amount of large agglomerates that is compensated by the increase in the proportion of particles ~ 1 µm for SQP and ~ 1 - 5 µm for DHP. Similar trend for viscosity of putties prepared from hard burned limes was monitored by previous study [7]. Authors propose aggregation of individual hexagonal plate-like particles to large clusters for freshly prepared putties. The original high viscosity decreases during this process, which can take weeks or even months. Subsequently, viscosity tends to increase after long-term storage (more than 1 year). Based on our results we propose that disaggregation of large clusters during aging and consequent enrichment of single number micron size particles can be one of the reasons for the continuous increment of the plasticity of lime putties during long-term aging. Calcination of limestone was found to be the ruling factor for consequent time-dependent rheological properties. The study dealing with microstructure and rheology of lime putty [7] claims that soft-burned lime putties show rheopectic behavior and vice versa hard-burned lime putties possess thixotropic properties. Our study shows that these properties are developing during aging. The microstructural mechanism described in [7] might be analogous.

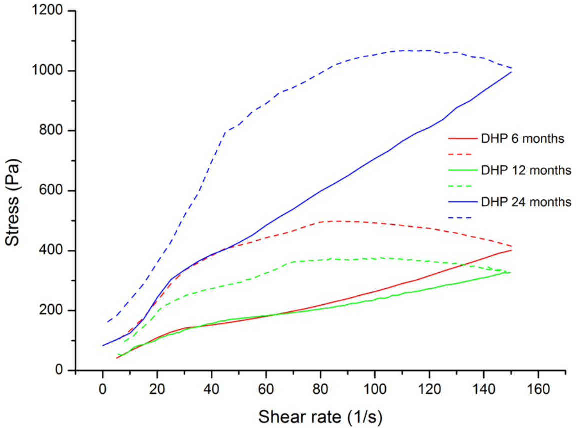


Fig. 5. The role of aging of DHP on its flow properties.

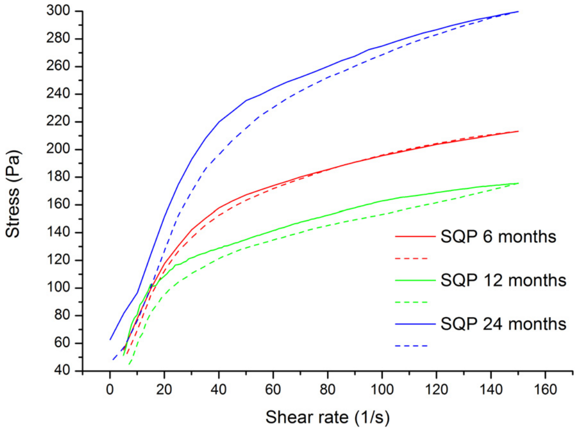


Fig. 6. The role of aging of SQP on its flow properties.

Table 2. Thixotropy/rheopexy (*Pa/s*).

Time of aging	DHP	SQP
6 month	-27106	280
1 year	-14029	306
2 years	-39465	785

4. Conclusions

The microstructure of DHP and SQP differed considerably in size and shape of the particles. SQP exhibited a variety of clusters that differed in size and shape meanwhile DHP showed round-shape clusters with size in microns during aging the microstructure of SQP became less porous and larger clusters were less abundant. DHP microstructure contained a larger amount of sub-micron sized particles after 24 months compared to 12 months.

Large clusters disaggregation during aging and resulting microstructural enrichment of micron-sized particles might be one of the reasons for the continuous increment of plasticity and yield stress of lime putties during long-term aging. Time-dependent rheological properties are affected by both calcination process and microstructure development during aging.

Acknowledgements

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