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ORIGINAL ARTICLE

A comprehensive review of the manufacturing process and properties of natural hydraulic limes

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Abstract Within the sub-group of hydraulic limes, natural hydraulic limes (NHL) are obtained by calcining limestone containing silica and alumina at temperatures of less than 1250 °C. The content of hydraulic phases generated at these temperatures depends on the raw material, the firing and cooling conditions inside the kiln, and the slaking method, giving rise to natural hydraulic limes with different hydraulic features. Despite these differences, the European standards classify NHL limes above all based on their free lime content and the compressive strength of the mortar after 28 days of curing. This means that there are natural hydraulic limes on the market today which despite having the same index number (NHL2, NHL3.5 or NHL5) have very different compositional and textural characteristics. The variations in the limes can in turn lead to mortars with different properties in both the fresh and hardened states. Although the standard establishes ranges for the compressive strength values for the different index numbers, these ranges overlap, so giving rise to ambiguities in the classification of these limes. This review paper aims to extend our knowledge as to how different aspects of the manufacturing process of NHLs influence their final properties, with the ultimate objective of achieving a more rigorous classification of these limes. If hydraulic limes with more precisely controlled compositional and textural characteristics were available on the market, this would have a positive impact, especially on architectural heritage conservation, as more suitable, more clearly defined and more compatible hydraulic mortars would be available to restorers.

Keywords Building limes · Hydraulicity · Calcination · Slaking · Composition · Setting

1 Introduction

According to the European standard EN459-1 on building limes [1], those with hydraulic properties "*consist mainly of calcium hydroxide, calcium silicates and calcium aluminates and have the property of setting and hardening when mixed with and/or under water*". The standard defines three subfamilies of limes with hydraulic properties: (1) natural hydraulic limes (NHL), (2) formulated limes (FL), and (3) hydraulic limes (HL). The first, natural hydraulic lime is defined as "*a lime produced by burning of more or less argillaceous or siliceous limestones (including chalk) with reduction to powder by slaking with or without grinding. (…). Grinding agents up to 0.1% are allowed. Natural hydraulic lime does not contain any other additions*".

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Natural hydraulic limes are classified into three grades: NHL2, for natural hydraulic lime 2; NHL3.5, for natural hydraulic lime 3.5; and NHL5, for natural hydraulic lime 5. This classification is based on the minimum compressive strength values obtained in standardised mortars made with these NHLs after 28 days of curing in accordance with EN459-1 [1]. As already highlighted by other researchers [2–4], the compressive strength ranges for the three types of natural hydraulic lime overlap, implying that some NHL might be misclassified. Such is the case of a natural hydraulic lime with a 28 day strength of around 6 MPa, which could be either a NHL2, a NHL3.5 or a NHL5 (Table 1).

Furthermore, the 28 day compressive strength test can be misleading when characterising and classifying feebly hydraulic NHL in which most of the strength is obtained through long-term carbonation, and therefore after a longer hardening period [2–7]. On average, NHL mortars only reach approximately 50% of their ultimate strength during the first 28 days of curing [6, 8–14]. And in fact, a curing time of at least 2 years is necessary to obtain a real indication of the strength gain in mortars made with NHL, at which point a NHL2 can reach even higher strengths than the weakest NHL5 at 28 days [2, 3, 15].

The European standard EN459-1 [1] also establishes different final setting times for each type of NHL (Table 1). However, it must be emphasised that these are the only physical parameters established in the standard that allow us to distinguish between the different NHLs.

As regards the chemical requirements, the lime available as $Ca(OH)_2$ (also called *free lime*) has to be controlled (Table 1), and the SO_3 content must be lower than 2% in all types of NHL. It is striking that the European regulations do not specify the approximate amounts of silica and alumina that must be present in the NHL, and/or even in the raw material to obtain this type of lime, especially considering that these compounds are responsible for the hydraulic nature of NHL (as also stated in the standard itself: “*the hydraulic properties* of NHL *exclusively result from the special chemical composition of the natural raw material*”).

Prior to the differentiation of natural hydraulic limes with indexes 2, 3.5 and 5, a more exhaustive categorisation, which defined the limes as *feebly*, *moderately* and *eminently* (or *moderate*,

Table 1 Main characteristics of natural hydraulic limes according to European standard [1, 35] and previous scientific literature [16, 19–22]

Binder type		Physical requirements (EN459-1 [1])		Chemical requirements (EN459-1 [1] and EN459-2 [35])	Other requirements					
Name	Acronym [1]	Compressive strength at 28 d (MPa)	Final setting times (h)	Available lime as $Ca(OH)_2$ (%)	Hydraulic degree [16]	Description [16, 18]	CI [20, 21]	HI [19, 22]	Content in clay phases [21]	Total reactive oxides ($SiO_2 + Al_2O_3 + Fe_2O_3$) [16, 18]
Natural hydraulic lime	NHL2	≥ 2 to ≤ 7	≤ 40	≥ 35	Moderate	Slightly or Feebly	0.3–0.5	0.1–0.2	~ 8%	< 12%
	NHL3.5	≥ 3.5 to ≤ 10	≤ 30	≥ 25	Intermediate	Moderate	0.5–0.7	–	~ 15%	12–18%
	NHL5	≥ 5 to ≤ 15*	≤ 15	≥ 15	High	Eminently	0.7–1.1	0.2–0.4	~ 25%	18–25%

CI cementation index, *HI* hydraulicity index

*The compressive strength at 7 days is only given for NHL5 and must be ≥ 2 MPa *intermediate* and *high*) hydraulic was used. This classification, which was introduced by Cowper [16], was based on the studies initiated in the eighteenth century by Smeaton, continued by Vicat [17, 18] and completed in the twentieth century by Eckel [19] and Boynton [20]. Cowper [16] defined hydraulic limes as very complex products consisting of silica (SiO_2), alumina (Al_2O_3) and lime (CaO), with or without magnesia (MgO) and iron oxide (Fe_2O_3). Holmes and Wingate [21] consider soluble silica as the most active component of the possible clays, while stating that alumina and ferric oxide also contribute to the hydraulicity. All these reactive oxides are regarded as responsible for the hydraulic properties of binders such as natural hydraulic lime, and precise ranges for the total reactive oxide content have been established for each type of lime (Table 1). These have been used to create indexes that define the total hydraulicity of each binder, i.e. the hydraulicity index (*HI*, Eq. 1) [9, 17, 19–24] and different versions there of [25, 26] (Eq. 2).

$$HI = \frac{\left(\%SiO_2\right) + \left(\%Al_2O_3\right)}{(\%CaO)} \tag{1}$$

$$HI = \frac{\left(\%SiO_2\right) + \left(\%Al_2O_3\right) + (\%Fe_2O_3)}{(\%CaO) + (\%MgO)} \tag{2}$$

However, the hydraulicity index does not assess the specific contribution made by each oxide to the formation of hydraulic phases. For this reason, another hydraulicity indicator known as the cementation index (*CI*, Eq. 3*)* was established, which considered the molecular proportions of each oxide when they combine to form the hydraulic compounds [19].

$$CI = \frac{2.8 \times \left(\%SiO_2\right) + 1.1 \times \left(\%Al_2O_3\right) + 0.7 \times (\%Fe_2O_3)}{(\%CaO) + 1.4 \times (\%MgO)} \tag{3}$$

Nowadays, *CI* is the most common index for classifying hydraulic limes, for determining the suitability of a raw material to produce a binder with a certain degree of hydraulicity and for establishing the boundaries between the different grades of hydraulic limes [27–32]. Even though different CI ranges have been established over time, the most generally accepted are those defined by Boynton [20, 33, 34], as indicated in Table 1.

However, as stated by Eckel a century ago [19], the cementation index "*cannot be the sole basis for classification, because the properties of a hydraulic cementing material* (..) *depend not only on its composition, but* also *on the conditions of its manufacture*".

Starting from this premise, the aim of this bibliographic review is to extend our knowledge of natural hydraulic lime and its applicable technical standards. To this end, this study will be focusing in particular on the manufacture of NHL and its use, especially in the field of Architectural Heritage conservation and restoration.

2 The manufacturing process of natural hydraulic lime

To understand why NHLs with such different properties are currently available on the market, it is necessary first to explain how they are manufactured at an industrial level, a topic about which little research has been conducted, as other authors have already pointed out [2, 3, 6, 12–14, 16, 19, 21, 25, 27–29, 31, 32, 36–51]. To this end, all the steps of the manufacturing process of natural hydraulic limes will be discussed in depth on the basis of the existing literature, according to which the most important factors affecting the final product are: (1) the chemical–mineralogical and textural composition of the raw materials, (2) the calcination conditions (e.g. temperature and residence time in the kiln), (3) the slaking process, and (4) the reactivity of the lime produced.

2.1 Raw materials

It has always been believed that the hydraulicity of NHLs is dependent on the presence of clays in the raw material. This is because the first definition of the degree of hydraulicity of NHLs referred to Smeaton's studies on English marly limestones, i.e. limestones containing clays. Even further back in time, Vicat [17, 18] produced an "artificial hydraulic lime" by mixing a "rich slaked lime" (obtained from chalk from the Upper Cretaceous carbonatic formation of the Paris Basin, according to Artioli et al. [52]) with a certain proportion of clay, and calcining the mixture, thus obtaining a product called ‘‘twice-kilned’’. And, in 1796, James Parker manufactured the first natural cement (also called *Roman cement* or *Parker cement*) by burning and grinding septaria, calcareous nodules with a clay nucleus [21, 52].

As a result, the presence of clays has become an essential prerequisite in all raw materials considered suitable for making NHLs. Even though the presence, content and type of clays (“active clays”, [21]) are important aspects to consider in the manufacture of NHLs, as the chemical–mineralogical composition of the clays can affect the silicates and aluminates formed [51, 53–55], different types of siliceous limestone (providing they have a *CI* of between 0.30 and 1.10 [19]), and even industrial sub-products [56] can also be used in the manufacture of natural hydraulic limes, as has been demonstrated in recent research.

These materials include stones containing diatoms (amorphous silicon oxide) [26], microcrystalline quartz (or silex), feldspars and plagioclases [27–32, 44, 46–48, 50, 57–64], waste from the paper industry (lime mud, [56]) and a mix of $Ca(OH)_2$ and SiO_2 [65].

Nowadays, it is more and more widely accepted that a natural hydraulic lime can be obtained not only from a limestone with a certain clay content, but also from a siliceous limestone (for example with silex or chert), providing that the silica present in the stone is reactive [32, 66].

The properties of natural hydraulic limes are directly influenced by the compositional and textural features of the raw materials used in their production [31]. This means that although the reactive oxide content is a determining factor in the development of hydraulicity, the heterogeneity [67], texture, granulometry and crystallinity of the rock influence not only the degree of hydraulicity, but also the physical properties of the calcined product [47–49, 59, 68–70]. For example, Wingate [37] found that crystalline rocks such as marbles, with low porosity and very coarse crystalline impurities, were hard to calcine. Other more recent research studies have investigated the influence of the petrographic features of the rock during the calcination phase [29, 31, 48, 49, 71]. In these studies, calcination was carried out in the laboratory and mostly on ground powder samples rather than on solid rock. In this way it was discovered that rocks with clastic textures are preferable to crystalline rocks because of their higher porosity and ease of decomposition, and that fine-grained or micritic (< 5 μm) calcite matrices are more prone to calcination than sparite-sized (> 5 μm) ones [31, 49, 71]. This is because the smaller the particle size, the larger the specific surface area of the grains. If these factors could be controlled, a better-quality quicklime (i.e. more reactive to water) could be produced using less energy, as will be discussed below.

2.2 Calcination

The hydraulicity and physical characteristics (e.g. colour, porosity, specific surface area, density, etc.) of the calcined product are influenced not only by the chemical and mineralogical composition of the raw materials, but also by the calcination conditions [9, 16, 21, 23, 24, 29, 36, 39–42, 71]. In particular, the degree of calcination of the limestone is highly dependent on the maximum temperature reached, the residence time in the kiln [29, 71] and the partial pressure of the surrounding CO_2 [34].

NHLs are obtained by calcination below the clinkering point, 1250 °C, a feature that differentiates these binders from ordinary Portland cement (OPC) and its varieties [72]. During the firing process, the following reactions occur [16, 21, 25, 73]:

- Between 400 and 600 °C, the clays, if any, are dehydrated and decompose partially or totally;
- Between 600 and 850 °C calcite decomposes into calcium oxide and CO_2 [74]. Above 1000 °C, CaO begins to undergo sintering, with an increase in crystallite size as the temperature rises [74], aspect that will have an impact on its reactivity towards water during the hydration step;
- Over 800 °C, a solid-state reaction occurs between unstable reactive ions (i.e., silicon, aluminium and iron) and calcium oxide, generating various silicates and calcium aluminates.

The calcination temperature used in most of the experimental studies reported in the literature ranges between 950 and 1050 °C [5], and 950–1250 °C [16, 25, 75], whilst temperatures higher than 1250 °C would favour solid-state and liquid-state sintering [61]. In some studies, hydraulic binders have been produced at lower calcination temperatures (850 °C, [26]). As is generally known for aerial lime, preheating and a gradual increase in temperature is preferable to shock calcination, so as to ensure the complete thermal decomposition of the calcite [40].

Heat is unevenly distributed inside traditional kilns in which different calcination temperatures can be reached. As a result, "*under-burned*", "*soft-burned*" and "*hard-burned*" (also called "*overburned*" and "*dead-burned*") lime [37] can be obtained. When the stone presents a residual core of non-decomposed calcite, due to an excessively low calcination temperature, the lime is considered to be *underburned* [37]. If the stone reaches sintering point, due to an excessively high temperature, the lime is said to be *hard-burned* (depending on the degree of sintering, this lime is then described as *overburned* or *deadburned*). In the latter, the CaO particles have a less porous structure and therefore a lower specific surface area, which means that the NHL quicklime is less reactive to slaking [41, 42, 49]. *Soft-burned* lime, by contrast, is obtained at lower temperatures and is more reactive than lime produced at higher temperatures or with longer residence times in the kiln [37, 40, 41, 50].

This problem was minimised with the invention of modern kilns in which, unlike the traditional ones, the heat is more homogeneously spread and calcination is less dependent on the position of the stone in the kiln. Previously, natural hydraulic lime had been obtained by burning large lumps of material, much larger than those used in the manufacture of Portland cement [76]. In traditional kilns (Fig. 1A), the size of the lump depended on its position in the kiln, which was filled from above and in layers so that the larger rock fragments were placed at the bottom, close to the fire, and the smaller pieces appeared in the upper layers [19]. However, with the introduction of modern industrial kilns (Figs. 1B and C) and machinery capable of reducing rock size to 6–8 cm (Fig. 2) [37], the calcination process was optimized.

Overburning is not only the product of high calcination temperatures, it is also influenced by the chemical and mineralogical composition of the raw material [7]. It is encouraged by the presence of silica, alumina and iron in the raw materials, which are known to clog the pores of the quicklime, decreasing its specific surface area and reactivity to hydration [40, 42]. This also affects the specific surface area of the lime, making it more impermeable to slaking water even if it has been calcined at optimum temperature.

In addition to its effects on the textural properties and reactivity to water of the NHL quicklime, the calcination temperature is also a determining factor in the resulting mineralogy of the NHL. For example,

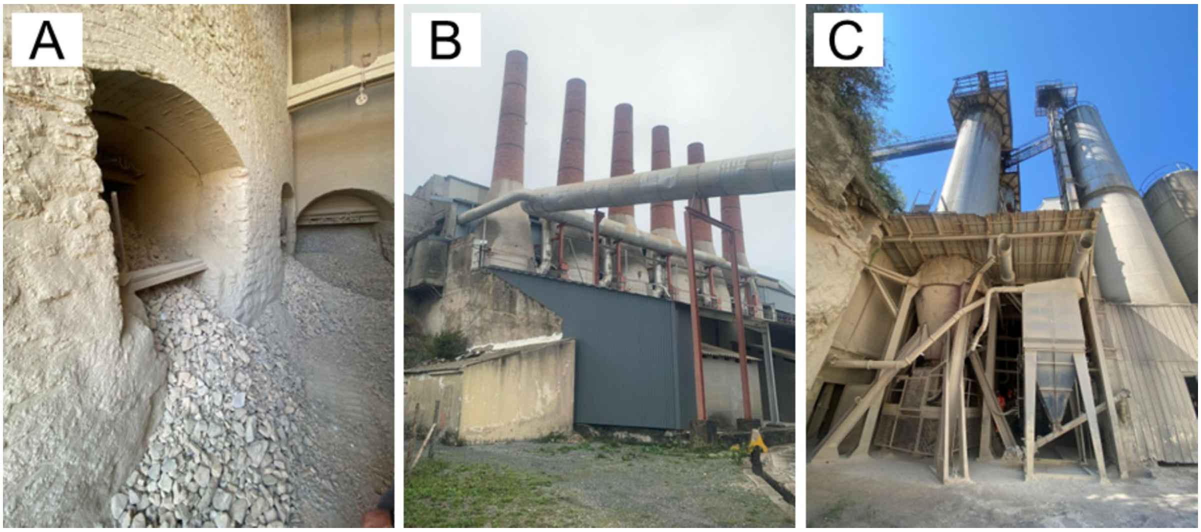

Fig. 1 Types of kiln used by different NHL manufacturers. **A** Traditional kiln from the Spanish company Cementos Tigre. **B** Industrial kiln from the Portuguese company Secil. **C** Industrial kiln from the French company Socli-Heidelberg. *Source* Photographs of the authors

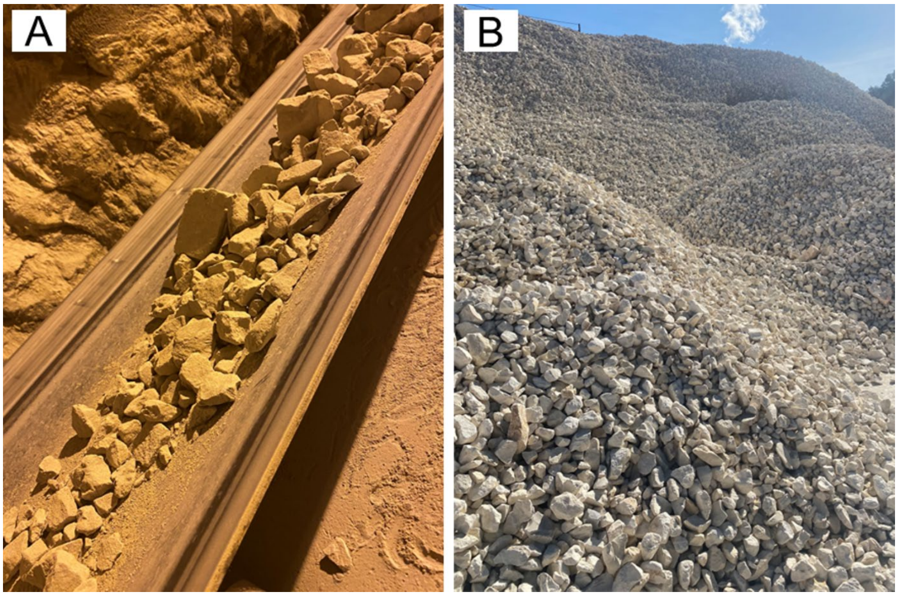

Fig. 2 **A** Raw material for NHL production on conveyor belts on the way to the kiln. Picture taken at the French company Saint Astier. **B** Raw materials of homogeneous size piled up by the French NHL producer Lafarge-Holcim. *Source* Photographs of the authors

the hydraulic phases (C_2S, C_3S, C_3A) and iron phases such as brownmillerite (C_4AF) appear in increasing amounts as calcination temperatures increase [28]. The development of larger amounts of Fe-bearing phases also modifies the physical properties of the lime, giving it a brownish tone [28, 29, 32, 46].

The influence of temperature in the resulting NHL was already observed in 1922 by Eckel [19], who stated that NHL can be produced in two different ways: (1) by the calcination of siliceous or argillaceous stones with a low CI (0.30–1.10), at a medium temperature, which would give rise to a "typical hydraulic lime"; or (2) by the calcination of stones with high CI (1.10–1.60) at a low temperature, which would result in a hydraulic lime with a large proportion of inert material, which Eckel refers to as an "imperfectly burned natural cement". This statement suggests that the same raw material can be used to obtain NHL with different degrees of hydraulicity, providing that a different calcination temperature is used.

Finally, the release of CO_2 in the kiln during calcination also influences the outcome of the calcination process in two main ways. Firstly, the resulting quicklime has a more porous structure, thus affecting the properties of the calcined product [40–42]. Secondly, it gives rise to silicon carbonates and back-reactions of carbonation inside the kiln when the CO_2 extraction system has insufficient capacity [20, 29, 32, 41, 46, 77]. This can be avoided by installing a more effective ventilation system or by a longer residence time at maximum temperature.

2.3 Hydration (slaking)

The calcined rock that gives rise to NHL is composed in part of a variable amount of calcium oxide that undergoes hydration to obtain calcium hydroxide (Eq. 4).

$$CaO + H_2O \rightarrow Ca(OH)_2 \tag{4}$$

This is a strong exothermic reaction [78] that causes an associated increase in surface area, weight and volume [20]. In theory, the part of the lime composed of silicates and other hydraulic phases will not slake during this stage [19].

Hydration (or slaking) can be carried out by different methods, as reported in the literature [58, 79]. In the case of air limes, the most common industrial method is "dry hydration", which consists of adding a stoichiometric amount of water to the CaO, by spraying or irrigation [52], so as to obtain a dry fine powder of $Ca(OH)_2$. Slaking under water, by contrast, involves the use of larger amounts of water to obtain calcium hydroxide in slurry or putty form [40, 52].

Slaking under water (also called *wet hydration*), is never used in the manufacture of NHLs, as it would lead to the undesired hydration of the calcium silicates and aluminates present in the NHL, which are supposed to react later in the mortar. As a result, a water/CaO ratio of 1:1 is used for slaking. According to the reactivity test regulated by the EN 459–2 standard [35], slaking is controlled by measuring the heat of hydration produced by a known weight of lime in a known volume of water.

The reactivity to water of CaO is influenced by a number of factors, including the characteristics of the fired limestone (e.g. composition, surface area, porosity, particle size, etc., [21, 37, 80]), the calcination conditions (e.g. kiln type, temperature and residence time, [81]), the existence of a storage period after calcination [41], the slaking method and the agitation mode [82], and the composition of the slaking water [45, 83, 84].

According to Leontakianakos et al. [45], the slaking process depends mostly on the composition and presence of impurities of the source material, and on the calcination conditions, rather than on the chemical composition of the slaking water. Factors such as the microstructure and texture of the raw material [39], and the magnesium and alumina content of the limestone seem to be key aspects in the progress of reactivity [84].

The use of high temperatures and long residence times during calcination leads to a reduction in the slaking rate due to the coalescence of the lime particles, and a decrease in their specific surface area [20, 39, 43, 49, 80, 82, 85, 86]. By contrast, soft-burned limes are more prone to hydration than hard-burned ones, because they are more porous and therefore more permeable to water [20].

The presence of CO_2 in the kiln and the storage also influence the reactivity of the quicklime towards water [41, 87]. The CaO formed during calcination is a thermodynamically unstable product that tends to react with other compounds such as CO_2 inside the kiln or with the water vapour in the atmosphere [34, 41]. The latter occurs because CaO has a high-water sorption capacity, which means that hydration can occur even in atmospheres with ~15% RH [20, 88]. CaO may be subject to both carbonation and pre-hydration reactions after calcination [34] and during a potential storage period [41], and therefore prior to the hydration process itself. If this occurs, the lime particles might be covered by a thin surface layer of calcium hydroxide that is known to influence their behaviour during the slaking process [40].

The slaking process can be carried out either: (i) directly on the lime lumps, which turn to dust when they come into contact with water, or (ii) on the previously ground quicklime powder. In general, the slaking of ground quicklime is the preferred option as it is quicker and more homogeneous, and smaller $Ca(OH)_2$ particles are obtained [20, 37].

Agitation during hydration positively impacts the rate of slaking, as it increases the dispersion of the lime particles and enables higher slaking temperatures to be reached [20, 82].

Finally, the chloride content of the slaking water seems to increase the reactivity of the lime towards water, while sulphates and carbonates delay the hydration reaction [83, 84].

According to Eckel [19], NHL was stored for approximately 10 days in bins in the plant, during which time the lime continued hydrating with the aid of the steam that was generated. Slaking was only considered to have been completed once this period had come to an end.

Similar traditional slaking methods exist in Oriental cultures [58, 79]. Among them, a method called *wind-slaking* [58], which involved exposing the quicklime to wet airflow, so producing better quality limes and mortars with greater mechanical strength. However, this method takes much longer than water-slaking, as it may need 21–40 days depending on the air flow (open or closed) [58].

Pesce et al. [89] have demonstrated the influence of the slaking method on the crystallinity of the mineral phases and on the type of hydrated phases formed. In particular, the enhanced mechanical properties shown by the final mortars could be due to the development of an amorphous precursor of portlandite, detected in limes and cement slaked with moisture from the air [32, 90–99].

In the final stage of the industrial manufacturing process, natural hydraulic limes are usually re-ground right

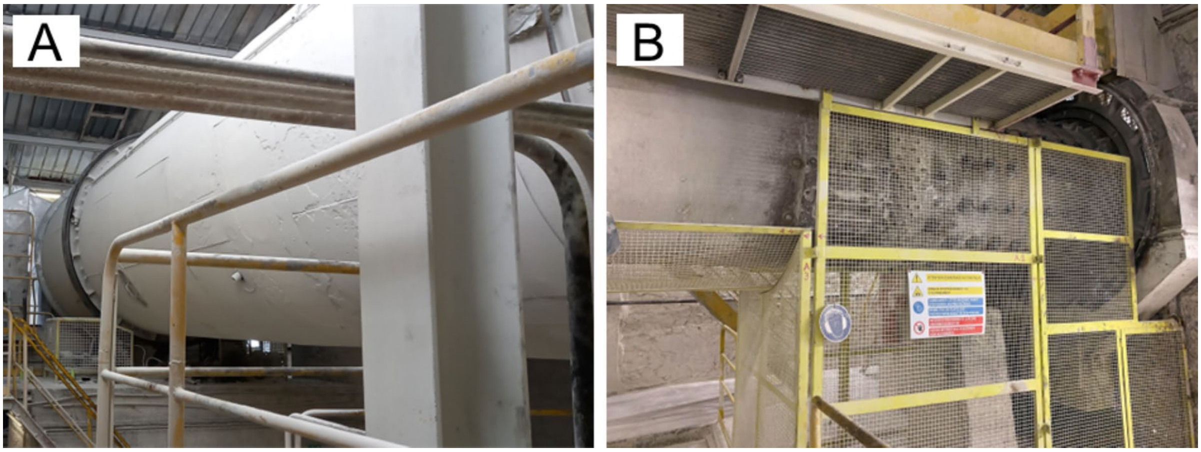

Fig. 3 **A** Tube for slaking of the calcined material. **B** Grinding ball mill for final crushing of NHL. Both images were taken at the French company Lafarge. *Source* Photographs of the authors

after slaking (Fig. 3), so as to obtain a finer powder that is now ready to be put on sale.

3 The composition of NHL

Natural hydraulic limes are composed, on the one hand, of an aerial fraction that consists mostly of calcium hydroxide ($Ca(OH)_2$, mineral phase *portlandite*, also referred to as *free lime*), and, on the other, of a hydraulic fraction formed by a series of more or less reactive compounds that depend on the raw material and manufacturing conditions, as commented above.

The predominant hydraulic phase in NHLs is di-calcium silicate (Ca_2SiO_4, mineral phase *larnite*, also known as *belite*, according to cement chemistry notation C_2S ($2\ CaO{\cdot}SiO_2$)) [8, 23, 25, 29, 31, 53, 65, 72, 96, 100, 101]. Other hydraulic phases likely to be found in NHLs are [7, 8, 23, 28, 29, 32, 46, 48, 100]:

- Tri-calcium silicate (Ca_3SiO_5, mineral phase *hatrurite*), also known as *alite*, C_3S ($3\ CaO{\cdot}SiO_2$). This phase is generally formed at higher temperatures than those used in NHL manufacture, but it can be found in NHL due to the occurrence of high-temperature points (hot-spots) in the kiln [25, 96].
- Tri-calcium aluminate, also known as *aluminate* or *celite*, C_3A ($3\ CaO{\cdot}Al_2O_3$);
- Tetra-calcium alumino-ferrite ($Ca_2(Al,Fe)_2O_5$, mineral phase *brownmillerite*) also known as *felite* or *ferrite*, C_4AF ($4\ CaO{\cdot}Al_2O_3{\cdot}Fe_2O_3$);
- Calcium aluminium silico-aluminate ($Ca_2Al(AlSiO_7)$, mineral phase *gehlenite*), also known as C_2AS ($2\ CaO{\cdot}Al_2O_3{\cdot}SiO_2$).

Wollastonite ($CaSiO_3$, CS) and its different polymorphs (e.g. *pseudowollastonite*, *parawollastonite*, etc.) are calcium silicates that can sometimes be detected in NHLs, even though they are not hydraulic phases [28]. Other non-hydraulic phases reported in hydraulic limes are *bredigite* ($Ca_7Mg(SiO_4)_4$) and *kilchoanite/rankinite* ($Ca_3Si_2O_7$) [32, 102].

In general, the higher proportion of C_2S compared to C_3S and the presence of gehlenite (C_2AS) are two distinctive aspects of natural hydraulic limes as compared to other hydraulic binders such as Portland cement [25].

Gehlenite can also be present in its hydrated form ($Ca_2Al(AlSi)O_7\ 8H_2O$, mineral phase *strätlingite*, C_2ASH_8) [23, 102] or in the form of other intermediate phases that form a solid solution with it. One example is the mineral phase *åkermanite* ($Ca_2MgSi_2O_7$), in which the aluminium is replaced by magnesium [103], a phase that can also be obtained from wollastonite if the system is rich in MgO [32, 104].

C_3A and C_4AF are formed within the calcination temperature range of NHL, although their presence is dependent on the content of reactive Al_2O_3 and Fe_2O_3 in the raw materials [29, 38]. When mixed with water and sometimes during the slaking process itself, these phases, also known as clinker phases [52], produce a series of intermediate or AFm phases [32, 52, 105]. These are predominantly *hydrocalumite* ($Ca_4Al_2(Cl,CO_3,OH)_2(OH)_{12\text{-}4}H_2O$) and *hydrotalcite* ($Mg_6Al_2(CO_3)(OH)_{16–4}(H_2O)$)), which are calcium and magnesium analogues [106], as well as *calcium carboaluminate* or *monocarboaluminate* ($C_4A\hat{C}H_{11}$) and other less stable hydrated phases such as *hydroxi-AFm* or *C_4A hydrates*, (C_4AH_{7+x}) and *hemicarboaluminate* ($C_4A\hat{C}_{0.5}H_{12}$) [102, 105, 107–110].

Other phases derived from the calcination process itself and likely to be detected in NHLs are *quartz* (SiO_2) and its polymorphs, *tridymite and cristobalite*.

Periclase (MgO) can also be present in NHLs if the raw material contained Mg-bearing carbonates (e.g., dolomite, magnesite) or other Mg phases, and trace CaO contents are sometimes found due to incomplete hydration.

Variable *calcite* contents may also be detected, due to incomplete thermal decomposition of this phase or as a result of carbonation of the free lime, when in contact with CO_2. Calcite polymorphs such as *aragonite* or *vaterite* can occasionally be found in NHL and their presence depends mostly on the carbonation conditions.

Silicon carbonates such as *spurrite* formed by recarbonation reactions with the CO_2 inside the kiln or back-reactions have also been reported in the literature [20, 29, 32, 41, 46, 77].

Another phase found by other authors in commercial NHLs is *anhydrite* [23, 96], which may be due to *gypsum* or other sulphur sources in the raw material.

It is worth stressing that, despite the high number of hydraulic phases that are potentially present in NHL, this binder only has to comply with the amounts of free lime established in the European standard EN459-1 [1] for each NHL class (≥ 35% for NHL2, ≥25% for NHL3.5, and ≥15% for NHL5), regardless of the other phases it may contain.

4 Setting process

Due to its composition, NHL setting (or hardening) consists of two main processes: (1) carbonation of calcium hydroxide when it comes into contact with atmospheric CO_2 (Eq. 5), and (2) hydration of the hydraulic phases when they come into contact with H_2O [16] (eqs. 6, 7, 8,9 and 10, [38, 75]. These processes are known to be in competition, although in NHL, hydration generally precedes carbonation [7, 111].

Carbonation reaction:

$$Ca(OH)_2 + CO_2 \rightarrow CaCO_3 + H_2O \tag{5}$$

Hydration reactions:
Larnite:

$$Ca_2SiO_4 + 4H_2O \rightarrow C-S-H + Ca(OH)_2 \tag{6}$$

Hatrurite:

$$Ca_3SiO_5 + 5H_2O \rightarrow C-S-H + 2Ca(OH)_2 \tag{7}$$

Tri-calcium aluminate:

$$Ca_3Al_2O_6 + 6H_2O \rightarrow C_3AH_6(\text{hydrogarnet}) \tag{8}$$

Brownmillerite:

$$\begin{aligned} &Ca_2AlFeO_5 + 5H_2O \\ &\rightarrow C_3AH_6(\text{hydrogarnet}) + Fe(OH)_3 \end{aligned} \tag{9}$$

Gehlenite:

$$Ca_2Al(AlSi)O_7 + 8H_2O \rightarrow C_2ASH_8(\text{strätlingite}) \tag{10}$$

Hydrated calcium silicates (or *calcium silicate hydrates*, C–S–H) are a family of mineral phases such as *jennite* ($C_9S_6H_{11}$), *tobermorite* ($C_5S_6H_5$) or *plombierite* ($C_5S_6H_8$) [102], characterised by disorder phenomena, low crystallinity and very small grain sizes [112], all of which are produced by the hydration of the hydraulic silicate phases C_2S and C_3S. According to Taylor [38], C_3S shows greater reactivity than C_2S, as after 28 days of curing, C_3S is responsible for 70% of cement hydraulicity, while C_2S is responsible for just 30%. However, the differences in the size of these components influence their specific area and therefore their reactivity. The average size of C_2S in cement is between 20 and 40 μm [38], while in NHL it is around 2 μm [32], which together with the lower C_3S content in NHL means that

C_2S is expected to make the largest contribution to the C–S–H, even though at a slower rate.

Aluminate phases (C_3A and C_4AF), which are known to be more reactive than C_2S [52], can also react to form AFm phases in the previous stages of hydration. These are hydroxy-AFm, hemi and monocarboaluminate and strätlingite, also known as gehlenite hydrate [105, 110], which tend to form more stable hydrated calcium aluminates (or *calcium aluminate hydrates*, C-A-H) [23]. Albeit to a lesser extent, C-A-H phases contribute to the mechanical properties of binders of this kind and can be detected in hardened NHL mortars [7]. In their crystalline form, C-A-H are commonly known as *hydrogarnet* ($Ca_3Al_2(OH)_{12}$) [102, 105]. This phase is considered to be the most stable phase, as all the AFm phases eventually tend towards it [23, 52, 102, 105]. The hydrogarnet phases may also include iron in their structure ($Ca_3(Al_xFe_{1-x})_2(SiO_4)_y(OH)_{4(3-y)}$, [113]) depending on the amount of C_4AF [114].

Other hydrated phases include *hydrated calcium silico-aluminates* or *calcium silico-aluminate hydrates* (C-A-S-H) and *hydrated magnesium silicates* or *magnesium silicate hydrates* (M-S-H), whose occurrence is closely related to the compositional characteristics of the binder and the raw material [115–121]. The hydrated phases that eventually form gels are hard to detect in NHLs as in many cases they are amorphous and are classified as amorphous phases [96]. They are more easily identified in cement pastes and mortars, where they appear in abundant amounts, and they have sometimes been detected in archaeological materials with pozzolanic activity [122–124].

Table 2 shows some of the most common mineral phases and compounds formed in natural hydraulic lime.

In summary, all natural hydraulic limes today are composed of lime (in the form of calcium hydroxide), silicates and calcium aluminates, in varying proportions depending on the initial composition of the raw material. They also contain a variable amount of inert material (normally *calcite*), whose percentages depend on their manufacturing process [96] and whose characteristics (e.g. granulometry and morphology) can influence the plasticity of the lime [125].

As a result of these key aspects, which are not taken into account in European standards, there are natural hydraulic limes on the market which, despite having the same index (2, 3.5 or 5) in their name or technical data sheet, have very different compositional and textural characteristics, an issue that has recently been addressed by various Asian researchers [30, 57, 58, 62, 126].

5 The use of NHL in heritage conservation and bio-construction: current debate

The aforementioned physical and chemical aspects of NHL are crucial for ensuring the best possible outcome of restoration works conducted with this binder, as will be discussed below.

Mortars made with natural hydraulic limes have certain specific characteristics such as lower shrinkage during curing compared to aerial limes and higher percentages of open porosity and pore sizes than modern artificial binders (such as hydraulic limes, i.e. limes blended with cement) that make them durable in historic masonry. This durability has been related to the delayed setting (*i.e. setting which starts after shrinkage has occurred*) of traditional hydraulic binders (e.g. lime with pozzolana and natural hydraulic lime), which is due to *a "major hydraulic component C_2S (belite) compared to cement*-based *binders that have C_3S (alite)"* [128].

These features result in moderate mechanical strengths and in permeability values that avoid excessive water retention and related pathologies [8, 21, 33, 129–132]. The plastic or ductile behaviour of NHL, which is capable of absorbing stresses and of adapting to differential settlements, also prevents cracking of the masonry, making it a flexible material [21, 128, 131, 133, 134]. Lime also has a long-term self-healing capacity, in which carbonate reprecipitation can occur in small cracks or fissures [129].

In chemical terms, unlike other non-natural hydraulic limes (HL) or formulated hydraulic limes (FL), NHL has no soluble salts [8, 126, 129] and it is mainly composed of calcium and silicon. The partially hydraulic nature of NHL means that it can be used, not only in the restoration of natural stone, mortars and earthen materials, but also in the stabilisation of soils [135, 136].

Another important aspect explaining its increased use in sustainable and bio-construction is its mineral

Table 2 Main compounds and mineral phases found in natural hydraulic lime before and after the hydration and carbonation processes (modified from Arizzi and Cultrone [102] and Mertens [127])

Cement chemistry notation	*Chemical formula*	*Name of the mineral phase*
Before hydration and carbonation		
CH	$Ca(OH)_2$	Portlandite/Free lime
C	CaO	Lime
–	SiO_2	Quartz-Trydimite-Cristobalite
M	MgO	Periclase
C_2S	Ca_2SiO_4	Larnite/Belite
C_3S	Ca_3SiO_5	Hatrurite/Alite
C_3A	$Ca_3Al_2O_6$	Aluminate
C_4AF	$Ca_2(Al,Fe)_2O_5$	Brownmillerite/Felite or ferrite
C_2AS	$Ca_2Al(AlSi)O_7$	Gehlenite
CS	$CaSiO_3$	Wollastonite
C_7MS_4	$(Ca_7Mg(SiO_4)_4)$	Bredigite
C_3S_2	$Ca_3Si_2O_7$	Kilchoanite/Rankinite
$C_5S_2\bar{C}$	$Ca_5(SiO_4)_2CO_3$	Spurrite
$C\bar{S}$	$CaSO_4$	Anhydrite
After hydration and carbonation		
–	$CaCO_3$	Calcite-Aragonite-Vaterite
C–S–H	$CaO–SiO_2–H_2O$	Calcium Silicate Hydrate
$C_9S_6H_{11}$	$Ca_9Si_6O_{18}(OH)_6 \cdot 8H_2O$	Jennite
$C_5S_6H_5$	$Ca_5Si_6O_{16}(OH)_2 \cdot 4H_2O$	Tobermorite (or 11 Å-Tobermorite)
$C_5S_6H_8$	$Ca_5Si_6O_{16}(OH)_2 \cdot 7H_2O$	Plombierite (or 14 Å-Tobermorite)
C-A-H	$CaO\text{-}Al_2O_3\text{-}H_2O$	Calcium Aluminum Hydrate
C_3AH_6	$Ca_3Al_2(OH)_{12}$	Hydrogarnet
C_2ASH_8	$Ca_2Al(AlSi)O_7 \cdot 8H_2O$	Strätlingite (gehlenite hydrate)
$C_4(A, F)X_2 \cdot y(H_2O)$	$Ca_4Al_2(Cl,CO_3,OH)_2(OH)_{12–4} \cdot H_2O$	Hydrocalumite
$M_6(A, F)X_2 \cdot y(H_2O)$	$Mg_6Al_2(CO_3)(OH)_{16–4}\cdot H_2O$	Hydrotalcite
$C_4A\hat{C}_{0.5}H_{12}$	$Ca_4Al_2O_7(CO_2)_{0.5} \cdot 12H_2O$	Hemicarboaluminate
$C_4A\hat{C}H_{11}$	$Ca_4Al_2O_6(CO_2) \cdot 11H_2O$	Monocarboaluminate
$C\bar{S}H_2$	$CaSO_4\cdot 2H_2O$	Gypsum

sequestration strategy. During its setting (carbonation) process, it sequesters larger amounts of CO_2 (a greenhouse gas) than OPC-based concrete, so reducing the environmental impact of its manufacture [29] and making it more environmentally friendly [131, 132, 137]. The more favourable CO_2 balance offered by NHLs, together with the lower energy consumption in their manufacturing process, make these hydraulic binders an interesting alternative to ordinary Portland cement. As a result, they are currently in high demand due to the increased consideration given to the environmental impacts and long-term consequences of construction work [131].

Other advantages applicable in the sustainable construction sector include the aforementioned permeability of NHL mortars. As Banfill and Forster [33] stated, permeability is related to the 'breathability' of the materials and therefore of the building itself. This has an impact on the indoor air quality inside the buildings as well as on the durability of the rest of the building materials [132, 138].

Given their physical compatibility with the generally 'softer' traditional building materials, there are multiple investigations that validate the use of NHLs in restoration work [3, 8, 25, 30, 67, 126, 128, 139–146], for either structural (masonry, bedding and pointing mortars), protective (finishing mortars such as plasters and renders), or decorative purposes (sgraffito, stucco, etc.).

NHL mortars are mainly used in the restoration of historic buildings to repair damaged original materials (e.g. stone, mortar), with specific applications such as volumetric reintegration in ashlars and decorative elements (Fig. 4), as well as rendering for façade protection [5, 6, 147–151].

Another common application is in injection grouts, a method that involves the pressurized injection of a fluid suspension into voids or cracks [152–156], which hardens in the absence of CO_2, developing high permeability and workability, and moderate levels of strength.

As a result, NHLs are nowadays considered as one of the best binders for use in the restoration of buildings, monuments and even mosaics [7, 139, 157, 158]. This is not surprising considering that some ancient mortars were made with a prototype of natural hydraulic lime that resulted from the calcination of impure or cherty limestones [66], which were probably used because there were no other geological resources available locally.

There are also several authors who criticise and question the use of NHL in conservation [9, 12–14, 159–161] due to unexpected long-term performances and the apparent high variability between NHLs with the same index number and from different manufacturers (Fig. 5), which can lead to mortars with final

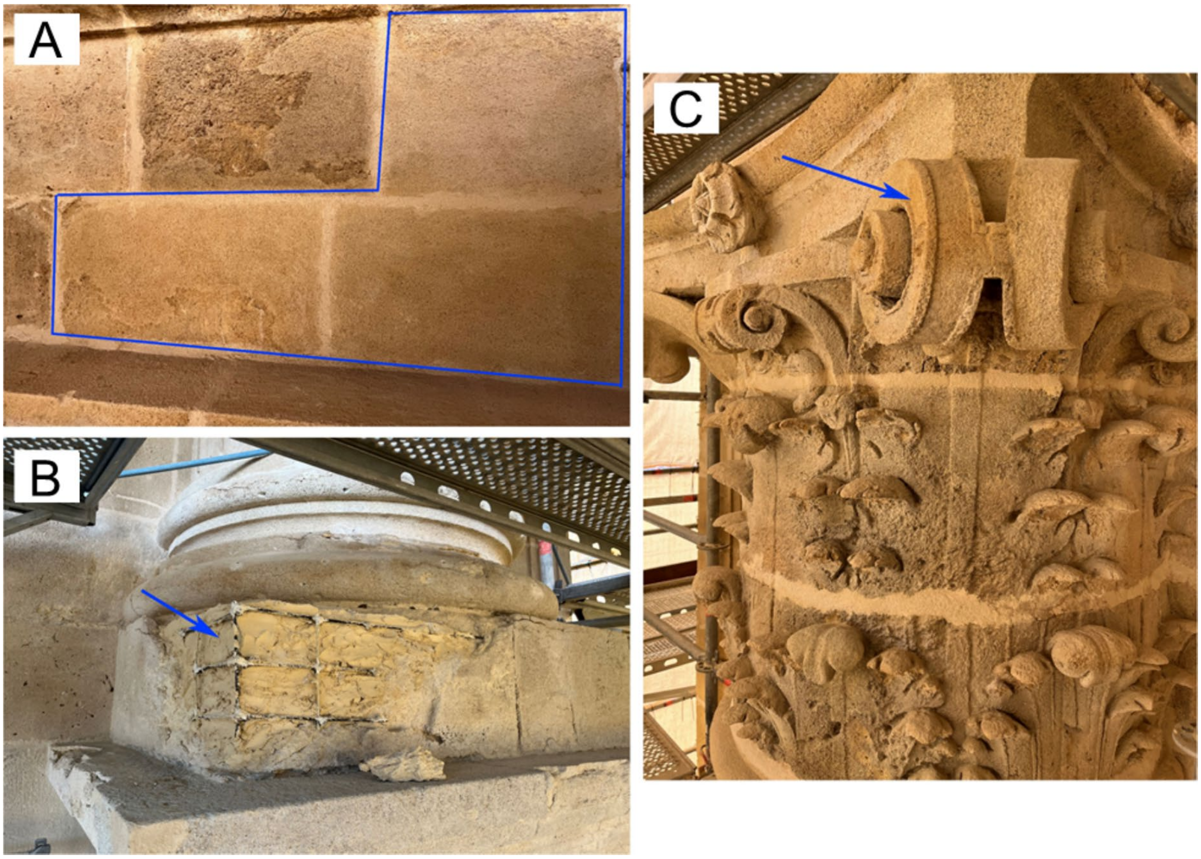

Fig. 4 Examples of applications of NHL mortars for restoration purposes. **A** Superficial reintegration of deteriorated stone ashlars (the blue line circumscribes the restored area); **B** Infill of an ashlar with glass rod structure for volumetric reintegration (the blue arrow indicates the NHL mortar that it is being used); **C** reintegration of decorative elements (the blue arrow indicates the appearance of the NHL mortars and its aesthetical compatibility with the original substrate). *Source* Photographs of the authors during the restoration of the tower of the Cathedral of Granada (Spain)

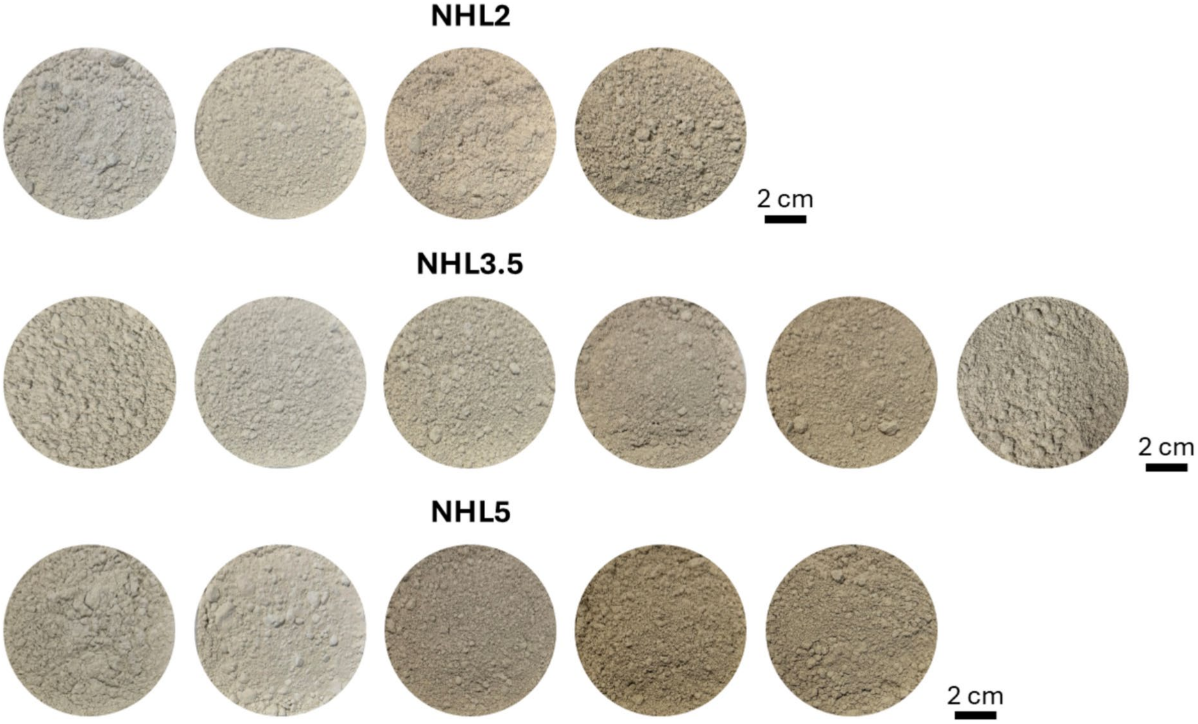

Fig. 5 Appearance and colour of different NHLs produced by the main European manufacturers from France, Spain and Portugal. *Source* Photographs of the authors

characteristics that differ greatly from those of their historic counterparts.

For this reason, restorers sometimes prefer the most traditional hydraulic lime mortars made with aerial lime and pozzolans (e.g. ceramic fragments, pumice powder, organic ashes, etc.) and other alternatives such as the hot-mixed or hot-lime mortars produced by mixing quicklime with sand [12, 13, 79, 162–167].

However, it is widely accepted that the final physical properties of lime mortars, in general, and NHL mortars in particular, are mostly influenced by the nature and dosage of sand, the water-to-binder ratio, and the curing time and conditions [8, 10, 53, 67, 111, 134, 141–144, 154, 168–173]. They are also affected by the presence of additives and admixtures [57, 145, 153, 155, 156, 174–192], regardless of the type of binder.

In this sense, the physical parameters set out in the European standard (EN459-1 [1]) are hardly applicable to real cases of construction and conservation works, where different types of sand and binder-to-sand ratios are used, and the exposure conditions vary over time. This is, however, a difficult issue to overcome from the perspective of a harmonised standard that seeks to define the binder rather than the final mortar. In this sense, it is more important to identify and regulate the factors that influence the chemical–mineralogical characteristics of the different natural hydraulic limes, in order to create commercial NHL products with more standardized compositional and textural characteristics, and therefore, with more predictable properties on site.

This incongruence was already observed by Mertens [127], who studied 90 hydraulic limes, most of which were manufactured in France. For their part, Callebaut et al. [25] stated that studies on the production process and characterisation of hydraulic lime mortars were very scarce. They emphasized the importance of acquiring detailed knowledge of the characteristics of hydraulic limes and their mortars as they were ideal materials for use in the conservation of historical buildings. After an in-depth chemical–mineralogical and petrographic characterisation of historical mortars from the

Tournai Cathedral and the Tongeren Basilica (Belgium), Mertens et al. [127, 193] stated that, despite being able to determine unequivocally that these mortars were hydraulic in nature, it was very difficult to decide whether this hydraulicity was due to pozzolanic-type reactions, to the use of hydraulic limes, or perhaps even to both. These studies show that it is difficult to identify the exact type of binder used in a hydraulic mortar.

If we consider the number of mortars on the market which, according to their technical data sheet, are made with hydraulic binders, an inevitable question arises as to the real composition of these mortars. In fact, there are a whole range of possibilities, from the use of hydraulic lime (NHL or HL) to the use of aerial lime with pozzolans, or in the worst case, the use of aerial limes mixed with cement (products that would be classified as formulated limes, FL [1]).

The difficulty of discerning one product from another means that there is great uncertainty about which hydraulic mortar would be most appropriate to ensure the successful restoration of a particular historic building, given that some of these products may not be fully compatible with the original traditional mortars.

6 Conclusions

This review aims to contribute to a greater, more in-depth knowledge of the characteristics and manufacturing process of natural hydraulic limes, with the ultimate objective of developing a more rigorous classification of this sub-group of hydraulic limes. As discussed here, it is evident that a more precise, more harmonized classification of the group of limes with hydraulic features, and in particular natural hydraulic limes, is needed. If the NHL on the European market had more precisely controlled compositional and textural characteristics, this would benefit the building sector as a whole, and the more specific field of historic heritage conservation and restoration in particular, in which NHL is being increasingly used as a compatible binder for repair mortars. This will be useful not only for researchers working in the field, but also for architects and restorers/conservators who will acquire more knowledge about the binders used and, finally, for the manufacturers who will have more detailed specifications to follow.

Three important aspects are missing from the definition of natural hydraulic lime in the EN459-1 standard [1]: (1) the chemical, mineralogical and textural specifications of the raw materials; (2) details about the optimum calcination conditions; and (3) instructions as to how to perform slaking.

On the basis of this review of the bibliography on natural hydraulic limes, we would like to make the following recommendations that could improve the EN459-1 standard [1]:

(1) To include, in addition to limestone that contains clay, other valid raw materials for NHL such as different types of siliceous limestone with reactive silica.
(2) To classify the different degrees of hydraulicity of the NHLs, not only on the basis of their free lime and compressive strength values at 28 days, but also on the reactive oxides content and the cementation indexes of the raw materials and final products.
(3) To advise that different degrees of hydraulicity can be obtained by applying different calcination temperatures (the higher the calcination temperature, the more hydraulic the NHL obtained), when only one type of valid raw material is available.
(4) To highlight that calcination temperatures of 950 ºC reduce the formation of iron-phases, thus favouring the obtention of whiter NHLs.
(5) To advise that water-slaking can give rise to the premature formation of C–S–H and C-A-H phases, something that can be reduced by using air moisture or steam.

The implementation of the regulatory framework for natural hydraulic limes is expected to have a positive impact on the classification of natural hydraulic limes, and to enable a clear distinction between natural hydraulic limes (NHL) and hydraulic (HL) or formulated limes (FL), in which lime is frequently blended with Portland cement.

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Declarations

Conflict of interest The authors report there are no competing interests to declare.

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