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CHEMICAL AND PHYSICAL CHARACTERISATION OF THREE NHL 2 BINDERS AND THE RELATIONSHIP WITH THE MORTAR PROPERTIES

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ABSTRACT

In conservation works, the physical properties of mortars, such as compressive strength and porosity, are by far the most important for compatibility with, and protection and durability of historic fabric. The classification of Natural Hydraulic Lime (NHL) binders by the EN 459-1, gives little information about these properties for mortars, due to the unrepresentative nature of the standard samples used to categorise these binders, especially after 28 days of aging. As a consequence, although important for quality assurance and consistency of binder production, the standard test tends not to reflect the performance of mortars as made and used on-site, since these use different aggregates and water/binder ratios.

In this work, three types of NHL 2 were analysed. These binders were characterised by means of X-ray diffraction and X-ray fluorescence. In addition to chemical tests, the surface area and bulk density data were also obtained. Mortar samples were manufactured using a sand aggregate which is appropriate for a conservation mortar with 1:2 ratio (binder:aggregate by volume). Sufficient water was added to produce a spread by flow table of 165±10 [mm]. The chemical and physical properties of the binders were related to the physical characteristics of the mortars.

The chemical and physical properties of different binders with the same NHL classification were found to vary greatly as did the properties of mortars at ages of 7, 14, 28, 90 and 180 days made with those binders. The need to develop a model to predict the performance of aged mortars based on the chemical and physical properties of the binders was identified.

1. INTRODUCTION

Natural hydraulic lime (NHL) mortars in conservation interventions of historic buildings and heritage are generally applied to repair eroded mortars, replace harmful strong cement and strong hydraulic mortars used in modern repairs and to protect historic fabric. As with any conservation material, these mortars are required to be compatible with the existing material in terms of aesthetics, mineralogical and chemical properties as well as physical and mechanical characteristics (Henry & Stewart 2011; Schueremans et al. 2011; Feilden 2003).

The application of materials that cause damage to the existing fabric is to be avoided in the search for compatibility. Therefore, surface characteristics of a mortar, its mechanical properties, related to the compressive and flexural strength and plasticity, and the porous structure are of great importance, along with the chemical compatibility. Compressive strength is usually more relevant when the mortar is load bearing; depending on the function, porosity and permeability or even flexural strength can be more important. The mortars can act as a sacrificial layer to protect masonry and the historic host fabric, having the ability to disintegrate being slightly weaker than the historic fabric, without damaging the substrate (Van Balen et al. 2005; Schueremans et al. 2011; Henry & Stewart 2011; Cizer et al. 2010; Forsyth 2008).

Hydraulic lime binders are manufactured from the calcining of crushed limestone containing clay. The clay minerals present in the limestone are sometimes called impurities. When burned at temperatures between 900°C and 1050°C the carbon dioxide is driven off. The silica and alumina from the clay then form reactive silicate and aluminate phases (Figure 1).

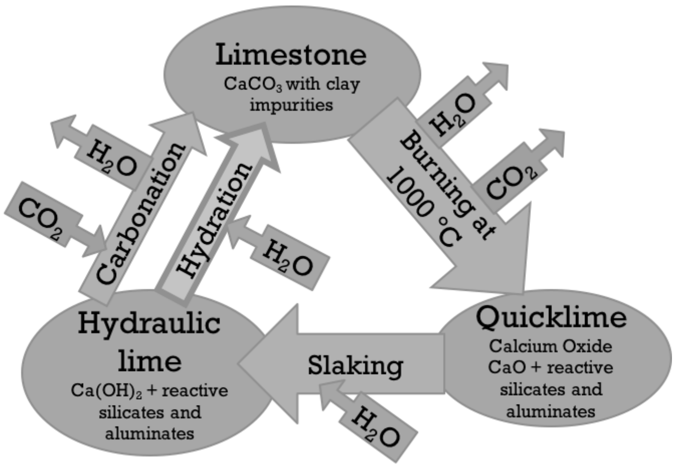

Figure 1: Natural Hydraulic Lime cycle

Hydraulic limes have the ability so set in damp conditions and under water. The initial set is much faster than that of air lime which is attributed to the hydraulic reactions. The calcium silicates and aluminates present react with water forming calcium silicate hydrates and calcium aluminate hydrates. Further strength results from the continued process of hydration and the slow carbonation of free lime. The CO_2 diffuses through the porous structure reacting with the calcium hydroxide and the hydration products, resulting in $CaCO_3$ and amorphous silica and alumina. The process of hydration and carbonation depend on the amount of hydraulic phases present and also on 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).

Prior to EN 459-1, Natural Hydraulic Limes (NHL) were classified according to the Cementation Index (CI) firstly suggested by Vicat (1837 (Facsmile1997)) as a method to predict the performance of hydraulic limes based on the likely hydraulicity of the raw materials of the binder. This Index balances the weight contribution of the different components that can be detected from chemical analysis of the limestone.

The most common expression found in the literature for the CI is Eq.1.
The Hydraulicity Index (HI) (Eq. 2) is also found in the literature as a method for hydraulic lime classification, balancing the most active oxides (Holmes & Wingate 2002; Elsen et al. 2012).

$$CI = \frac{2.8SiO_2 + 1.1Al_2O_3 + 0.7Fe_2O_3}{CaO + 1.4MgO} \quad \text{(Eq. 1)}$$

$$HI = \frac{SiO_2 + Al_2O_3}{CaO} \quad \text{(Eq. 2)}$$

The common classification of limes reported by Holmes & Wingate (2002) is described in Table 1.

Table 1: Cementation Index for the various types of building lime

Lime description	Cementation index (CI)	Active clay in the limestone
Fat limes	Close to zero	Very little clay
Slightly hydraulic limes	0.3 to 0.5	Around 8%
Moderately hydraulic limes	0.5 to 0.7	Around 15%
Eminently hydraulic limes	0.7 to 1.1	Around 25%
Natural cement	1.7	Up to 45%

These earlier classifications have now been superseded by BS EN 459-1:2010 which classifies the NHL according to the minimum quantity of available lime, as $Ca(OH)_2$, and the compressive strength at 28 days as shown in Table 2.

Table 2: NHL classification and tolerances according to EN 459-1:2010

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)

There is wide overlap among the three classifications allowing 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).

NHL2 binders are often preferred for conservation applications where low strength is required however the EN 459-1 classification is insufficient to guarantee undesirable higher strengths will not be achieved. There is currently a need for a characterisation method which takes into account the lime setting processes and better predicts the strength of mortars manufactured from limes over the long term.

The results presented in this work show the distinct properties that can be found in mortars manufactured with a selection of NHL2 binders for a given binder:aggregate ratio, a particular aggregate and workability, highlighting the need to improve NHL classification and selection.

2. MATERIALS AND METHODS

To study the differences and similarities between NHL2 binders available on the European market, three NHLs were chosen from different manufactures, identified as NHL2_A, NHL2_B and NHL2_C.

These binders were physical and chemically characterised to elucidate the implications for the resulting mortar properties.

2.1. Binders

Bulk density was determined using the process described in BS EN 459-2:2010 and the surface area was determined by BET nitrogen adsorption analysis using a Micromeritics 3Flex.

XRD analysis 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-ray and $\lambda = 1.5405$ Å. The step was 0.02°, from 4 to 75 ° (2θ).

XRF analysis was performed on pellets of diameter 40mm and thickness 2mm pressed from the binders and analysed using an Energy Dispersive XRF spectrometer. The Loss on Ignition (LOI) was determined by burning 1g of material [±0.001] at 950°C until sample mass stabilization.

2.2. Mortars

To establish the volumetric formulations, bulk density of the aggregate was determined using BS EN 1097-3:1998. The quarzitic nature was assessed from XRF and XRD characterisation where the major oxide detected was SiO_2 corresponding to the mineral quartz. Mortar prims of dimensions 160×40×40 [mm] were prepared using NHL 2 binders sourced from three different manufacturers with a binder:aggregate ratio of 1:2 and a spread, measured by flow table (BS EN 1015-3:1999) of 165±10 [mm]. Specimens were prepared and cured according to the BS EN 1015-11:1999. Compressive and flexural strength was then measured at 7, 14, 28, 91 and 180 days, following the method described in BS EN 1015-11:1999. Table 3 shows the spread and the water/binder (w/b) ratio in mass of the formulations manufactured.

Table 3: Spread and water/binder ratios of the mortars

Binder	Spread (mm)	w/b (g/g)
NHL2_A	160.0	0.95
NHL2_B	160.0	1.12
NHL2_C	159.0	1.08

3. RESULTS

3.1. Binders

An important part of this work was to establish the similarities and differences between three binders classified as NHL 2 by the EN 459-1. The results present in this section show that, while in the same grade, NHL 2 binders can have distinct physical and chemical characteristics.

Table 4 shows the bulk density and surface area of the three NHL2 binders.

Table 4: Physical properties of the binders: bulk density and surface area

Binder	bulk density (g/cm^3)	surface area (m^2/g)
NHL2_A	0.64	5.46
NHL2_B	0.58	10.04
NHL2_C	0.67	9.40

While the bulk density has similar values across the three binders, the surface area of NHL2_A is significantly lower than the surface area of the other binders. This will increase the water demand required to achieve a specific workability.

The main phases detected by XRD are presented in Table 5, subtle differences in calcite concentration were observed however the most significant differences correspond to the hydraulic oxides C_2S (Belite) and C_3S (Alite) as these are most influential on strength development. This analysis was performed using the software Match! 2 supplied by Crystal Impact. The software is specifically used for phase identification from powder diffraction using the Crystallography Open Database REV129424. Phase identifications were further confirmed by comparison with the literature including Forster et al. (2014).

Table 5: XRD qualitative mineral composition. **++** Strong signal, identified by 3 or more major peaks; **+** Moderate signal, identified by 3 peaks of intensity <20% of maximum; **R** Residual concentration.

Binder	$Ca(OH)_2$ Portlandite	$CaCO_3$ Calcite	Ca_2SiO_4 Belite	Ca_3SiO_5 Alite
NHL2_A	++	+	++	+
NHL2_B	++	++	+	R
NHL2_C	++	++	+	

Although a quantitative analysis of the mineral phases existing in the binders has not been undertaken this analysis indicates that mortars produced using the NHL2_A binder will exhibit a more hydraulic set due to the greater amounts of C_2S and C_3S in this binder. Particularly, the detection of C_3S in NHL2_B and NHL2_C was residual or non-existent when compared to the NHL2_A.

Table 6 presents the chemical composition in terms of oxides percentage of weight obtained from XRF analysis.

Table 6: Oxide composition. Cementation and hydraulicity index according to (1) and (2)

Oxide	NHL2_A	NHL2_B	NHL2_C
CaO	66.38	66.03	66.41
SiO_2	7.80	9.35	4.85
Al_2O_3	1.63	0.38	0.12
MgO	2.37	0.44	1.19
Fe_2O_3	2.10	0.38	0.55
SO_3	0.37	0.46	1.19
K_2O	0.89	0.33	0.46
Na_2O	0.31	0.49	0.49
TiO_2	0.16	0.09	0.09
MnO	0.05	0.01	0.01
LOI	17.95	22.03	24.64
CI	0.36	0.40	0.21
HI	0.14	0.15	0.07

The quantity of CaO is almost identical in all three binders. NHL2_A has a higher quantity of Al, Mg and Fe oxides. NHL2_B, on the other hand, as a higher quantity of Si oxide. When comparing NHL2_C with both NHL2_A and NHL2_B, NHL2_C has a lower quantity of oxides Si and Al oxides which are the main compounds giving hydraulic properties to the binders. From this analysis it is expected that NHL2_A and NHL2_B are both, more hydraulically reactive compared to NHL2_C. This is also notable when comparing CI and HI values, both similar and higher in NHL2_A and NHL2_B when compared to NHL2_C.

3.2. Mortar

The mechanical properties of the three mortars tested were measured at 7, 14, 28, 91 and 180 days. Average values for the flexural and compressive strengths of the different mortar types are shown in Figure 2 and Figure 3 respectively.

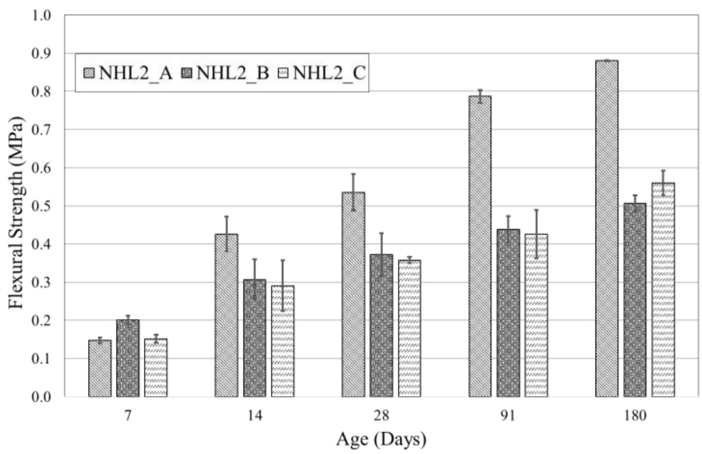

Figure 2: Flexural strength of the mortars at 7, 14, 28, 91 and 180 days.

Although, the flexural strength increases for every mortar, the mortar with the NHL2_A binder shows a higher strength gain up to 180 days. NHL2_B and NHL2_C mortars have similar behaviour, with the exception of the test at 7 days.

Compressive strength develops in a similar trend with every sample gaining strength until the 180 day test.

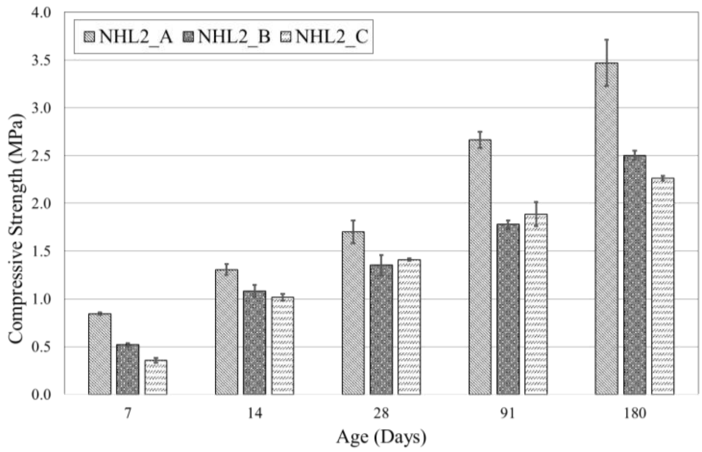

Figure 3: Compressive strength of the mortars at 7, 14, 28, 91 and 180 days.

Across all ages, NHL2_A mortar is the strongest of the three; NHL2_B and NHL2_C present similar values. From 7 to 28 days the gain in strength is almost parallel when comparing the three mortars. After this period the NHL2_A rate of strength gain is higher than B and C mortars.

4. DISCUSSION

Chemical composition and physical characteristics of the binders highlights the variability of the existing products available on the market. This variability can stem from the raw materials to produce the binders and also the temperatures used to burn them. Usually a higher temperature produces more C_3S as was the case for NHL2_A.

The compressive strength of the different mortars reflects two factors: water/binder ratio and the presence of hydraulic mineral phases in the binders. NHL2_A required less water to achieve the same workability (here represented by the spread measured by flow table) mainly due to the lower surface area. Combining the lower w/b ratio and the higher abundance of hydraulic phases in NHL2_A, resulted in a higher compressive strength. This was especially remarkable after the 28 days compressive strength measurement where the rate of strength gain in NHL2_A was higher than the

NHL2_B and NHL2_C increase in strength. There appears to be a relationship between the chemical/mineral composition of the binders, the physical properties such as surface area, and the mortar strength characteristics. A model to establish this connexion has the potential to be studied.

The 28 day strength of common formulated mortars are unrepresentative when compared to those manufactured following EN 459-1. The three hydraulic lime mortars had compressive strengths below 2 MPa at 28 days. At 91 days, NHL2_A had achieved the 2 MPa threshold and by 180 days all three mortars exhibited higher compressive strengths than the minimum for their classification. Although all three mortars remained within the tolerance values for their classification (2 + 5MPa), at least one had achieved the minimum compressive strength for the next classification group (NHL3.5).

Where a conservator wishes to design a mortar to achieve a maximum long term compressive strength according to the assumed standard classification the following points should be taken into account:

1. Compressive strengths achieved at 28 days can be as much as 50% less than the long term compressive strength.
2. The classification allows for a high range of variation in compressive strength, such that an NHL2 could be within acceptable limits with a 28 day compressive strength of 7MPa, which might represent an ultimate compressive strength of up to 14MPa
3. NHL binders from different manufacturers can show a variation in ultimate compressive strength of up to 50%, and yet still remain within the classification.

Mortars based on the minimal value of the anticipated compressive strength as described by the standard classification can lead to an underestimation of eventual strength. This is demonstrated by the 180 day strength for the NHL2_A binder which had a measured compressive strength of 3.5 MPa.

5. CONCLUSIONS

The results presented show a variability in the chemical and physical properties of binders classified as NHL 2 by the current standard EN 459-1.
The relationships summarised below were identified between the chemical and physical characteristics of the binders and the final properties of mortars formulated for a given binder/aggregate ratio:

- lower surface area and higher quantity of hydraulic phases leads to higher compressive strength;
- higher abundance of Alite results in higher compressive strength at earlier ages;
- a higher strength gain for ages over 28 days is related to a higher abundance of belite.

Conservators should exercise caution when using EN 459-1 to predict mortar characteristics. At ages greater than 28 days, mortars can achieve higher compressive strengths than those implied by the binder classification.

The results presented will form the basis of a model relating the chemical composition and the physical characteristics of the binders. Such a model will aid the appropriate selection of binders for conservation work.

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