# What is NHL?
## Does it have a role in conservation?

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## 1  INTRODUCTION

The use of Natural Hydraulic Lime (NHL) has become extremely common in conservation work in recent years.  The reasons for this are not clear, although a complete ignorance of what the material consists of, coupled with hard selling by the manufacturers, are probably the two main factors.  Sadly the ease with which poor information can now be spread electronically makes matters worse.  A quick search for 'hydraulic lime' on Wikipedia demonstrates this well, the information supplied on the web-site not only being wrong, it is extremely misleading.  This note will try to clarify the true nature of NHL and what happens when it is transformed into a mortar using aggregate and water.  Even the materials name is misleading :

**N**atural  it is not.  It is completely man-made in a manner similar to cement.

**H**ydraulic  it is only partly, and variably, hydraulic.

**L**ime  it is only partly, and variably, a lime.

Each of these terms will be clarified, starting in reverse order, since it is lime which NHLs are attempting to supercede.

## 2  LIME

This is the common name of calcium oxide CaO.  It is traditionally made by calcination, that is heating a limestone to temperature in excess of about $900°C$.  Limestone is essentially a sedimentary rock which contains predominantly calcium carbonate, either in the form of calcite or aragonite, or a mixture of calcium and magnesium carbonates, the most well known being dolomite, although magnesium can replace some of the calcium in calcite in variable quantities.  Some sources suggest that the carbonate content should be at least 80%, although this may be a little restrictive.  The reaction which occurs when limestone is calcined is the dissociation of calcium carbonate into calcium oxide and carbon dioxide :

$$CaCO_3 \rightarrow CaO + CO_2$$
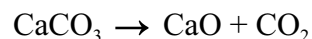
The lime produced by this reaction is more correctly referred to as 'quick lime'.

'Slaked lime', also loosely referred to as lime, is calcium hydroxide formed when water is added to calcium oxide. The chemical reaction is as follows :

$$CaO + H_2O \rightarrow Ca(OH)_2$$
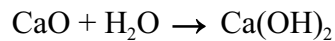
The 'setting' of lime, that is its hardening to a point where it retains any shape into which it has been formed, although still being relatively soft, and its final hardening after a considerable period of time, is due to the reaction between the calcium hydroxide and atmospheric carbon dioxide, in the presence of moisture.

$$Ca(OH)_2 + CO_2 \rightarrow CaCO_3 + H_2O$$
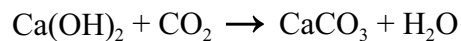
The moisture is required as a carrier for the carbon dioxide, the two being in equilibrium as carbonic acid :

$$CO_2 + H_2O \rightleftharpoons H_2CO_3$$
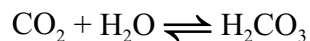
Although water is required initially to start the reaction, and make the mortar workable, the generation of water by the carbonation reaction results in the reaction being self-sustaining as long as carbon dioxide is present. However, if the mortar dries out, the reaction will cease.

## 3 HYDRAULIC MATERIALS

Basically meaning of, or pertaining to, fluids, the term 'hydraulic' has been used in the context of mortars to refer to the ability to set or harden under water. As a result, it covers a number of different chemical reactions. It is the lack of appreciation of this fact that has caused much of the confusion regarding different types of mortar. In his introduction to the 1997 reprint of Smith's 1837 translation of Vicat's 1828 volume on la Fabrication des Mortiers et Ciments Calcaire (calcareous Mortars and Cements), Michael Wingate defines hydraulic limes as those which "can develop strength under water". Vicat's classification of 'rich lime', 'poor lime', 'moderately hydraulic lime', 'hydraulic lime' and 'eminently hydraulic lime', is based on the setting times, or lack of set, under water. Some descriptions given in the book of the appearance and properties of the eminently hydraulic limes as they are removed from the kiln, suggest that it was very similar to Portland cement clinker rather than to lime. Clearly the term hydraulic is used by Vicat as a property which has been acquired during the burning of the raw materials in the kiln. It is

interesting to note that although his hydraulic lime is normally made from impure limestone, he also discusses making an hydraulic lime by burning limestone and clay. This he terms 'artificial hydraulic lime'.
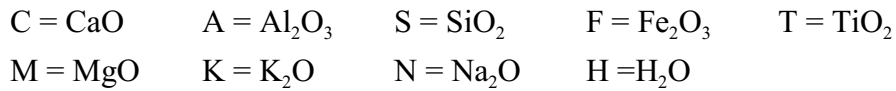
If, however, if we look at Cowper's definition in his 1927 book *Lime and Lime Mortars*, published by the Building Research Station, he states that "the Romans were noted for their fine public works executed in stone and hydraulic lime mortar, the mortar being made with an addition of the pozzolanic sands abounding in the volcanic districts around Baiae and Mount Vesuvius". He also notes that Smeaton's hydraulic mortar used for the Eddystone Lighthouse consisted of burnt and slaked lime from the Blue Lias of Aberthaw, an argillaceous limestone, **mixed** (*my emphasis*) with pozzolan from Civita Vecchia near Rome. Clearly the term hydraulic is being used here for a largely pozzolanic lime.

Since the 'hydraulic minerals' formed during the burning process in the lime kiln and the 'pozzolanic' minerals found in pozzolans, whether natural or man-made, are completely different, it is essential that a distinction is made between mortars made from these different materials. This distinction is even more important when it is appreciated that the reactions involved in the setting and the development of the strength of the two types of mortar, are also completely different.

### 3.1 Pozzolanic lime mortars

The term pozzolan is derived from the name of a village, Pozzuoli, from the neighbourhood of which the Romans obtained a source of volcanic tuff for preparing their 'Roman cement'. Pozzolans, whether natural or man-made, all have one thing in common, this being they contain reactive silica. This can be glassy non-crystalline silicates created due to very rapid cooling, as in volcanic ash, or biochemically formed opal, such as that formed by diatoms and found as deposits of diatomaceous earth. Man-made pozzolans range from materials which are the by-product of an industrial process, such as the fly ash formed when the ash from boilers fired by pulverised coal is carried out of the system by the gases, to those materials, such as calcined clays, which are deliberately activated by heat, the temperature used varying with the clay mineral concerned and can range from $540°C$ to $980°C$.

In pozzolanic lime mortars the calcium hydroxide in the slaked lime reacts with the reactive silica or silicate in the pozzolan to form a 3-D framework of calcium silicates and aluminates, giving a rigid material. The reactions require no oxygen or carbon dioxide and therefore can take place underwater. The minerals formed during this reaction vary with the type of pozzolan used. These compounds can be relatively complex and it is convenient to illustrate their chemistry using the notation developed in the cement industry where such minerals are common. This 'chemical shorthand' is based on abbreviating the chemical oxides found in cement and related minerals :

$$C = CaO \quad\quad A = Al_2O_3 \quad\quad S = SiO_2 \quad\quad F = Fe_2O_3 \quad\quad T = TiO_2$$
$$M = MgO \quad\quad K = K_2O \quad\quad N = Na_2O \quad\quad H = H_2O$$

The mineral gehlenite, dicalcium alumino silicate, $2CaO.Al_2O_3.SiO_2$, therefore becomes $C_2AS$.

Examples of some of the minerals formed during the setting of pozzolanic lime mortars are shown in Table 1.  The time and temperature of curing can also affect the final combination of minerals.

| | Bacoli pozzolan | | Segni pozzolan | | Calcined kaolin | | Neapolitan yellow tuff | | Rhine trass | |
|---|---|---|---|---|---|---|---|---|---|---|
| | (a) | (b) | (a) | (b) | (a) | (b) | (a) | (b) | (a) | (b) |
| C-S-H | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ |
| $C_2ASH_8$ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ |
| $C_4AH_{13}$ | | | | | | | ✓ | | ✓ | ✓ |
| $C_3A.CaCO_3.H_{12}$ | | ✓ | ✓ | ✓ | | | | ✓ | | |
| $C_3AS_3\text{-}C_3AH_6$ | | | ✓ | | | | | | | |
| (a) The reaction time 90 days. | | | | | | | | | | |
| (b)  Water/solid ratio = 0.40;  pastes cured for 5 years | | | | | | | | | | |
| Table 1.  Hydrates formed in pozzolan-lime by the reaction of pozzolan with calcium hydroxide in saturated lime solution and in paste.    After Sersale R *et al*. 1970. *Zement-Kalk-Gips* | | | | | | | | | | |

## 3.2  Hydraulic lime mortars

These are mortars which contain hydraulic minerals which, even in the absence of any other material, will react with water to form a hard hydrated mass.  This is of course unlike pozzolans which require hydrated lime as well as water to form a hard solid material.  Since the hydraulic minerals will react with water as soon as it is encountered, they very rarely occur in nature, being restricted to areas of volcanic activity.  As a result they have to be manufactured using some form of furnace.  They are, therefore, always man-made.  Modern so-called Natural Hydraulic Lime is a 'hydraulic' material in the sense used by Vicat and not that used by Smeaton or those who compare it to Roman mortars or cements, all of which involve pozzolanic reactions.

The reactions which take place during the hardening of true hydraulic mortar are completely different to those in pozzolanic mortars.  In the case of hydraulic minerals, they react purely with water to form a 3-D framework of calcium silicates and aluminates, giving a rigid material.  The

rate of reaction varies between minerals and the reactions do not require oxygen, carbon dioxide or calcium hydroxide. The reactive minerals involved are entirely dependent upon the chemistry of the raw materials which are burnt in the kiln and on the conditions, not only within the kiln, but also on the rate of cooling of the material discharged from the kiln. As a result the actual composition of hydraulic lime has varied both in time and location. In the UK, the burning of various mixtures of impure limestone occurred following Smeaton's use of so-called hydraulic mortar. In 1824 Aspdin was granted his well known patent for Portland cement. However, this material was made at too low a temperature to actually be what we now know as Portland cement. It was his son, William Aspdin, who actually made the true precursor to modern cement, having found that hard overburnt lumps from the kiln, normally discarded, made a better hydraulic material when finely ground. At about the same time I C Johnson discovered the same fact, resulting in what is still an ongoing debate as to who actually discovered Portland cement.

The setting and hardening of lime has been discussed above. In order to understand the setting and hardening of hydraulic calcareous materials we need to determine their chemical and mineralogical composition. Since hydraulic limes are produced by burning either an impure limestone, in particular one containing clay minerals and quartz, or by deliberately mixing a pure limestone with clay or shale prior to calcining, it is convenient to consider the minerals which are formed during the manufacture of Portland cement. This only differs from hydraulic lime in that it is manufactured from a mixture of limestone and clay or shale, blended together in such proportions that all the limestone combines with the other materials to form hydraulic minerals, leaving very little, if any, to be converted into lime. Furthermore, considerable research has been carried out into the chemistry of cement minerals.

There are four main minerals produced when the limestone and argillaceous materials are burnt to form cement clinker. These are as follows.

Tricalcium silicate, $3CaO.SiO_2$, or $C_3S$ in the cement chemistry notation.
> This makes up about 60% of the cement clinker and reacts with water as soon as it is added to the cement. It gains strength steadily, accounting for much of the strength in cement up to 28 days. In fact the mineral is normally impure, containing other elements as well as calcium, silicon and oxygen, this impure form being termed Alite.

Dicalcium silicate, $2CaO.SiO_2$, or $C_2S$ in the cement shorthand.
> About 15% of cement clinker is made up of $C_2S$. It hydrates slower than $C_3S$ and makes its contribution to strength development after about 28 days. It is also normally impure and is termed Belite.

Tricalcium aluminate,  $3CaO.Al_2O_3$, or $C_3A$ in the cement notation.

Although cement clinker may contain about 10% $C_3A$, its contribution to the strength of hydrated cement is low, despite the fact that it can hydrate very fast, giving what is known as a 'flash set'.  To counter this reaction, the mineral gypsum is added to the cement clinker at the grinding stage, when the nodules of clinker are converted to the familiar cement powder. The gypsum, $CaSO_4.2H_2O$, reacts with the aluminate to form the mineral ettringite, which coats the crystals of $C_3A$ and slows down the hydration reaction.

Aluminoferrite phase, or 'Ferrite',  $4CaO.Al_2O_3.Fe_2O_3$, or  $C_4AF$.

Although traditionally the formula was indicated as $C_4AF$, the phase is actually a solid solution based on $C_2A_{1-x}F_x$ and $C_4AF$ is only one of a number of chemical compositions which can exist.  Less than about 10% of ferrite occurs in cement clinker and, although contributing a little more that $C_3A$ to the final strength of cement, its contribution is still not all that great.

Although the important hydraulic minerals in cement are calcium silicates, the temperatures required to react silica, for example in the form of quartz, and calcium in the form of calcium oxide, are much too high to be used commercially, especially in a cement or lime kiln.  In cement manufacture, it is the alumina and ferric oxide from the clay or shale, coupled with very fine grinding and thorough blending of the raw materials before the kiln, which enable the sintering of the materials to form the correct hydraulic minerals in the kiln.  The aluminium and iron oxides act as fluxes which enable the reactions between silicon and calcium to take place at economically viable temperatures.

In order to produce the correct mixture of hydraulic minerals in cement clinker, three carefully controlled processes are essential.

1. The correct chemical composition of the mix.
2. A thoroughly homogeneous and very fine-grained mixture of the raw materials.
3. A temperature of between about $1,450°C$ and $1,500°C$ maintained for a controlled time to allow the reactions to occur.

However, the mineralogy of the hydraulic minerals complicates this further.  If the clinker, at a temperature of about $1,500°C$ is cooled down to ambient temperature too slowly, there can be a partial transition of some of the alite, which provides early strength to the cement, to belite which contributes mainly to the post-28 day strength.  Furthermore, the mineral belite occurs as a number of polymorphs, designated α, β and γ.  The α form, of which there are a number of types, occurs

at high temperatures, whereas below about 650°C this changes to the β form. This is the important type of dicalcium silicate, being hydraulic. However, below about 500°C this starts to change into the γ form which is not hydraulic. Although the change is not rapid, the cooling process has to be fast enough to 'freeze' the belite in the β form.

The complexity of the cement industry is clearly much greater than that of the lime industry, where the raw materials tend to be burnt in lump form in vertical shaft kilns. There is, therefore, limited chemical control of the feed to the kiln, unless the limestone is very uniform in composition. Similarly, unless this uniformity exists, there is no homogeneity to the feed. Except on very modern shaft kilns, the maintenance of a uniform burning regime is also difficult. The burning temperature in lime kilns is also lower than used in cement kilns, for non-hydraulic lime being between about 900°C and 1,100°C, and for hydraulic lime between about 950°C and 1,250°C, depending upon the type of NHL being produced. Although modern high-technology lime plants can produce a relatively uniform hydraulic lime, it is not surprising that the output from simple plants, such as that which was at one time making natural hydraulic lime in Somerset, tend to have a very variable product.

Unlike Portland cement, the Standards for NHL are relatively simple, being shown in Table 2.

| Type of natural hydraulic lime | Compressive strength (MPa) | | $SO_3$ | Available lime as $Ca(OH)_2$ |
|---|---|---|---|---|
| | 7 days | 28 days | Values in mass fraction in % | |
| NHL 2 | - | ≥2 to ≤7 | ≤2 | ≥35 |
| NHL 3.5 | - | ≥3.5 to ≤10 | ≤2 | ≥25 |
| NHL 5 | ≥2 | ≥5 to ≤15 | ≤2 | ≥15 |
| Table 2. The main specification criteria for natural hydraulic limes (EN 459-1:2010) | | | | |

There are other requirements such as particle size, free water content, soundness and mortar tests, which are similar to normal lime. There is, however, one test which could be misleading if the nature of natural hydraulic lime is not thoroughly understood, that being the 'setting times'. The values required are shown in Table 3.

The setting time is defined as the time when the needle of the Vicat apparatus first penetrates the mortar only 0.5 mm. The problem lies with the understanding of the rather unscientific concept of 'setting'. A mortar is considered to have 'set' when it first retains any shape into which it has been moulded. Any attempt to alter that shape will result in some degree of fracture. The term has no connection with the 'curing' of a mortar, which in a normal slaked lime is the total conversion of the calcium hydroxide to calcium carbonate by reaction with carbon dioxide in the

| Type of natural hydraulic lime | Setting times | |
|---|---|---|
| | Initial | Final |
| | hours | |
| NHL 2 | >1 | ≤40 |
| NHL 3.5 | | ≤30 |
| NHL 5 | | ≤15 |
| Table 3.  Specified setting times of NHL | | |

air.  In addition to this total carbonation, a pozzolanic lime will only be cured when all the reactions between the calcium hydroxide and the active pozzolan have ceased, and in a natural hydraulic lime when all the silicates and aluminates have converted to their hydrates.  In an NHL 3.5 therefore, although it must have reached its 'final set' in less than 30 hours, its calcium hydroxide content, which must be greater than 25%, will continue to 'cure' for at least 90 days and probably longer.  In fact its silicate content could continue to cure for a number of years.

| Manufacturer | A | B | C | C | D | D | E | F | F | F | Slaked lime |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Specification | NHL 3.5 | NHL 2 | NHL 3.5 | NHL 5 | NHL 3.5 | NHL 5 | NHL 5 | NHL 5 | NHL 3.5 | NHL 3.5 | |
| Strength 7 d  (MPa) | | | | ≥2.0 | | | 2.33 | 4.5 | 3 | 3 | |
| Strength 28 d  (MPa) | 4.8 | | ≥3.5 ≤10.0 | ≥5.0 ≤15.0 | 3.5 | 5.0 | 5.76 | 7.5 | 5 | 4.5 | |
| $SiO_2$ | 11.55 | 5.32 | 11.46 | 13.84 | 18.20 | 17.12 | 13.07 | 21.0 | 18.0 | 18.0 | |
| $Al_2O_3$ | 3.25 | 1.50 | 3.06 | 3.71 | 1.99 | 1.69 | 4.48 | 5.0 | 4.5 | 3.0 | |
| $Fe_2O_3$ | 1.33 | 0.685 | 1.26 | 1.58 | 0.806 | 0.673 | 1.61 | 3.5 | 3.0 | 4.5 | |
| CaO | 61.63 | 67.11 | 58.69 | 56.64 | 56.81 | 56.53 | 56.81 | 62.0 | 68.0 | 68.0 | 75.7 |
| MgO | 1.72 | 0.305 | 1.77 | 2.22 | 0.707 | 0.595 | 5.86 | 1.0 | 0.8 | 0.8 | |
| $K_2O$ | 1.14 | 0.314 | 0.821 | 0.97 | 0.294 | 0.245 | 1.21 | 0.7 | 0.6 | 0.6 | |
| $Na_2O$ | 0.25 | | | 0.0192 | | 0.0068 | 0.04 | 0.3 | 0.3 | 0.3 | |
| $P_2O_5$ | 0.11 | 0.0765 | 0.11 | 0.16 | 0.09 | 0.07 | 0.07 | | | | |
| SrO | 0.14 | 0.115 | 0.0973 | 0.0929 | 0.121 | | 0.03 | | | | |
| $SO_3$ | 0.62 | 0.0320 | 2.57 | 3.18 | 0.430 | 0.390 | 2.06 | 1.6 | 1.5 | 1.5 | |
| MnO | 0.02 | 0.234 | 0.0195 | 0.0266 | 0.0240 | 0.0200 | 0.02 | | | | |
| $TiO_2$ | 0.17 | | | | | | | | | | |
| LOI | | 24.20 | 19.88 | 17.26 | 20.45 | 22.69 | 14.85 | | | | 24.3 |

Table 4.  Chemical analyses of a range of NHLs.

The most complete of the analyses are a result of analysing actual samples, others are taken from manufacturer's data.

In order to understand what is happening when aggregate and water are added to NHLs it is important to know what they are made of. Table 4 provides examples of analyses of a number of commercially available natural hydraulic limes. Apart from a single NHL 2, the analyses are of NHL 3.5 and NHL 5. When the analyses are compared there are significant variations. Obviously, there will be differences in the analyses between NHL 2, NHL 3.5 and NHL 5, as they are made from different materials. However, even within an individual type of lime there are large variations. For example, in the case of NHL 3.5, the silica content varies between 11.46% and 18.20%, a relative increase of 59%. In the NHL 5, the calcium oxide varies between 56.53% and 62.0%, a relative increase of 10%. Overall the total alkali content of the limes, that is the sum of potassium and sodium oxide, ranges from 0.25% to 1.39%, a relative increase of 456%. Even this is smaller than the range of sulphur content in the limes. Within the NHL 3.5 for example, the $SO_3$ can be as low as 0.43% and as high as 2.57%, a relative increase in concentration of almost 500%.

These chemical analyses represent the mixture of minerals which determine the setting, curing and strength development of the lime. With such a range of analyses, it would appear likely that the range of minerals within the limes would also vary. As a result of such a variation the properties of the lime would also vary. Although this is expected between the different types of lime, since they are designed to cure at different rates, it is also possible that the mineralogy of different limes of the same grade could vary. This would result in, for examples, different NHL 3.5 limes from different sources, setting and curing at different rates, with completely different strength development patterns.

In order to investigate the possible range of minerals in the different NHLs, X-ray diffraction (XRD) studies have been undertaken on a number of limes from different manufacturers. The output from this type of analysis is a trace consisting of peaks of different heights. Every individual mineral produces a number of different peaks. As a result, it is possible to distinguish individual minerals, even if some of the peaks from one mineral coincide with those from another. The determination of the individual minerals is carried out by computer, using extremely large databases containing the peak data for a considerable number of minerals, both natural and man-made. However, as noted previously, the calcium silicates produced in cement and lime kilns are frequently impure, resulting in some unusual chemical compositions. They may not, therefore, be identified precisely as, for example, as tricalcium silicate, but as a complex mineral defined only by its composition. Interpretation of the data is therefore often required.

Three simplified XRD scans are shown in Figure 1, two different NHL 3.5 products and an NHL 5. The figure is intended to demonstrate not only the complexity of the limes, but also how even two materials with the same designation can vary. Note that although the scale on the
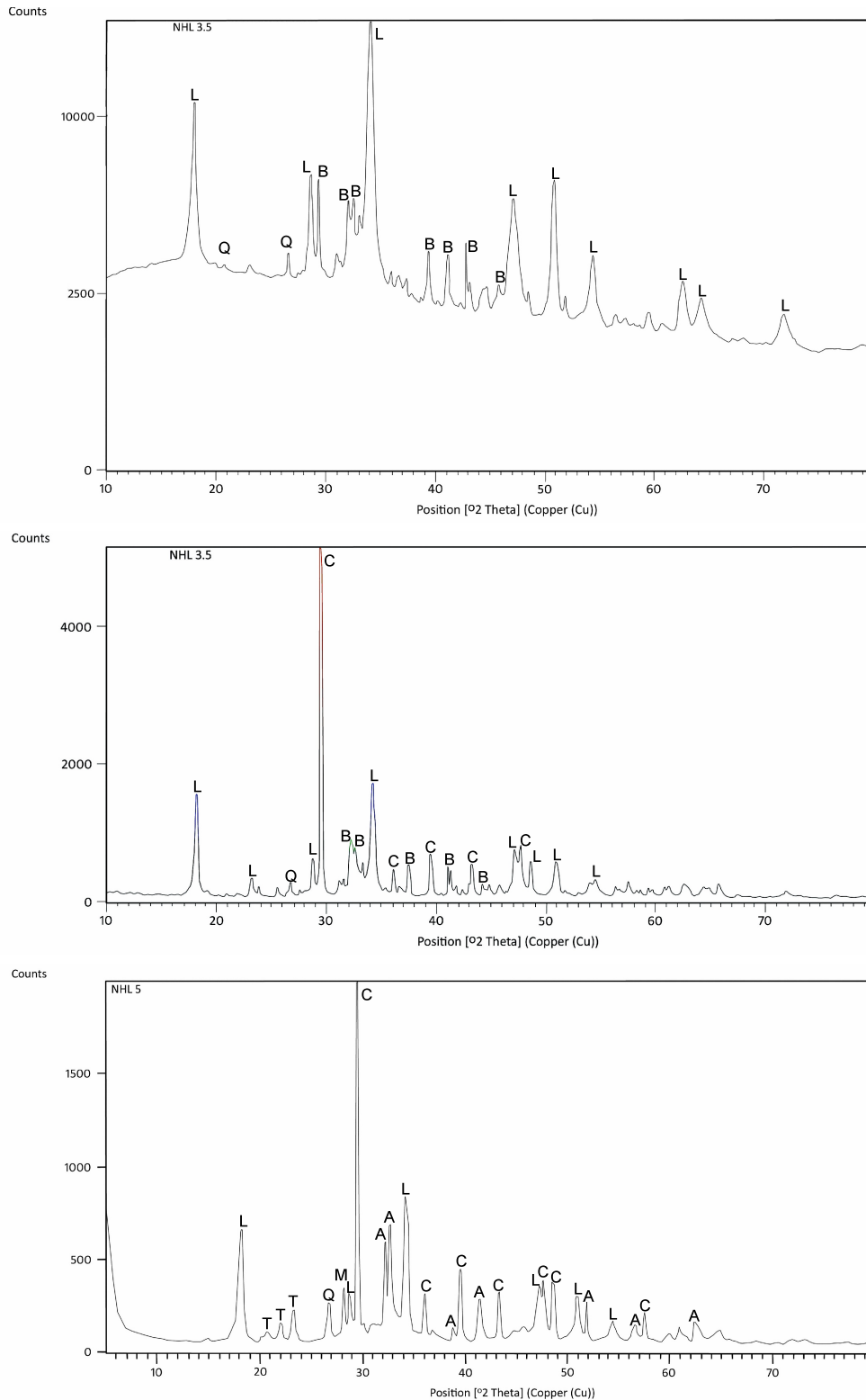
Figure 1. X-ray diffraction traces of two sample of NHL 3.5 and one sample of NHL 5. A selection of peaks have been labelled so as to indicate the minerals they represent.
'C' = calcium carbonate, 'L' = calcium hydroxide (slaked lime), 'B' = belite (dicalcium silicate), 'A' = alite (tricalcium silicate), 'M' = magnesium silicate, 'Q' = quartz and 'T' = tridymite.

abscissa is the same on all three traces, the scale on the ordinate varies and may, as in the case of the top trace, be logarithmic. This allows the peaks to be made more prominent where detailed studies are required of a specific area.

Although a number of different minerals have been identified in each of the limes, only the more prominent ones have been labelled. As would be expected, all the limes contain calcium hydroxide and calcium silicate. In the samples of NHL 3.5 this is dicalcium silicate, whereas in the NHL 5 it is an extremely impure tricalcium silicate. A significant difference between the two samples of NHL 3.5 is the presence of calcium carbonate in the second material; this mineral, in the form of calcite, also occurs in the NHL 5. Although this could be due to unburnt limestone in the lime, this would be most unusual in a product manufactured using modern kiln technology. It is assumed that the carbonate has been deliberately added in the form of limestone in order to adjust the strength development of the material. The quartz in the limes is assumed to have been present in the original limestone raw material, although in the NHL 5, the mineral tridymite, a high temperature form of silica, is also present, perhaps reflecting the higher burning temperature used in the manufacture of this product.

Using both the chemical data and the X-ray diffraction data, it is possible to characterise the different types of NHL of different grades and from different sources. Table 5, although incomplete due to full analyses of XRD data not being available, summarises the mineral content of the limes listed in Table 4.

| Manufacturer | A | B | C | C | D | D | E | F | F | F |
|---|---|---|---|---|---|---|---|---|---|---|
| Specification | NHL 3.5 | NHL 2 | NHL 3.5 | NHL 5 | NHL 3.5 | NHL 5 | NHL 5 | NHL 5 | NHL 3.5 | NHL 3.5 |
| $CaCO_3$ | | | 28 (calc) | 26 (calc) | | | 14.79 | | | |
| Hydrated lime | 32 | | ≥25.0 (33 calc) | ≥15.0 (25 calc) | | | 23.3 | | | |
| $C_2S$ (belite) | | 15 | 22 (calc) | | yes not calc. | | | | | |
| $C_3S$ (alite) | | | | 24 (calc) | | yes not calc. | | 0 | 0 | 0 |
| $C_3A$ | | | 9 | 10 (calc) | | | | 0 | 0 | 0 |
| Additives | | | gypsum limestone | gypsum limestone | some detected | | limestone | no | probably | no |

Table 5. Calculated composition of some 'Natural Hydraulic Limes'.

An important aspect of this mineralogy is the ratio of hydraulic minerals to calcium hydroxide since this will not only have an effect on setting and curing times, but also on the manner in which the material is used. For example whether or not the mortar can be "reworked" in a

similar manner to traditional non-hydraulic lime. As noted previously, 'setting' is the process of permanently taking the shape into which lime mortar has been moulded, and is not related directly to strength. The final set for NHL 3.5, for example, should be equal to, or less than, 30 hours. At this point the mortar has a moderately rigid three-dimensional form, created by the needle-like crystals of calcium silicate hydrate, formed by the reaction of dicalcium silicate with water. This framework will not react further, although the remaining dicalcium silicate and virtually all the calcium hydroxide will continue to react for a considerable time, steadily increasing the strength of the mortar. Since the initial set is provided by completely reacted silicate, if the mortar is re-mixed after the set is achieved, the three-dimensional framework will be destroyed and the resulting particles merely act as aggregate, in a mass which will then have to rely on the remaining unreacted silicate to create a brand new rigid framework, always assuming sufficient unreacted silicate remains. In practical terms this means that an NHL 3.5, if re-mixed after 24 hours, could start to act as an NHL 2, the lime:silicate ratio having increased. An NHL 2, if re-mixed after a period of time, could have lost virtually all its hydraulic nature and act as if it were a pure calcium hydroxide lime. It has been noted in the literature from one manufacturer, that their NHLs can be reworked 8 to 24 hours after the initial addition of water. However, they do not provide any information on the setting time and strength development of their limes after such treatment.

Quantification of the damage caused by reworking a partially set NHL is difficult to determine. The fineness of the lime, the aggregate:lime:water ratio, and even the size of the aggregate, could affect the setting time and strength development if the mortar is reworked after a period of time. However, if it is assumed that the relative hydration development remains the same, whatever the time interval from initial wetting to final hydration, it is possible to roughly estimate the amount of damage that reworking could inflict on the mortar. Studies have produced a hydration development curve, which suggests that reaction in fine-grained commercial lime will start in less than one hour from mixing, and that there is a slow but steady reaction for the next two hours. The reaction then speeds up and the hydration then continues at a much faster rate for the next sixteen or seventeen days or so. This is followed by a slightly slower rate of hydration which continues until the process is completed. This may take of the order of one and a half to two years. It is estimated that ten hours after adding water, about 5% of the silicate will have hydrated, and after 20 hours about 8% will have finished reacting. If therefore the mortar is reworked after twenty hours, the resulting mixture will have the same quantity of calcium hydroxide present, but only about 92% of the original dicalcium silicate. There will also be an effective increase in the amount of aggregate present, since the framework of reacted silicate will have been broken up and now only act as inert fine-grained aggregate. Moreover, as the hydration of the silicate produces calcium hydroxide, this together with the increase in the calcium hydroxide to silicate ratio created by the hydration of the silicate, will start to alter the

composition of the NHL from, for example, an NHL 3.5, towards an NHL 2. The effective increase in aggregate will start to move, from for example, a 2.5:1 aggregate to lime ratio, towards a 3:1 ratio, potentially reducing the final strength of the mixture.

An important consideration when using natural hydraulic lime is the water requirement of the mix. In pure natural limes the water takes no part in the reaction, merely facilitating the absorption of carbon dioxide by the calcium hydroxide to produce calcium carbonate. In fact water is generated during this reaction. In the hydration of calcium silicates, water is actually absorbed by the silicate to form calcium silicate hydrate. In the case of dicalcium silicate, one kilogram of this mineral requires over 0.2 kilogram of water to hydrate completely; the reaction also producing a little under half a kilogram of calcium hydroxide. When using an NHL therefore, it is necessary to add more water than would be required to maintain the moisture level in a normal fat lime. It should also be noted that the hydration of calcium silicates is exothermal, possibly about 300 KJ/kg being evolved during the hydration process, with a maximum rate of heat evolution of about 3 W/kg being achieved after about ten hours. Eventual cooling could conceivably result in cracking of the set mortar.

Another potential problem is indicated in Table 5, that is the presence of gypsum. This was first identified when attempting to convert the chemical analyses into minerals known to occur in NHLs. The sulphur content often created problems during this calculation and it was found that by converting the sulphur into gypsum, it was possible to reconcile items such as 'loss on ignition' with the elements present. Studies of the published data on the manufacturing plants eventually located a flow chart for one plant which included the provision to add both raw material and gypsum to the lime after it had been produced in the kiln. The gypsum is probably required, as it is in the manufacture of Portland cement, to control the rapid hydration of tricalcium aluminate, which would result in a 'flash' set. Unfortunately the addition of sulphate to the fabric of an historic building, which may well be suffering from degradation due to sulphate salts from elsewhere, is unlikely to be in the best interests of conservation.

## 4 CONCLUSIONS

'Natural Hydraulic Limes' are a mixture of slaked lime, silicates and aluminates. The latter two materials are essentially the same compounds as those found in Portland cement, albeit in different proportions. The grain size of powdered NHL as received from the manufacturer is largely below 90 microns, as is cement. The aim of the grinding of both products is to release the individual minerals in order that, on the addition of water, they can react freely and allow the development of the strength of the mortar to take place in a planned manner, thereby fulfilling

the requirements of the relevant Standards. NHL can therefore be considered as a mixture of particles of calcium hydroxide and cement minerals such as dicalcium silicate. Portland cement takes the form of a mixture of cement minerals with very few particles of calcium hydroxide or calcium oxide. Whereas the composition of the mixture of minerals in cement is relatively constant, that in NHL can vary. One reason for this is the fact that lime is burnt in lump form and the raw material is inhomogeneous, whereas the raw materials which are used for cement manufacture are finely ground and thoroughly homogenised in order to ensure that the chemistry and mineralogy of the product is constant. It could be argued that, in order to obtain a more uniform NHL, a uniform hydrated lime could be gauged with an homogenous Portland cement, or even a belite cement, a process which has, for some time, been strongly disapproved of when repairing historic buildings.

The two types of mineral which make up NHL react completely differently with water. The silicates start to react with water immediately to form silicate hydrates and calcium hydroxide, the reaction taking place at different rates depending upon the type of silicate; the same is also true of the aluminates which can be present. In contrast, there is no reaction between calcium hydroxide and water, the latter merely providing the medium through which the hydroxide can react with carbon dioxide from the air to produce calcium carbonate. This reaction is slow, at least three months being required before a significant quantity of carbonate is formed. Furthermore, should the permeability of the mortar be reduced, for example through the development of silicate hydrate, the flow of carbon dioxide into the mixture can be restricted, resulting in even longer carbonation times. Two independent hardening processes are therefore taking place in an NHL mortar, processes which can result in one hindering the development of the other. This may well be the cause of the failure of some NHL mortars following their first exposure to winter conditions.

It is therefore suggested that, as there is no advantage in terms of strength development of a mortar prepared with NHL, and there may well be problems with decreased permeability, the use of NHL-based mortars is avoided when repairing historic stone buildings.