



The difference in behaviour between calcitic and dolomitic lime mortars set under dry conditions: The relationship between textural and physical–mechanical properties

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ABSTRACT

Differences in the texture, mineralogy, hygric and mechanical properties of mortars prepared with dry hydrated limes of calcitic and dolomitic composition are investigated in this work. Special attention is given to the influence of the lime microstructure and the mortars curing condition. The effect of using two different aggregates (natural and crushed of calcitic and siliceous composition) is also examined. Results showed that the use of dolomitic lime is not recommendable if mortars are applied in dry areas since, under these conditions, a great shrinkage occurs and no strength improvement is induced. Moreover, dolomitic mortars presented a pore network that negatively affects the water transfer properties. On the contrary, calcitic mortars present higher carbonation degree and better physical–mechanical properties. Finally, the use of a calcareous aggregate is preferred because it produces better cohesion in the mortar.

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1. Introduction

At the present time, when designing repair mortars, nobody questions the recommended preference for aerial or hydraulic limes [1–3] with respect to Portland cement, knowing the deleterious effects that this binder has provoked in ancient building [4,5].

If an aerial binder is selected, often the question is which lime, whether calcitic or dolomitic, has to be preferred for elaborating repair mortars.

In the past, this choice depended mostly on the availability of the geological source (namely the proximity to stone quarries to be exploited for obtaining the raw material), as demonstrated recently by Diekamp et al. [6] who identified dolomite in more than 250 samples of renders and plasters collected in buildings from Northern (Austria) and Southern Tyrol (Italy).

However, the choice can be controversial if it is grounded on the properties that each lime confers to the mortar. One of the reasons is that the quality of a lime depends on different factors, burning [7] and slaking [7,8] are some of them, which are in part overcome by the adoption of standardised limes [9], in which the amounts of portlandite ($\text{Ca}(\text{OH})_2$), brucite ($\text{Mg}(\text{OH})_2$) and calcite (CaCO_3) are strictly controlled. However, although standardisation guarantees the production of limes with the same compositional quality, potential differences in their microstructure may still exist depending on the manufacturing

process of the lime (industrial or traditional). This can be influential on the out coming of the carbonation process [10] and, therefore, on the final quality of the mortar, together with other factors, such as curing conditions [11] and aggregate type [12,13].

Conflicting results about the characteristics of the dolomitic limes in suspension are published in literature. Arizzi et al. [14] stated that dolomitic dry hydrated limes show a much more pronounced plasticity than the calcitic ones, therefore the dolomitic lime requires higher amount of water to attain the same consistence as calcitic lime suspensions. On the contrary, Chever et al. [15] found that the dolomitic lime possesses a lower water demand than the calcitic one although, finally, it leads to a greater shrinkage.

Further uncertainty exists regarding the hardened performances of dolomitic lime mortars. Some studies agree that dolomitic lime mortars are good for masonry mortars [6,15] because of their expected durability. On the other hand, Cultrone et al. [16] strictly warned not to use dolomitic lime for the elaboration of repair mortars exposed to urban environment, since the sulphation of this binder leads to the formation of highly soluble and deleterious hydrated magnesium sulphates, such as epsomite and hexahydrate, and the total amount of sulphates developed is higher compared to calcitic limes.

With respect to the physical–mechanical properties of dolomitic lime mortars, previous studies agree that they show higher mechanical strengths and lower porosity and capillary suction than the corresponding calcitic mortars [13,15,17]. Dheilly et al. [17] attributed the higher strength of dolomitic lime mortars to the formation, under high moist conditions ($\text{RH} = 98\%$), of a network of fine plate-like particles of hydromagnesite ($\text{Mg}_5(\text{CO}_3)_4(\text{OH})_2 \cdot 4\text{H}_2\text{O}$) that improve the

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cohesion between binder and aggregate grains. Similarly, other authors observed that the Mg-lime binders perform superiorly in areas subject to presence of moisture [18]. This can be explained with a feeble hydraulic character that the dolomitic lime seems to possess [19].

Since the formation of magnesite and hydromagnesite is kinetically hindered below 52 °C [20], this strength enhancement is not expected to occur under dry conditions. Lanas et al.'s study [13] on dolomitic lime mortars set under atmospheric conditions ($T=20\pm 5$ °C and $RH=60\pm 10\%$) reports that the strength enhancement is due to the formation of portlandite and calcite after a dedolomitization process, which occurs when dolomite is present in the mortar.

In this work, dry hydrated dolomitic and calcitic limes are used, with the consequence that the microtextural characteristics of the lime can be consistently different than those of a lime slaked manually from a light calcined calcite or dolomite (as in Lanas et al.'s study [13]). The microstructure and flow behaviour of the limes used have been studied previously [14] and this allowed us to find a relation between the rheological properties of calcitic and dolomitic limes, and the quality in the fresh and hardening state of the mortars prepared with them.

In this work we compared the mineralogical, textural, hygric and mechanical properties of calcitic and dolomitic lime mortars, in order to find out which lime (whether calcitic or dolomitic) is the most appropriate for the elaboration of repair rendering mortars to be applied in dry or low-moist zones. Especially, we claim to know if mortars prepared with a dry hydrated dolomitic lime still show good physical-mechanical properties under a dry environment and to investigate the cause of the possible improvement.

In this sense, it is important to remember that when a mortar is applied as coating of wall or building facades, mechanical strength is not a crucial property as it may be in masonry mortars, whilst water capillary absorption, porosity and shrinkage are characteristics that need to be strictly controlled.

The influence of the characteristics and mineralogy of the aggregate is also investigated.

2. Materials and methods

2.1. Limes and aggregates

The calcitic lime (CL) chosen is a CL90-S [9], produced by ANCASA (Seville, Spain) whilst the dolomitic lime (DL) is a DL85-S [9], produced in the USA and supplied by LHOIST enterprise (Nivelles, Belgium).

Two aggregates of calcareous (CA, $0.063<\phi<1.5$ mm) and siliceous (SA, $0.1<\phi<0.5$ mm) composition were used. Following the European standard classification for aggregate grading [21], CA and SA can be classified as fine aggregates.

2.1.1. Characterisation of the limes

The mineralogical phases of the limes were determined by X-ray diffraction (XRD), using a Philips PW-1710 (disoriented powder method). Analysis conditions were: radiation $\text{CuK}\alpha$ ($\lambda=1.5405$ Å), 3 to $60^\circ 2\theta$ explored area, 40 kV voltage, 40 mA current intensity and goniometer speed of $0.1^\circ 2\theta/\text{s}$. The interpretation and quantification of the mineral phases were performed by using the X-Powder software package [22].

Specific surface area (SSA) and micropore volume (determined with BET [23] and BJH [24] methods, respectively) were measured by using the N_2 Adsorption technique, by means of an equipment Micromeritics 3000 Tristar that works under continuous adsorption conditions at a temperature of 77 K. Prior to the measurements, two samples per lime were outgassed at 10^{-3} Torr and 110 °C for 4 h, by means of a Micromeritics Flowprep.

Solid density (ρ , g/cm^3) of the limes was measured by pycnometer analysis. Measurements were carried out according to the ASTM D

854-92 standard [25]; pycnometers were calibrated and filled with white spirit.

The bulk density of the limes was measured without (ρ_b , g/cm^3) and with (ρ_b^* , g/cm^3) compaction. In the first case, the limes were poured loosely into a container without any additional compaction. In the second one, the bulk density was determined after vibrating them at 0.3 mm of amplitude and 50 Hz of frequency during 300 s.

2.2. Mortars preparation and curing

Four types of mortars were prepared with a binder-to-aggregate ratio of 1:3 by weight. Their names and composition are shown in Table 1. The water amount (Table 1) was determined in order to obtain mortars with a plastic consistence. The flow was calculated as the average of the spread diameter (in mm) measured on three fresh samples during the flowability assay [26] and it was equal to 150 ± 5 mm. After the preparation [27], mortars were cured for 7 days in normalised steel moulds ($4\times 4\times 16$ cm) at $RH=60\pm 5\%$ y $T=20\pm 5$ °C and, after demoulded, cured for further 21 days in the same laboratory (modification of the standard UNE-EN 1015-2 [27] proposed by Cazalla [28]). Mortars samples were cured at $RH=60\pm 5\%$ y $T=20\pm 5$ °C for the whole period of the study.

2.3. Mortars characterisation

In order to follow mineralogical, textural and physical mortars changes due to the carbonation process, mortar samples were analysed after 28 days and 2 months since their elaboration.

2.3.1. Carbonation degree

The mineralogical phases of mortars were determined by means of thermogravimetric analyses (TGA), by using a Shimadzu TGA-50H equipment. Approximately 50 mg of sample was heated in an alumina crucible, in a flushed-air atmosphere (100 mL/min), at a heating rate of $5^\circ/\text{min}$ and 25–950 °C interval. TGA data treatment was carried out according to the standard UNE-EN ISO 11358 [29]. Mortars phases were determined by measuring the weight loss corresponding to the stoichiometric reactions of brucite ($300<T<400$ °C) and portlandite ($450<T<550$ °C) dehydroxylation and calcite thermal decomposition ($700<T<900$ °C). The decrease in portlandite and brucite content was taken as a reference to estimate the carbonation degree index (I_{CD} , in %) at the same time intervals indicated above, according to the equation:

$$I_{\text{CD}} = \frac{(P_0 + B_0) - (P_x + B_x)}{(P_0 + B_0)} \times 100 \quad (1)$$

where P_x and B_x are the amounts of portlandite and brucite at the time x and P_0 and B_0 are the initial contents of portlandite and brucite (at the time 0).

2.3.2. Textural study

The observation of internal and external zones of the mortars microstructure (morphology, cohesion, porosity) was carried out by means of optical (OM) and field emission scanning electron microscopy (FESEM). In the first case, thin sections were observed by using an Olympus

Table 1

Composition, names and water amount (W, expressed in % on the total mass) of the four mortars studied, with a binder-to-aggregate ratio of 1:3 by weight. CL: calcitic lime; DL: dolomitic lime; CA: calcareous aggregate; SA: siliceous aggregate.

Mortar name	CC	CS	DC	DS
Lime	CL	CL	DL	DL
Aggregate	CA	SA	CA	SA
W (%)	31	27	35	34

BX-60 microscope equipped with digital microphotography camera (Olympus DP10). In the second case, mortars fragments previously dried and carbon coated were analysed by using a Carl Zeiss, Leo-Gemini 1530 microscope. The application of FESEM was also useful for the observation of the aggregate morphology at micro-scale whilst the use of OM on hardening mortars allowed observing the cohesion of mortars samples.

Both external (1 cm from the surface to the core) and internal (core) zones of the mortars samples were periodically analysed.

2.3.3. Pore system

The pore system was evaluated by means of mercury intrusion porosimetry (MIP). Open porosity (P_o , %) and pore size distribution (PSD, in a range of $0.002 < r < 200 \mu\text{m}$) were determined using a Micromeritics Autopore III 9410 porosimeter with a maximum injection pressure of 414 MPa. Three measurements were performed on mortar fragments of ca. 1 cm^3 collected in the internal and external zones, which were oven-dried for 24 h at 60°C before the analysis.

2.3.4. Hygric properties

The water capillary imbibition test was performed to study mortars hygric properties after 2 months of carbonation. Three samples ($4 \times 4 \times 16 \text{ cm}$) per mortar were oven-dried at 100°C during 24 h before the measures. Two imbibition coefficients (A and B) were determined from the mass uptake per surface unit and the height during the time, according to Beck et al. [30] procedure.

2.3.5. Mechanical properties

Flexural and compressive strength were measured by means of a hydraulic press INCOTECNIC-Matest. According to the UNE-EN 1015-11 [31] standard, flexural assays were carried out on three samples per mortar (of $4 \times 4 \times 16 \text{ cm}$). The six samples obtained after the flexural rupture were used for the compressive assays.

3. Results and discussion

3.1. Mineralogy of limes

The main mineral phases detected by means of XRD (Fig. 1) are portlandite and brucite (the latter only in DL). The X-ray pattern of the limes also shows the presence of a small quantity of calcite (around 5%), which reveals that a little carbonation occurred during limes storage and use. Even if it is preferable to use non-carbonated limes, the amount of calcite found is very low and it cannot affect importantly the limes reactivity.

3.2. Behaviour of mortars in the fresh state

In agreement with a previous study [14], the dolomitic lime conferred a higher plasticity to the mortar pastes and required a bigger amount of water compared to CL (Table 1). This is due to the higher values of specific surface area (SSA) and micropore volume ($\mu\text{-Vol}$) of DL (Table 2) and depends on the differences in the microstructure of the dry limes, which give rise to opposite behaviours when the limes are in suspension [14]. SSA and $\mu\text{-Vol}$ are the parameters that influence the water content rather than the lime composition. In fact, the finer the lime, the higher the water demand. In a similar way, Chever et al. [15] reported that calcitic mortar pastes show a higher water demand than the dolomitic ones to achieve a specific flow ($175 \pm 10 \text{ mm}$), since the calcitic lime they studied had a greater fineness than the dolomitic one. In our opinion, differences in the microstructure of limes with the same composition can be caused by variations in the manufacturing process that produced them. Notwithstanding, knowing the morphology of $\text{Mg}(\text{OH})_2$ and $\text{Ca}(\text{OH})_2$ particles (brucite particles are thinner and larger than portlandite ones [14]), we would expect always a greater fineness in the dry hydrated lime of dolomitic composition.

Differences in the amount of kneading water were also observed depending on the type of aggregate used: mortars elaborated with the calcareous aggregate required more water than those prepared with the siliceous one (Table 1). This is because CA is a crushed aggregate, formed by angular and porous grains, whilst SA is characterised by rounded, harder and smoother grains that absorb less water.

3.3. Characteristics of mortars in the hardening state

3.3.1. Carbonation degree of mortars

According to TGA curves (Fig. 2), the amount of portlandite (P) decreased in time, always faster in the exterior than in the interior of mortars. On the other hand, the amount of brucite (B) remained almost unvaried for the all duration of the study, being only a 1% less in the internal zones of the samples at every time interval. This is because in dolomitic lime mortars (DC and DS) only a part of the lime, corresponding to portlandite ($\text{Ca}(\text{OH})_2$), is involved in the carbonation process, whilst the rest of the binder, composed of brucite ($\text{Mg}(\text{OH})_2$), does not undergo to any transformation at these curing conditions, as also observed by other authors [13]. This is why the carbonation degree index is lower in dolomitic lime mortars at the end of this study (Table 3).

In mortars with siliceous aggregate (CS and DS) the weight loss recorded is much lower since quartz does not undergo any transformation in the range of temperature analysed during thermogravimetric analyses (see Section 2.3.1).

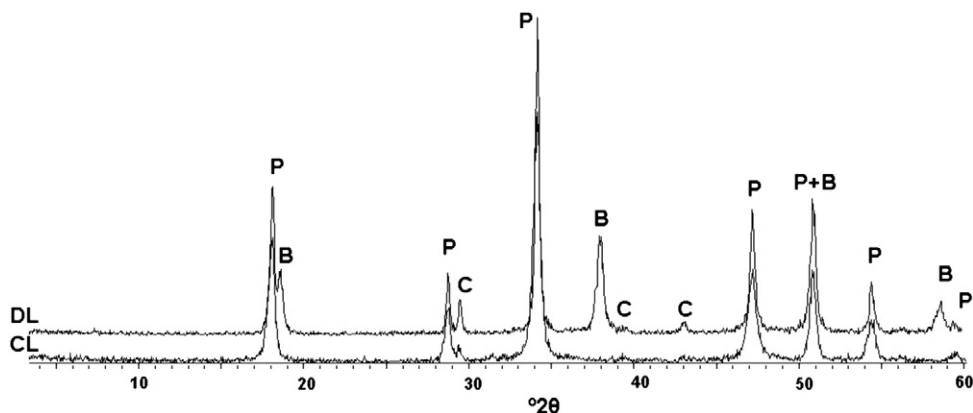


Fig. 1. X-ray diffraction patterns of the calcitic (CL) and dolomitic (DL) limes: P, portlandite; B, brucite; C, calcite.

Table 2

Particle properties of the dry powders of calcitic (CL) and dolomitic (DL) limes: specific surface (SSA, m²/g); micropores volume (μ -Vol, cm³·g); solid density (ρ , cm³/g); bulk density determined without (ρ_b , cm³/g) and with (ρ_b^* , cm³/g) compaction.

	CL	DL
SSA	13.8	23.1
μ -Vol	0.0569	0.0898
ρ	2.42	2.38
ρ_b	0.496	0.416
ρ_b^*	0.611	0.496

3.3.2. Mortars texture and morphology

FESEM images show the loss of some siliceous grains from the surface of CS and DS samples (Fig. 3a and b). The rounded and smooth surface of the siliceous aggregate does not allow a strong attachment of the matrix particles (formed by the binder and the newly-formed calcite) to the surface of the aggregate grains (Fig. 3c), thus causing desegregation in some cases. A better cohesion is observed in CC and DC mortars, because of the rough and more porous surface of the calcareous aggregate (Fig. 3d and e).

Table 3

Carbonation degree index (I_{CD} , in %) of the external (Ex) and internal (In) zones of the four mortars at the end of the study (2 months of carbonation). CC: calcitic lime + calcareous aggregate; CS: calcitic lime + siliceous aggregate; DC: dolomitic lime + calcareous aggregate; DS: dolomitic lime + siliceous aggregate.

Mortar name	I_{CD} (%)	
	Ex	In
CC	74.3	53.8
CS	73.0	16.8
DC	50.6	20.8
DS	51.9	32.1

The particles of calcite formed after carbonation of portlandite have different morphology in calcitic and dolomitic lime mortars (Fig. 4a and b). Distinguishing them in the matrix was possible only in limited zones of the samples observed, where they appear more compact than the matrix (Fig. 4c and d).

The calcitic lime is composed by agglomerates of nano- and, occasionally, micro-crystals (around 1 μ m in size) of portlandite with hexagonal habit (plate-like particles) (Fig. 4e). On the other hand, the dolomitic lime is predominantly characterised by nanoparticles that present certain homogeneity in size (not bigger than 500 nm) (Fig. 4f), confirming the previous study by Arizzi et al. [14]. FESEM observations of the mortars samples also revealed that the morphology of the new particles of calcite precipitated after carbonation is conditioned by that of the original particles of portlandite. In fact, in dolomitic mortars, the calcite particles are smaller and their shape is homogeneous (Fig. 4b). In calcitic lime mortars, by contrast, the calcite particles present different morphology and sizes (Fig. 4a), as well as the portlandite particles from which they originate (Fig. 4e).

By means of optical microscopy little dark spots (between 5 and 40 μ m in size) were observed in some localised areas of the dolomitic mortars (Fig. 5). These spots were defined by Diekamp et al. [32] as “brownish patches” or “magnesium enriched areas” of size comprised between 20 and 300 μ m (larger than the ones observed here), because of the higher concentration of Mg in these zones. A proof of the preferential localisation of Mg is the sporadic identification of hydromagnesite particles, by means of FESEM (Fig. 6), in pores of around 10 μ m in size, which probably correspond to some zones with high Mg content recognised by optical microscopy. In 28-days old samples, hydromagnesite is characterised by nanometric plate-like particles (up to 1 μ m in size) (Fig. 6a) as those formed under moist conditions described by Dheilley et al. [17]. In 60-day old samples, the hydromagnesite particles appear more elongated (Fig. 6b), being more similar to the phases observed by Diekamp et al. [32] in old dolomitic mortars samples. This indicates a growth of the hydromagnesite particles over time. If nesquehonite formation is favoured at atmospheric conditions this is not the case of hydromagnesite ($T=20$ °C, according to Lanas et al. [13]), unless it has grown under disequilibrium conditions [32]. The identification of hydromagnesite is an unexpected finding since until now it was found only in old mortars or in young samples cured under moist conditions. However, its amount is very low in the mortar because it was not detected by TG analyses at any time during the study. Interestingly, hydromagnesite has been detected in the core of the mortar, which is a zone characterised by a much slower drying than the exterior. Then, we can assume that the formation of hydromagnesite, although very scarce, has been favoured by the combined presence of a higher humidity together with the high concentration of magnesium in this zone.

The transformation of a small content of Mg(OH)₂ into hydromagnesite would explain the little variations in its amount found by means of TGA (see Section 3.3.1).

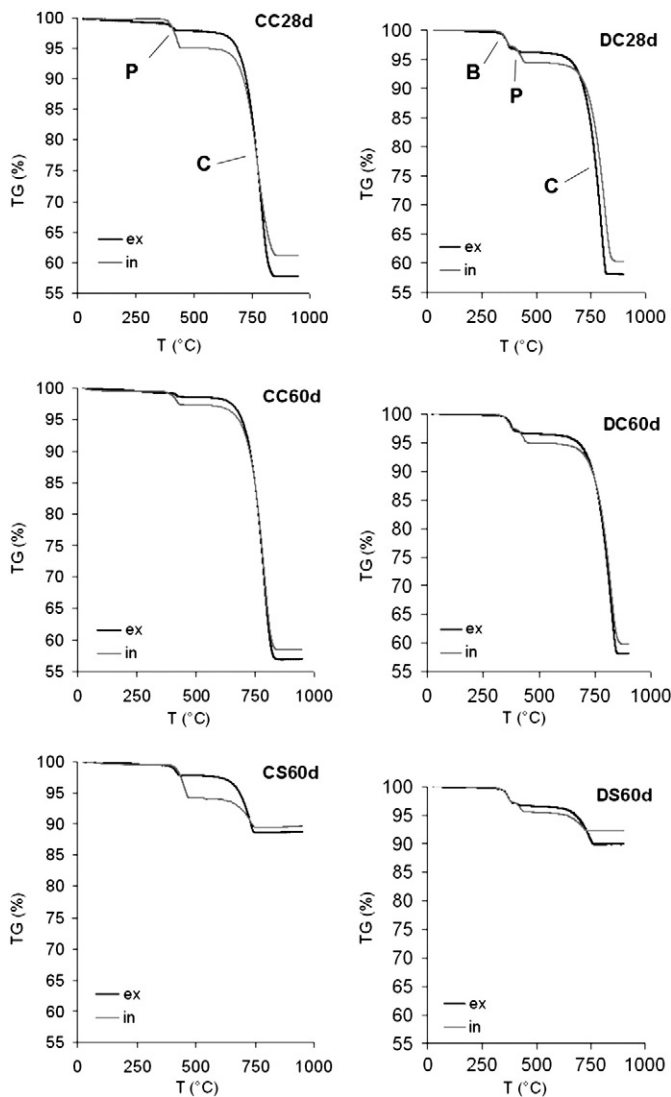


Fig. 2. Most representative TGA curves of the four types of mortars after 28 and 60 days of carbonation. CC: calcitic lime + calcareous aggregate; CS: calcitic lime + siliceous aggregate; DC: dolomitic lime + calcareous aggregate; DS: dolomitic lime + siliceous aggregate; P: portlandite; B: brucite; C: calcite.

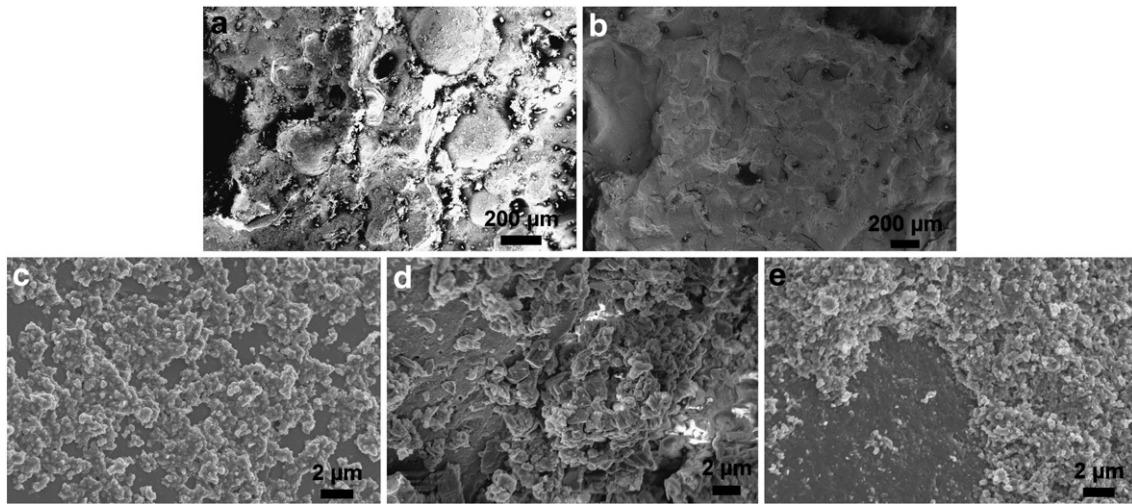


Fig. 3. FESEM images of calcitic (a and d) and dolomitic (b, c and e) lime mortars: loss of some siliceous grain from the matrix of CS (a) and DS (b); cohesion between the matrix and the siliceous (c) and calcareous (d and e) grains.

3.3.3. Pore system of the mortars

Calcitic and dolomitic lime mortars present very different pore size distribution curves (Fig. 7). On the one hand, the PSD of CC and CS is characterised by a main peak comprised between 0.1 and 1 μm

(Fig. 7a and b), which is typical of calcitic lime pastes and mortars [28,33,34]. On the other hand, DC and DS present two main families of pores with different volumes: one of them includes pores with radius equal to 0.01–0.5 μm , the other peak correspond to pores whose

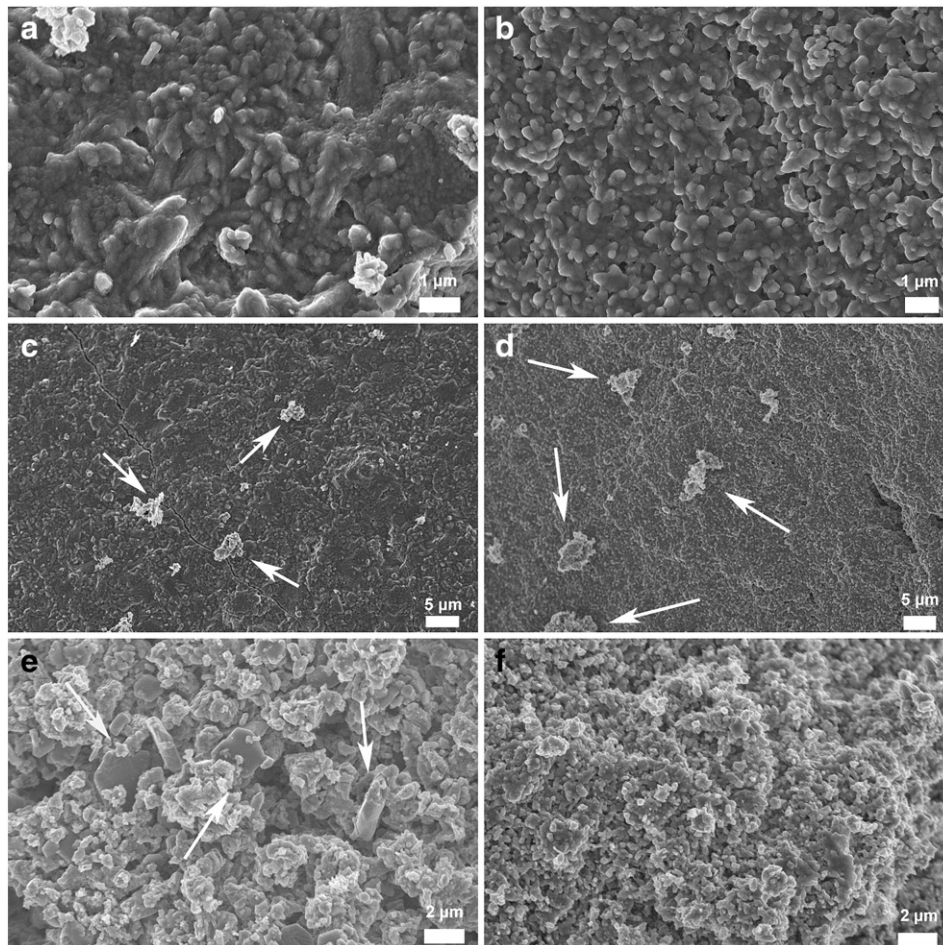


Fig. 4. FESEM images of calcitic (a, c and e) and dolomitic (b, d and f) lime mortars: newly-formed calcite in calcitic (a and c) and dolomitic (b and d) lime mortars; the clearer agglomerates indicated by the arrows (in c and d) are formed by the binder particles. Calcitic (e) and dolomitic (f) lime in mortars; the arrows (in e) indicate the hexagonal plate-like sub-micro particles of portlandite, whose size is around 2 μm , which are present in calcitic lime mortars.

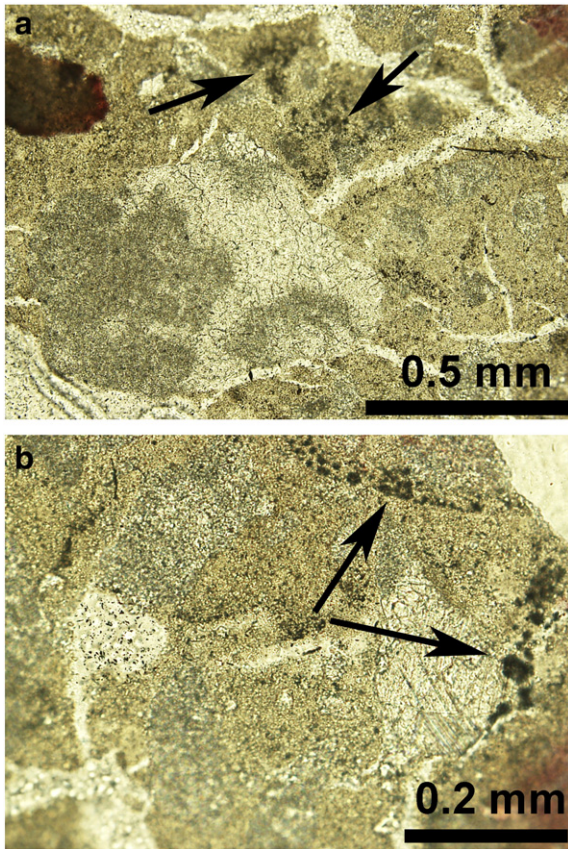


Fig. 5. OM images of the black spots in dolomitic lime mortars.

radius is comprised between 2 and 25 μm (Fig. 7c and d). Bimodal curves in the dolomitic lime mortars were also observed by other authors [16,28] who calcined the dolomite and slaked the lime manually for the preparation of the dolomitic lime mortars.

The similarities found in the pore size distribution curves between our dry hydrated limes and other limes differently produced may suggest that the lime manufacturing processes do not affect very much the pore size distribution of the mortar. The composition of the lime, in turn, influences strongly the mortar pore system.

Another factor to take into account is the effect of the aggregate on the volume of the bigger pores of the mortars. In calcitic lime mortars, the siliceous aggregate gives rise to the formation of a small family of pores in the range of $1 < r < 10 \mu\text{m}$ (Fig. 7b). In the dolomitic ones, the presence of the same aggregate produces an increase of the pores of radius comprised between 2 and 25 μm (DS, Fig. 7d). This porosity has to be related to the poor cohesion between the matrix and the aggregate grains found in mortars with siliceous aggregate (see Section 3.3.2).

During carbonation, the volume of the main pores decreases slowly in the four mortars types (Fig. 7), because the lime is progressively transformed into calcite. Nevertheless, the open porosity values found after 60 days are in some cases higher (in CC and CS, Table 4) or remain almost unvaried (DC and DS, Table 4). This can be due to the formation of small calcite particles that fill the pores left by the portlandite and brucite particles but, at the same time, create new smaller pores ($r \sim 0.01 \mu\text{m}$) that are especially visible in CC mortar (Fig. 7a), since the carbonation process in dolomitic mortars is slower.

3.3.4. Hygric behaviour

3.3.4.1. *Water capillary imbibition.* Fig. 8 shows the different behaviour of mortars during the water capillary uptake. We have to mention

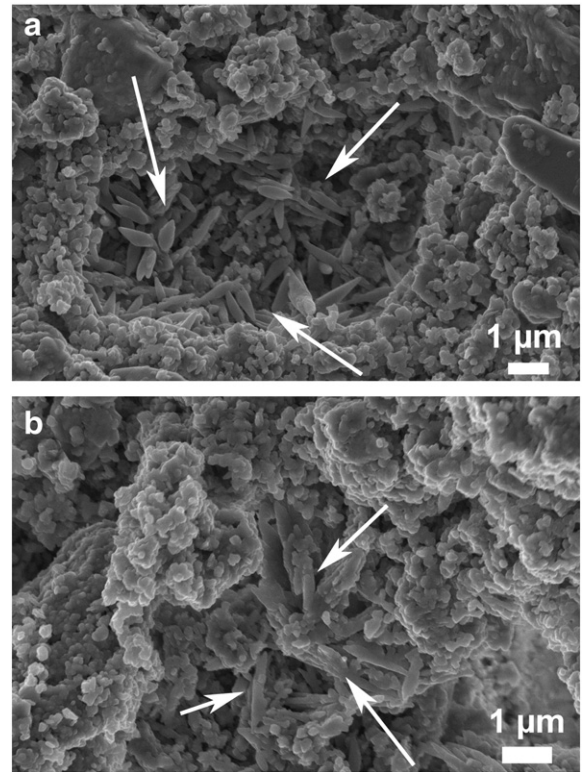


Fig. 6. FESEM image of the internal samples of dolomitic lime mortar after 28 (a) and 60 (b) days of curing. Arrows indicate some nanometric plate-like (up to 1 μm in size) (a) and more elongated (b) particles of hydromagnesite.

that mortars samples were not totally carbonated when the capillary test was performed, therefore potential reactions between water and the binders might have occurred, thus influencing the results. Between the calcitic lime mortars, CC absorbs the biggest amount of water, due to its higher porosity (Table 4), but the weight saturation is reached almost at the same time than in CS (Fig. 8a). The same occurs with the visual saturation of CC and CS samples, which is attained when the capillary front achieves the top of the samples (Fig. 8b). At the end of the capillary test, in calcitic mortars samples all connected pores are filled and both mass and visual saturations are achieved because the majority of the pores are in the same range of size ($0.1 < r < 1 \mu\text{m}$, Fig. 7a and b).

On the other hand, in dolomitic mortars (DC and DS), the water absorbed during time is much lower than in calcitic ones. Moreover, the curve representing the mass taking over time (Fig. 8a) is not linear but it is formed by two sections with different slopes, due to the fact that the pore system of these mortars is characterised by two main families of pores with small ($0.01 < r < 0.5 \mu\text{m}$) and big ($2 < r < 25 \mu\text{m}$) radius [30] (Fig. 7c and d). In this kind of pore network, water is absorbed faster by the biggest pores, through which it reaches the top of the sample (as shown in Fig. 8b). However, sample continues absorbing water even after the visual saturation because the smallest pores, in which the capillary pressure is higher (according to Laplace's equation), absorb water from the biggest ones [35–37]. This causes a time lag between the visual and the real saturation of the sample [30] (Fig. 8). The test was ended after the total saturation of the calcitic lime mortars; it is evident that DC and DS mortars have still not reached a constant weight and further increase is expected considering their higher porosity (Table 4) and the characteristics of their pore system (Fig. 7c and d).

3.3.4.2. *Shrinkage and water-retention capacity.* Dolomitic lime mortars experimented a much bigger shrinkage compared to the calcitic ones,

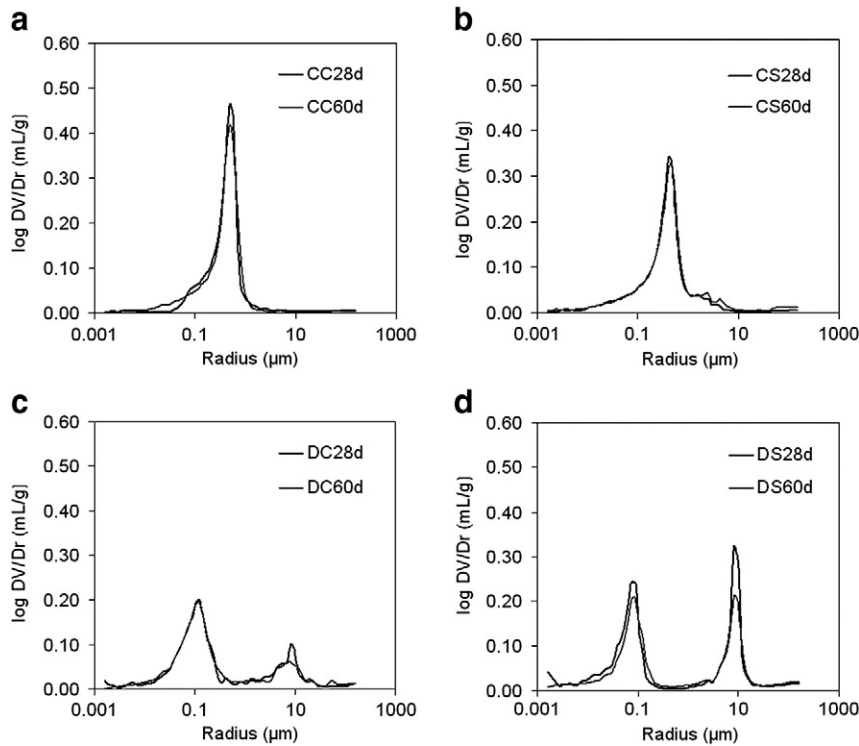


Fig. 7. Pore size distribution curves of the calcitic (CC and CS) (a and b) and dolomitic (DC and DS) (c and d) lime mortars with calcareous (CC and DC) (a and c) and siliceous (CS and DS) (b and d) aggregate after 28 (28 d) and 60 (60 d) days from their elaboration.

as observed by means of optical and electron microscopy (Fig. 9). The plastic shrinkage, namely the mortar volume reduction due to water evaporation, depends on the amount of water in excess present in the mixture but, above all, it is related to the water-retention capacity of the lime. Generally, a lime with a higher specific surface area gives rise to a mixture with higher viscosity and better water-retention capacity [38]. The dolomitic lime presents these characteristics (see SSA value in Table 1) and, in fact, the DC and DS fresh mixtures showed a higher viscosity and needed a bigger amount of water with respect to CC and CS (Table 2). Then, we wondered why DC and DS are characterised by such big shrinkage. Since the shrinkage is a consequence of the water evaporation, it is sensible to relate the drying behaviour of the dolomitic mortars to the water transport properties and, as a consequence, to the pore system of these mortars. According to Scherer [39], the shrinkage due to drying of a solid porous body is the result of internal stresses produced by capillary forces and the probability of cracking is related to the strength of the pore network, among other factors. In a heterogeneous pore system, the largest pores empty first and the capillary pressure compresses the smaller pores, causing great tensions that finally crack the network. This is what occurred in the dolomitic mortars, which are characterised by both large and small pores (see Section 3.3.3). As consequence of the formation of shrinkage fissures, an increase in the volume of the largest pores is likely to have occurred, especially in the DS mortars (Fig. 7d).

Table 4
Open porosity (P_o , in %) values and standard deviation of the four mortars types after 28 (28 d) and 60 (60 d) days from their elaboration.

Mortar name	P_o (%)	
	28 d	60 d
CC	32.5 ± 2.74	35.0 ± 1.10
CS	32.8 ± 3.34	34.3 ± 3.39
DC	34.4 ± 1.56	34.2 ± 0.64
DS	36.4 ± 1.17	37.5 ± 2.01

3.3.5. Mechanical behaviour

After 28 days of curing, mortars achieve quite low mechanical strengths (Table 5) because mortars are in the early stage of carbonation and resistances are not extensively developed yet. Contrary to that studied by other authors, dolomitic lime mortars are characterised by very low mechanical strengths, especially DS. In fact, when the siliceous aggregate was used, extremely weak dolomitic mortars samples were obtained, to such a degree that their strength could not be measured by the mechanical press.

Our results disagree with Dheilly et al.'s study [17] on the mechanical resistances of dolomitic lime mortars after 28 days of curing. However the curing conditions in this study were not the same (we exposed mortars to a dry environment instead to a moist one) and this seems to be a crucial factor on the development of strengths. Moreover, the fragility shown by the dolomitic lime mortars was expected since they have been subjected to internal stresses, due to shrinkage, that obviously affected the mechanical performances.

In addition to this, it is important to point out that the formation of hydromagnesite in some small areas of the dolomitic mortars samples (see Section 3.3.2) did not yield any strength improvement, as expected due to the low amount of this phase.

4. Conclusions

This work claims to clarify the uncertainty that arises due to different and, sometimes, conflicting results published in literature about the performances of dolomitic lime mortars; uncertainty that makes controversial the choice of the correct lime for the elaboration of repair mortars.

There are two interesting aspects of this research: 1) the calcitic and dolomitic limes used were standardised limes industrially manufactured in the state of dry powder (i.e. dry hydrated limes); 2) the mortars were cured under dry conditions. By comparing our results with those published in literature up to now, we have understood that the manufacturing process of the dolomitic lime (i.e. manually

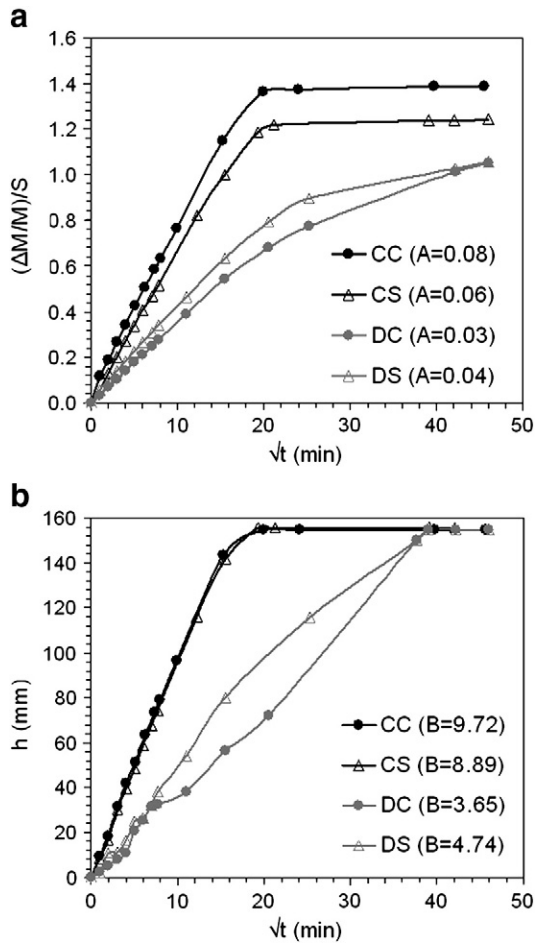


Fig. 8. Capillarity curves of calcitic and dolomitic lime mortars after 60 days of carbonation, representing the weight increase (ΔM , in g) per surface unit (S , in m^2) and the height of the capillary front (h , in mm) versus the square of time (\sqrt{t} , in $min^{-1/2}$). The imbibition coefficients (A , in $g/cm^2 min^{1/2}$ and B , in $cm/min^{1/2}$), which correspond to the slope of the two curves, are indicated in each graphic.

or industrially calcined and slaked) and the curing conditions (dry or moist) are the main causes of the variability of the mortars' properties. The first factor affects the microstructure of the lime, then the

Table 5

Flexural (R_f , in MPa) and compressive (R_c , in MPa) strengths and standard deviation of the four mortars types after 28 days since their elaboration.

Mortar name	R_f	R_c
CC	1.43 ± 0.16	1.03 ± 0.03
CS	1.35 ± 0.16	0.05 ± 0.00
DC	1.15 ± 0.16	0.90 ± 0.19
DS	-	-

water demand and the viscosity of the fresh mortar mixture; the second one influences the formation of different mineralogic phases, then the development of strength. With respect to this last point, we have observed that the brucite amount remains almost unvaried during carbonation, unless it turns into small amounts of hydromagnesite. We found that the formation of hydromagnesite is possible at ambient conditions if a low humidity is present, but its presence does not increase the mechanical resistances of the dolomitic mortar. A great strength improvement can be expected only in dolomitic mortars exposed to moisture areas.

The heterogeneous pore network of the dolomitic lime mortars, characterised by micropores connected to large pores, has demonstrated to be crucial in the capillary imbibition behaviour and the drying kinetics, which caused a great shrinkage and produced low mechanical strengths. These microstructural characteristics and the fragility of the dolomitic mortars studied here indicate that they might be more susceptible to weathering than the calcitic mortars.

The textural characterisation of calcitic and dolomitic lime mortars showed that the calcite particles formed during carbonation are similar in morphology (shape and size) to the original particles of portlandite from which they originate. In this sense, the dolomitic lime generates a more uniform texture.

Finally, differences due to the aggregate type are especially visible in the textural properties of the mortars, more specifically in the degree of cohesion between the surface of the grains and the matrix. About this, calcareous aggregates, which present an angular, rough and porous surface, perform better than siliceous aggregates, with a smoother and rounded surface.

The main conclusion that can be drawn from this study is that the use of a calcitic dry hydrated lime should be preferred to a dolomitic one for the elaboration of repair mortars to be applied in dry zones. In practice, however, it is possible to reduce the shrinkage of dolomitic

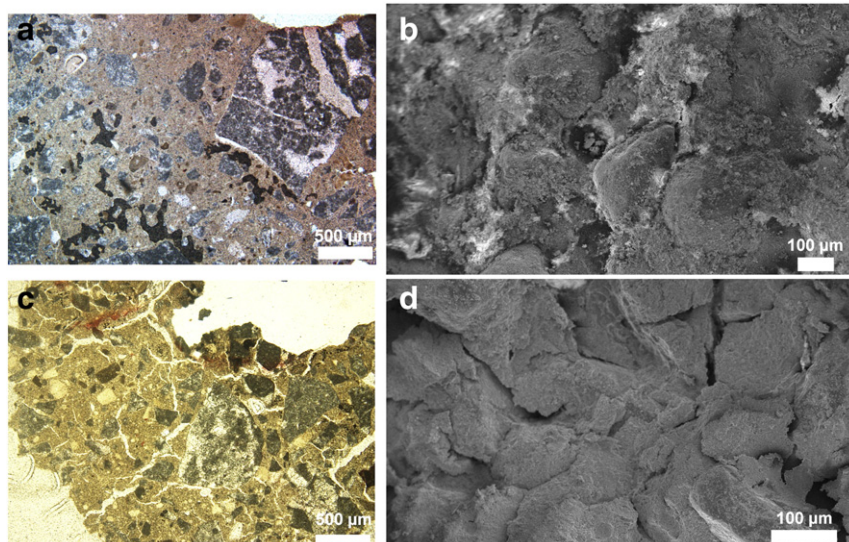


Fig. 9. OM (a and c) and FESEM (b and d) images of the shrinkage fissures observed in calcitic (a and b) and dolomitic (c and d) limes mortars.

mortars by wetting the surface during rendering and by keeping the render moist during the initial setting. Moreover, we rely on the better performances that the dolomitic lime generally confers to mortars when cured in moist areas.

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References

- [1] A.D. Cowper, Lime and lime mortars. Donhead Ed. (1927), reprinted by building Research Establishment Ltd. In 1998.
- [2] C. Groot, P. Bartos, J. Huges, Historic mortars: characteristics and test concluding summary and state of the art, International Workshop on Historic mortars, Paisley, UK, 1999, pp. 443–454.
- [3] A.H.P. Maurenbrecher, Mortars for repair of traditional masonry, *Pract. Period. Struct. Des. Constr.* 9 (2) (2004) 62–65.
- [4] K. Callebaut, J. Elsen, K. Van Balen, W. Viaene, Nineteenth century hydraulic resaturation mortars in the Saint Michael's Church (Leuven, Belgium). *Natural hydraulic lime or cement? Cem. Concr. Res.* 31 (2001) 397–403.
- [5] F. Veniale, M. Setti, C. Rodriguez-Navarro, S. Lodola, W. Palestra, A. Busetto, Thaumate as decay product of cement mortar in brick masonry of a church near Venice, *Cem. Concr. Compos.* 25 (2003) 1123–1129.
- [6] A. Diekamp, J. Konzett, W. Wertl, R. Tessadri, P.W. Mirwald, Dolomitic lime mortar—a commonly used material for medieval buildings in western Austria and northern Italy, *Proceedings of the 11th International Congress on deterioration and conservation of stone*, Torun, Poland, 2008, pp. 597–604.
- [7] C. Atzeni, L. Massidda, U. Sanna, Magnesian lime. Experimental contribution to interpreting historical data, *Sci. Technol. Cult. Herit.* 5 (2) (1995) 29–36.
- [8] G.F. Dornap, The slaking of lime—effect on quality of calcium hydroxide, (English translation), *Zement Kalkund Gips*, no. 1/77, 1977, pp. 34–39.
- [9] UNE-EN 459–1, Cales para la construcción. Parte I: definiciones, especificaciones y criterios de conformidad para los cementos comunes, AENOR, Madrid, 2000.
- [10] O. Cazalla, C. Rodriguez-Navarro, E. Sebastián, G. Cultrone, M.J. De La Torre, Aging of lime putty: effects on traditional lime mortar carbonation, *J. Am. Ceram. Soc.* 83 (5) (2000) 1070–1076.
- [11] K. Van Balen, Carbonation reaction of lime, kinetics at ambient temperature, *Cem. Concr. Res.* 35 (2005) 647–657.
- [12] S. Pavía, B. Toomey, Influence of the aggregate quality on the physical properties of natural feebly-hydraulic lime mortars, *Mater. Struct.* 41 (2008) 559–569.
- [13] J. Lanás, J.L. Perez Bernal, M.A. Bello, J.I. Alvarez, Mechanical properties of masonry repair dolomitic lime-based mortars, *Cem. Concr. Res.* 36 (2006) 951–960.
- [14] A. Arizzi, R. Hendrickx, G. Cultrone, K. Van Balen, Differences in the rheological properties of calcitic and dolomitic lime slurries: influence of particle characteristics and practical implications in lime-based mortar manufacturing, *Mater. Constr.* 60 (2012), doi:10.3989/mc.2011.00311.
- [15] L. Chever, S. Pavía, R. Howard, Physical properties of magnesian lime mortars, *Mater. Struct.* 43 (2010) 283–296.
- [16] G. Cultrone, A. Arizzi, E. Sebastián, C. Rodriguez-Navarro, Sulfation of calcitic and dolomitic lime mortars in the presence of diesel particulate matter, *Environ. Geol.* 56 (2008) 741–752.
- [17] R.M. Dheilly, A. Bouguerra, B. Beaudoin, J. Tudo, M. Queneudec, Hydromagnesite development in magnesian lime mortars, *Mater. Sci. Eng. A268* (1999) 127–131.
- [18] S. Pavía, B. Fitzgerald, R. Howard, Evaluation of properties of magnesian lime mortar, in: C.A. Brebbia, A. Torpiano (Eds.), *WIT Transactions on The Built Environment*, 83, WIT Press, 2005, pp. 375–384.
- [19] L.J. Vicat, *Mortars and cements*, Donhead, Shaftesbury, 1837 2003.
- [20] J. Lanás, J.I. Alvarez, Dolomitic limes: evolution of the slaking process under different conditions, *Thermochim. Acta* 423 (2004) 1–12.
- [21] UNE EN 933–2, Ensayos para determinar las propiedades geométricas de los áridos, Parte 2: Determinación de la granulometría de las partículas. Tamices de ensayo, tamaño nominal de las aberturas, AENOR, Madrid, 1999.
- [22] J.D. Martín Ramos, X Powder. A software package for powder X-ray diffraction analysis (Lgl. Dep. GR 1001/04), 2004.
- [23] S. Brunauer, P.H. Emmet, J. Teller, Adsorption of gases in multimolecular layers, *J. Am. Chem. Soc.* 60 (1938) 309–319.
- [24] E.P. Barret, L.J. Joyner, P. Halenda, The determination of pore volume and area distributions in porous substances. I. Computations from nitrogen isotherms, *J. Am. Chem. Soc.* 73 (1951) 373–380.
- [25] ASTM D 854–92, Test Method for Specific Gravity of Soils, 1993.
- [26] UNE EN 1015–3, Métodos de ensayo de los morteros para albañilería, Parte 3: Determinación de la consistencia del mortero fresco (por la mesa de sacudidas), AENOR, Madrid, 1998.
- [27] UNE EN 1015–2, Métodos de ensayo de los morteros para albañilería, Parte 2: Toma de muestra total de morteros y preparación de los morteros para ensayo, AENOR, Madrid, 1999.
- [28] O. Cazalla Morteros de cal. Aplicación en el patrimonio histórico. PhD Thesis, University of Granada (2002).
- [29] UNE-EN ISO 11358, Plásticos. Termogravimetría (TG) de polímeros. Principios generales, AENOR, Madrid, 1997.
- [30] K. Beck, M. Al-Mukhatat, O. Rozenbaum, M. Rautureau, Characterization, water transfer properties and deterioration in tuffeau: building material in the Loire valley-France, *Build. Environ.* 38 (2003) 1151–1162.
- [31] UNE-EN 1015–11, Métodos de ensayo de los morteros para albañilería, Parte 11: Determinación de la resistencia a flexión y a compresión del mortero endurecido, AENOR, Madrid, 2000.
- [32] A. Diekamp, J. Konzett, P.W. Mirwald, Magnesian lime mortars—identification of magnesium-phases in medieval mortars and plasters with imaging techniques, 12th Euroseminar on Microscopy Applied to Building Materials, Dortmund, Germany, 2009.
- [33] M. Arandigoyen, J.L. Pérez Bernal, M.A. Bello López, J.I. Alvarez, Lime-pastes with different kneading water: pore structure and capillary porosity, *Appl. Surf. Sci.* 252 (2005) 1449–1459.
- [34] R.M. Lawrence, T.J. Mays, S. Rigby, P. Walker, D. D'Ayala, Effects of carbonation on the pore structure of non-hydraulic lime mortars, *Cem. Concr. Res.* 37 (2007) 1059–1069.
- [35] D. Benavente, P. Lock, M.A. García del Cura, S. Ordóñez, Predicting the capillary imbibition of porous rocks from microstructure, *Transport Porous Med.* 49 (2002) 59–76.
- [36] M. Mamillan, Connaissances actuelles des problèmes de remontées d'eau par capillarité dans les murs, The conservation of stone II. Cent per la Conservazione delle Sculture all'aperto, 1981, pp. 59–72, (Bologna).
- [37] C. Hall, W.D. Hoff, Water transport in brick, stone and concrete, (Ed.) Taylor and Francis, London and New York, 2002.
- [38] Boletín AFAM, Morteros. Guía General, 2003.
- [39] G.W. Scherer, Theory of drying, *J. Am. Ceram. Soc.* 73 (1) (1990) 3–14.