THE OPTIMIZATION OF HYDRATED LIME PUTTIES AND LIME MORTARS USING NOPAL PECTIN

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ABSTRACT

Considered the base material of millenary building systems in Mexico, hydrated lime has been traditionally produced since pre-Hispanic times. This implies intangible heritage that is currently at risk of being lost due to the high costs involved in its manufacture, especially during its hydration stage, which involves a resting time of several months before it develops the mechanical and rheological properties that make it useful in construction and works of restoration. Multidisciplinary research was carried out to reduce the cost of manufacture and to revitalize an ancient technique. It involved several experimental phases of physicochemical, architectural and constructive analysis that resulted in the discovery of a key substance contained in the nopal mucilage. This substance not only enabled a good chemical interaction with lime, but also managed to function as a catalyst in the hydration and aging process of lime putties from its crystallographic modification. Moreover, it had a significant impact on the optimization of the mechanical and rheological properties of the mortars prepared with them, as well as on their behavior during the carbonation process and their ability to absorb moisture. The results that allowed to conclude this optimization were obtained from the characterization and comparison of the behavior of the new lime putties with pectin and the mortars prepared with them through analysis in SEM, XRD, as well as the adaptation of some established methods of analysis and many others proposed in the research for this binder and its by-products. The theories produced from this research open the door to new lines of exploration that involve further research about the interference that mortar dosage has and the interaction with pectin compared to other fruits.

INTRODUCTION

The optimization of base materials of historical and archaeological construction systems, such as hydrated lime, is worthy not only in terms of the conservation of cultural and social heritage, but also in favor of promoting multi and transdisciplinary research in architecture, still under development in Mexico. Regarding the conservation of heritage, the hydration of lime is an ancient technique at risk of disappearing in our country due to the high costs generated by its traditional means of production, which has caused the material to be undervalued in the construction industry. The high cost of the material due to industrialization also makes it unattainable for the low-income population that mostly inhabits a variety of buildings with similar construction systems planned around hydrated lime. On the other hand, the reduction of costs in lime production techniques and generally unfounded efforts to improve its properties result in poor quality mortars. One of the main causes of the increase in the costs of the traditional production of hydrated lime is the time it must rest submerged in its hydration medium until it reaches desirable mechanical and rheological properties for construction purposes. Consequently, the direct optimization of lime putty aims to catalyze the 12–14-month physicochemical process that leads to the improvement of its properties [5] [6], automatically reducing production and marketing costs.

The optimization of lime putties has a direct impact on the improvement of the mortars that are manufactured with this binder [2] [8]. The optimization that is proposed in this research, has its origin in a pre-Hispanic practice of the northern Mayan region, where the gums of the bark of some trees, rich in polysaccharides, were combined with the water they used to hydrate quicklime and produced lime putties with good rheological and mechanical behavior [1] [2]. In Mexico, nopal, a cactus rich in polysaccharides that is affordable for practically the entire population, is known in the restoration industry as a natural additive to mixtures and mortars in the earliest stages of their manufacture process, that is, in the hydration phase of the binder [8] [10]. The optimization proposal with nopal required multidisciplinary work distributed into different experimental phases, the first one with a focus on the identification of the chemical compound responsible for an effective interaction between lime and nopal mucilage.

EXPERIMENTAL

In the chemistry laboratory, it was discovered that galacturonic acid is responsible for facilitating the successful chemical interaction between nopal mucilage and quicklime (CaO) [11].

Galacturonic acid is the main component of nopal pectin and pectin the major component of the nopal carbohydrates, so pectin was isolated in order to be tested as a hydrating agent for quicklime (CaO) as an alternative to water [3] [12]. To obtain the nopal mucilage from which the pectin would be extracted, different extraction methods were tested [3]. These extraction methods were divided into two groups: those that involved water to obtain the mucilage from the cladodes and the ones that obtained the mucilage directly from the plant without any other substance (Fig. 1a-1c) [3][9]. In line with the hypothesis that galacturonic acid is responsible for the desirable chemical interaction between nopal mucilage and lime, the acid-base titration phase of the products obtained from the different tested extraction methods was carried out in this stage. The greater the amount of sodium hydroxide needed to produce a significant increase in pH to basic values in each extract, the more galacturonic acid the mucilage contained [3] [11]. From extraction methods that correspond to the group where water is used in the process, the one that reflected a higher content of galacturonic acid and a high volume of the mucilaginous substance was the one in which cladodes of opuntia streptacantha, native to Tetla, Tlaxcala, were used with temperature elevation and constant stirring during the extraction process [3].

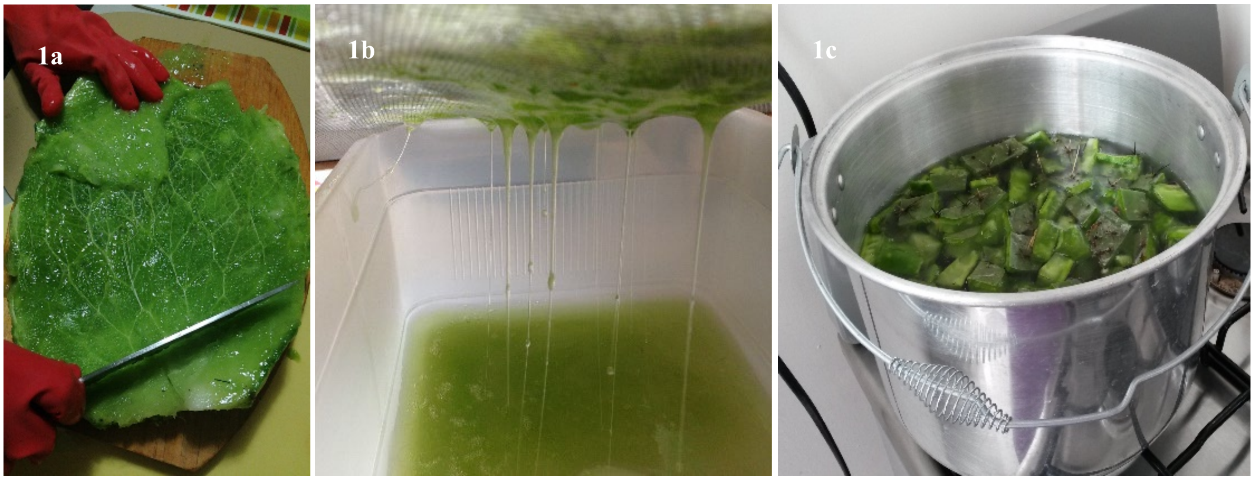


Figure 1a-1b: Nopal mucilage extracted directly from de cladode. 1c: Mucilage extraction method that involves water in the process, temperature elevation and constant stirring.

Acid hydrolysis was the extraction method selected to obtain nopal pectin from the chosen nopal mucilage. The product was poured into beakers and its pH was adjusted to a value of 2 using 98 % sulfuric acid. Immediately after, solution was elevated to 90°C +-1 for about 30 minutes, constantly stirred and then filtered. 96 % ethanol was added to the solution in a ratio of 1:0.5 and the resulting product was separated carefully by decantation. The procedure was then repeated; the more repetitions, the greater amount of pectin obtained. Pectin was dried for 18 hours in a laboratory oven, before being pulverized in a mortar, ground in a blender, and finally passed through a mesh (# 40), the last two steps were repeated several times in order to obtain the highest amount of fine-grained pectin (Fig. 2a-2d) [3].

Figure 2a: Mucilage pH adjustment to 2 with sulfuric acid. 2b: Filtration process with ethanol. 2c: Pectin separation by decantation. 2d: Dried and powdered nopal pectin.

In a previous examination phase, quicklime was hydrated using nopal mucilage solution at different concentrations (20 %, 60 %, 100 %) to determine which concentration enhanced the rheological properties of lime putties [3] [9]. Putties hydrated in mucilage solution in a concentration of 20 % presented the best rheological behaviour, so nopal pectin solution was prepared using the equivalent amount of pectin contained in a solution of mucilage in a concentration of 20 % [3].

The lime hydration process was executed using a proportion ratio of 1:2 by weight between quicklime and nopal pectin solution in a concentration of 20 %. Simultaneously, the quicklime

(CaO) hydration process was carried out using water as a control solution in order to compare the behaviour of the proposed lime putty with the traditional one. Once both lime putties were obtained, the characterization phase of each lime putty began [3].

Lime putties were analysed and characterized in different phases throughout their production process, from the earliest stage, through 28 days and then, up to 400 days of aging. The analysis of putties required the characterization of their crystallographic behaviour, for which a 7800 Scanning Electron Microscope (SEM) was used to determine whether the nopal pectin had an influence on the transformation speed of crystallographic patterns in lime putties. The physical changes of the putties at the different aging stages were evaluated with an X-ray Diffractometer (XRD) Bruker D8, to determine their physicochemical evolution over time [12]. The Abrams cone was used due to the lack of a normative framework for the evaluation of the plasticity of lime putties; therefore, the plasticity of the paste was qualified based on the slump that it showed in the cone. The evaluation was also carried out empirically by tactual exploration of the material when manufacturing fresh lime putty spheres (Fig. 3a-3c). A chemical characterization of lime putties was also carried out by EDS Analysis, Energy Dispersive X-ray Spectroscopy to confirm the presence of nopal pectin [3] [12].

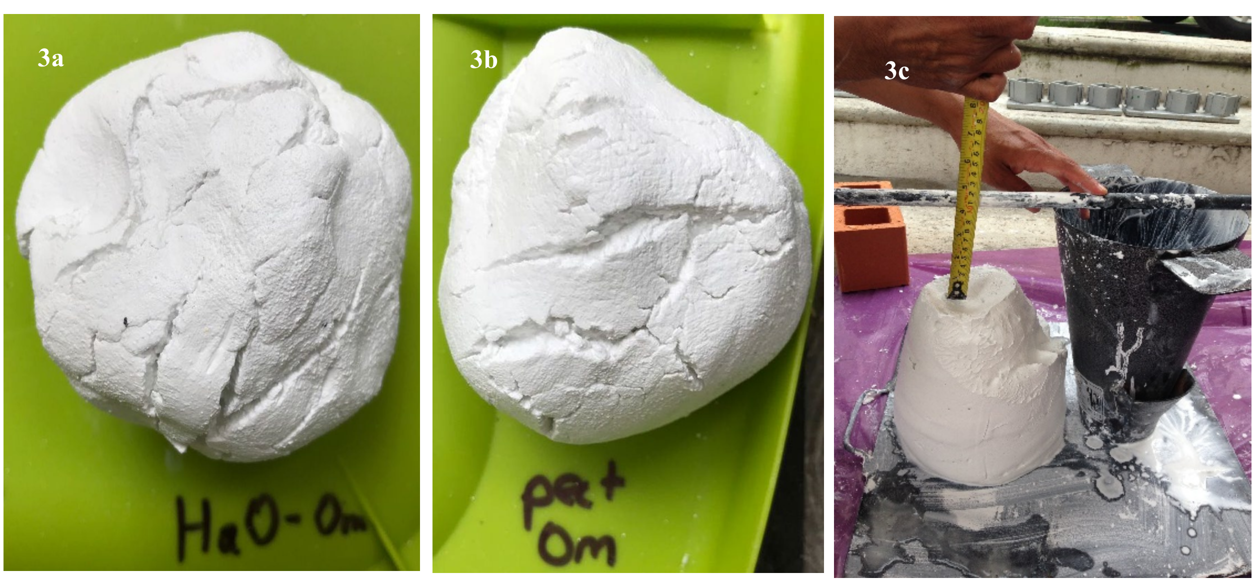


Figure 3a: Lime putty hydrated in water sphere and 3b: lime putty hydrated in pectin solution sphere to evaluate plasticity empirically. 3c: Abrams cone test for fresh lime putties.

Optimized lime mortars

A type of mortar for each type of lime putty was produced and different mortar samples were prepared in the selected aging periods. The properties of the mortars that were selected for their characterization and comparison were prioritized according to the desirable rheological and structural requests of the material in the restoration and preservation of buildings with historical construction systems. In light of this, mortars were tested to measure their resistance to compression and adhesive capacity [12]. Also, a mortar's readiness to carbonation is closely related to its exposure to CO2 in a building and to the control of coating cracking, so mortar specimens were also evaluated to determine their propensity for carbonation using phenolphthalein as an indicator. It becomes important to prioritize the speed of moisture absorption by capillarity and the drying lapse of mortars as they were originally designed to allow controlled vertical moisture to transit from the subsoil, through the foundation, through the structure of the wall until it finally evaporates through the covering mortars.

The calculation of lime mortars capillary absorption capacity was carried out based on the NORMAL 11/85 standard [3] [12]. Lime mortars were formulated using a ratio of 1:3 by weight, regarding the lime and arid ratio and the procedure for preparing mortars and their specimens (cubic specimens about 125 cm3), was based mainly on ASTM C270 – 02, ASTM D752000 and ASTM C-109 standards [12].

Lime mortar analysis methods

It is clear that hydrated lime mortars are different from cement mortars, so they cannot be evaluated under the same criteria. As Mexico does not have a regulatory framework that stipulates guidelines to test hydrated lime mortars, some analysis methods were implemented as a new proposal and some tests were adapted from those originally intended for cement mortars while some others have their origin in the construction or restoration sites from an empirical approach [3]. The mortar specimens were evaluated and compared among each other at 45, 100 and 200 days of aging. To evaluate mortar strength, cubic specimens were subjected to compressive stress on the manual digital press type machine model E657-2 (Fig. 4c). To evaluate mortar adhesion capacity, an adaptation to the Mexican standard NMX-C-082-1974 used for cement mortars was made. To evaluate the force required to separate the parts, several specimens prepared by joining together three bricks in two-thirds of their length were placed in a vertical position inside of the manual digital press type machine model E657-2 (Fig. 4a-4b) [12]. Mortar plasticity was measured by using the Abrams cone and the evaluation was also done empirically to the touch when manufacturing fresh mortar spheres [12]. In terms of the capillary absorption capacity of mortars, cubic specimens were moistened and weighed in an Ohaus Precision Balance at equal time intervals to determine the time of absorption, evaporation and drying, as well as the difference between dry weight and moisture saturated weight. The fewer the differences in dry weight and wet weight of the specimens, the shorter the drying time, and, therefore, the better the performance (Fig. 5a).

Cracking control in the different mortar coverings manufactured was evaluated by observing and counting cracks in 4 cm thick rectangular specimens placed on a masonry wall (Fig. 6). And finally, the mortar propensity to carbonation, was determined by using the phenolphthalein method, which consists of cutting cubic mortar test specimens in half to evaluate the level of carbonation in both the exterior and interior faces with different exposure to CO2. The addition of phenolphthalein to the test specimens will expose a dark pink color if there is less carbonation while the surface will be colorless when it presents a higher degree of carbonation, which is desirable (Fig. 5b) [3] [12].

Figure 4a: Brick specimen to test the adhesion of lime mortars. 4b: Brick specimen separated in parts after the test. 4c: Cubic specimen to test mortars strength.

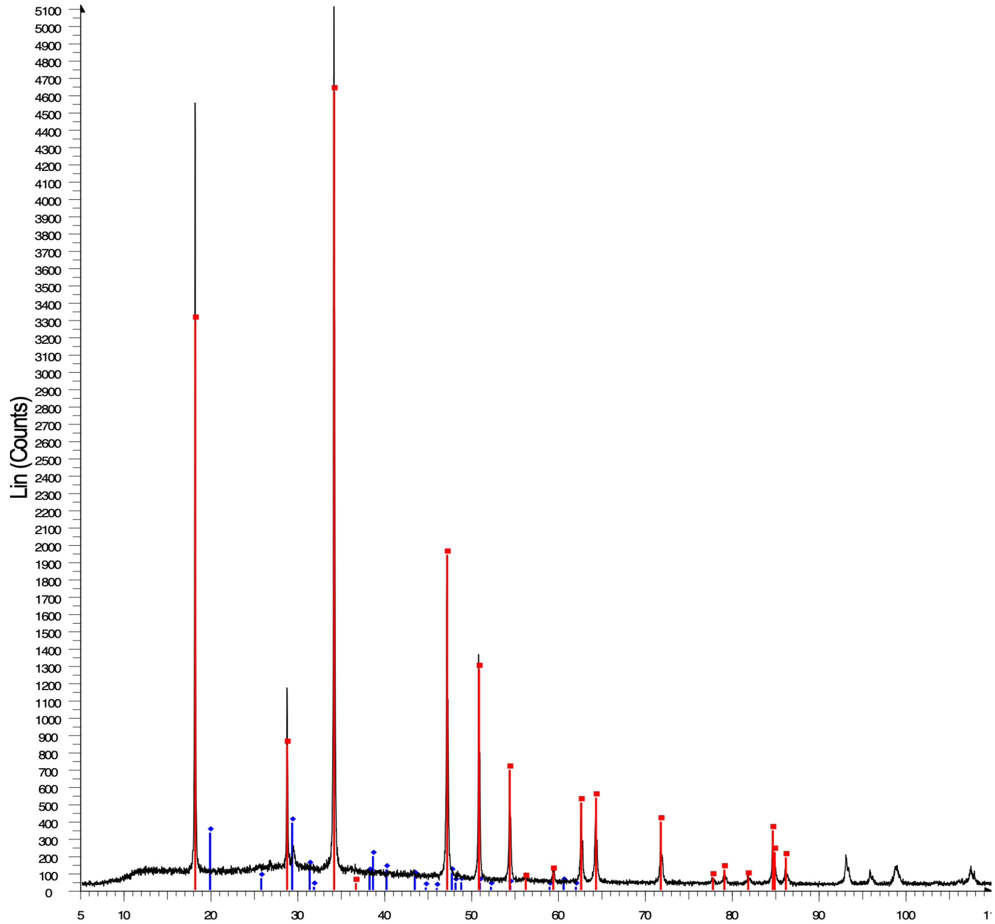
Figure 5a: Mortar specimens during capillary absorption capacity test. 5b: phenolphthalein application procedure to test lime mortars propensity to carbonation.

Figure 6: Rectangular mortar specimens to measure cracking control.

RESULTS AND DISCUSSION

Physicochemical XRD analyses showed calcite phases in lime putty samples that had been hydrated in nopal pectin for only 28 days, which suggests an immediate start of the carbonation process. This does not happen in the absence of nopal pectin during the lime putties' hydration stage, wherein only portlandite phases could be detected, that is, without initiating the carbonation process (Fig. 7-8). Early carbonation in the pectin-containing putties coincides with the 100 % carbonation of the lime mortar specimens with pectin, even on the inner faces of the cubes that did not have direct exposure to CO2 from the environment [12].

A greater propensity for the carbonation process and the increase in its speed are desirable for the mechanical applications of masonry unit bonding mortars, but it could also lead to more frequent cracking of the coating mortars due to the rapid loss of moisture during the process. However, the specimens manufactured for the evaluation of cracking showed a 50 % decrease in the fractures of the coatings. The carbonation speed and the loss of humidity during those processes are consistent with the results obtained from the analyses of the mortars' capacity for moisture absorption, where it was concluded that mortars containing lime putty hydrated in nopal pectin showed a reduction of 50% in their capillary absorption capacity directly linked to its drying speed up to 35 minutes faster compared to those mortars that did not include pectin [3] [12]. In the SEM images, changes in crystalline morphology could be identified from the very first day of aging in the lime putties that were hydrated with nopal pectin, where nanometric-sized laminar patterns were identified and contrasted against the prismatic patterns that could be observed in the lime putties that did not include nopal pectin in their production process (Fig. 9-11). Nano-sized laminar patterns are usually identified in lime putties aged from 12 to 14 months. These laminar patterns show evidence of a lime putty with better colloidal characteristics that translate into an improvement in its rheological and mechanical properties, probably explained by the carboxyl and hydroxyl groups present in nopal pectin sugars and by the degradation alkaline of its bioproducts deprotonate at a high pH. This deprotonation is produced during hydration of quicklime and achieve a strong interaction with the newly formed calcium hydroxides Ca(OH)2, acting both as inhibitors of the process of nucleation, thus promoting the formation of nano-sized crystals, and as habit modifiers, favoring the development of a planar habit following the adsorption which takes place on the positively charged faces [4] [5]. Adsorption of polysaccharides in calcium hydroxide crystals Ca(OH)2 prevents the formation of large particles resulting in a highly reactive nano-sized lime putty [6] [7].The examination performed using empirical tests agreed with the quantitative assessment, as the spheres made on site showed a better performance in adherence and plasticity when it came to mortars containing nopal pectin [3]. Furthermore, the EDS analyses on mortars containing cactus pectin shows that the pectin remains even after the exothermic reaction generated during the hydration of quicklime. The behavior of the mortars was analyzed in samples of 7, 14, 28 and 45 days old, as determined by the regulatory framework for cement mortars [3] [12]. In a first battery of analyses and results, it was determined that the mechanical behavior was reflected in longer time intervals and it was proposed to carry out the analysis of results in mortars at 45, 100 and 200 days of age. The specimens that were subjected to compression forces, showed an increase of 67 % in the compressive strength for mortars containing lime putty with pectin, compared to those mortars that did not contain this substance. In the same way, an increase of 35 % in adhesion capacity over the control mortar was reported. The compressive strength of lime mortars cannot be compared with that of cement mortars since the materials behave differently during the drying and hardening process. Lime mortars will always report less resistance to compression than that of cement mortars aged for at least 200 days, although the mechanical demands of historical structural systems are satisfied with the strength offered by lime mortars, an increase in this property is desirable because it shows an optimization of the material. An increase in the adherent capacity of lime mortars is relevant, because its use as a coating requires thicknesses that ranges between 2.5 and 4 cm, finally, the plasticity of lime mortars containing nopal pectin also suffered an increase that facilitates not only the workability of the material, but also the application of mortars in thin layers [3] [12]



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01-084-1263 © - Calcium Hydroxide – $Ca(OH)_2$ – Y: 90.34 % - d x by: 1. – WL: 1.5406 – Hexagonal – a3.59180 – b3.59180 – c4.90630 – alpha 90.000-

00-024-0223 (*) – Hydrophilite [NR] – $CaCl_2$ – Y: 7.57 % - d x by: 1. – WL: 1.5406 – Orthorhombic – a 6.26100 – b6.42900 – c4.16700 – alpha 90.000 - bet

Figure 7: Diffractogram corresponding to lime putty hydrated in water for 28 days where portlandite phases were identified.

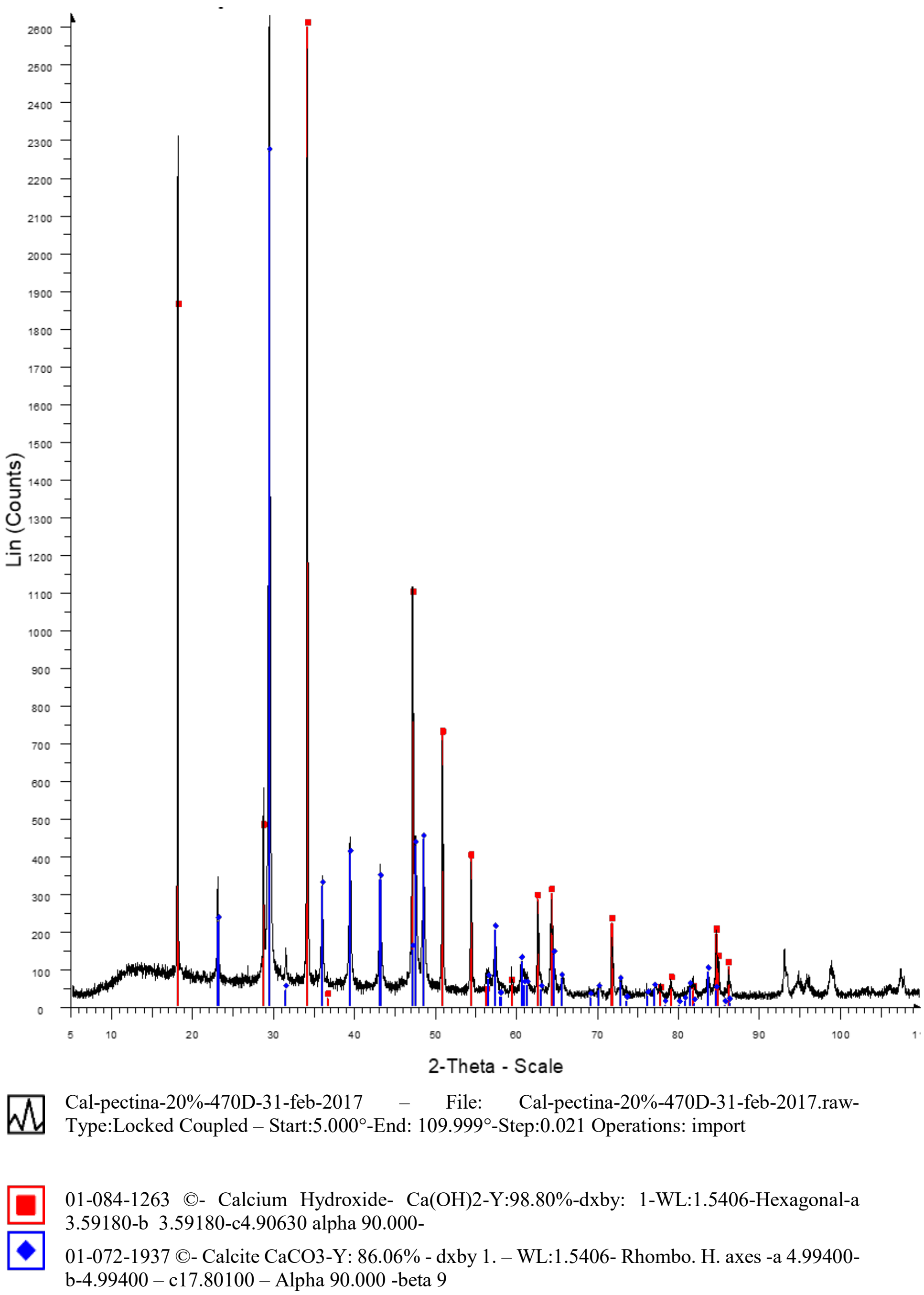

Figure 8: Diffractogram corresponding to lime putty hydrated in nopal pectin of 28 days of aging where calcite phases were identified.

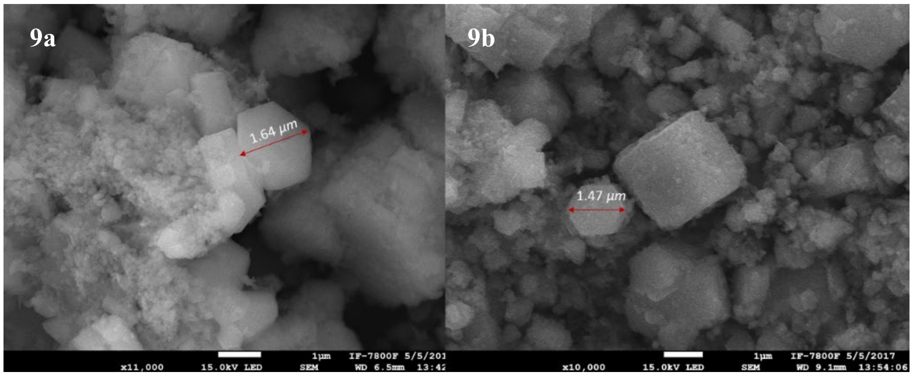

Figure 9 a: SEM image corresponding to lime putty slaked in nopal pectin at 28 days. 9 b: SEM image corresponding to lime putty hydrated in water at 28 days. In both images, crystallographic structures of prismatic hexagonal morphology micrometric size can be identified.

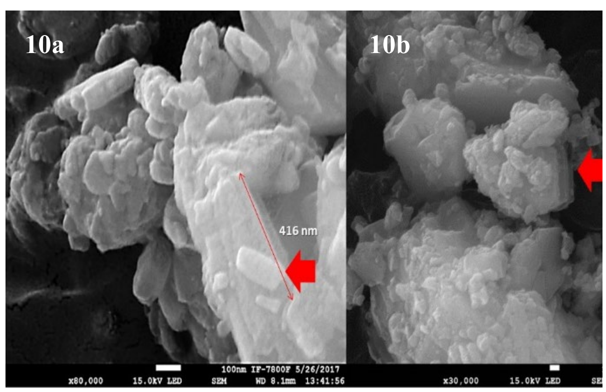

Figure 10 a: SEM image corresponding to lime putty slaked in nopal pectin at 28 days. 10 b: SEM image corresponding to lime putty hydrated in water at 28 days. In both images, micrometric sized crystallographic structures of prismatic hexagonal morphology can be identified.

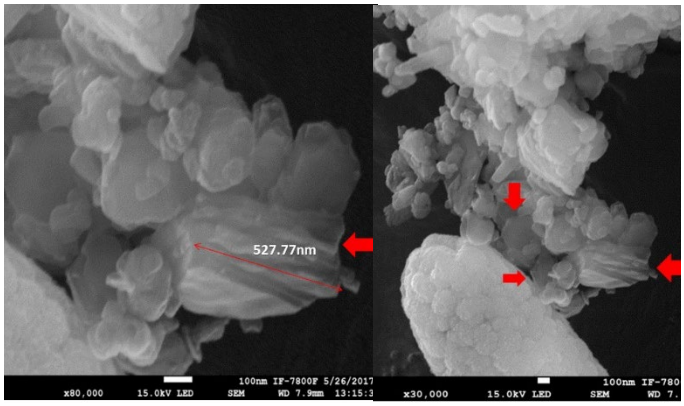

Figure 11 a-b : Both SEM images show lime putty hydrated in water for 110 days. Nanosized hexagonal plate patterns can be identified in the two pictures.

CONCLUSIONS

It is possible to conclude that the pectin of the nopal contains a significant amount of galacturonic acid, responsible for an effective interaction between pectin and lime [3]. Secondly, pectin conditions a morphological transformation in Ca(OH)2 crystals with a prismatic hexagonal morphology towards nano-sized laminar patterns with a higher surface area, compared to the control putty (which is produced by hydration of CaO in water). According to the observations in scanning electron microscope, this results in improved workability and consistency of slaked lime putties starting at 28 days of aging when they are compared to the behavior of the control putty [3] [12]. Furthermore, nopal pectin, conditions a greater propensity of the carbonation of the lime putties that contain it, from 28 days of aging, compared to that in the control putty. Regarding the improvement of properties of lime mortars, greater workability, a better consistency and less cracking are achieved with the presence of pectin, even at barely 28 days of aging of lime putties and in comparison, with the control mortar. Compressive strength and adhesive capacity of mortars are significantly increased in the presence of nopal pectin, even when mortars are made with 28-day aged lime putty, compared to the control mortar. Nopal pectin enables a greater impermeability to the mortars that contain it, from the production of lime and reduces the drying time of mortars. The waterproof and hydrophobic capacity that pectin gives to the mortar enables a greater protection to the factory of the support elements from its core to its outer faces that, together, reach a couple of meters thick depending on the time of construction. After analyzing the results obtained, it can be concluded that nopal pectin has a catalytic effect in the hydration of CaO with regard to the properties of workability, consistency, propensity to carbonation and adhesion of slaked lime putties starting at 28 days of aging. All this shows the value of preserving and revaluing this pre-Hispanic production technique and its use in the restoration of historical construction systems, ensuring compatibility with those original to the buildings [3] [12]. Finally, the proposed theories open doors of multidisciplinary research regarding species of nopal, synthetic pectin and other fruits, as well as the deepening of the role played by the dosage of mortars produced [3].

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript. ‡These authors contributed equally.

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