Crystallization and Colloidal Stabilization of Ca(OH)$_2$ in the Presence of Nopal Juice (Opuntia ficus indica): Implications in Architectural Heritage Conservation

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Supporting Information

ABSTRACT: Hydrated lime (Ca(OH)$_2$) is a vernacular art and building material produced following slaking of CaO in water. If excess water is used, a slurry, called lime putty, forms, which has been the preferred craftsman selection for formulating lime mortars since Roman times. A variety of natural additives were traditionally added to the lime putty to improve its quality. The mucilaginous juice extracted from nopal cladodes has been and still is used as additive incorporated in the slaking water for formulation of lime mortars and plasters, both in ancient Mesoamerica and in the USA Southwest. Little is known on the ultimate effects of this additive on the crystallization and microstructure of hydrated lime. Here, we show that significant changes in habit and size of portlandite crystals occur following slaking in the presence of nopal juice as well as compositionally similar citrus pectin. Both additives contain polysaccharides made up of galacturonic acid and neutral sugar residues. The carboxyl (and hydroxyl) functional groups present in these residues and in their alkaline degradation byproducts, which are deprotonated at the high pH (12.4) produced during lime slaking, strongly interact with newly formed Ca(OH)$_2$ crystals acting in two ways: (a) as nucleation inhibitors, promoting the formation of nanosized crystals, and (b) as habit modifiers, favoring the development of planar habit following their adsorption onto positively charged (0001)Ca(OH)$_2$ faces. Adsorption of polysaccharides on Ca(OH)$_2$ crystals prevents the development of large particles, resulting in a very reactive, nanosized portlandite slurry. It also promotes steric stabilization, which limits aggregation, thus enhancing the colloidal nature of the lime putty. Overall, these effects are very favorable for the preparation of highly plastic lime mortars with enhanced properties.

INTRODUCTION

The hydration of quicklime (CaO) results in the production of hydrated or slaked lime (Ca(OH)$_2$, the mineral portlandite), a process known to mankind since millennia. If water is added in excess to the stoichiometric amount, a slaked lime putty (an aqueous dispersion of Ca(OH)$_2$ particles) is produced. Lime putty was the traditional binder used in ancient lime mortars and plasters, and currently is the binder of choice for the preparation of compatible mortars and plasters used in the conservation and restoration of architectural heritage. Several factors, such as the reactivity of the oxide and the retention of heat through control of the water to oxide ratio during lime slaking, affect the size, shape, and particle size distribution of portlandite crystals. The textural and structural features of portlandite crystals in turn affect the rheological properties of the putty and wet mortar mix, the carbonation reaction, speed of setting, and development of strength and porosity of a mortar, as well as its ultimate performance as a building material. Calcium hydroxide crystals formed by a slaking process can undergo significant morphological and microstructural changes upon long-term storage under water. This so-called “lime putty aging”, a process known since Roman times, brings several benefits that have fostered the use of aged lime putties in architectural conservation. Aging (months to years) induces the separation of large prismatic portlandite crystals along (0001) basal planes into numerous smaller plate-like crystals. It also leads to secondary crystallization of sub-micrometer-sized plate-like portlandite. As a result, a significant increase in hydrated lime surface area takes place, which positively correlates with enhanced reactivity, rheology (higher plasticity and workability), water retention, and faster carbonation. Comparatively, the aged lime-based mortars ultimately achieve a higher durability. However, aging of

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lime putty is a slow and lengthy process. The finding of faster alternative ways to improve the quality of lime-based binders could have significant practical implications in the conservation of architectural heritage.

Organic substances such as animal glue, egg yolk, blood, beer, casein, linseed oil, fig juice, sticky rice, and curd, as well as carboxylic acids (tartaric and citric acids), have been used since antiquity as additives to improve lime mortar quality.2,9 There is ethnographic and ethnohistoric evidence showing that lime-based binders in Latin America were commonly mixed with the water-soluble extract (juice) of tree barks (e.g., *Pithecolobium albicans*), plants leaves (e.g., *Agave spp.*), or cacti, such as nopal (*Opuntia ficus indica*) cladodes (or paddles), and their use as additives has been reported for ancient pre-Hispanic Mesoamerican Mayan and Aztec mortars, plasters, and stuccos.10-13 A traditional procedure used in ancient Mesoamerica (currently used in Mexico and the USA Southwest) involved the slaking of quicklime in nopal aqueous extract.14 Such a vernacular technology produced high quality lime mortars and plasters that withstood weathering in a hot and humid environment up until present times. In general, it is agreed that the hydrocolloid that withstood weathering in a hot and humid environment up until present times. In general, it is agreed that the hydrocolloid technology produced high quality lime mortars and plasters (that includes nongelling mucilage and gelling pectin)18 was order to determine which component(s) of the nopal juice presence of a range of organic compounds results in significant morphological and textural modifications, typically involving a change from (short) prism to thin plate-like (nano)-crystals.20-23 Such additive-induced changes resemble those achieved by aging of lime putty but are obtained in a quicker manner. A similar effect could be brought about by nopal juice. Nonetheless, the microstructural changes of Ca(OH)2 crystals induced by nopal juice during lime slaking have not been examined yet.

Here we studied the crystallographic and (micro)textural modifications undergone by Ca(OH)2 crystals formed following lime slaking in the presence of nopal aqueous extract. In order to determine which component(s) of the nopal juice (that includes nongelling mucilage and gelling pectin) was most critical for the changes in Ca(OH)2 crystals, we also studied the changes induced by the addition of pure citrus pectin, a widely available well-characterized polysaccharide with an overall composition very similar to that of the nopal juice.18,24,25 Our aim was to elucidate which nanoscale changes in terms of crystal size, shape, and ultrastructure, as well as colloidal stabilization, are brought upon by the presence of polysaccharides in slaking water and to disclose if these changes are similar to those resulting from lime putty aging. Ultimately, we strive to understand why some pre-Hispanic Mayan and Aztec lime mortars and plasters that included organic additives were of such an unmatched quality and to develop a simple technology for producing high quality lime putties for heritage conservation.

## MATERIALS AND METHODS

### Raw Materials and Preparation of Lime Putties

Quicklime (CaO) designated “Graymont” for the preparation of slaked lime putty was obtained from Genlime (USA) and used as received. The calcium oxide was slaked under vigorous stirring in an initial quicklime to water mass ratio of 1:3. Three batches of slaked lime were prepared: (a) quicklime slaked in water (this slaked lime was used as a reference); (b) quicklime slaked in aqueous nopal juice extract; and (c) quicklime slaked in 0.5 wt % pectin aqueous solution. The nopal juice extract was prepared as follows:15 (i) young nopal cactus paddles (cladodes) were obtained from nopal growing wild locally in Southern California (The Getty Center, Los Angeles); (ii) the paddles were cut into 1 in. slices, covered with water, and left to soak for 3 days; and (iii) the resulting viscous solution was strained and further diluted 1:1 with water immediately prior to use in putty preparation. The dry solid content of the nopal extract slaking water was 0.5 wt %, The putty was supplied from SIGMA Chemical Co. designated “pectin from citrus peels” [CAS No. 9000-69-5; EC No. 232-353-0] and contains >74 wt % (dry basis) poly-o-galacturonic acid. Deionized water was used throughout (water conductivity less than 5S μS cm-1). Putties were stored in covered containers under excess water throughout the length of testing. Immediately before testing, excess water was decanted. To avoid carbonation during storage and testing, containers were flushed with N2 before airtight capping.

### Reactivity Tests

The kinetics of lime slaking in the absence and presence of nopal juice and citrus pectin were determined by the continuous measurement of the temperature (T) increase taking place during the slaking process. In addition to T variations, pH and conductivity of the slaking water were measured using a glass electrode and a 856 conductivity probe coupled to a Titrino 905 titrator manufactured by Metrom. In all cases, however, both the pH and the conductivity of the solutions experienced a sudden increase right after the addition of water (with or without the additives) to CaO, followed by a T-inducing monotonic decrease (Supporting Information Figure S1), showing no differences among the different runs. For this reason, only the results of the time (t)-evolution of T are presented and discussed here. Measurements were performed under constant stirring using a magnetic stirrer. Reactivity analyses enabled disclosure of the possible nucleation inhibition effect of carbohydrate additives during Ca(OH)2 crystallization following lime slaking.

### Titration Experiments

In order to evaluate the effects of both nopal and pectin additives on ion binding during the precipitation stage, as well as their effect on the induction time (i.e., time elapsed before the onset of calcium hydroxide precipitation), titration experiments were performed at pH 12.4 ± 0.2, following the method outlined elsewhere.20 Titration experiments were performed using the above-described Titrino 905 equipment. For these homogeneous precipitation experiments, a 250 mM CaCl2 solution was continuously added to a 100 mM NaOH solution at a rate of 4 μL/s. A standard 1 M NaOH solution (Sigma-Aldrich) was used to prepare the corresponding 100 mM NaOH solutions with and without the two tested additives. Before addition of CaCl2 solution and during all the titration experiments, N2 gas was continuously bubbled into the solution placed in the reactor at a rate of 30 L/h in order to avoid the presence of CO2 in the reaction medium. During all experiments, the Ca2+ potential (i.e., free-Ca concentration) was continuously measured using an ion-selective electrode (ISE, Mettler-Toledo, DX337-Ca). This electrode was calibrated twice a day by titration of a 100 mM CaCl2 standard solution into a NaCl solution of the same ionic strength, both purchased from Sigma-Aldrich. The pH was measured using a glass electrode (Unitrode, Metrom) with a Pt100 sensor for T monitoring. T was maintained constant at 25 °C (water-cooled jacketed reactor). Solution conductivity (five-ring conductivity measuring cell, Metrom) and transmittance at 610 nm (Optrode, Metrom) were also continuously monitored. Initially, we tested an additive concentration of 5000 ppm (i.e., 0.5 wt % used during lime slaking tests). However, we observed complete inhibition (over a period of more than 12 h) of calcium hydroxide nucleation when either nopal or pectin were dosed at such a concentration. Then, we...
tested a concentration 1 order of magnitude lower (500 ppm) and observed complete inhibition after 6000 s. Finally, we chose to use a 2 orders of magnitude lower concentration (50 ppm) in order to be able to get statistically significant results (at least 5 replicates/run) in a reasonable period of time. The overall features of the titration curves (free-Ca vs t) were, however, similar regardless of the additive concentration (i.e., changes in the initial slope during the premunition stage and drop in free-Ca concentration at the nucleation stage). Note that it was not feasible to perform such a detailed analysis of the pre- and postnucleation events during the precipitation of Ca(OH)₂ following direct lime slaking because this reaction was extremely exothermic and fast (see above).

Characterization of Ca(OH)₂ Particles. Phase composition and crystallite size of slaked limes were determined by means of X-ray diffraction (XRD). Oriented aggregate mounts were prepared. Aliquots of 0.5 mL each of lime putty were deposited on glass slides, evenly spread using a stainless steel spatula, and dried under N₂ atmosphere. The oriented aggregates of calcium hydroxide crystals, presumably lying on their [0001] faces, were analyzed by means of XRD. XRD analyses were performed using a Philips PW-1710 diffractometer with an automatic slit, Cu Kα radiation (λ = 1.5405 Å), 3–60° 2θ range, with steps of 0.025° 2θ and 0.01° 2θ s⁻¹ goniometer speed. Crystallinity or "crystallite size", Dₘₐₓ (i.e., coherent X-ray scattering domains), and nonuniform strain, ε, of Ca(OH)₂ were calculated using the Williamson–Hall method implementing the routine in the XPowder 1.2 software package, which enables background subtraction, Kβ₂ stripping, and instrumental broadening correction.⁴⁸ Peak profile fitting was performed using Gaussian, Lorentzian, and pseudo-Voigt functions. Best fits were obtained using a pseudo-Voigt function.

Analysis of the shape, size, and ultrastructure of particles was performed by means of field emission scanning electron microscopy (FESEM) using a Leo Gemini 1530 and transmission electron microscopy (TEM) using a Philips CM20, operated at a 200 kV (FESEM) using a Leo Gemini 1530 and transmission electron microscopy (TEM) using a Philips CM20, operated at a 200 kV. To further evaluate habit changes associated with the presence of additives (nopal juice and citrus pectin). For kinetic stability tests, three batches of lime putty samples were prepared: (a) slaked lime putty; (b) slaked lime putty prepared with nopal juice; and (c) slaked lime putty prepared with citrus pectin. A 0.25 mL aliquot of each putty (with a solid volume fraction, ϕ = 0.25) was dispersed in 12 mL of saturated Ca(OH)₂ aqueous solution (i.e., ϕ = 0.02) and vigorously stirred at room T. The relative kinetic stability of the dispersions was determined by continuous measurement (for a period of up to 30 min) of the optical density of the dispersions measured at 600 nm (UV–vis spectrometer, Thermo Scientific UNICAM UV 300). Analyses were performed in triplicate.

RESULTS AND DISCUSSION

Reactivity. Figure 1 shows representative results of the reactivity tests. The slaking rate of the control sample (i.e., quicklime slaked in DI water) was the highest of all tested samples as shown by the faster increase in lime putty T upon addition of CaO to the slaking water. Both samples that included nopal juice and citrus pectin in the slaking water displayed a slower increase in T, particularly evident in the case of the sample including nopal juice. A contrasting behavior.
between the two additives was observed regarding the maximum temperature, $T_{\text{max}}$ reached and the time, $t_{\text{max}}$, to reach such a $T_{\text{max}}$. As compared with the control, $T_{\text{max}}$ and $t_{\text{max}}$ were lower in samples with nopal juice, whereas $T_{\text{max}}$ and $t_{\text{max}}$ were higher in the case of pectin. Apparently, dissipation of the heat produced by the highly exothermic slaking reaction was less effective in the latter case. This is likely due to the observed high viscosity of this lime putty (i.e., gelling of the citrus pectin solution due to the high pH and calcium addition), which in some runs even prevented the proper stirring of the dispersion. No such high viscosity increase was observed in the case of the slaked lime putty with nopal juice or the control. Heat dissipation was thus favored during stirring of the reactor in the latter cases. These results show that the additives acted as nucleation inhibitors, delaying Ca(OH)$_2$ crystallization. Note that several mono-, di-, and polysaccharides have been shown to delay the crystallization of portlandite, as well as other decomposition of polysaccharides, (3) dehydroxylation of Ca(OH)$_2$, lime putties corresponding to (1) dehydration of ACC, (2) portlandite was the main crystalline phase in all studied samples exposure to atmospheric CO$_2$ during preparation of oriented samples. This phase presumably formed following accidental (Figure 2). Trace amounts of calcite were detected in all phases such as CaCO$_3$.31

**Phases and Crystallinity.** XRD analyses showed that portlandite was the main crystalline phase in all studied samples (Figure 2). Trace amounts of calcite were detected in all samples. This phase presumably formed following accidental exposure to atmospheric CO$_2$ during preparation of oriented aggregates and XRD analysis. $D_{\text{lat}}$ (and $\epsilon$) values varied from 26 to 30 nm ($\epsilon = 0.09 \pm 0.02$) of the lime putty with nopal juice and 27 $\pm$ 2 nm ($\epsilon = 0.02 \pm 0.01$) of the lime putty with citrus pectin addition, up to 61 $\pm$ 11 nm ($\epsilon = 0.18 \pm 0.03$) of the control lime putty. Note that $D_{\text{lat}}$ values of freshly hydrated lime typically range between 37 and 60 nm, while a 12 month aged slaked lime putty reaches a $D_{\text{lat}}$ value of 28 nm. The Lorentzian contribution to the pseudo-Voight was generally over 90%, confirming that the microstrain contribution to broadening was minimal, which is in agreement with measured $\epsilon$ values. The absence of macrostrain due to lattice distortion (i.e., Bragg peaks showed no detectable shift to lower or higher 20 angles compared to portlandite standard: Joint Committee for Powder Diffraction Standards JCPDS Card No. 44-1481) and the negligible microstrain demonstrate that organics occlusion within portlandite crystals was negligible. Barker et al. also observed negligible lattice strain and microstrain in the case of portlandite precipitated in the presence of different sulfonate additives (superplasticizers). Note that occlusion of organics within crystalline phases, such as biogenic and biomimetic calcite, typically results in the development of macro- and microstrain, detectable using XRD.33 Our results suggest that the interaction of organics with portlandite crystals was constrained to an adsorption process at the crystal–solution interface (see below). They also show that, in terms of crystallite size, the presence of either nopal juice or citrus pectin enables, in a nearly instantaneous way, the production of Ca(OH)$_2$ crystals with the microstructural features that are achieved via long-term aging of lime putties.

Figure 2b shows the TG traces of the different Ca(OH)$_2$ samples. The control showed a first weight loss at 395–550 °C corresponding to the dehydroxylation of portlandite (Ca(OH)$_2$ = CaO + H$_2$O), and a second weight loss at 550–800 °C corresponding to the decomposition of calcite (CaCO$_3$ = CaO + CO$_2$). There was also a small weight loss at 110–330 °C, associated with the dehydration of amorphous calcium carbonate (ACC$_2$ with the overall formula CaCO$_3$.1.5H$_2$O). From these results, and according to the methodology for the quantification of both crystalline and amorphous phases formed during portlandite carbonation using TG and outlined in Rodriguez-Navarro et al., the composition of the control lime putty was 93 wt % portlandite, 4 wt % calcite, and 3 wt % ACC. Similar weight loss events were observed in the case of the lime putties with nopal juice and citrus pectin. However, in these two latter cases, the weight loss preceding Ca(OH)$_2$ decomposition was substantially higher. This is in part due to the presence of larger amounts of ACC due to faster carbonation during sample handling, which is evidence of very high reactivity of these slaked lime samples. However, from the total amount of CO$_2$ released during the thermal decomposition of CaCO$_3$ (corresponding to both ACC and calcite), an additional weight loss had to be considered for the T interval 100–395 °C. This additional weight loss corresponded to the thermal decomposition of the organic additives adsorbed on portlandite crystals and/or distributed among such crystals. Overall, the composition of these lime putties was as follows: (i) nopal lime putty, 78 wt % Ca(OH)$_2$, 7 wt % calcite, 10 wt % ACC, and 5 wt % nopal extract; (ii) citrus pectin lime putty, 67 wt % Ca(OH)$_2$, 14 wt % calcite, 10 wt % ACC, and 9 wt % pectin.

**Morphology of Ca(OH)$_2$ Particles and Aggregates.** FESEM observations showed the presence of abundant, large (up to 1.5 μm in size), short hexagonal prisms (~300–600 nm
the presence of poly(acrylic acid).

The case of calcite growth (via ACC nanoparticle attachment) in structure was favored by the organics, as recently reported for mechanism, and the preservation of such a nanogranular crystal coarsening involved a nonclassical aggregation-based making up larger plate-like portlandite crystals suggests that crystals in the control lime putty (Figure 3a). Panels b and c of

Figure 3. SEM photomicrographs of (a) control lime putty showing micrometer-sized (short) prisms of portlandite, (b) sub-micrometer-sized plate-like portlandite crystals surrounded by nanometer-sized aggregates of the same phase formed in the presence of nopal juice, (c) detail of nanometer-sized portlandite particles formed in the presence of nopal juice, and (d) thin plate-like and nanogranular portlandite crystals in the lime putty slaked in the presence of citrus pectin.

Figure 3 show the textural features of lime slaked in the presence of nopal aqueous extract. The larger crystals (∼300–1500 nm) displayed a hexagonal plate-like habit (plate thickness, ∼100–300 nm; Figure 3b and Figure S2a) and were surrounded by aggregates made up of nanometer-sized Ca(OH)₂ grains (∼30–50 nm in size) that were more abundant than in the control sample (Figure 3c and Figure S2a). Interestingly, some plate-like portlandite crystals displayed a nanogranular surface texture made up of such nanoparticles (Figure 3b and Figure S2b). The size of the smallest nanoparticles matched the crystallite size determined from Bragg peak broadening analysis (see above). Similar features were observed in the lime putty prepared using citrus pectin (Figure 3d and Figure S2c). We also observed the polysaccharide covering and binding different plate-like portlandite crystals (Figure S2d). The presence of nanocrystals making up larger plate-like portlandite crystals suggests that crystal coarsening involved a nonclassical aggregation-based mechanism, and the preservation of such a nanogranular structure was favored by the organics, as recently reported for the case of calcite growth (via ACC nanoparticle attachment) in the presence of poly(acrylic acid).

Optical microscopy and ESEM observations of portlandite crystals formed via homogeneous synthesis (counterdiffusion experiments) showed large hexagonal prismatic crystals (some of them a few millimeters long and twinned) in the control aqueous solution, whereas thin hexagonal plate-like crystals, apparently clumped together with organic material, were formed in the presence of nopal juice (Figure 4). Despite the fact that these crystals were much larger than those in the slaked lime putties, they did show a very similar and definite effect of nopal juice on portlandite habit. This is in accord with previous studies showing that a range of organic additives (e.g., polyelectrolytes) promote the formation of hexagonal plate-like portlandite crystal following their preferential adsorption on the (0001) basal planes.

TEM observations of precipitates collected right after lime slaking showed that irrespectively of the presence or absence of additives, the first solid phase formed was nanosized (Figure S5a) and amorphous, as demonstrated by the diffuse haloes of its SAED pattern (inset in Figure 5a). These amorphous calcium hydroxide nanoparticles (∼20–30 nm in size) were slightly rounded, formed porous aggregates, and were more abundant in samples slaked in the presence of the additives. Remarkably, these nanoparticles had a shape and size similar to the individual nanoparticles making up the portlandite structures observed using FESEM (e.g., Figure 3b–d). Samples collected once slaking was completed (ca. 1 h after addition of water to quicklime) showed aggregates of the above-mentioned nanoparticles along with sub-micrometric hexagonal plate-like portlandite crystals (Figure 5b). A careful examination of Figure 5b suggests that the nanoparticles, which at this stage it was not clear if they were amorphous or crystalline, attached to developing hexagonal portlandite crystals, contributing to their growth in a fashion similar to that reported for the nonclassical growth of calcite via attachment of ACC nanoparticles.

Remarkably, lime slaking in the presence of the additives favored the early development of porous aggregates made up of numerous oriented Ca(OH)₂ nanoparticles ∼30 to ∼60 nm in size (Figure 5c). The nanostructural features of such aggregates, including the low angular spreading (∼9–16°) of diffraction spots (see SAED pattern in inset of Figure 5c), are indicative of a mesocrystalline structure. These results show that the crystallization of Ca(OH)₂ followed a nonclassical route involving the formation of solid amorphous calcium hydroxide nanoparticles that subsequently underwent coarsening via nanoparticle aggregation. The latter was likely preceded by or was concomitant with an amorphous-to-crystalline transformation, which facilitated the oriented aggregation of the nanoparticles, forming the observed hexagonal plate-like portlandite particles. Samples collected at latter stages, once the slaked lime was left to set for at least 24 h, showed larger portlandite crystals and aggregates (Figure 6). Panels a and b of Figure 6 show the two main portlandite crystal morphologies of control putties observed with TEM. In agreement with FESEM
observations, portlandite crystals appeared either as large hexagonal crystals or as aggregates of nanosized crystals, with rounded or irregular habit. Interestingly, a sample of the control lime putty collected following 12 months aging showed sections of large prismatic crystals separating along (0001) planes (Figure 6b). Rupture along the basal planes was not limited to the prisms’ surface but nearly affected the whole crystal. This is a clear evidence of incipient putty evolution upon aging. Minor amounts of ACC nanospheres forming aggregates were also detected. Their amorphous nature was confirmed by the diffuse haloes in the SAED pattern (inset in Figure 6c). As indicated above (TG results), this metastable
calcium carbonate phase formed during the early carbonation of the lime putty. ACC reportedly precedes the formation of crystalline calcium carbonate phases (vaterite, aragonite, and calcite) during carbonation (in air) of portlandite crystals. The addition of nopal juice during lime slaking clearly altered portlandite crystals morphology and size (Figure 6d,e). The bimodal particle size distribution described above (see also PSD results, below) was also observed. However, nanometer-sized crystals were much more abundant, and in some cases aggregated (nonoriented aggregation) forming loose porous micrometer-sized structures (Figure 6e). Separation of individual crystals along (0001) planes was also observed (Figure 6f). In this case, however, such an effect cannot be ascribed to aging, because the sample was collected and analyzed right after slaking. Separation along basal planes was thus associated with the presence of nopal extract, which likely adsorbed on and intercalated within (0001) planes. A similar separation along basal planes in the presence of sulfonated melamine formaldehyde, which adsorbed onto (0001)Ca(OH)₂ crystals, has been reported. Addition of citrus pectin produced very similar effects on portlandite, in terms of habit, size, and nanostructure, as nopal juice addition (Figure 6g). The presence of nopal juice or citrus pectin limited crystal growth, especially along the [001] direction, thereby resulting in thin, plate-like crystals, as also observed in the case of the large crystals precipitated homogeneously via counterdiffusion in the presence of nopal juice. Both additives also limited coarsening via (irreversible) oriented attachment of Ca(OH)₂ crystals.

Figure 7a shows representative N₂ sorption isotherms of the different lime putties. All of them were of Type II, with Type H3 hysteresis loop. These features are typical for nonpore solids forming aggregates of slit-shaped pores. A slightly more marked/extended hysteresis loop was observed in lime putties formed in the presence of the organic additives. The changes in the hysteresis loop are related to an increase in the amount of slit-shaped pores, associated with more abundant plate-like crystals in the lime putties with additives as compared to the control. The BET surface area varied from 15 ± 1 m²/g in the control, up to 21 ± 2 and 24 ± 6 m²/g in the case of the lime putties prepared with nopal and citrus pectin, respectively. Such a significant surface area increase is consistent with PSD analyses showing a reduction in the amount of particles larger than 2 μm (aggregates of primary nanoparticles and larger individual crystals), and a parallel increase in the amount of particles 20–200 nm in size (i.e., primary nanoparticles), in the case of the lime putties slaked in the presence of nopal juice and citrus pectin (Figure 7b). N₂ sorption and PSD results are consistent with FESEM and TEM results (see above) showing an overall decrease in crystal size and degree of aggregation of portlandite particles formed in the presence of both additives.

Spectroscopic Study of Additives and Lime Putties. Figure 8a shows the FTIR spectra of both the dried nopal extract and the citrus pectin. Both spectra showed a broad band centered at ~3440 cm⁻¹, corresponding to the O–H stretching of carboxylic acids and polysaccharides. The small bands at 2880–3016 cm⁻¹ corresponded to the C–H stretching in CH₂ and CH₃ groups of carboxylic acids and esters in polysaccharides. The bands at 1613 (nopal) and 1638 cm⁻¹ (citrus pectin) corresponded to the ν asym(COO⁻) stretching, whereas the band at 1429 cm⁻¹ (citrus pectin) corresponded to the ν sym(COO⁻) stretching. The bands at 1727 (nopal) and 1738 cm⁻¹ (citrus pectin) corresponded to C==O stretching and can be assigned to protonated carboxyl groups (COOH) in carboxylic acids (e.g., galacturonic acid). Note, however, that esterification (methylation) of carboxyl groups strongly contributes to the absorbance intensity of this carbonyl band. The higher value of the ratio between the absorbance intensity of the 1613 and 1727 cm⁻¹ bands in nopal as compared to citrus pectin, indicates that the former had a lower degree of esterification than the latter. These results are consistent with previous studies showing that the aqueous extract of nopal includes ~10 wt % galacturonic acid residues with a low degree of (methyl)esterification (~9%). The strong carboxylate band at 1429 cm⁻¹ in the nopal extract corroborates the presence of abundant free carboxylic acids (galacturonic acids). The weak band at 1321 cm⁻¹ has been assigned to the C–H vibration in haired zones of polysaccharides. A very weak band at 1516 cm⁻¹, which can be ascribed to amide II, suggests that a small amount of proteins might be present in nopal juice. However, the overlap of the amide A, B, I and III bands with those of the polysaccharides precluded an unambiguous identification of proteins in the studied aqueous extract of nopal. Both additives showed numerous bands between 1200 and 800 cm⁻¹, the so-called “fingerprint” region of polysaccharides. Despite its complexity, in the case of the nopal extract, the band at 1051 cm⁻¹ was ascribed to amide II, corresponding to C==O stretching
been termed (nongelling) mucilage and (gelling) pectin, respectively.\textsuperscript{18} Mucilage and pectin from \textit{O. ficus indica} can be distinguished based on the higher amount of polygalacturonic acid in the latter fraction.\textsuperscript{18} The main structural component of pectins is a backbone of homopolymeric partially methylated poly-\textalpha{}(1\rightarrow4)-\textalpha{}-galacturonic acid residues (known as the “smooth” region), along with “hairy” nongelling areas with neutral sugars such as \textbeta{}-xylene, \texti{}-rhamnose, \texti{}-arabinose, and \textbeta{}-galactose.\textsuperscript{45} The existence of abundant carboxylic acid groups is responsible for the gelling behavior of pectin. A pH increase and/or addition of divalent cations such as \texttext{Ca}^{2+} can trigger the gelling of an aqueous solution of (low methoxylated) pectin,\textsuperscript{18,24} via the formation of a rigid “egg-box” structure.\textsuperscript{46} In our case, and in agreement with published results,\textsuperscript{18,24,25,37} the juice of nopal cladodes included both mucilage and pectin according to the polysaccharide composition identified using FTIR. It is thus expected that the gelling pectin fraction in the aqueous extract of nopal cladodes contributes to the amelioration of macroscopic properties observed upon its addition to lime-based mortars and mortars (i.e., increased viscosity, plasticity, and workability, as well as reduced cracking).\textsuperscript{16,17} However, the gelling behavior of pectin in nopal juice does seem to be the only or main factor that contributes to obtaining a lime binder of superior quality: the changes in \texttext{Ca(OH)}_{2} crystals’ morphology, size, and degree of aggregation observed upon lime slaking in the presence of both nopal juice and citrus pectin seem to be more important factors. Further insights on the interaction of the nopal juice and the citrus pectin with \texttext{Ca(OH)}_{2} crystals were gained through spectroscopic analysis of the lime putties slaked in the presence of these additives.

Figure 8. FTIR spectra of (a) the dry nopal juice and the dry citrus pectin and (b) the dry lime putties slaked in the absence (control, blue line) and presence of nopal juice (green line) and citrus pectin (red line). The shaded bars in panel a show the main regions for the different absorption bands of the groups in the organic additives.

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broad ν3 band of CO32− groups centered at 1480 cm−1. Interestingly, both the sharp band at 3642 cm−1 and the broad band at 442 cm−1 of portlandite underwent a small reduction in intensity in the presence of nopal juice and citrus pectin. Raju et al. observed a similar effect upon interaction of a polysaccharide (dextrin) with portlandite and concluded that this was due to the formation of a chemical complex between the carbohydrate and Ca(OH)2 crystals. In contrast, Moreira et al. suggested that a reduction in the intensity of the νOH band of another alkaline-earth hydroxide (brucite, Mg(OH)2) following interaction with pectin was due to H-bonding. Note, however, that both H-bonding and electrostatic interactions have been shown to operate during the adsorption of polysaccharides onto minerals including structural OH groups. In our case, it is thus likely that both electrostatic interactions leading to chemisorption and H-bonding played a role in the adsorption of the polysaccharides onto portlandite. Overall, our FTIR results show that the polysaccharides used as additives were affected by the highly alkaline environment in the Ca(OH)2 lime putty, and strongly interacted with, and were adsorbed onto, the portlandite crystals.

Figure 9a shows the diffuse reflectance UV–vis–near-IR spectra of dry nopal extract and citrus pectin. The nopal extract showed two weak bands at ~230 and ~272 nm and a shoulder centered at ~320 nm. The citrus pectin showed a band at ~275 nm and a well-defined shoulder at ~320 nm. In both cases, no distinctive bands were observed in the visible and near-IR regions. Absorption bands at ~230 and ~280 nm are characteristic of nopal mucilage and pectins. The appearance of a band at ~230–235 nm has been associated with the formation of an unsaturated compound following glycosidic bond cleavage in poly-D-galacturonic acids via β-elimination, a degradative (depolymerization) process which is promoted at high pH, and in the presence of cations such as Ca2+. The band at ~280 nm has been associated with the presence of carbonyl groups in galacturonic acid units. The band at 320 nm could be associated with carbonyl groups in reducing sugar end units (n → π* transitions of a saturated aldehyde or ketone). Our UV results show that the nopal extract displayed a higher degree of depolymerization (after β-elimination) than the citrus pectin. This is likely due to mucilage degradation during aqueous extraction and sample preparation.

Figure 9b shows the diffuse reflectance UV–vis–near-IR spectra of slaked lime putty powders with and without additives. The control lime putty only showed a small shoulder at 260 nm, as reported in the literature. This shoulder is likely related to the presence of carbonate groups (i.e., ACC and calcite). If compared with the spectrum of pure nopal extract, the main change that took place upon its interaction with the
lime putty was the relative increase in the intensity of both the shoulder at \( \sim 235 \) nm (due to \( \beta \)-elimination and depolymerization) and the broad band/shoulder centered at \( \sim 280 \) nm and spanning up to \( 320 \) nm (associated with free carboxylic groups and reducing sugar end groups). Reportedly, enolization of reducing sugar units in alkaline solution strongly contributes to the intensity of the band at \( \sim 320 \) nm.\(^{53}\) In the case of the citrus pectin, the main changes after lime slaking were as follows: (i) the appearance of a shoulder at \( \sim 235 \) nm due to \( \beta \)-elimination, promoted by the high initial degree of methyl esterification of this polysaccharide;\(^{53}\) (ii) reduction in the intensity of the carbonyl band at \( 287 \) nm, likely due to de-esterification at high pH;\(^{50}\) and (iii) the increase in the intensity of the shoulder at \( 320 \) nm, due to an increase in the abundance of reducing sugar end groups associated with depolymerization and their alkali-induced enolization.\(^{53}\) The observed changes in bands/shoulders show that the polysaccharides underwent important structural changes in the presence of Ca(OH)\(_2\), which, in addition to de-esterification and depolymerization of poly-D-galacturonic acids via \( \beta \)-elimination and alkaline hydrolysis,\(^{50,51}\) likely were associated with adsorption of the two additives on Ca(OH)\(_2\) crystals. Indeed, an increase of the band/shoulder at \( \sim 320 \) nm has been associated with the formation of calcium–polysaccharide complexes following interaction of carbohydrates with Ca(OH)\(_2\) crystals in solution.\(^{53}\) Finally, no significant differences were detected among the different samples in the visible and near-infrared region. The \( \nu_\text{OH} \) stretching band at \( 1413 \) nm (\( 7077 \) cm\(^{-1}\)) and the overtone (\( 3\nu_\text{OH} \)) at \( 914 \) nm (\( 10298 \) cm\(^{-1}\)) associated with portlandite were clearly observed in all samples.

To gain further insights into the structural changes and possible binding mechanism of the polysaccharides in nopal juice and citrus pectin at the relevant conditions existing in a slaked lime putty (pH = 12.4 and 20 mM Ca\(^{2+}\)),\(^{7}\) we performed UV–vis spectroscopic analyses of aqueous solutions of nopal extract and citrus pectin with and without dissolved Ca(OH)\(_2\) (i.e., limewater; Figure 9c,d). The spectrum of the saturated Ca(OH)\(_2\) solution had no distinctive features, other than a marked monotonic decrease in absorbance with increasing wavelength in the interval 200–230 nm. In contrast, both the nopal extract (Figure 9c) and citrus pectin (Figure 9d) solutions showed a strong band centered at \( \sim 210 \) nm corresponding to carboxyl groups (i.e., \( n \rightarrow \pi^* \) transitions),\(^{54}\) which did not change position or intensity upon pH increase up to 11.4–11.6 and presence of Ca\(^{2+}\). Bands associated with unsaturated sugar residues formed upon cleavage of glycosidic bond (\( \sim 240 \) nm) and carbonyl (\( \sim 280 \) nm) groups of carbohydrate in nopal solution at its natural pH of 4.1 experienced a red shift upon addition of the saturated Ca(OH)\(_2\) solution, likely associated with (limited) Ca\(^{2+}\)–carbohydrate complex formation. In the case of the citrus pectin solution, the pH increase from 3.7 to 11.6 resulted in the appearance of a strong shoulder at \( \sim 240 \) nm, consistent with a \( \beta \)-elimination process. The reduction in intensity of the small shoulder at \( 280 \) nm and the appearance of a well-defined and stronger band at \( 340 \) nm in the limewater solution suggest that alkaline degradation involving formation of abundant unsaturated reducing sugar end groups and their enolization and \( \beta \)-elimination (and final transformation into carboxylic and/or hydroxycarboxylic acids, see below), as well as complexation between the carboxyl groups in galacturonic acids (and/or other degradative byproducts) and Ca\(^{2+}\) ions took place. Indeed, the increase in intensity and shift of the band at \( 320 \) to \( 340 \) nm has been associated with Ca-complex formation following alkaline degradation of carbohydrates exposed to calcium hydroxide solutions.\(^{53}\) Ca complexation is consistent with the observation that (unlike the nopal juice) the citrus pectin underwent gelling following addition of limewater. Note, however, that the capacity of pectin for complexing Ca\(^{2+}\) (in alkaline solutions), although enough to form an egg box structure, has been shown to be very limited.\(^{31}\) It is thus considered that the complexation effect of polysaccharides in nopal juice (and citrus pectin) should be very limited in the lime putties and constrained to the binding of small amounts of free calcium (up to 20 mM) present in the solution where the Ca(OH)\(_2\) particles were dispersed.

Overall, the spectroscopic results show that the polysaccharides in nopal aqueous extract and citrus pectin suffered significant structural modifications in contact with the slaked lime putty, and such modifications (alkaline hydrolysis and \( \beta \)-elimination leading to de-esterification and depolymerization) resulted in a strong interaction (adsorption) between the polysaccharides (and their degradative byproducts; see below) and the portlandite crystals formed upon quicklime slaking, which were dispersed in a high pH solution (i.e., lime putty). Our UV–vis results also demonstrate that (limited) interaction (complexation) between the polysaccharides and Ca\(^{2+}\) in solution also took place at the alkaline pH of the lime putties.

**ζ-Potential and Kinetic Stability of Lime Putties.** The adsorption of the polysaccharides onto portlandite particles was further confirmed by \( \zeta \)-potential measurements. The \( \zeta \) potential changed from a high positive value (26 ± 4 mV) in naked portlandite particles to a lower positive value (15 ± 2 mV) in the presence of citrus pectin, and a value close to zero (0.5 ± 2 mV) in the presence of nopal. These results confirm that adsorption of such organic additives onto Ca(OH)\(_2\) particles took place. In principle, a reduction in surface charge to values closer to 0 mV should promote particle agglomeration and settling. However, kinetic stability measurements showed an increase in the stability of the dispersions of Ca(OH)\(_2\) particles with either nopal juice or citrus pectin compared to the control, as reflected by their slower settling rate (Figure 10). The latter results demonstrate that the stabilization effect brought about by the adsorbed polysaccharides was not mainly due to electrostatic interactions but rather to steric stabilization (i.e.,

![Figure 10: Colloidal stability test results showing the variation in absorbance at 600 nm of the Ca(OH)\(_2\) dispersions prepared from lime putties with and without organic additives.](image)
osmotic and elastic—steric repulsion). Pectin adsorption on nanoparticles (e.g., silver nanoparticles) has been reported to prevent their agglomeration and to contribute to their colloidal stabilization via steric hindrance.55

**Mechanisms of Polysaccharide–Ca(OH)2 Crystal Interaction.** Our results show that the mucus (and pectin) in the nopal aqueous extract and the citrus pectin are polysaccharides that have very similar effects on Ca(OH)2 crystals and their aqueous dispersions. Based on the literature and our experimental results, the following mechanisms can be proposed to explain the effects of these carbohydrates (i) as crystallization inhibitors, leading to the reduction in the slaking rate and resulting in the observed abundance of nanometer-sized crystals; (ii) as habit modifiers, leading to the formation of thin plate-like particles; and (iii) as colloidal stabilizers, leading to the observed increase in the colloidal stability of lime putty dispersions.

Regarding crystallization inhibition it could be argued that carbohydrates reduce the effective supersaturation of the system with respect to portlandite via chelation of Ca2+. However, chelating agents stronger than carbohydrates, such as EDTA, are not as effective portlandite crystallization inhibitors as carbohydrates.30 Banfill,30 who discarded the previous “chelating” hypothesis, proposed that the effectiveness of carbohydrates to inhibit Ca(OH)2 crystallization (and to delay cement setting) was due to nuclei poisoning. However, it was not clear from a mechanistic point of view how such a nuclei poisoning operated. Recently, and within the context of nonclassical nucleation involving (stable) prenucleation clusters (PNC),26 it has been shown that a range of organic additives, including polysaccharides, have manifold effects on the nucleation and growth of different phases (e.g., CaCO3 and CaC2O4·nH2O) depending on how and at what stage of the crystallization process they act, and with what species (solute species, PNC, liquid precursors, or solid products) they interact.31,56,57 Up to nine types of independent actions occurring at both pre- and postnucleation stages have been identified in different additive systems.57 At the prenucleation stage, it has been observed that stabilization of PNCs by adsorption of additive molecules leads to nucleation inhibition, because such an adsorption effect prevents PNCs clustering, similarly to colloidal stabilization.57 Conversely, destabilization of PNC induced by additives also inhibits nucleation.31 In both cases nucleation eventually occurs, typically after long waiting times and at a very high supersaturation. Overall, these effects result in a high density of small crystals. Recent experimental results have shown that pectin is a good nucleation inhibitor for CaCO3 because it induces PNC destabilization.31 It is thus likely that similar PNCs (de)stabilization effects operated here in the case of Ca(OH)2, both in the presence of the citrus pectin and the nopal aqueous extract, leading to nucleation inhibition (i.e., “poisoning effect“). In order to check this hypothesis we performed titration experiments in which a CaCl2 solution was added at a constant rate to a NaOH solution placed in a reactor with and without dissolved nopal juice or citrus pectin (see Materials and Methods). Figure 11 shows representative results of the t-evolution of free-Ca and transmittance for the control run and the runs performed in the presence of 50 ppm nopal and pectin. In all cases the slope of the initial (nearly) linear part of the free-Ca evolution curve was lower than the slope of dosed Ca. This effect has been reported to be due to the formation of prenucleation ion associates (i.e., PNC)58 and suggests that the system undergoes a nonclassical nucleation pathway involving the formation of PNC prior to the appearance of the amorphous calcium hydroxide nanoparticles observed using TEM (see Figure 5).35 Moreover, in the case of nopal addition, the slope of the initial part of the curve was steeper than that of the control. This shows that this additive destabilized PNC. Such a destabilization led to a marked increase in the waiting time for nucleation, which was detected by the reduction in transmittance and the drop in measured free-Ca. In contrast, in the case of pectin addition the slope of the initial portion of the free-Ca vs time curve was lower than that of the control. However, the presence of pectin also increased the waiting time before the onset of nucleation, although to a lower extent than in the case of nopal. These results demonstrate that both additives are strong nucleation inhibitors,56,57 although nopal is a more effective nucleation inhibitor than pectin. Nonetheless, while both additives show a Type II behavior according to the classification of additives proposed by Gebauer et al.,56 (i.e., influence on the prenucleation clusters equilibria in solution), their effect on PNC was opposite. Nopal delayed nucleation because it apparently destabilized PNC, thereby making the formation of a new phase (e.g., an amorphous solid, see TEM results) via coalescence of PNC difficult.55 Conversely, pectin apparently stabilized PNC, a colloidal stabilization effect that has been reported to hamper phase separation via aggregation of PNC.56 It is likely that the different behavior of nopal and pectin at the prenucleation stage and their differing effectiveness as nucleation inhibitors are related to compositional differences between the two carbohydrates. Galacturonic acids, which are the main component of citrus pectin, seem to favor PNC stabilization due to their high content of carboxylic groups. Conversely, the abundance of neutral sugar residues in the nopal juice appears to favor PNC destabilization. However, the detailed mechanism responsible for such a distinct behavior is not clear and might be related to charge, chain length, branching, and conformation of polysaccharides,51 as well as to the effects of the different alkaline degradation byproducts

![Figure 11. Free-Ca profiles measured during addition of CaCl2 solutions into NaOH solutions in the absence (control, blue solid line) and presence of 50 ppm nopal (green solid line) or 50 ppm pectin (red solid line). The black solid curve represents the evolution of total added Ca. The sudden change in the slope of the free-Ca vs t curves, matching the drop in transmittance (dashed lines; same color code as in the case of free-Ca curves), corresponds to the onset of precipitation.](https://doi.org/10.1021/acs.langmuir.7b02423)
formed in each case (see below). Collectively, these results suggest that PNC played a role in the precipitation of Ca(OH)₂, similar to that observed in the case of other inorganic phases such as calcium carbonates, calcium oxalates, silica, iron oxy(hydr)oxides, and amino acids (see ref 35 and references therein). Note, however, that although our titration experiments point to the existence of PNC, further complementary analyses (e.g., ultracentrifugation and/or cryo-TEM) would be required to confirm their presence in our system. Our results also show that both nopal and pectin (and their alkaline degradation byproducts) have a high inhibition capacity in the case of Ca(OH)₂ nucleation, an effect also displayed by several carbohydrates (including pectin) in the case of CaCO₃ precipitation. However, no significant complexation was detected for both nopal and pectin as demonstrated by the lack of an offset (delay) in the t-evolution of free-Ca concentration at the beginning of the titration runs.

Regarding the effect of the studied additives as habit modifiers, it can be hypothesized that polysaccharide molecules can preferentially be adsorbed onto portlandite (0001) crystal faces. The growth of basal faces will thus be slowed so that these faces should become morphologically more important, giving rise to the observed change in morphology from short prismatic to thin plate-like crystals. Additive adsorption on (0001) limits growth along the [001] direction, resulting in plate-like crystals. Adsorbed polysaccharides prevent particle aggregation via steric hindrance, thereby providing a high colloidal stability to the limewash dispersion.

Figure 12. Structure of portlandite projected along (a) [100] and (b) [001]. (c) Simplified structural features of the poly-D-galacturonic acids constituting the backbone of nopal juice and citrus pectin prior to and after alkaline degradation. (d) Scheme showing the proposed adsorption of the polysaccharides on portlandite (0001) basal planes. Deprotonation of carboxyl groups in the partially degraded polysaccharides enable their chemisorption on the (0001) basal planes of portlandite. Adsorption on (0001) limits growth along the [001] direction, resulting in plate-like crystals. Degradation products of the polysaccharides and their degradative byproducts (Figure 12c) can be the active groups involved in the chemisorption process (i.e., formation of reducing sugars and carboxylic acid byproducts) has been proposed to explain the observed morphological change.
set retarding effect of carbohydrates in Portland cement.\textsuperscript{61} Furthermore, the interaction between the polysaccharides and portlandite crystals at the alkaline pH (12.4) of the lime putty may also involve deprotonated hydroxyl groups of neutral sugar residues. Note that the pKₐ (25 °C) of some of the neutral sugar residues in nopal extract and pectin, such as mannose (12.08), xylose (12.15), and galactose (12.39), are below pH 12.4.\textsuperscript{62} Indeed, it has been proposed that hydroxyl groups in carbohydrates are involved in chemisorption on metal (Ca and Ba) hydroxides.\textsuperscript{37}

Adsorption could also take place via H-bonding between ionized carboxyl and hydroxyl groups in the polysaccharides and neutral >CaO\textsuperscript{2+} surface sites on (0001) faces of portlandite via the reaction >CaOH\textsuperscript{+} + ^−\text{OOC−R} = >CaOH−OOC−R. Both chemisorption and H-bonding of nopal and citrus pectin polysaccharides on portlandite are consistent with our FTIR and UV results. However, the observed reduction in ζ-potential from a highly positive value to values close to zero following adsorption of the polysaccharides onto portlandite suggests that electrostatic interactions leading to chemisorption likely are the dominant adsorption mechanism in our studied systems.

Upon adsorption, polysaccharides would prevent aggregation of Ca(OH)\textsubscript{2} particles mainly due to steric repulsion effects (Figure 12d), thus stabilizing the dispersion as observed here (Figure 10). Ultimately, the adsorbed organic coating will also interfere with the coarsening (via oriented attachment) and aggregation of nanoparticles undergoing Brownian motion in the aqueous dispersion. On the other hand, the organic “protective” coating will also limit dissolution of such small, unstable nanoparticles, thereby limiting Ostwald ripening. Despite their coating effect, the water-holding character of polysaccharides may preclude a reduction of lime putty plasticity and workability.\textsuperscript{15}

\section{CONCLUSIONS}

Our results show that both the aqueous extract (mucilage) of nopal cladodes and a commercially available pectin (citrus pectin) have significant and very similar effects on the size, habit (shape), and colloidal stability of Ca(OH)\textsubscript{2} crystals in lime putties prepared following slaking of quicklime.

The nopal juice includes abundant polysaccharides with overall composition very similar to that of the tested citrus pectin: galacturonic acid and neutral sugar residues. The most marked differences between the two polysaccharides are the lower content of galacturonic acids (i.e., low gelling capacity) in the nopal juice and their lower degree of methylation.

The high pH (12.4) of the lime putty formed after lime slaking promotes alkaline hydrolysis and β-elimination of the polysaccharides, resulting in de-esterification and depolymerization and, possibly, formation of carboxylic and/or hydroxycarboxylic acid byproducts. These degradative processes, in addition to deprotonation of carboxyl and (to a lesser extent) hydroxyl groups, favor a very strong interaction between the carbohydrate additives and prenucleation species, resulting in nucleation inhibition and crystallization at a high supersaturation. These effects foster the formation of abundant nanosized portlandite crystals after an amorphous nanosized precursor. All in all, these results demonstrate that the system follows a nonclassical crystallization pathway.

Postnucleation effects of the additives are associated with their preferential adsorption on (0001) planes of Ca(OH)\textsubscript{2}, resulting in habit modification from (short) hexagonal prisms to plate-like crystals. Adsorption predominantly occurs via electrostatic interactions (chemisorption) between deprotonated carboxyl groups of polysaccharides and the abundant positively charged >CaOH\textsuperscript{+} surface species on (0001)\textsubscript{portlandite}. Adsorption via a H-bonding between deprotonated carboxyl and hydroxyl groups in the polysaccharides and the OH groups present on (0001)\textsubscript{portlandite} also occurs (to a minor extent).

The minor amounts of Ca\textsuperscript{2+} ions present in the alkaline solution (up to 20 mM) interact with the polysaccharides and their degradative byproducts, likely via complexation. Complexity, however, seems to be very limited due to the low amount of Ca in solution compared to the large volume of Ca(OH)\textsubscript{2} particles in the lime putty dispersion.

The adsorption of the polysaccharides onto Ca(OH)\textsubscript{2} crystals leads to a strong colloidal stabilization mainly via steric interactions. Additive adsorption apparently also prevents limits Ostwald ripening and coarsening due to particle aggregation, two detrimental processes that can to some extent be reverted by aging of slaked lime. However, the addition of nopal juice or citrus pectin allows the production of a high quality lime putty with high surface area, small particle size, and plate-like morphology, right after lime slaking. These features positively affect reactivity, water retention and rheology of the lime paste and may lead to easier and faster carbonation during setting and hardening of lime mortars and plasters. This quality improvement is an important fact to consider in practical architectural conservation interventions using lime-based mortars and plasters.

Both the nopal juice and the citrus pectin have very similar positive effects on the microstructure and colloidal behavior of Ca(OH)\textsubscript{2} crystals. Nonetheless, from a practical and economical point of view, the use of nopal juice will be preferable for the formulation of lime mortars and plasters used in architectural conservation.

Finally, our results contribute to shed light on the origin of the high quality and durability of pre-Hispanic Mayan and Aztec lime mortars and plasters that reportedly included in their formulation polysaccharide-rich plant extracts, such as nopal juice.

\section{ASSOCIATED CONTENT}

\subsection*{Supporting Information}

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.langmuir.7b02423.

Information on the methodology used for the calculation of portlandite surface speciation and supporting figures including results from reactivity tests, SEM analysis, and pH-dependent surface speciation, and also supporting references(PDF)

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