

# Effect of lignosulfonates on the morphology of calcium hydroxide crystals

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## Abstract

Lignosulfonates are commonly used in concrete as superplasticisers. Their presence can affect crystallisation and carbonation kinetics of calcium hydroxide (CH), which is an important phase in hydrated cement since it plays a crucial role in the durability and performance of concrete. In this work, lime pastes were produced by slaking quicklime in distilled water. Ca lignosulfonate (CaLS) was added to them, either before or after the slaking process to investigate the effects of temperature on the CaLS-CH interaction. All samples were characterised at 0 and 6 months from slaking with the aim of investigating the effects of CaLS on CH crystallisation. Scanning electron microscopy and X-ray diffraction were used to investigate CH crystal size and morphology, whereas microchemical analyses contributed to the investigation of the chemistry of pore solutions. Results suggest that the addition of CaLS (both, during and after slaking) affects the CH crystals habit and size, which, in turn, can have an effect on the reactivity of CH and, consequently, on the properties of fresh and hardened concrete.

## 1. Introduction

Calcium hydroxide (CH) is currently used in several industrial processes, including in construction where it has been used since antiquity as a binder in lime mortars and plasters [1]. CH is also a major component (15-25% wt) of hydrated Portland cement and its presence is vital in reinforced concrete structures to maintain an appropriate high pH to preserve reinforcement bars from corrosion [2], [3]. Changes in morphology of CH crystals can result in changes in reactivity, mechanical and rheological properties of the mixture, and can significantly affect the durability of cement and concrete [3], [4]. One of the factors that can play a role in modifying CH crystals is the presence of organic compounds that can affect CH nucleation and growth and consequently its reactivity towards CO<sub>2</sub> [4]. During concrete manufacturing, a wide variety of chemicals are routinely used to modify the properties of the mixture. In particular, plasticisers and water-reducers are commonly used to obtain cement pastes of high fluidity at low w/b ratios [5]. Among these, lignosulfonates (highly-soluble polymers obtained as by-products of the wood pulping industry) are largely employed [6]. Some studies [4], [7]–[10] have shown that the presence of lignosulfonates in solution influences the crystallisation process of CH through mechanisms that have not been completely elucidated yet. In this work, the effect of CaLS on the morphology of CH crystals in lime pastes are investigated to provide further insight on the mechanism underlying the lignosulfonates action on CH crystallisation.

## 2. Materials and Methods

In this work, 3 lime putties were prepared and analysed: a control putty (referred to as ‘C’ hereafter), prepared by slaking CaO in water at 1:3 mass ratio; a CaLS-modified putty (‘LS-1’ hereafter), prepared by slaking CaO in a 1.5% aqueous solution of CaLS at 1:3 mass ratio; a modified putty prepared by adding a quota of CaLS

(1.5% w/v of water as for the previous batch) to a putty obtained as for the control, immediately after the slaking process. To produce all the putties, ‘Calbux Granular 15’ CaO (CL90 type) with nominal particle size <15 mm was supplied by Tarmac Buxton Lime (UK). Microstructural and mineralogical characterisation of CaO is reported in [12]. Calcium lignosulfonate (80% pure with 15% reducing sugars) from Sigma-Aldrich and ethanol >99.8% from Fisher Scientific were used in these experiments. The putties and their supernatant solutions were characterised using a variety of analytical techniques when fresh and after 6 months of ageing (i.e. storage under water). Prior to each analysis, a sample from each putty was collected from the core of the batch and quenched in ethanol. For microstructural analysis a quote of each quenched putty was transferred onto a metal stab, vacuum-dried for 1 hour at 50°C, Pt-coated, and observed with a Tescan Mira3 Scanning Electron Microscope (SEM) in high-vacuum mode. For mineralogical analysis samples were prepared as described in [18] and analysed with a Rigaku SmartLab X-ray diffractometer (XRD), with Cu-K $\alpha$  radiation, parallel beam geometry, 10°-90° 2 $\theta$  scan range, 0.5° scan step, at 50kV and 40mA. The estimation of CH platelets abundance was calculated as in [18]. The mean crystallite size was estimated from the XRD data using the Halder-Wagner method [19] implemented in the Rigaku SmartLab Studio II software package. The particle size distribution (PSD) of the putties was measured via laser diffraction using a Mastersizer 3000 (Malvern Panalytical). Agglomeration was limited through sonication and by using ethanol as dispersant. The total Ca concentration in the supernatant solutions was estimated by using a Perkin Elmer Optima 8000 Inductively Coupled Plasma - Optical Emission Spectrometer (ICP-OES). For this analysis a sample of each solution was filtered through a 0.1  $\mu$ m PTFE syringe filter and diluted (x100 or x1000) in a 2% H $_2$ NO $_3$  solution.

### 3. Results and discussion

#### 3.1 SEM analysis

Selected SEM images of all putties are reported in Figure 2, showing that CH crystals in all putties are varied in size and shape. In the fresh control putty (Figure 2a), crystals display short rod-like (about 0.5  $\mu$ m), hexagonal platelet (about 1  $\mu$ m), bipyramidal, and nanogranular shape. In the aged control, the nanogranular crystals seem more abundant. These textural features are typical of CH crystals formed upon lime slaking in water [15]. In sample LS-1 (CaLS solution), CH crystals display a regular hexagonal plate-like habit (0.1-1  $\mu$ m size) with largely overdeveloped basal {001} and small vertical {100} faces (Figure 2b). Smaller crystals also display a regular platelet-like shape. Very few nanogranular crystals are visible. The aged LS-1 shows a similar microstructure. The fresh LS-2 (CaLS solid, Figure 2c) has a microstructure similar to the aged control: hexagonal platelets (0.5-1  $\mu$ m size) and abundant nanogranular crystals. In the aged LS-2, the nanogranular crystals seem more abundant.

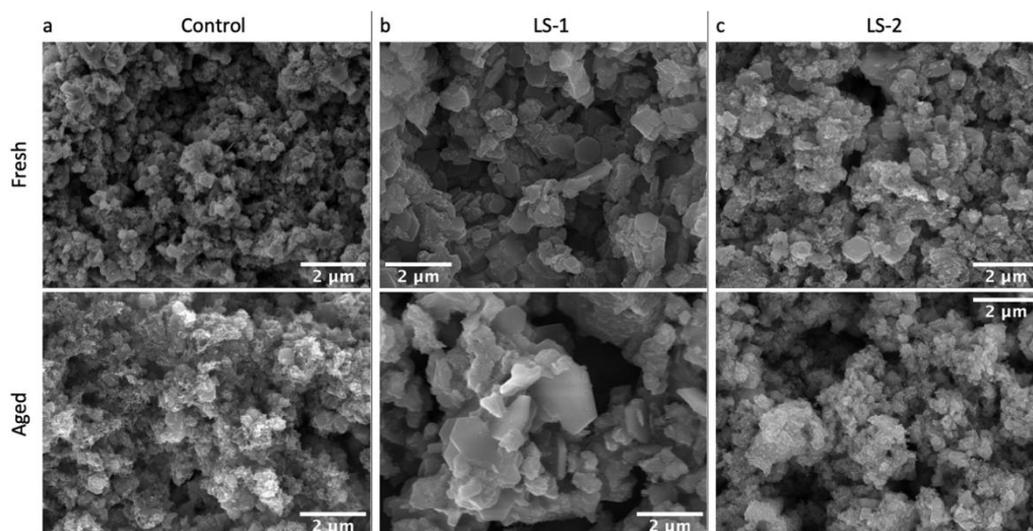


Figure 2. SEM images of the putties: (a) control; (b) LS-1 putty slaked in CaLS solution; (c) LS-2 putty with addition of solid CaLS. The first and second rows show fresh and aged samples, respectively.

Overall, the microstructure of CaLS-modified putties shows various  $\mu\text{m}$ -sized crystals with a clear tabular shape and with significantly overdeveloped  $\{00.1\}$  basal faces. These results are in agreement with previous studies [9], [10] which attribute this morphological change the preferential absorption of CaLS onto the  $\{001\}$  basal CH faces. Arguably, such adsorption occurs via interaction of the sulfonate moieties of CaLS with the  $\text{CaOH}_2^+$  species that cover the surface of basal CH faces, analogously to the reaction between pectin carboxylate groups and  $\text{CaOH}_2^+$  proposed in a previous work by Rodriguez-Navarro *et al.* [16].

### 3.2 XRD analysis

The quantitative phase analysis of the putties showed that CH was expectedly the main phase in all putties. Some traces ( $<3\%$ ) of calcite and monohydrocalcite were detected in the fresh LS-2 putty, likely formed upon carbonation in air during sample preparation. The platelets abundance ( $A_{001}$ ) and mean crystallite size of the putties are shown in Table 1.  $A_{001}$  increases with ageing in all samples and the values of both CaLS-modified putties are similar to the control. The observed increase with ageing is in agreement with literature and with the known morphological evolution of CH under water [13]. However, our SEM images show a clear platelet habit assumed by CH in Ca-LS modified putties which is not reflected by an increase in  $A_{001}$  value. Our XRD data also show a crystallite size reduction in the CaLS-modified putties compared to the control sample, which is in agreement with results of other researchers [8], [9]. As regards the ageing, our results do not support previous work where crystallite size reduction has been reported [13], [17], whereas they are in agreement with the known Ostwald's ripening mechanism, which predicts an increase of big particles overtime at the expense of the smaller [18].

Table 2. Calculations from XRD data of mineralogical characteristics of the putties.

Parameter	Fresh			Aged		
	C	LS-1	LS-2	C	LS-1	LS-2
$A_{001}$	0.70	0.58	0.74	0.88	0.69	0.78
Crystallite Size (nm)	35	19	24	36	19	30

### 3.3 Supernatant solutions analysis

The total Ca concentration in the supernatant solutions are reported in Table 2. Results show that in all CaLS-modified samples the Ca concentration is close to the control, also regardless of the ageing time. This suggests that the presence of CaLS does not (or to a very limited extent) raise Ca solubility, e.g. by complex formation, unlike other organic compounds such as sucrose [19].

Table 2. Results of the microchemical analyses of the supernatant solutions.

Parameter	Fresh			Aged		
	C	LS-1	LS-2	C	LS-1	LS-2
[Ca] (mg/L)	937	970	1010	797	873	948

## 4. Conclusions

From these results we can draw the following conclusions: i) the addition of CaLS to lime pastes produces visible changes in the morphology of CH crystals, which exhibit a tabular shape with overdeveloped basal faces in place of the rod-shape habit usually visible in a pure lime putty; ii) crystallite size is smaller in CaLS-modified systems than in pure CH system, suggesting that the additive plays a role in the nucleation stage of CH; iii) the interaction mechanism of CaLS with CH is most likely preferential adsorption onto CH crystals' basal faces rather than complex formation; iv) CaLS addition seems to inhibit the formation of nanogranular crystals upon ageing, unlike what is usually observed in a pure lime putty. Further research should elucidate whether CaLS addition to lime pastes affects the carbonation kinetics, which is a crucial aspect when CH has the role of buffering cement in reinforced concrete.

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## 6. References

- [1] R. S. Boynton, *Chemistry and Technology of Lime and Limestone*. New York: John Wiley & Sons, Inc., 1980.
- [2] I. Galan, F. P. Glasser, D. Baza, and C. Andrade, “Assessment of the protective effect of carbonation on portlandite crystals,” *Cem. Concr. Res.*, vol. 74, pp. 68–77, 2015.
- [3] S. Galmarini and P. Bowen, “Cement and Concrete Research Atomistic simulation of the adsorption of calcium and hydroxyl ions onto portlandite surfaces — towards crystal growth mechanisms,” *Cem. Concr. Res.*, vol. 81, pp. 16–23, 2016.
- [4] A. P. Barker, N. H. Brett, and J. H. Sharp, “Influence of organic additives on the morphology and X-ray diffraction line profiles of synthetic calcium hydroxide,” *J. Mater. Sci.*, vol. 22, no. 9, pp. 3253–3260, 1987.
- [5] A. Colombo, M. R. Geiker, H. Justnes, R. A. Lauten, and K. De Weerd, “On the effect of calcium lignosulfonate on the rheology and setting time of cement paste,” *Cem. Concr. Res.*, vol. 100, no. June, pp. 435–444, 2017.
- [6] R. Flatt and I. Schöber, “Superplasticizers and the rheology of concrete,” in *Understanding the Rheology of Concrete*, N. Roussel, Ed. Woodhead Publishing, 2012, pp. 144–208.
- [7] I. Jawed, W. A. Klemm, and J. Skalný, “Hydration of Cement-Lignosulfonate-Alkali Carbonate System,” *J. Am. Ceram. Soc.*, vol. 62, no. 9–10, pp. 461–464, 1979.
- [8] D. A. Kirchgessner and J. M. Lorrain, “Lignosulfonate-Modified Calcium Hydroxide for Sulfur Dioxide Control,” *Ind. Eng. Chem. Res.*, vol. 26, no. 11, pp. 2397–2400, 1987.
- [9] R. J. Lee, C. Hsia, and L. -S Fan, “Characterization of lignosulfonate-modified hydrated lime powders,” *AIChE J.*, vol. 41, no. 2, pp. 435–438, 1995.
- [10] V. T. Yilmaz and F. P. Glasser, “Crystallization of calcium hydroxide in the presence of sulphonated melamine formaldehyde superplasticizer,” *J. Mater. Sci. Lett.*, vol. 10, no. 12, pp. 712–715, 1991.
- [11] British Standards Institution, “Building lime. Definitions, specifications and conformity criteria,” *BS EN 459-1:2015*, 2015.
- [12] C. Pesce and G. Pesce, “Effects of Steam Slaking on the Characteristics of Portlandite Crystals,” *Proc. 39th Cem. Concr. Sci. Conf.*, pp. 58–61, 2019.
- [13] C. Rodriguez-Navarro, E. Hansen, and W. S. Ginell, “Calcium Hydroxide Crystal Evolution upon Aging of Lime Putty,” *J. Am. Ceram. Soc.*, vol. 81, no. 11, pp. 3032–3034, 1998.
- [14] N. C. Halder and C. N. J. Wagner, “Separation of particle size and lattice strain in integral breadth measurements,” *Acta Crystallogr.*, vol. 20, no. 2, pp. 312–313, 1966.
- [15] E. Navrátilová, E. Tihlaříková, V. Neděla, P. Rovnaníková, and J. Pavlík, “Effect of the preparation of lime putties on their properties,” *Sci. Rep.*, vol. 7, no. 1, pp. 1–9, 2017.
- [16] C. Rodriguez-Navarro, E. Ruiz-Agudo, A. Burgos-Cara, K. Elert, and E. F. Hansen, “Crystallization and Colloidal Stabilization of Ca(OH)<sub>2</sub> in the Presence of Nopal Juice (*Opuntia ficus indica*): Implications in Architectural Heritage Conservation,” *Langmuir*, vol. 33, no. 41, pp. 10936–10950, 2017.
- [17] G. Mascolo, M. C. Mascolo, A. Vitale, and O. Marino, “Microstructure evolution of lime putty upon aging,” *J. Cryst. Growth*, vol. 312, no. 16–17, pp. 2363–2368, 2010.
- [18] W. Ostwald, “Studien über die Bildung und Umwandlung fester Körper,” *Zeitschrift für Phys. Chemie*, vol. 22, pp. 289–330, 1897.
- [19] S. Martínez-Ramírez, L. R. Higuera, I. Cascales, M. Martín-Garrido, and M. T. Blanco-Varela, “New approach to nanolime synthesis at ambient temperature,” *SN Appl. Sci.*, vol. 1, no. 1, pp. 1–8, 2019.