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Aging of Lime Putty: Effects on Traditional Lime Mortar Carbonation

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The influence of storing slaked lime under water for extended periods of time (i.e., aging) on $Ca(OH)_2$ crystal morphology, texture, and carbonation evolution of various lime mortars has been studied by the combined use of X-ray diffractometry, phenolphthalein tests, porosity measurements, electron microscopy, and ultrasonic wave propagation analyses. Mortars prepared using traditional aged lime putties (up to 14 years storage under water) show rapid, extensive carbonation, resulting in porosity reduction and ultrasonic speed increase. The aged hydrated lime mortar carbonation reaction (i.e., $Ca(OH)_2 + CO_2 = CaCO_3 + H_2O$) follows a complex diffusive path, resulting in periodic calcite precipitation as Liesegang rings. In this case, binder:aggregate ratios $>$1:4 result in crack development. Nonaged commercial hydrated lime mortars show slower carbonation and need a higher binder:aggregate ratio (1:3). The carbonation of nonaged lime mortars follows a normal diffusion-limited continuous path progressing from the mortar sample surface toward the core. Differences between aged and nonaged lime mortar carbonation evolution are explained considering $Ca(OH)_2$ crystal shape changes (from prisms to platelike crystals) and size reduction that occurs on aging of lime putty. Implications of these results on historic building conservation using traditional lime mortars are discussed.

I. Introduction

MILLENARY traditional lime technology has been neglected for decades by the construction and research communities.[1,2] Besides the widespread use and thorough study of the role of calcium hydroxide ($Ca(OH)_2$; the mineral phase portlandite, also known as slaked lime or hydrated lime) in many technological and industrial processes—including portland cement production[3] and hardening,[4,5] metallurgy,[6] and a variety of chemical processes[7]—hydrated-lime-based mortars and plasters have been used only sporadically as building materials during the past century. Moreover, little or no research has been dedicated to their study in recent decades. However, a revival of lime-based mortar technology has occurred recently in connection with the conservation of historic buildings,[2,8,9] where compatibility, respect for traditional materials, and the advantages of hydrated lime—if compared with portland cement[10]—are important issues. The lack of practical experience on the use of lime mortars has generally resulted in the consultation of historical sources, e.g., "The Ten Books of Architecture," by Vitruvius,[11] where a detailed description of lime-burning, slaking, and mortar preparation is given. Nonetheless, lime slaking remains a controversial issue with regard to the parameters—such as water:lime ratio, temperature, and stirring rate and duration—to be controlled during this process.[12,13] Long-term slaking of burned lime is recognized as an important factor for the proper performance of lime mortars, because previously nonhydrated calcium oxide (CaO) particles would hydrate and "popping" following their application prevented.[14] Moreover, it is observed that long-term storage of slaked lime under water (a process also known as aging) results in a significant improvement of $Ca(OH)_2$ plasticity and water retention.[13]

Many researchers agree on the necessity of keeping slaked lime under water for an extended period of time before its use as a building material.[15–18] Nevertheless, there is no consensus on an optimum aging time.[2] Ashurst[2] has stated that lime putty, with a shallow covering of water, should be kept for a minimum of two month before its use. Pliny and Vitruvius both stated that mortar quality would increase through prolonged storage (years).[2,11] In fact, an ancient Roman law required the lime to be slaked and stored under water three years before its use.[2] As a common practice, lime was slaked and stored under water to be used by next generations.[19] Bonell[20] indicates that experience has shown that slaked lime undergoes a certain amount of aging on storage in contact with excess water. He stated that only lime putty (if compared with fresh "dry" hydrated lime) has the workability and water retention necessary to prepare a good mortar or plaster. However, until very recently, little has been known about how aging changes $Ca(OH)_2$ properties.

Initially, the original characteristics of the raw limestone, the burning temperature, and the slaking conditions affect $Ca(OH)_2$ particle size and shape, thereby controlling properties such as plasticity, water retention, and workability.[13,20,21] Later, the aging process may homogenize initial differences among various slaked limes. In a previous paper,[22] we have shown that, on the aging of lime putty, $Ca(OH)_2$ undergoes both significant morphologic changes (from prisms to platelike crystals) and particle-size reduction because of (i) differences in solubility between $\{0001\}$ basal pinacoid faces and $\{10\bar{1}0\}$ prism faces caused by surface energy (γ) differences between both faces (i.e., $\gamma_{\{0001\}} < \gamma_{\{10\bar{1}0\}}$) and (ii) heterogeneous secondary nucleation of nanometer-scale platelike portlandite crystals on preexisting larger $Ca(OH)_2$ crystals. The overall $Ca(OH)_2$ particle-size reduction and the resulting surface area increase may explain the observed improvement of plasticity, workability, and water retention of aged hydrated lime. However, little is known about how these changes affect lime mortar carbonation, thereby determining the quality and future behavior of the mortar as a building material.

The main purpose of this work is to study the effects of lime putty aging on traditional lime mortar carbonation evolution. The evolution of the carbonation is evaluated through the combined use of various analytical techniques.

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II. Materials and Methods

Table I shows the lime mortars prepared using various traditionally aged lime putties and a commercial nonaged lime powder. The main difference among the various aged lime putties was the aging time. Mortar samples A, B, C, and D were prepared by adding the aggregate to the aged lime putty. Sample E was prepared by adding water to the $Ca(OH)_2$ powder, forming a lime putty that was mixed with the aggregate. Sample F was prepared by mixing the lime powder with the aggregate, followed by the addition of water. To avoid undesired chemical interactions between the binder and the aggregate and to quantify calcite formed by $Ca(OH)_2$ carbonation, no carbonates were used as aggregate; quartz sand was used instead. The Instituto E. Torroja (Madrid, Spain) supplied the sand. The quartz grains were normalized[23] and rounded, with controlled granulometry and silica content $>98\%$. The water:binder ratio in the mortar samples ranged from 0.5 to 1, depending on the lime content in the mortar, which was the highest in the 1:4 binder:aggregate ratio mortars. The mortars were prepared manually following the UNE (Spanish Society for Testing and Standards) normative, with modifications as described by Sebastian *et al.*[24] To facilitate CO_2 access to the mortar pore system, samples were kept in a ventilated room. The room temperature and relative humidity were controlled at 18° ± 5°C and 60% ± 5%, respectively.

The traditionally aged lime putties were obtained from two local craftsmen that follow "ancient" recipes to obtain slaked lime. These ancient recipes include limestone burning in an open kiln, lime slaking with excess water in an open trench, and slaked lime storage under water for an extended period of time.

Tests and analyses were conducted using the techniques described below after curing times (i.e., carbonation) of 10, 28, 49, and 63 d (short-term evolution) and 6, 9, and 12 months (long-term evolution).

Mineral phases in the hydrated limes and the mortars, as well as the calcite:portlandite ratio (R) evolution on carbonation were studied by powder X-ray diffractometry (XRD; Model PW 1710, Philips, Eindhoven, The Netherlands). The platelet abundance ($A_{(0001)}$), which indirectly gives an estimate of the degree of $Ca(OH)_2$ crystal evolution of the aged lime putties, was calculated as follows:[22]

$$A_{(0001)} = \frac{I_{(0001)}}{I_{(10\bar{1}1)}} \qquad (1)$$

where $I_{(0001)}$ and $I_{(10\bar{1}1)}$ are the intensities of the (0001) and $(10\bar{1}1)$ portlandite diffraction peaks, respectively.

XRD analyses of the lime mortars were performed on freshly cut (minimum CO_2 exposure) surfaces normal to the longest sample axis (4 cm × 4 cm × 16 cm sample size). One 4 cm × 4 cm × 4 cm cube was cut for each analysis. The carbonation degree was evaluated by analyzing two samples: one collected from the surface and one collected from the core of the cube.

Portlandite crystal morphology and size were studied using transmission electron microscopy (TEM; 200 kV, Model CM 20, Philips) coupled with energy-dispersive X-ray (EDX) microanalysis. Diluted ethyl alcohol–portlandite suspensions were deposited on 3 mm diameter copper grids. The samples were carbon coated.

Details of mortar texture, binder–aggregate three-dimensional structure, pore geometry, and fissure evolution on carbonation were observed at high magnification using scanning electron microscopy (SEM; Model DSM 950, Karl Zeiss, Inc., Thornwood, NY) coupled with EDX microanalysis (Link Systems, High Wycombe, U.K.). Samples were either gold or carbon coated. Calcite grain-size distribution was evaluated using digital image analysis of scanned SEM photomicrographs, using Adobe PHOTOSHOP 4.0 (Adobe Systems, Inc., San Jose, CA) computer software.

Ultrasound speed (V_p) propagation through the mortars and its evolution on mortar carbonation were evaluated using an ultrasound tester (Model BP-5, Steinkamp); best results were achieved using 100 kHz transducers. Measurements were performed attaching the transducers to two opposite faces of a 4 cm × 4 cm × 4 cm sample. Appropriate contact between the transducer and the mortar surface was achieved by applying a thin layer of silicone gel. Direct-transmission V_p data were obtained from three samples of each mortar type. V_{p1}, V_{p2}, and V_{p3} (in ms^{-1}) values corresponding to the three normal directions of the samples were determined.[25,26]

The carbonation degree was qualitatively evaluated by spraying freshly cut mortar surfaces with a phenolphthalein- ($C_{20}H_{14}O_4$) saturated ethyl alcohol solution. Phenolphthalein shows red coloration in alkaline media (i.e., where $Ca(OH)_2$ is abundant), and it is white at neutral pH (i.e., areas where $CaCO_3$ is more abundant). The degree of carbonation is proportional to the degree of whiteness of the sample, normally showing an outer whitish ring, with reddish core.

Open porosity (P, in percent), i.e., pores that can be filled with water, was evaluated according to the water saturation RILEM Commission PEM-25 test,[27] using three samples of each mortar type.

III. Results and Discussion

TEM analysis of the hydrated lime (Fig. 1) shows large (micrometer-sized) prismatic portlandite crystals in the nonaged commercial slaked lime, whereas smaller, submicrometer (colloidal) platelike portlandite crystals are more abundant in the aged lime putties, particularly in the 14 year old sample. Four crystal morphologies have been identified in the aged lime putties: prismatic hexagonal crystals; tabular, platelike crystals (most common);[28] fibrous crystals; and nanometer-sized spherical aggregates (reported to correspond either to portlandite[28] or to colloidal calcite[29]). Nonaged commercial hydrated lime powder shows no spherical morphologies. XRD analyses show calcite as a trace phase in all the hydrated limes; its proportion is ≥5% in the 14 year old lime putty (Fig. 2) because of limited CO_2 exposure on aging. $A_{(0001)}$ values (Table I) are consistent with TEM observations: The greatest $A_{(0001)}$ value (4.0) is obtained in the 14 year old lime putty, where the highest amount of platelike portlandite crystals are found. On the other hand, the smallest $A_{(0001)}$ value (0.3) appears in the nonaged commercial hydrated lime. Figure 3 shows calculated surface area variations versus portlandite crystal size (L) measured along the {0001} basal face parallel to the

Table I. Lime Materials Used and Mortars Prepared

Lime	Aging time[†] (year)	Composition (%)[‡]		Platelet abundance $A_{(0001)}$[§]	Samples prepared	Binder:aggregate ratio
		P	Cc			
Aged lime putty (Malaga, Spain)	14	≤95	≥5	4.0	A	1:3
					B	1:4
Aged lime putty (Granada, Spain)	1	97	3	0.8	C	1:3
					D	1:4
Nonaged commercial lime powder (Malaga, Spain)	0	≥95	≤5	0.3	E (putty)	1:3
					F (powder)	1:3

[†] Storage under water. [‡] XRD data. P is portlandite ($Ca(OH)_2$) and Cc is calcite ($Ca(CO)_3$). [§] Calculated from XRD data using Eq. (1).

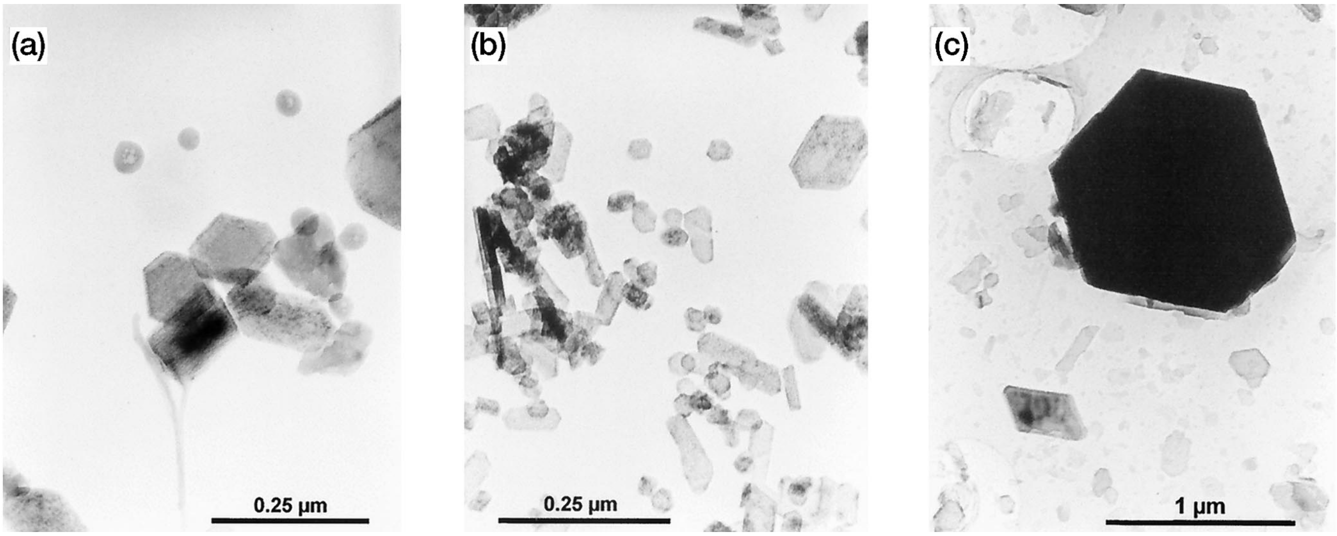

Fig. 1. Representative TEM photomicrographs of portlandite crystals in (a) 1 and (b) 14 year old lime putties and (c) nonaged commercial hydrated lime powder.

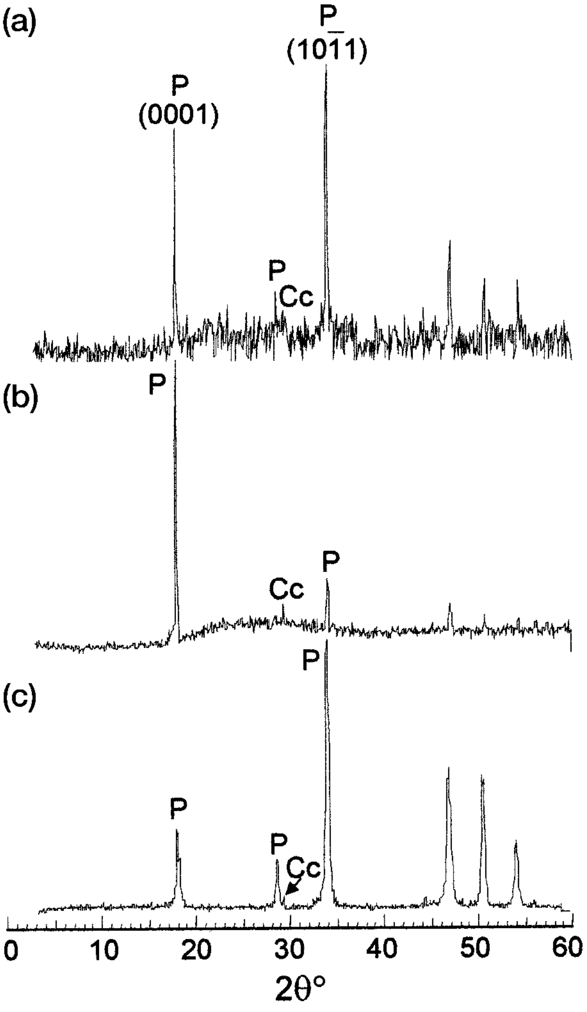

Fig. 2. XRD patterns of (a) 1 and (b) 14 year old lime putties and (c) nonaged commercial hydrated lime powder (Cu*K*α X-ray radiation; P is portlandite and Cc is calcite).

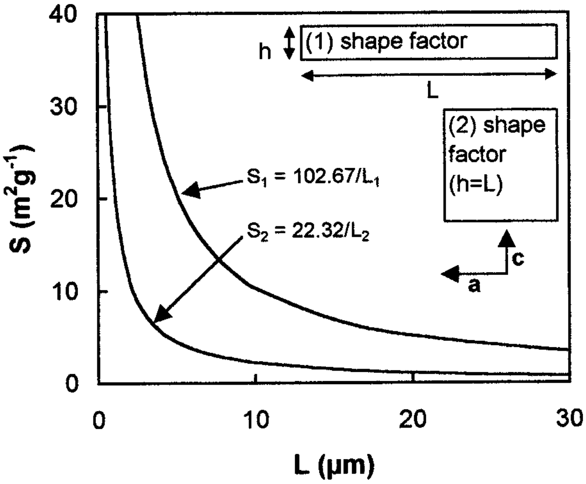

Fig. 3. Calculated surface area (*S*) versus portlandite crystal size (*L*) along *a*-axis (directions of *a*-axis and *c*-axis are indicated with arrows) for various crystal morphologies (insets). Case (1) is platelike crystal with 1:10 length:height aspect ratio. Case (2) is prismatic crystal with 1:1 length: height aspect ratio. Equations for each morphology surface area calculation (S_1 and S_2) are indicated.

crystallographic *a*-axis for various portlandite crystal morphologies. For equal crystal sizes, platelike crystals with 1:10 height: length aspect ratio have a surface area ~5 times larger than prismatic crystals with 1:1 height:length aspect ratio. Supposing that the fresh hydrated lime and the 14 year old lime putty show equal-sized 1 µm crystals, the platelike crystals in the aged lime putty have a surface area of 102.6 $m^2 \cdot g^{-1}$, whereas the prismatic crystals in the fresh hydrated lime have a surface area of 22.2 $m^2 \cdot g^{-1}$. Because the platelike crystals in the aged putty are smaller, the surface area difference between aged and nonaged $Ca(OH)_2$ crystals becomes even more significant. The influence of surface area differences among the tested hydrated limes on lime mortar carbonation is discussed latter.

Figure 4 shows calcite:portlandite ratio (*R*) versus time. Faster carbonation occurs at the surface compared with the core of the mortar samples. Fourteen year old lime putty mortars (samples A and B) show the fastest overall carbonation, with maximum *R* values ranging from 3.5 to 4. The higher *R* value is about double the ones of the nonaged commercial hydrated lime-based mortars (samples E and F) that range from 1.2 to 1.8. One year old lime putty mortars (samples C and D) show no major differences in *R* values if compared with the commercial nonaged lime mortars. Following 1 year exposure to air, the carbonation process is not completed, as indicated by the positive (nonzero) slope of the carbonation curves in Fig. 4. Following 6 month CO_2 exposure, the aged lime putty mortar (A and B in particular) carbonation speed shows a significant increase. Sample E shows very slow carbonation, whereas sample F shows a slightly higher carbonation speed.

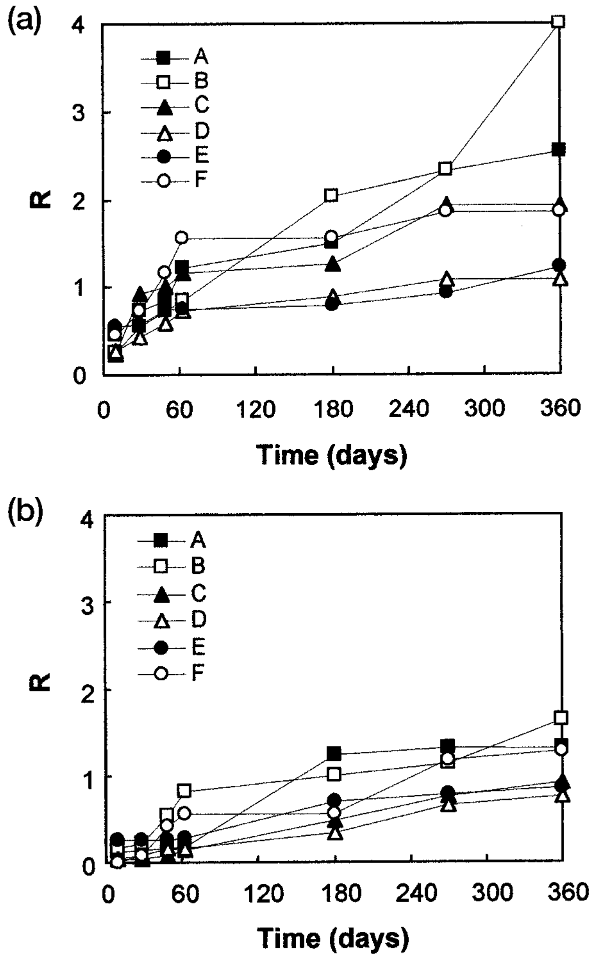

Fig. 4. Calcite:portlandite ratio (R) versus carbonation time of the various tested lime mortars: (a) external and (b) internal (core) zones of the samples are compared.

This seems to be influenced by the higher porosity of F samples compared with E samples (Table II), which enhances CO_2 transport toward reaction sites.

SEM analyses of the aged lime putty mortars show a significant number of pores and some cracks developing on drying. The binder–aggregate contact zone shows discontinuities (fissures) initially, that disappear after extensive carbonation. In general, increased carbonation time results in a porosity decrease (Table II), a fact consistent with the reported 11.8% solid volume increase when portlandite ($\rho = 2.24$ g·cm^{-3}; 33.0 cm^{-3} molar volume) transforms to calcite ($\rho = 2.70$ g·cm^{-3}; 36.9 cm^{-3} molar volume).[30] Cracks are more abundant in the 1:3 than in the 1:4 binder:aggregate ratio mortars. This is consistent with the higher porosity of 1:3 mortars following carbonation (Table II). Cracks are more abundant in samples A and C, whereas few or no cracks are observed in samples E and F. Digital image analysis of calcite crystal-size distribution in carbonated mortars (Fig. 5) shows that 14 year old lime mortars have the smallest average particle size (0.35 μm), whereas the largest average particle size appears in the mortars with commercial hydrated lime (0.85 μm). Intermediate values are obtained in the 1 year old lime putty mortars (0.79 μm). Apparently, the original portlandite crystal size, which, in turn, controls final calcite crystal size (i.e., carbonation can be considered as a replacement reaction[30]) is important in crack development. It seems that the high water retention of the small portlandite crystals in the aged lime putties[31,32] induces crack formation on drying, especially at high binder:aggregate ratios. The large portlandite crystals in the commercial lime powder, having limited water retention, do not show this behavior. However, the smaller portlandite crystals in the aged lime putty mortars, especially in the 14 year old lime putty mortar, once transformed into small calcite crystals (Figs. 5(a) and 5(b)), result in a more-interlocked and, therefore, more-resistant cement.

Table II. Mean Porosity Values after 6 and 12 Month Air Exposure (Carbonation)

Mortar type	Porosity (%)	
	6 months	12 months
A	24.1	23.5
B	23.6	23.2
C	34.0	28.0
D	31.8	28.5
E	19.2	19.1
F	31.0	29.2

V_p values show little differences when the various mortars tested are compared. The slowest V_p values correspond to the direction normal to the compaction of the mortar (V_{p1}). Slightly higher V_p values are observed along directions parallel to the compaction plane (V_{p2} and V_{p3}). Figure 6 shows lime mortar mean V_p values (i.e., $V_p = (V_{p1} + V_{p2} + V_{p3})/3$) versus carbonation time. Following 1 year carbonation, the highest V_p value (2476 m·s^{-1}) corresponds to sample E. Slightly lower V_p values are measured in the aged lime putty mortars, whereas sample F shows the minimum V_p value. An inverse linear correlation is observed between porosity and V_p data (i.e., high porosity results in low V_p values). In fact, E samples have the lowest porosity, whereas F samples have the highest (Table II). Some V_p differences are observed when comparing the various aged lime putty mortars. Higher V_p values are found in the aged lime putty mortars with binder:aggregate ratios of 1:4 (2359 m·s^{-1} in sample B and 2388 m·s^{-1} in sample D; whereas samples A and C have V_p values of 2295 and 2154 m·s^{-1}, respectively; all data correspond to 12 month carbonation time). Following 12 month carbonation time, there are no significant porosity differences between 1:3 and 1:4 aged lime putty mortar samples; therefore, these later V_p results might be explained considering that the presence of higher amounts of aggregate (quartz) results in higher V_p values in the 1:4 mortars and that the higher degree of carbonation of the aged lime putty mortars with lower binder:aggregate ratio (1:4), which are more rigid and with fewer cracks because of drying, also contributes to a higher V_p value.

Phenolphthalein tests show significant differences in carbonation rim development toward the sample core when aged and nonaged lime putty mortars are compared. After 6 months of carbonation, no major differences are observed; however, 12 months of carbonation results in alternating calcite-rich and portlandite-rich rings in the aged lime putty mortars, particularly in the 14 year old lime putty mortars (Fig. 7). This pattern is similar to the so-called Liesegang rings.[33,34] The Liesegang phenomenon is a periodic, intermittent precipitation commonly found in far-from-equilibrium counterdiffusive systems.[35,36] The nonaged hydrated lime mortars show gradual, homogeneous carbonation that progresses from the sample surface toward the sample core (Fig. 7). However, the total amount of portlandite transformed to calcite in the nonaged hydrated lime mortars is smaller when compared with the aged lime mortars, as evidenced by XRD data and the pinkish-white homogeneous color in the nonaged lime mortar sample outer parts, changing to dark red toward the noncarbonated core.

The carbonation of lime mortars takes place via the transformation of portlandite to calcite. This is a two-stage process that takes place according to the following reactions.[37] First, carbon dioxide dissolves in water:

$$CO_2 + H_2O = H_2CO_3 \tag{2}$$

Second, calcium hydroxide reacts with the carbonic acid in solution:

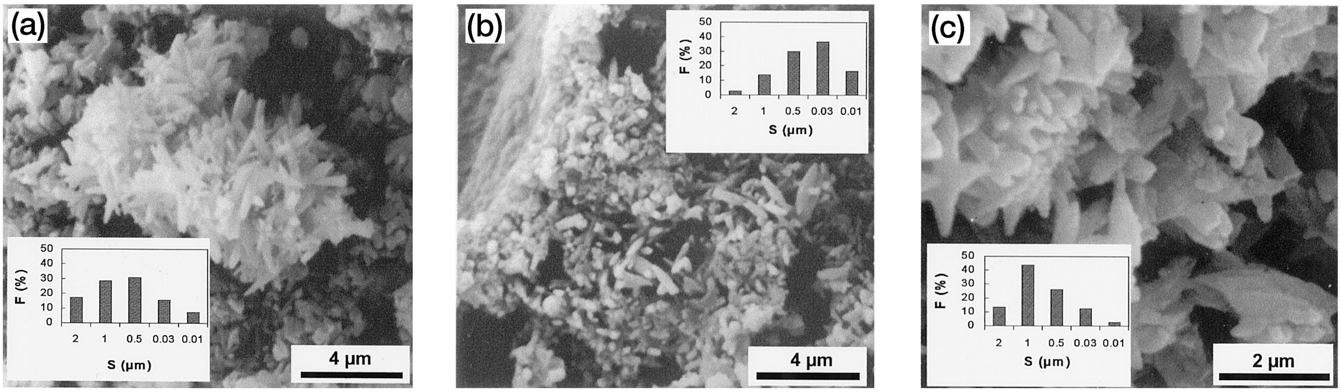

Fig. 5. SEM photomicrographs of (a) 1 and (b) 14 year old lime putty mortar texture of carbonated areas (i.e., calcite replacing portlandite crystals). (c) Detail of the carbonated nonaged hydrated lime mortar. Insets show histograms of calcite grain size (S, in micrometers) versus frequency (F, in percent).

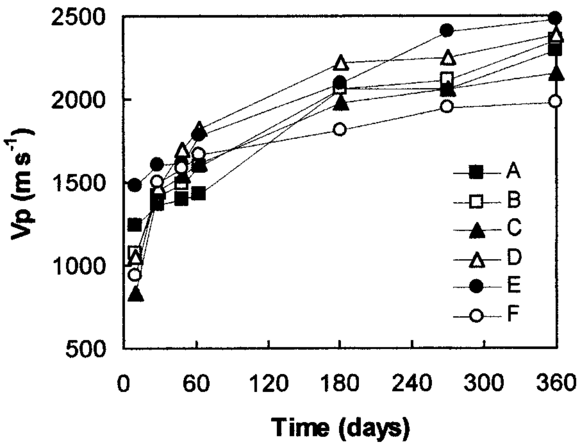

Fig. 6. V_p evolution versus carbonation time for the various tested mortars.

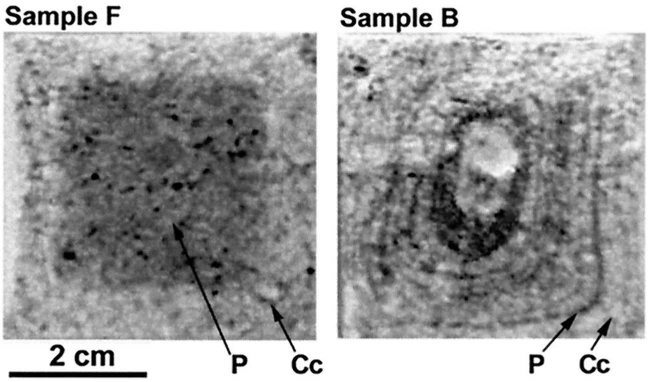

Fig. 7. Appearance of freshly cut faces of 12 month carbonated mortar samples treated with phenolphthalein. General view of (left) sample F, prepared using nonaged hydrated lime, and (right) sample B, prepared using 14 year old lime putty. Liesegang ring pattern is observed on the aged lime mortar (dark rings correspond to $Ca(OH)_2$-rich areas, while white rings are $CaCO_3$-rich areas; P is portlandite and Cc is calcite).

$$Ca(OH)_2 + H_2CO_3 = CaCO_3 + 2H_2O \tag{3}$$

The presence of water is necessary for the reaction to occur, a fact confirmed by many researchers who have observed very slow carbonation at low relative humidity, whereas carbonation is very fast at high relative humidity.[30]

It seems that the presence of the smaller portlandite crystals with larger surface areas in the aged lime putty mortars, if compared with the nonaged commercial hydrated lime, results in faster dissolution of $Ca(OH)_2$ in the CO_3^{2-} saturated solution formed when CO_2 dissolves into the water. This is due to the higher solubility of small crystals compared with large crystals, as given by the modified Kelvin equation:[38]

$$\frac{S}{S_0} = \exp\left(\frac{2\gamma V}{RTr}\right) \tag{4}$$

where S is the solubility of a crystal with a radius r, S_0 the bulk solubility of the crystal, γ the surface free energy, V the molar volume, R the gas constant, and T the temperature (in kelvin).

The higher solubility of the very small portlandite crystals in the aged lime putty results in rapid supersaturation with respect to $CaCO_3$ in the solution existing in the mortar pores (i.e., water condensed in the pores that dissolves CO_2 and $Ca(OH)_2$), followed by rapid calcite precipitation at high supersaturation ratios. This crystallization behavior may lead to ion (i.e., Ca^{2+} and CO_3^{2-}) diffusion and, possibly, solution mass transport from the saturated surrounding areas toward the precipitation front where reactive concentration depletion (due to calcite precipitation) occurs. Therefore, an outer calcite ring forms surrounding an inner, thin, almost dry, portlandite-rich ring with very high pH, resulting in conditions that promote an increase of calcite solubility[39] and prevent carbonation. Moorehead[30] has emphasized that hydrated lime carbonation is a self-limiting process, where water availability for the dissolution of $Ca(OH)_2$ and CO_2 is the primary limiting factor. Because calcite precipitation is an exothermic process ($\Delta G = 74$ kJ·mol^{-1}), water produced in reaction (3) evaporates eventually, stopping the carbonation process in the area of precipitation. The loss of aqueous solution around the carbonated ring results in CO_2 diffusion toward an inner zone, where sufficient aqueous solution (i.e., water with Ca^{2+} and CO_3^{2-} in solution) is available, and the above-described self-limiting precipitation process again occurs. The progression of this diffusive–precipitating system toward the sample core finally results in the formation of a Liesegang pattern with alternating wide calcite-rich and thinner portlandite-rich rings.

Low supersaturation ratios in the commercial nonaged hydrated lime mortars with large portlandite crystals (less soluble, according to Eq. (4)) result in limited calcite precipitation at low supersaturation ratios as larger $CaCO_3$ crystals, as evidenced by SEM. In this case, carbonation occurs in a closer-to-equilibrium diffusion-limited system.

The above-described overall portlandite-dissolution–calcite-precipitation process is important in understanding the differences in the behavior of the tested hydrated lime mortars. Precipitation of calcite in the aged lime putty mortars is kinetically faster (as demonstrated by the carbonation curves in Fig. 4), resulting in smaller, more interlocked crystals, that create a rigid three-dimensional structure. However, even though the aged lime mortar shows higher carbonation degree than the nonaged ones, noncarbonated thin rings remain after 1 year of air exposure, indicating that the carbonation of lime mortars is a very slow, long-term process. In fact, the presence of portlandite (not transformed to calcite) has been reported in ancient medieval (12th century) and Roman (~2000 years old) nonhydraulic lime mortars.[40,41] The carbonation of aged lime putty mortars following the described Liesegang pattern might explain the latter observations, because some parts in the lime mortar may have been readily carbonated and others not carbonated. Carbonation does not seem to have a negative influence on the lime mortar performance. In fact, the Romans used long-term aged lime putty,[2,11] achieving excellent lime mortars that have withstood weathering until the present time.[2,41]

IV. Conclusions

Significant carbonation evolution differences have been found among various lime mortars, depending on the aging time of the hydrated lime. Parameters have been identified that allow the evaluation of lime mortar quality and, thus, the selection of suitable hydrated limes and binder:aggregate ratios for mortars to be used in the conservation of historical buildings.

When 14 year old (samples A and B) and 1 year old (samples C and D) lime putty mortars are compared with nonaged hydrated lime mortars (samples E and F), the fastest and highest degree of carbonation is obtained in the long-term aged lime putty mortars (i.e., 14 year old), in particular those samples with a low binder aggregate ratio (1:4). This is consistent with $A_{(0001)}$ values and TEM observations showing a high amount of submicrometer, platelike portlandite crystals in the 14 year old lime putty. The small, high-surface-area crystals are very reactive and, therefore, result in rapid carbonation. Ultrasonic testing shows a good correlation between mortar carbonation degree and evolution, and V_p values, i.e., the higher the extent of carbonation (R values), the higher the V_p values. However, mortar sample E, prepared using nonaged hydrated lime as a putty, shows an anomalous behavior, having the highest V_p values but slow, limited carbonation. This behavior is interpreted considering the presence of larger portlandite crystals in this nonaged lime mortar if compared with aged lime mortars. The high water retention of small portlandite crystals in the aged lime putty mortars may induce crack formation on drying when high binder:aggregate ratios are used, therefore resulting in a decrease of V_p values. Thus, recommendations in traditional recipes for lime mortar preparation that suggest the use of either low binder:aggregate ratios or the application of pressure during lime mortar curing,[42,43] become understandable.

It is demonstrated that long-term storage of slaked lime under water, the so-called aging process, results in a significant improvement of mortar quality when using the above-mentioned low binder:aggregate ratios. This is due to the significant portlandite crystal-size reduction (from micrometer- to submicrometer- or nanometer-sized particles) and shape transformation (from prisms to hexagonal platelets). These changes initially result in increased mortar paste plasticity, workability, and water retention.[32] $Ca(OH)_2$ crystals later change on aging, resulting in significant kinetic and morphologic differences in the mortar carbonation evolution in the aged and nonaged hydrated limes: (i) continuous, slow, diffusion-controlled carbonation progressing from the surface to the core in the recent, nonaged hydrated lime mortars samples; and (ii) fast carbonation showing a Liesegang pattern in the aged lime putty mortars.

These results have some practical implications for historical building conservation interventions: (i) conservation lime mortars should be prepared with long-term aged lime putty (>1 year) with binder:aggregate ratios ≤1:4 (Low binder:aggregate ratios result in a significant decrease of the mortar cost, and the final product shows faster carbonation with less crack development.); and (ii) if aged lime putty is not available, commercial lime powder can be used if a putty is prepared before mixing with the aggregate (A 1:3 binder:aggregate ratio is recommended.).

The need of preservation of historical buildings using compatible traditional lime materials has reopened a very promising research field. Future work should focus on a better understanding of how carbonation of various hydrated lime products takes place at the molecular scale. Current work is being undertaken on how lime mortar carbonation and performance can be optimized.

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