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Is EN459-1 fit for purpose in the context of conservation?

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ABSTRACT

Natural Hydraulic Lime (NHL) binders consist mainly of portlandite, reactive silicates and aluminates formed from the reaction of crushed limestone, containing clays or other impurities, during calcination. By their nature these binders have a variable chemical and mineral composition, depending on the geographical location of the limestone extraction (initial composition) and the manufacturing process. The NHL (Natural Hydraulic Lime) classification, as specified in the EN459-1 standard, does not consistently give a representative evaluation of the mortar properties, resulting in similarly classified limes often exhibiting very different properties and behaviour thereby hindering the ease of user specification for mortars. A representative selection of binders was characterised using calorimetric analysis, XRD, XRF and particle size analysis. The varying proportions of reactive silicates and portlandite between the limes was used to determine the kinetics of the hydraulic reaction NHL binders. These properties were related to the chemical and physical properties of the binders. A relationship has been established between the chemical and physical properties of the binders and the NHL characteristics. These results will be used to validate a model predicting the long-term behaviour of NHL mortars for conservation interventions on heritage and historic buildings.

1. INTRODUCTION

Lime based mortars are one of the most ancient man-made materials and can be found in a large proportion of buildings constructed before the twentieth century which are still standing.

Natural Hydraulic Lime (NHL) plays a major role in the conservation process presenting some of the beneficial characteristics of an air-lime based mortar such as good pore structure, allowing water vapor diffusion, and the ability to accommodate movement through flexibility. Unlike air-lime mortars, they have a faster initial set and the ability to harden in damp conditions or even under water (Van Balen et al. 2005; Schueremans et al. 2011; Henry & Stewart 2011; Cizer et al. 2010; Forsyth 2008).

NHL results from the calcining of crushed limestone containing clay at temperatures between 950˚C and 1050˚C. The ability to set under water and the faster setting time is dependent on the amount of hydraulic phases which is in turn related to the raw materials composition and the calcination temperature. The initial set of hydraulic lime mortars is much faster than that of air lime, which is attributed to the hydraulic reactions. The calcium silicates and aluminates react with water forming calcium silicate hydrates and calcium aluminate hydrates. Further strength develops from the continued process of hydration and over the longer term carbonation of free lime. CO_2 diffuses through the porous structure reacting with the calcium hydroxide and the hydration products, forming $CaCO_3$, amorphous silica and alumina. Hydration and carbonation depend on the amount of hydraulic phases and the calcination temperature of the original limestone (Holmes & Wingate 2002; Forsyth 2008; Henry & Stewart 2011; Allen et al. 2003; Lanas et al. 2004; El-Turki et al. 2010; Livesey 2002).

The classification of NHL binders in the European market is regulated by the EN 459-1:2015 and is based on the compressive strength of a standard mix at 28 days and the minimum weight content of available lime (Table 1).

Table 1. NHL classification and tolerances according to EN 459-1:2015

Lime type	Available lime as $Ca(OH)_2$ (%)	Minimum compressive strength at 28 days - tolerance values in brackets (MPa)
NHL2	≥35	2 (2-7)
NHL3.5	≥25	3.5 (3.5-10)
NHL5	≥15	5 (5-15)

The wide overlap among the three classifications allows a high variability of limes to be classified as the same type. The test at 28 days can also be misleading when characterising and classifying less hydraulic limes where the majority of strength is gained through carbonation over the longer term (Henry & Stewart 2011; Elsen et al. 2012).

The hydration process of lime based binders is frequently studied using diffraction and spectroscopic techniques (Jerman et al. 2016). In this study, isothermal calorimetry is used to relate the reactivity of NHL binders to the mechanical properties of corresponding lime based mortars.

Understanding of the variability of NHL binder properties and how these characteristics influence mortar performance will facilitate more informed selection of materials, particularly in conservation works were the preservation of the historic fabric is one of the most important factors.

2. Materials and methods

To study how the presence of hydraulic phases affect the reactivity of NHL binders, three binders from a single manufacturer and one from a different producer were selected, which presented a diverse range of physical and chemical properties. Bulk density was determined using the process described in the BS EN 459-2:2010 and the surface area was determined by BET nitrogen adsorption analysis using a Micromeritics 3Flex (Table 2). Particle size distribution was obtained by testing the dry powder in a Malvern Mastersizer 2000 and obtaining the frequency of the particle size related to the volume (Figure 1).

Table 2. Physical properties of the binders: bulk density and surface area

Binder	Bulk density (g/cm^3)	Surface area (m^2/g)
NHL2	0.58	10.04
NHL3.5	0.67	6.24
NHL5	0.79	4.14
NHL2B	0.64	5.46

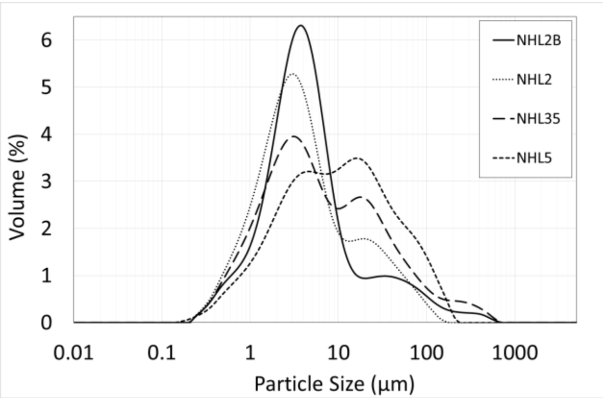

Figure 1. Particle size distribution.

XRF analysis (Table 3) was performed on 40mm diameter pellets of thickness 2mm pressed from the binders and analysed using an EDAX Eagle II Energy Dispersive XRF spectrometer with Rhodium X-ray, operated at 25kV and 1mA for 100 seconds in multiple spots per sample for the spectrum acquisition. The Loss on Ignition (LOI) was determined by burning 1g of material [±0.001] at 950°C until the sample mass had stabilised.

Table 3. XRF main oxide composition in % of weight

Binder	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	LOI
NHL2	9.3	0.4	0.4	66.0	0.4	0.5	22.0
NHL3.5	15.2	1.0	0.5	61.4	0.6	0.5	19.8
NHL5	15.6	0.9	0.6	60.7	0.9	0.6	19.7
NHL2B	7.8	1.6	2.1	66.4	2.4	0.4	18.0

XRD analysis (Table 4) was performed at ambient temperature using a Bruker-AXS D8 powder X-ray diffractometer. The equipment was operated at 40kV, 40mA and the source of radiation was Cu-K_α X-rays. The step was 0.02°, from 4 to 75 ° (2θ).

Table 4. XRD qualitative mineral composition. ++ Strong signal, identified by 3 or more major peaks; + Moderate signal, identified by 3 peaks of intensity <20% of maximum.

Binder	Portlandite	Calcite	Belite	Alite
NHL2	++	+	+	+
NHL3.5	++	++	+	+
NHL5	++	++	++	++
NHL2B	++	+	++	+

Mortar prisms 160×40×40 [mm] were prepared with a binder:aggregate (b/a) volumetric ratio of 1:2 and a spread, measured by flow table (BS EN 1015-3:1999) of 165±10 [mm]. Compressive and flexure tested was carried out at 7, 14, 28, 91 and 180 days according to the BS EN 1015-11:1999. Table 5 shows the characteristics of the formulations manufactured by volume, the spread and the water/binder (w/b) ratio in mass.

Table 5. Formulations characteristics (1:2 b/a volumetric formulation).

Binder	Binder (kg)	Sand (kg)	Water (kg)	b/a (w/w)	Spread (mm)	w/b (w/w)
NHL2	2.42	11.83	2.70	1:4.89	160	1.12
NHL3.5	2.75	11.56	3.28	1:4.20	174	1.19
NHL5	3.30	11.72	2.97	1:3.55	174	0.90
NHL2B	2.64	11.68	2.51	1:4.42	160	0.95

The iso-thermal calorimetric tests were performed using a Calmetrix I-Cal 4000 with F/P-Cal logger software. The heat of the reaction was recorded for 72 hours.

3. Results and discussion

Calorimetric results (Figure 2) show the specific hydration heat power per 1 g of material. The initial peak represents the first contact of the binder with water. NHL2 and NHL3.5 present a slower decrease of heat flow, indicating initiation of hydration in the first few hours of testing.

NHL5 shows a small peak around 8 hours (1) of testing related to the Alite content, faster to react. While NHL2B presents a peak at 13 hours (2) that can be related to the Belite phase.

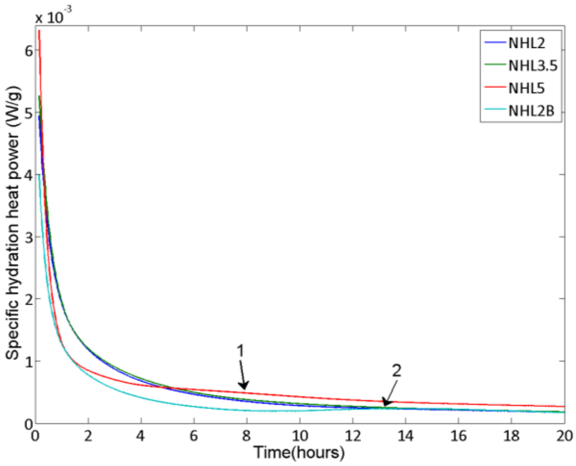

Figure 2. Calorimetric analysis for the first 20 hours.

The specific heat of hydration (Figure 3) demonstrates that all the binders continue to have hydraulic reactions until the end of the test. NHL2 and NHL3.5 reaction process is faster in the beginning but tend to slow down after 10 hours. NHL2B reaction at around 13h is also detectable in these data. NHL5 reaction process is slower than NHL2 and NHL3.5 in the beginning of the test, but after 10 hours it demonstrated to have the faster reaction.

It appears that within the same manufacturer, NHL2, NHL3.5 and NHL5, the higher surface area improves the speed of reaction. NHL2 and NHL3.5 shown similar initial reaction kinetics, related to the higher surface area of the NHL2 binder and the higher content of SiO_2 in NHL3.5. The slower reaction of NHL5 is probably related to the low surface area and it is therefore potentially less reactive, at the beginning of the calorimetric test.

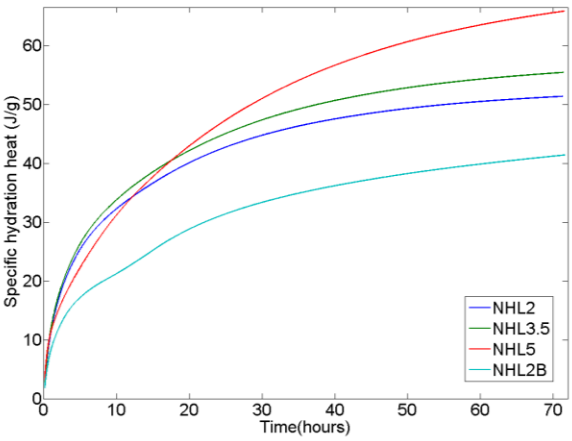

Figure 3. Specific hydration heat per 1 g of binder.

Compressive strengths are shown in Figure 4, Similar to the calorimetric tests, NHL2 and NHL3.5 present similarities in the compressive strength across all ages.

NHL 5 is consistently the stronger binder, with NHL2B achieving similar results at 360 days. This demonstrates the importance of carbonation in hydraulic lime based mortars, where the MgO in the form of Dolomite also contributes to the gain of strength along with the CaO in the form of Portlandite.

NHL5 and NHL3.5 have similar chemical compositions by XRF, the calorimetric and compressive test results highlight the differences in phase composition, where NHL5 contained more Alite and lower specific surface area. NHL5 with a lower surface area demanded less water for the same workability, helping to achieve a stronger mortar.

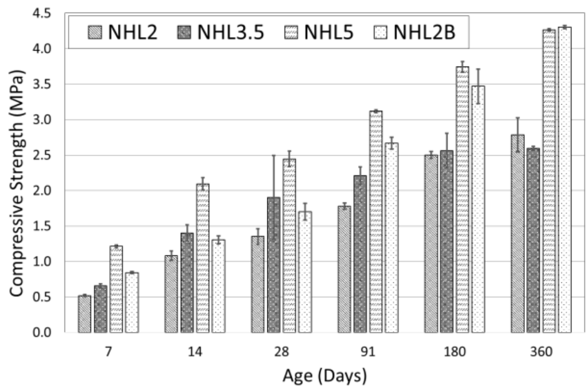

Figure 4. Compressive strength results.

These results show the importance of the chemical and mineral composition. The physical properties of the binders should be taken in consideration when predicting the behaviour of mortars. NHL5, with a higher content of Alite and Belite, achieved higher strengths. NHL2B achieved the same compressive strength as the NHL5 mortar due to carbonation, at later ages

NHL2 and NHL3.5, with differences in the SiO_2 content, demonstrated similar behaviour in both the calorimetric tests, where NHL3.5 showed the higher SiO_2 with slightly higher specific heat of hydration, and strength development. This reflects the chemical similarities and the higher w/b ratio of the NHL3.5 mortar leading to similar compressive strengths between the two mortars.

NHL2 and NHL2B binders, have the same classification, although presenting very distinct behaviour in both the calorimetric analysis and the compressive strength measurements across all ages. NHL2 and NHL3.5 represent binders from different classifications, achieving similar results. NHL5 and NHL2B, despite being classified differently by BS EN 459-1 achieved the same compressive strength at one year.

The variability of the final properties of the mortars, when the binders present similar chemical characteristics, is determined by their physical properties. Therefore, a model to predict mortar properties over long-term periods should consider both chemical and physical parameters. It is expected that a model considering these properties to be achieved and therefore aid industry professionals to make an appropriate selection of materials for intervention in historic fabric and new build.

3. Conclusions

Hydraulic reactions are dependent not only on the chemical and mineral characteristics but also on the physical properties of the binders.

The calorimetric tests can be useful to study the hydraulic reactions of NHL binders and to establish the differences and similarities between the binders.

The standard classification, given by the EN-459, does not reflect the final properties of commonly volumetric formulated mortars, therefore caution should be used when using this standard to predict mortar properties. Mortars that show lower strength at early ages (until 28 days) can achieve much higher strengths for later periods (over 90 days) and therefore damage the weak masonry units. On the other hand, some binders have the possibility of never achieving the strength related to their classification.

A model predicting the long-term behaviour of NHL mortars will be developed using the chemical and physical properties of the binders.

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