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The influence of slaking time on lime putty

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ABSTRACT

A new interest in the preservation of mortars, plasters and decorative finishings in façades has emerged in certain European countries in the past thirty to forty years, with a view to understanding how they have evolved throughout History. There is a growing interest in learning about the composition and execution techniques of original surfaces and a number of Heritage Institutions have encouraged the systematic application of conservation in this area.

Up to the XX century, limes were often used in work as lime putty. After the transformation of quicklime into lime putty the latter was stored to maintain its characteristics. Tanks or large pits were used to store the lime putty, always covered with water in order to prevent its carbonation. The quality of the material was guaranteed for many years with this process.

The evolution of the storage processes for materials has led to a change in this procedure and in most cases binders are now used as powders.

The influence of the maturation time of lime putty has been studied. The aim of this paper is to present the physical and microstructural changes on lime putty due to the effect of ageing, focusing on the particle size of the portlandite crystals and on the reorganization of the internal structure.

KEYWORDS Mortar, air lime binders, lime putty, slaking time

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1 INTRODUCTION

The fine conditions in which many ancient mortars still are today proves beyond doubt that the binder preferably used for centuries, lime, has high quality.
Slaked lime putty stored with excess water guaranteed the material's quality for many years. As an example Duquesnay [1883] refers that in Landsberg, near Meiningen in Germany, a lime pit 300 years old was found with lime putty carbonated only to a few centimeters of depth, the rest remaining in good conditions even if a bit dry.
There are references to the need for the slaking period of the lime to be extended to guarantee its quality. Plinius for example stood for a three-year delay before lime were used [Millar, 1897].
Plasticity gained during this slaking time has been empirically known for a long time. Nowadays this property is attributed to the morphology and dimensions of the portlandite crystals and to the water retention capacity [Rodrigues -Navarro, 1998, Margalha, 2010].
The improvement of lime mortars quality, based on quality factors involving its constituent materials, namely lime, the aggregate or the addition of other components, is important for them to acquire proper characteristics with the usual resource to hydraulic binders such as Portland cement.
It is necessary to know all the potential of lime for its use to be reactivated in adequate conditions. Since this binder was used for centuries as putty with large slaking periods in mortars that are still in a good conservation state, it is important to understand the factors that have contributed to that.

2 EXPERIMENTAL WORK

2.1 Techniques

The set of tests selected mainly aimed at understanding the physical and microstructural changes of lime putties due to the effects of aging.
The thermo gravimetric and differential thermal analyses, TGA-DTA, are both thermal techniques of materials characterization that allow measuring continuously the mass and temperature variations, as a function of the temperature imposed and of time, in samples that are heated (or cooled) at a constant rate.
The microstructure of lime putty was analyzed in an environmental scanning electron microscope (ESEM) complemented by an x-ray microanalysis spectrometer (EDS). The ESEM analysis allowed visualizing the damp samples, at amplifications of 8000x and 10000x, and verifying microstructural changes with time. These observations were complemented with the use of a high-resolution ionic beam microscope (FIB), at amplifications of 15000x and 25000x, which emits a beam of ions of varying energy and allows the observation in depth of the microstructure of materials.

2.2 Materials

The industrial slaked lime putty used (CL90) is produced from Alcanede limestone. The chemical characteristics of the limestone and corresponding lime are presented in Table 1.

Table 1. Chemical composition of Alcanede limestone and lime (mass %)

Sample	*CaO*	*Fe_2O_3*	*Al_2O_3*	*SiO_2*	*MgO*	*SO_3*	*Fe_2O_3*	*K_2O*	*MnO*	*CuO*	*LOI**
Alcanede limestone	52.3	0.1	0.7	0.4	1.5	0.2	0.1	0.8	0.06	0.06	44
Alcanede lime	71.9	-	0.1	0.2	-	0.2	0.03	-	-	-	27.6

* Loss of ignition determined by ATG-ATD in the range 20 ºC to 1000 ºC

The TGA-DTA tests were performed on limes with maturation times of 1 month, 1, 3 and 5 years. Using ESEM the initial extinction phase was observed for 20 minutes and after approximate maturation times of 4 and 24 hours, 1, 8 and 9 months and 5 years. Using FIB limes aged lime putties were observed with 4 months and 5 years.

3 RESULTS AND DISCUSSION

3.1 TGA-DTA analysis

Lime putty incorporates water in different ways. Part of this water is chemically unbound and is easily separated from lime through drying, at 100 ºC, being identified as free water or capillary water. Water may also be adsorbed linked to lime particles by physical forces, only to be released at higher temperature, of 350 ºC. Finally, chemically combined water present within $Ca(OH)_2$ is released between 350 ºC and 600 ºC.

By drying limes at 100 ºC a direct relationship was established between lime slaking time and amount of free water incorporated (Table 2). In the older lime putties, from 3 years upwards, the amount of free water is kept practically constant and close to 50%. In the intermediate lime putty, 1 year, a higher amount of free water was registered, i.e. 58%, by weight. In the more recent putties, with slaking time of 48 hours and 1 month, the amount of free water incorporated in the putty is even higher, around 64%.

Table 2. Determination of mass loss of lime putties when heated at 100 ºC

	Slaking time				
	48 hours	*1 month*	*1 year*	*3 years*	*5 years*
Lime putty left to dry (g)	42.06	50.09	39.36	36.97	40.49
Dried lime (g)	15.12	18.10	16.65	19.06	19.90
Free water within the sample, by weigtht (%)	64.05	63.87	57.69	48.44	50.85

In limes putties dried at 40 ºC (Table 3) the greatest percentage of free water incorporated in the putty is lost, even though further loss is reported when heating at 100 ºC. The most recent putties, 1 month or less old, contain more free and adsorbed water in their composition. Slightly higher values of water chemically bound were also registered in these limes. During lime maturation the paste gradually becomes more compact, i.e. the same percentage of calcium hydroxide takes up less volume.

Table 3. Water (in %, by weight) within limes with different slaking times previously dried at 40 ºC

Samples (slaking time)	*Temperature range (ºC)*		
	25→350	*350→600*	
	Free and adsorbed water	*Chemically bound water*	*Total loss*
1 month lime	3.5	21.5	25
1 year lime	0.8	20.8	22
3 years lime	0.7	17.2	18
5 years lime	0.9	19.2	20

In the TGA/DTA readings (Figure 1) of limes dried at 40 ºC it is clear that most free water has already been eliminated since low mass losses are registered in the 25-200 ºC temperature range. The main differences found are in the most recently slaked lime (1 month) where a higher intensity peak around 100 ºC is found, corresponding to loss of free water. Since this is the lime putty with the shortest maturation time it is also the one that loses the most water at low temperatures. The percentage of $CaCO_3$, corresponding to the mass loss between 550 ºc and 850 ºC, is higher in the limes with the longer maturation time (5 and 3 years) and lower in the 1 month lime. This is due essentially to the greater carbonation rate of the older limes that can be related to the size of the calcium hydroxide crystals.

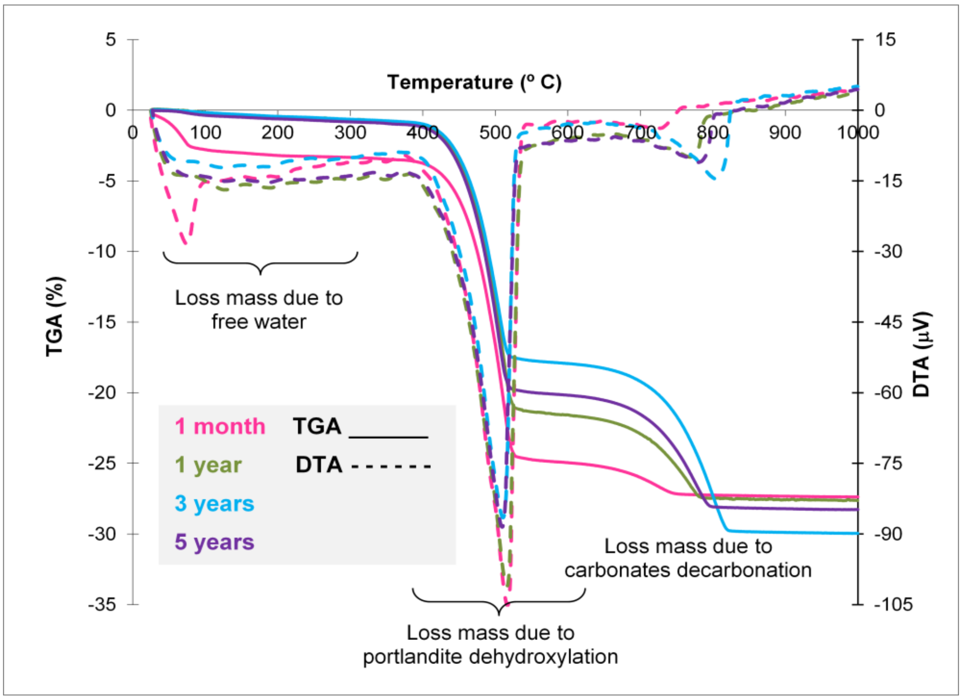

Figure 1. TGA/DTA chart of the 1 month, 1, 3 and 5 years, lime putty previously dried at 40 ºC

3.2 ESEM and EDS analyses

The observations made with ESEM aimed at analyzing lime putty, with no previous drying, at different slaking stages and also at observing a lime whose slaking occurred within the chamber for a 20 minute period. The initial slaking stage of the quicklime was observed by letting water inside the chamber.

An Electroscan 2020 ESEM with a Peltier stage was employed. The sample was introduced into the chamber and imaged using the standard procedure at 733 kPa. The sample was then cooled to 5^{o}C and the chamber pressure increased to 1040 kPa. Water was allowed to condense on the surface of the sample holder sufficient to just cover the calcium oxide particles. The pressure was then adjusted manually to maintain the desired water film thickness. Following the reaction of calcium oxide with water, the pressure decreased to 733 kPa and the sample temperature increased to 15^{o}C. The procedure described above was repeated at intervals allowing the sample to be imaged after total exposure times to the water film of 5, 10 and 20 minutes.

The condensation of water became visible on the sample surface after the chamber pressure had been increased to 1040 kPa with the sample at 5 ^{o}C. The water shows up as dark patches on the sample which grow during the sequence.

Figures 2 and 5 show sets of images taken at exposure times of 0, 5, 10 and 20 minutes respectively. Each set of images contains typical structures viewed at magnifications of 8000x.

Changes in the morphology of the sample throughout the experiment were observed. Figure 2 shows the morphology of the calcium oxide before hydration in water. The angular nature of these crystals suggests that sintering has not occurred and burning has been efficient. Figure 3 shows the structure of the calcium oxide after 5 minutes in water. Small crystals are visible on the surface of the oxide particles in Figure 3. The structure after 10 minutes is shown in Figure 4. A dramatic change in morphology is observed. A complex structure, shown in Figure 4, was observed in material adjacent to the aluminum stub. Figure 4 shows a crystal with edges resembling portlandite. After 20 minutes in contact with water the recognizable hexagonally angled facets of portlandite plates are clearly visible in Figure 5. These crystals are particularly noticeable in the centre of the image in Figure 5. The crystals range in size up to approximately 5 microns. The calcium oxide was successfully hydrated in situ within the ESEM. Crystals clearly resembling portlandite are shown after 20 minutes.

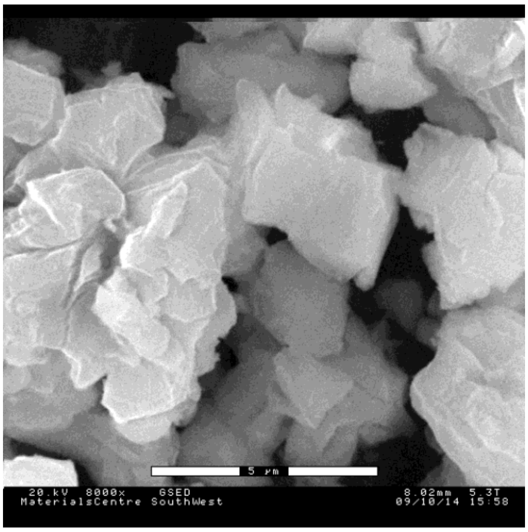

Figure 2. Un-hydrated calcium oxide after immediate insertion into ESEM (8000x)

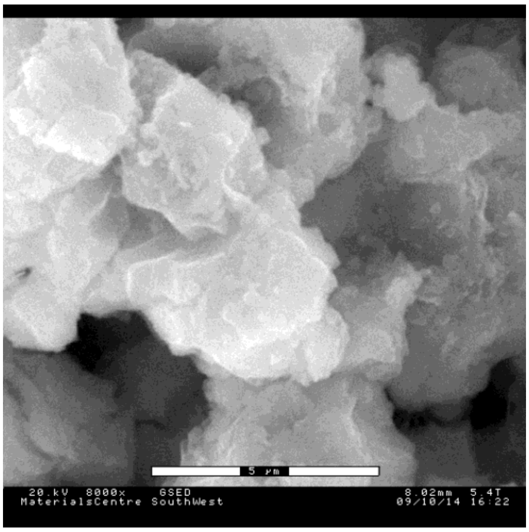

Figure 3. ESEM image of calcium oxide after 5 minutes of hydration (8000x)

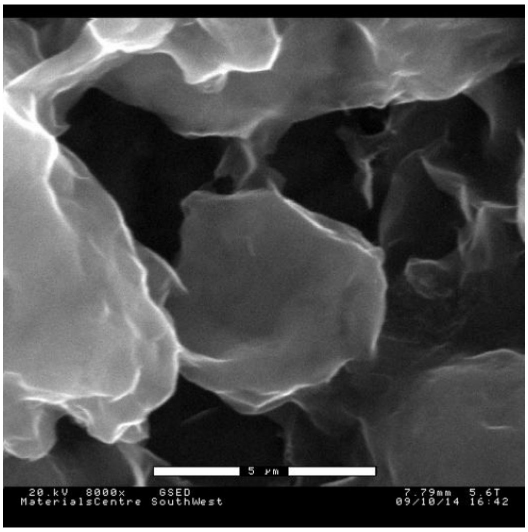

Figure 4. ESEM image of calcium oxide after 10 minutes of hydration (8000x)

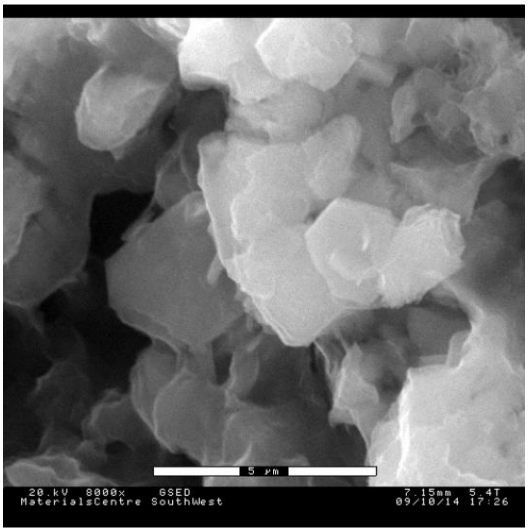

Figure 5. ESEM image of calcium oxide after 20 minutes of hydration (8000x)

Limes observed with 24 hours, 1 and 8 months and 5 years of slaking time were previously kept for a few seconds under a water surface because it would not be viable to keep them inside the chamber for very long periods. Lime putties with 24 hours and 1 month have a less defined structure than older lime putties with 8 months and 5 years (Figures 6 to 9). A densification of the putty that becomes less porous with aging time is visible. There is a change in size of the crystals within the lime putty. The lime putty with 24 hours has an incipient structure made of prisms. After 1 month the structure is still ill-defined but start the formation of hexagonal portlandite crystals packed in layers. In the 8 month aged lime these crystals are already well defined and started to separate into finer crystals. The 5 year putty compared with the 8 month putty shows separated finer crystals, with a great decrease in particle size generally with a diameter on the hexagonal surface smaller than 1.3 µm.
According to some authors [Rodriguez-Navarro et al., 1998; Cazalla et al., 2000; ELERT et al., 2002; HANSEN et al., 2008], who observed fresh and aged lime putties with 2 months, 1 year and 14 years, the portlandite crystals change their shape over time from prisms to thin plate-like crystals.
Hansen et al. [2005], who have studied two limes from distinct origins, industrial and traditional, concluded that 1 year maturation changed the size of the crystals and their morphology, and using DRX they registered a reduction of the prismatic particles and an increase of the small plates.

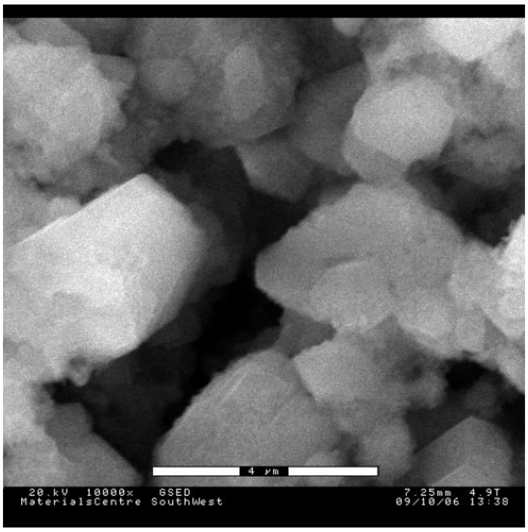

Figure 6. ESEM image of a lime putty after 24 hours (10000x)

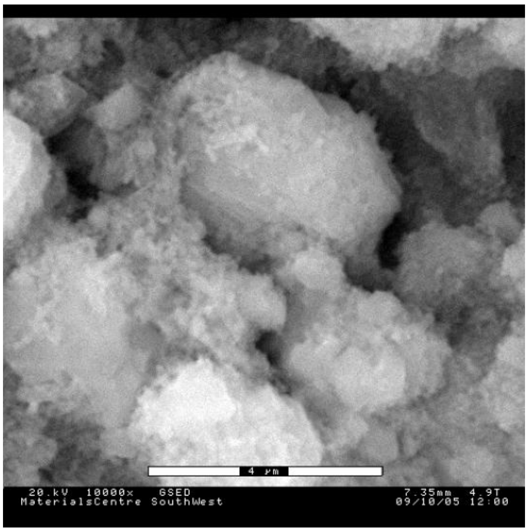

Figure 7. ESEM image of a lime putty after 1 month (10000x)

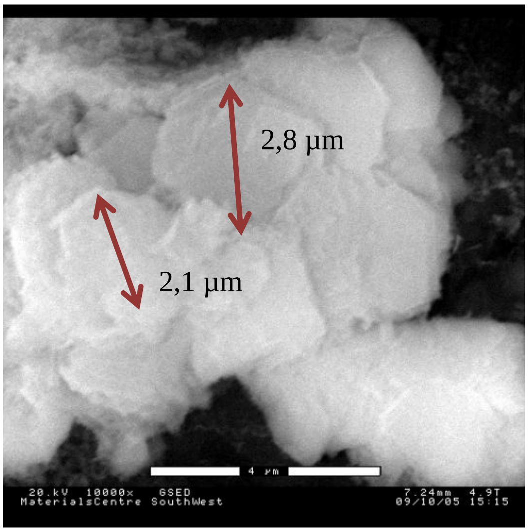

Figure 8. ESEM image of a lime putty with 8 months (10000x)

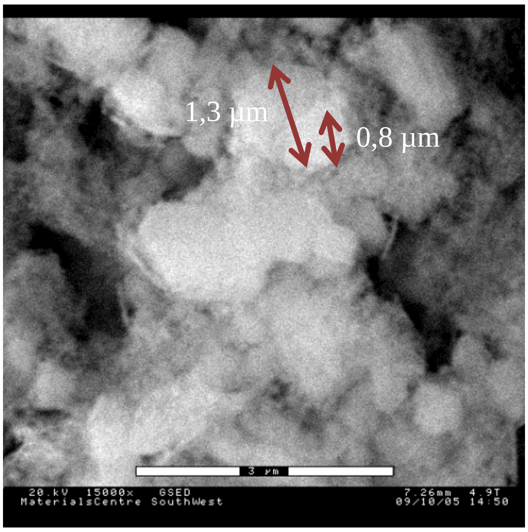

Figure 9. ESEM image of a lime putty with 5 years (10000x)

Lime putty gets more compact and takes up less space as the maturation time increases in agreement with the results obtained in the TGA-DTA observations where it was found that aged lime putties contained smaller amounts of free water. The EDS analysis of limes with 4 hours, 9 months and 5 years (Figure 10) show that oxygen content increases with maturation time, which correlates well with the greater percentage of $Ca(OH)_2$ in the aged lime putties.

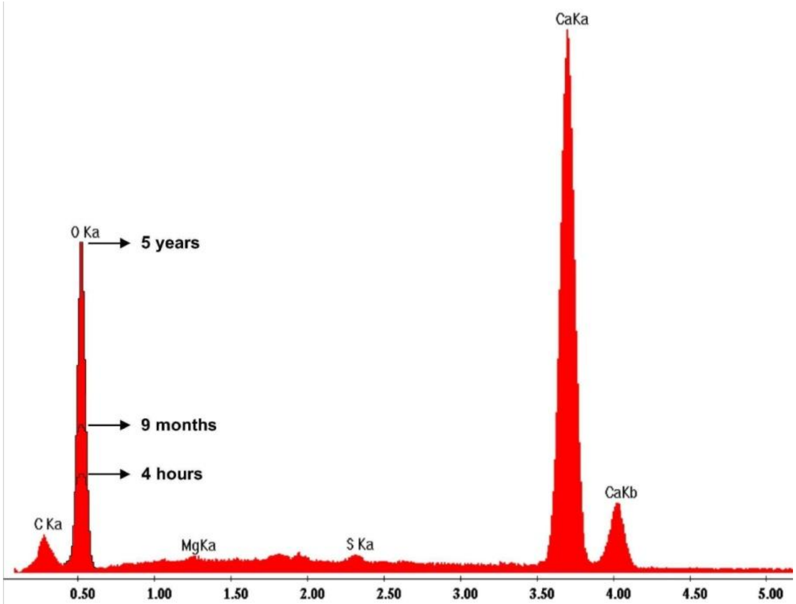

Figure 10. EDS spectrum of a lime putty after 4 hours, 9 months and 5 years

3.4 Observations in FIB

Visualizing the samples in FIB revealed a dense structure of the 5 year lime putty and a more open structure of the 4 month lime putty. The hexagonal shaped portlandite crystals are not completely visible but the shape can be glimpsed underneath the carbonated skin, with much finer dimensions in the 5 year lime (Figures 11 to 14).

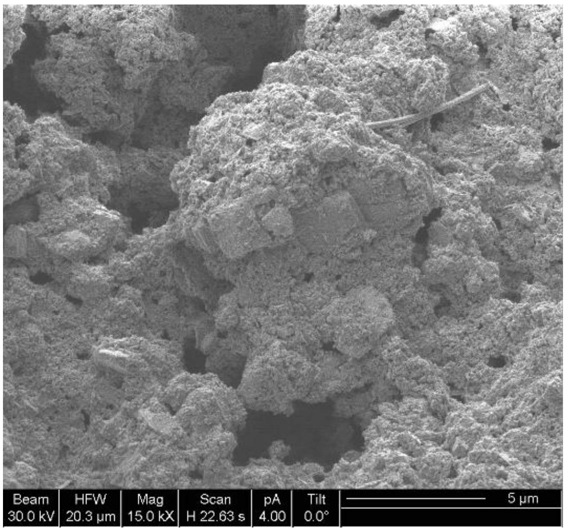

Figure 11. FIB image of a lime putty with 4 months : 15000x

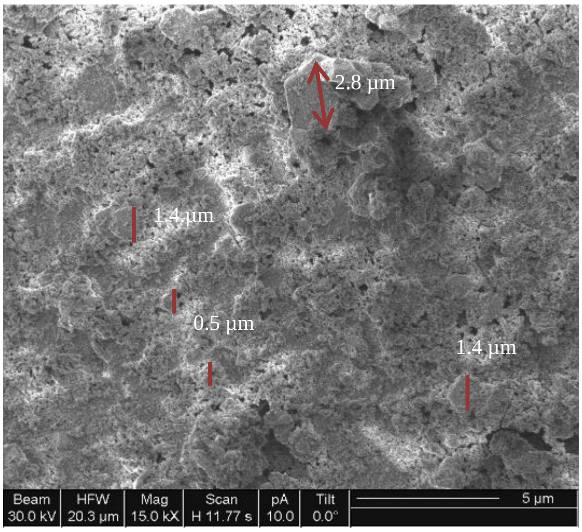

Figure 12. FIB image of a lime putty with 5 years: 15000x

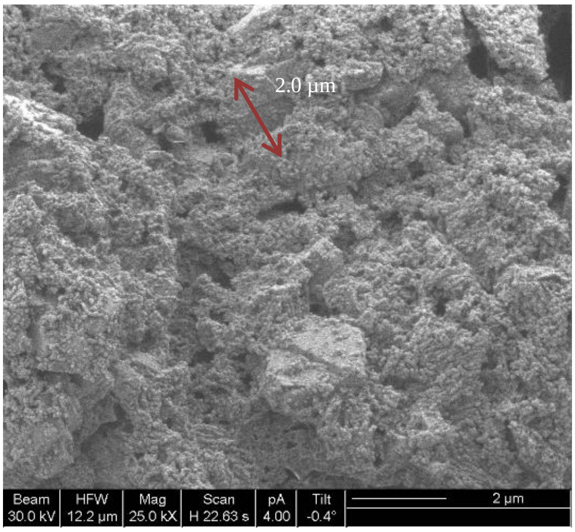

Figure 13. FIB image of a lime putty with 4 months: 25000x

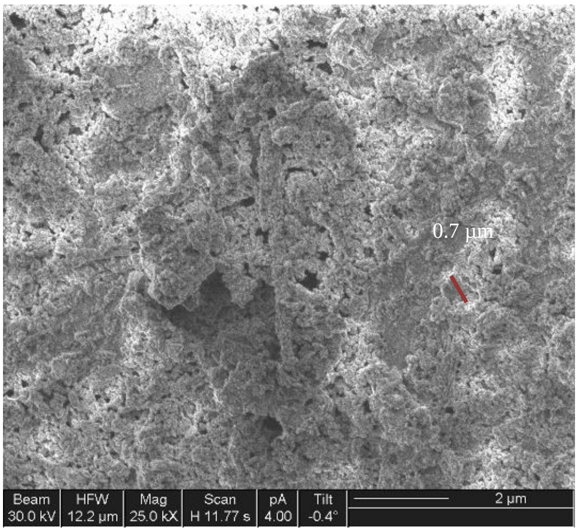

Figure 14. FIB image of a lime putty with 5 years: 25000x

The observations in ESEM and FIB allow concluding that portlandite particles decrease in size as maturation time increases and, also according to the preliminary TGA tests, free water separates itself from the putty with aging and a densification of the crystalline structure.

4. Conclusions

Slaking lime putty has the great advantage of not loosing qualities with storing since water is a slow diffuser of carbon dioxide and therefore stops lime from carbonating, thus remaining indefinitely as calcium hydroxide. Lime putties with a shorter aging time contain more free water that those with a longer time. It was found that the greater part of this mass is lost by drying at 40 ºC.
The various techniques of analysis used allowed confirming the change of physical and microstructural characteristics of lime putty with aging time.
The crystals of calcium hydroxide mostly hexagonal shaped are smaller in the aged lime putties (5 years), mostly < 1.4 µm, with a great quantity of particles near 0.5 µm, while in the 8 and 4 month putties these sizes range from 2.0 µm to 2.8 µm. This small dimension of the calcium hydroxide particles in the aged lime putties seems to justify the greater reactivity they usually display [Cazalla et al., 2000; Margalha, 2010].
Lime and particularly lime putty has played a unique role in construction throughout History and its use must be reactivated mostly when the intention is to preserve or restore ancient buildings, since it is the binder most securely compatible with the materials that make up ancient walls.

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