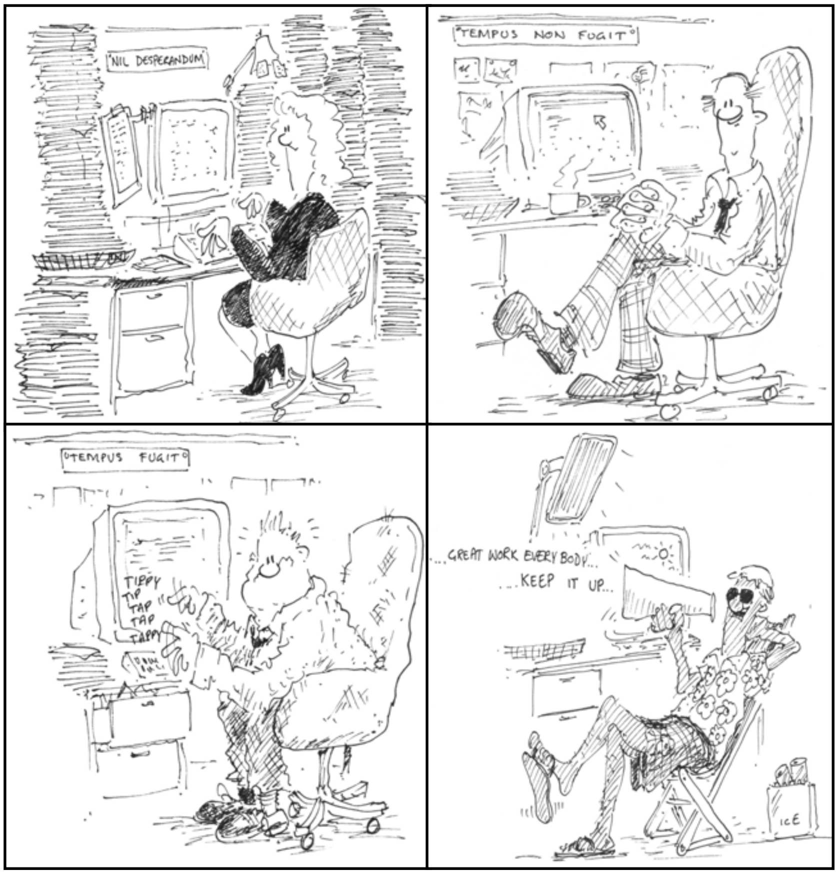

SCOTTISH
LIME
CENTRE

HOW HYDRAULIC LIME BINDERS WORK

hydraulicity for beginners
and
the hydraulic lime family

By Alan M. Forster

This publication, drawing on simplified information from his PhD thesis, was written by
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Dr Forster qualified as a building surveyor from Heriot Watt University, Edinburgh. He was awarded a travelling scholarship with the Society for the Protection of Ancient Buildings in 2001, and gained his PhD in building conservation materials science, with particular reference to the hydraulicity and water vapour permeability of lime based mortars, from Heriot Watt University in 2002. Currently employed by the Scottish Lime Centre Trust as a building surveyor / technical training manager, he has published several papers on lime science, technology and specification and contributed to various research projects.

The Scottish Lime Centre Trust (SLCT) was established in 1994. The Trust is a centre of excellence for traditional building skills, specifically those associated with traditional masonry buildings in Scotland. Activities include provision of consultancy services to building owners, professionals and contractors; development and provision of specialist practical and industry training, provision of continuing professional development (CPD) and other educational services; practical conservation projects, including management of the EC-funded Limeworks project, participation in research projects and drafting of technical advice. The Trust collaborates with a wide range of other bodies in Scotland, the UK and overseas and works closely with Historic Scotland on a number of initiatives.

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1 Introduction

This short publication sets out to make the subject of hydraulicity in lime mortars more accessible for practical people. Processes and descriptions have been simplified to try to identify and explain the main mechanisms and set characteristics of hydraulic lime mortars. The discussion generally is focussed on modern hydraulic lime mortars. In the case of surviving historic mortars the same principles are relevant to their understanding but, with less control over material selection, firing and processing, the characteristics (and component reactive compounds) of the mortars are likely to be more variable than those of modern hydraulic lime mortars.

Hydraulic limes are binders with the ability to undergo a chemical set in the presence of water. They are usually combined with fillers such as sand, and processed into a workable material (namely mortar). We use this in a myriad of construction processes including wall construction, repair / repointing, wall coatings, grouts and lime washes / paint systems, etc.

The ultimate behaviour of hydraulic lime mortars depends on the original ingredients (both lime and sand or other filler, etc), the methods of processing the lime (i.e. burning and hydration) and on techniques of use and curing. By understanding hydration and hydraulic set it is hoped that certain key questions can be clarified, such as – Why is curing important? – Why should hydraulic lime mortars be protected from rapid drying out? – Why do certain materials set faster than others? and – What bearing can these factors have on mortar performance?

It appears that the long term stability of the hydrate in the mortar binder may be one of the most important issues in durability, perhaps more so than the measure of compressive strength currently more commonly used for assessing potential durability.

This publication does not attempt to cover the practical site use of hydraulic lime mortars: guidance on this is available in a number of other publications (see 'Further Reading').

2 Formal standards & definitions

The term 'NHL' signifies natural hydraulic lime, as opposed to an artificial hydraulic lime. An artificial hydraulic lime is made from a relatively pure non-hydraulic lime with the addition of pozzolan or cement.

All building limes, including hydraulic limes are covered by formal standards for their production. BS EN459 classifies hydraulic building limes under 3 categories – NHL2, NHL3.5 and NHL5 based on minimum compressive strength of the cured lime (not of a typical site mortar) at 28 days. These definitions are somewhat unsatisfactory, since the extent of overlap between categories is so wide that, in some instances, one material may be described by any of the three categories. The three categories equate roughly with the traditional descriptions of 'feebly', 'moderately' and 'eminemtly' hydraulic limes.

Standards for mortar are covered by BS EN 998-1 Specification for mortar for masonry - Rendering and plastering mortar; and by BS EN 998-2 Specification for mortar for masonry - Masonry mortar.

Workmanship is covered by relevant parts of BS 8000.

3 What does 'hydraulic' mean?

Hydraulic set has been defined as
'… the chemical combination of lime, burnt clay or other pozzolanic material and water to form a stable compound, even under water.'[i]

Hydraulic limes vary in their degree of hydraulicity, ranging from feebly through to eminently hydraulic in nature. In all hydraulic limes (but not in cements) two set mechanisms occur simultaneously. These are:

- A hydraulic reaction – put simply this means setting with water.
  The most basic way to view a hydraulic set is to consider it in terms of a material's ability to set in the presence of water. The degree to which this reaction can occur depends on the quantity of hydraulically reactive components present, twinned with sufficient water. In hydraulic lime mortars hydraulic set occurs as a result of the hydration (i.e. reaction with water) of certain compounds within the fresh mortar.
- A carbonation reaction – absorbing of carbon dioxide and release of water, leading to a degree of hardening of the material.
  Carbonation occurs in all lime mortars – in non-hydraulic materials carbonation and controlled drying are the means by which the material hardens.

In addition to hydraulicity, which influences the strength of the material, the speed of reaction, or 'reactivity', is important in a hydraulic lime. A high degree of reactivity may result in a quick set which may be beneficial in ensuring the stability of the mortar in its early days. However, certain fast formed components may be susceptible to longer term deterioration.

4 Some considerations for carbonation

All hydraulic lime mortars undergo a carbonation reaction in addition to their hydraulic set. Generally, the higher the hydraulicity of the binder the less is the carbonation requirement and vice versa. Table 1 indicates the approximate ratio of hydraulic set to carbonation set in some common binders.

binder type	degree of hydraulic set	degree of carbonation set	compressive strength
non-hydraulic lime	0%	100%	2-3 N/mm^2
NHL2 $^{\phi}$ (feebly hydraulic lime)	45%-50%	50-55%	2-7 N/mm^2
NHL3.5 $^{\phi}$ (moderately hydraulic lime)	75-80%	20-25%	3.5-10 N/mm^2
NHL5 $^{\phi}$ (eminently hydraulic lime)	80-85%	15-20%	5-15 N/mm^2
OPC	100%	0%	35 N/mm^2 +

ϕ These values will vary depending on the composition of the lime and have been based on the St Astier range of hydraulic limes

Table 1: Approximate hydraulic set versus carbonation set

Many people (mistakenly) believe that if they use a strong hydraulic lime, such as NHL5, then it is not necessary to ensure carbonation of the material via normal curing methods. This generally has disastrous results and it is considered advisable to cure hydraulic lime mortars whatever their classification. The provision of suitable aftercare and protection to ensure good carbonation and hydraulic set is of paramount importance. A good contractor should always be aware of the 3 'Ps' in lime work – namely protection, protection and protection! Lime-based materials can be likened to young children, requiring babysitting in their infancy!

5 Materials for making lime

Hydraulic lime is manufactured from a mixture of calcium carbonate (normally limestone) and clay based and/or other silicate or silicate/aluminate minerals. Where these materials are available in a naturally occurring mixture the resultant lime is called Natural Hydraulic Lime (NHL). Hydraulic lime may also be manufactured from pure calcium carbonate with the addition of pozzolans, when it is known as Artifical Hydraulic Lime.

5.1 Impure limestones (with essential minerals!)

The use of the term 'impurities' to define the clayey minerals which form an essential part of hydraulic limes is somewhat misleading and tends to conjurer up a picture of unwanted components. This could not be further from the truth as these 'impurities' are required in order to confer a hydraulic set. The term '*essential minerals*' is a better description.

Geologically, impure limestones have similarities to pure limestones; but with the natural inclusion of other minerals such as clay. These additional minerals are generally derived from eroded rock, transported to the sea via rivers. Clay is primarily silica, required for the hydrauilic set, with secondary components including aluminium, iron, potassium, etc, which can also influence the hydraulic set. Interestingly, silicon is the second most abundant element on the planet so it is not difficult to appreciate how it could end up in limestone.

Some 'impure' limestones are much more akin to pure limestones but with the presence of clearly defined nodules of silica.

5.2 Pure limestones

Geologically, limestones can be formed in various ways. Generally the most familiar of these is skeletal deposition. Bill Bryson describes this process, '*So what keeps the planet stable and cool? Life does. Trillions upon trillions of tiny marine organisms that most of us have never heard of – foraminiferans and coccoliths and calcareous algae – capture atmospheric carbon, in the form of carbon dioxide, when it falls as rain and use it (in combination with other things) to make their tiny shells. By locking the carbon up in their shells, they keep it from being re-evaporated into the atmosphere where it would build up dangerously as a greenhouse gas. Eventually all the tiny forminiferans and coccoliths and so on die and fall to the bottom of the sea, where they are compressed into limestone. It is remarkable, when you behold an extraordinary natural feature like the white Cliffs of Dover in England …. A six inch cube of Dover chalk will contain well over a thousand litres of compressed carbon dioxide that would otherwise be doing us no good at all*'.' [ii]

These forms of limestone are relatively pure, with approximately 95%+ calcium carbonate. When converted into a lime the material is described as a non-hydraulic and will not set without the availability of CO_2 and drying conditions. Pure limestones can be used, in conjunction with pozzolans, in the production of 'artificial' hydraulic lime.

5.3 Pozzolans

Pozzolans, in very simple terms, are clay-based minerals that have been fired through natural (i.e. volcanic) or human processes (such as the manufacture of soft-fired brick and tiles). They are essentially minerals or impurities which can be added to a non-hydraulic lime to make an artificial hydraulic lime. This is what the Romans excelled at, mixing pure limes with soft fired clay to make high performance artificial hydraulic limes for civil engineering projects. In the 18th century engineers developed the practice of combining pozzolans and hydraulic limes to produce strong mortars which would set rapidly under water

6 Hydraulicity

6.1 Factors affecting hydraulicity

The degree to which a material may become hydraulic is governed by various factors:

i) The proportion of clayey materials (or other relevant minerals) within the stone.

ii) The degree to which these are available for reaction (e.g. silica nodules within a relatively pure limestone require to be crushed before firing to gain higher reactivity).

iii) The temperature of the firing process to which the material is subjected.

iv) The duration of the firing process.

v) The rate of cooling.

Generally the higher the proportion of clay in a limestone (up to 40%), twinned with an appropriately high firing temperature, the greater will be the degree of hydraulicity. Conversely there is some pragmatic evidence that lower firing temperatures may increase the rate of reactivity.

6.2 Development of hydraulicity in the kiln

Reaction processes within a kiln are very complex. Equilibrium phase diagrams (see fig 1) provide a way of describing these, illustrating the effect of temperature (and pressure) on a material. In the following diagram the materials illustrated are calcium oxide [CaO] and silica di-oxide [SiO_2]). These are two of the most important components in hydraulic limes and in most cements.

The 'x' axis, along the bottom, indicates the concentration of the material (in the form of component oxides); on the left hand side we have 100% calcium oxide (CaO) and on the right hand side we have 100% silica (SiO_2). The 'y' axis along the side indicates temperature, ranging from 0°C (32°F) to 2600°C (4680°F). For the sake of clarity the diagram does not take account of other mineral components that would also be forming simultaneously, such as aluminium and iron. The effects of vapour and gas pressures within the kiln are also not shown on this simplified diagram.

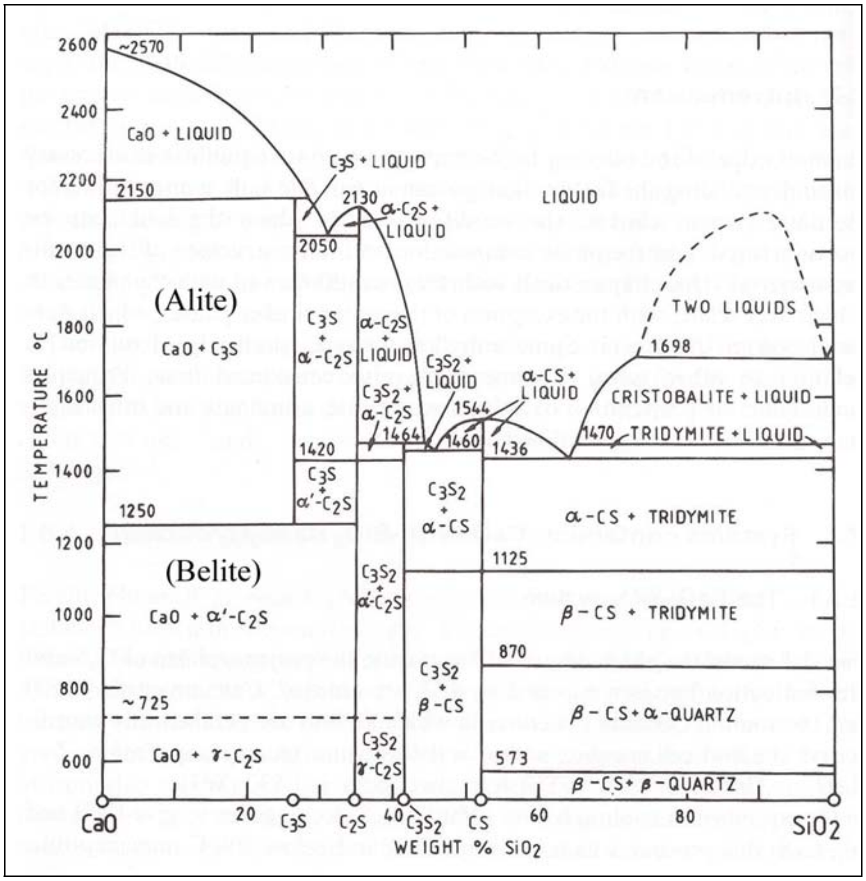

Figure 1: The phase system - CaO-SiO_2 [iii] Taylor

With a known mineral composition of limestone (in the form of its component elements) and a given temperature in the kiln, phase digrams can predict the components and potential performance of the resulting lime.

To take a modern example:- with a limestone composed of 20% SiO_2 and 80% CaO and fired at approximately 900°C (1620°F) the resulting compound will be in the form of C_2S (belite, or di-calcium silicate). Hence we have generated a combined silica and lime component and an additional part of uncombined quicklime (this would be the free lime). Now simply alter the temperature to 1350°C (2430°F) and we generate C_3S (alite, or tri-calcium silicate) which, when hydrated, forms the primary cementing compound in cement. Generally an increase in calcination temperature will lead to an increase in the quantity of combined (soluble) silica, with stage development of silicates following mono, di- and tri-calciums at increasing temperatures.

In the case of historic lime burning, where a consistent and intimate mix of all the component minerals prior to firing was not normally achieved, and where firing conditions within the kiln were less likely to be consistent, the nature of the final product was likely to be more variable.

6.3 Reactivity – Overburn, under burn and optimal firing

Reactivity (that is the speed and ease with which the material hydrates to give a hydraulic set) is influenced by methods of production. With modern production and handling of materials the situations described below are unlikely to occur. However it is worth noting the potential. If the limestone mix is burnt at too high a temperature the reactivity of the lime product may be reduced by the formation of a compound that will not readily react with water (this is due to the radical alteration of its crystalline lattice structure). Reactivity of the product may also be influenced by the fineness of the particles and, where the material has been ground down, by the time elapsed since grinding – freshly ground material is more reactive than older material. Storage, particularly if conditions are humid or damp, can also allow the hydration processes to begin, resulting in a material which is less reactive and which cannot attain the anticipated hydraulic set. Binders that have been subjected to this phenomenon are generally said to be 'blown'.

Underburning, either through too low a temperature or too short a period of residence in the kiln, (or historically through use of over large pieces of limestone) will result in only partial conversion of the material. In such conditions the degree of hydraulicity obtained may not match the potential of the raw materials and, if the product is subsequently ground down the final material will contain a proportion of unburnt stone forming, in effect, a very fine aggregate. Controlled use of these processes can produce a range of limes of differing hydraulicity from basically the same raw material.

There are also some indications that rapid cooling of the quicklime after burning *may* increase reactivity of the final material. This is currently little understood.

7 Hydration theory

7.1 The hydration process

The various (anhydrous) compounds formed in the kiln will react with water in a process known as hydration. Each type of compound will yield a different hydrate when in the presence of water, some being hydraulic and others being non-hydraulic in nature.

Hydration of modern hydraulic limes takes place in two stages. In general terms when the calcined or clinkered material has been removed from the kiln it is cooled and partially slaked (often in steam) to hydrate the vast majority of the quicklime, or calcium oxide, (CaO) into calcium hydroxide ($Ca(OH)_2$), but without sufficient water to hydrate the hydraulic compounds and cause the hydraulic reaction to occur. Hydration causes the particles to break down into a fine powder (grinding processes may also be adopted) which is then bagged. Proper dry storage is important to prevent hydration by moisture in the air. This is the stage at which we buy powdered hydraulic lime binder from the merchants.

Further hydration (by the addition of water to the dry material) is required before use to convert the hydraulic compounds into reactive materials which will undergo a hydraulic set.

When these hydraulic compounds are hydrated they can be classified into broad groups according to the primary hydrated forms, namely calcium silicate hydrates (C-S-H), if they have formed from calcium and silica based compounds or calcium aluminate hydrates (C-A-H), if they have formed from calcium and aluminium based materials. It is important to realise that cement chemists use their own symbols to represent elements, i.e. C = calcium and not carbon.

For example belite (C_2S) would hydrate into jennite-based C-S-H (the main cementing component in hydraulic lime); this is hydraulically reactive and therefore sets with water – it is not dependent on the presence of carbon dioxide (CO_2). However, when the dry ($Ca(OH)_2$) component, previously slaked from CaO, is further treated with water it will react with any available CO_2 to form calcite, but will not set under water and is non-hydraulic in nature.

The primary hydration products associated with hydraulic limes include, mono-calcium silicate (CS), di-calcium silicate (C_2S), calcium aluminate (CA) and di-calcium alumino-silicate (C_2AS).

starting phase	reaction product	in cement	in hydraulic lime
Alite - C_3S (+H)	C-S-H + CH	Yes	? in some historic limes
Belite - β-C_2S (+H)	C-S-H + CH	Yes	Yes
Ettringite - C_3A	C_3AH	Yes	in certain hydraulic limes
Brownmillerite - C_4AF	$C_3(A,F)H_6$	Yes	in certain hydraulic limes

Table 2: Common hydraulic compounds in OPC and hydraulic limes

7.2 Hydration of compound phases

The development of hydraulicity may also be associated with solubility. When the limestone with its 'impurities', or essential minerals, is heated in a kiln the once inactive, insoluble clay (primarily silica) becomes soluble. This allows a reaction between calcium and silica to occur via a series of complex precipitation and dissolution reactions before the final compounds, mainly calcium silicate hydrates (C-S-H) and calcium aluminate hydrates (C-A-H), achieve their final forms.

Other hydrates are also formed. The diagram below shows the sequence and relationship of the main reactions and reaction products involved in cement or hydraulic lime mortar from raw material through to set product.

It is important to remember that an individual particle of hydraulic lime can have a complex and variable composition and may not simply be a product of two elements (i.e. silica and calcium).

found in the raw material

component elements

these are chemically combined into various minerals which disassociate in the kiln

in cement	in hydraulic lime
O_2 (oxygen) Si (silica) Ca (calcium) Al (aluminium) Fe (iron)	**O_2 (oxygen) Si (silica) Ca (calcium) Al (aluminium) Fe (iron)**

⇓

from firing processes

component oxides

these form as the various elements combine with oxygen at high temperatures

in cement	in hydraulic lime
Si Ca Al Fe	**Si Ca Al Fe**

⇓

as bagged product

binder compounds

these form in the kiln from combinations of the component oxides, and are relatively stable unless exposed to water when they will start to hydrate

in cement	in hydraulic lime
C_3S C_2S C_3A C_4AF	**C_2S C_3A C_4AF**

⇓

as set material

hydration products

these develop as the binder compounds hydrate, forming interlocking crystalline and amorphous structures

in cement	in hydraulic lime
C-S-H C-A-H A-S-H + $Ca(OH)_2$	**C-S-H C-A-H A-S-H + $Ca(OH)_2$**

Figure 2: Commonly applied terms for OPC and hydraulic limes

7.3 Solubility and hydration

As outlined above firing a material in a kiln at a specified temperature for a set duration may create compounds that are hydraulically reactive. When silica is heated it may be turned from an insoluble material into a soluble one, which can dissolve in water.

The basic solubility reaction may be explained by looking at a cup of hot coffee. When we add sugar to the coffee it dissolves; however as we increase the quantity of sugar in the coffee we reach a point at which no more sugar can dissolve. The liquid has become saturated with sugar. When we drink our coffee and reach the bottom of the cup a sugary sediment will be seen (and if we continue to drink it a sugar rush will ensue!).

Several things have occurred in this process, namely,

i) We have created a saturated solution.
ii) No more sugar can dissolve until the quantity of sugar held in solution in the liquid is reduced.
iii) Under these conditions the sugar would have a tendency to precipitate into sugar crystals / grains (especially when the temperature cools in the liquid).

This process also occurs with hydraulic lime and cement. The particles of binder compound start to dissolve into the water until a saturated solution occurs. The lime and other elemental components in the solution then precipitate in new combinations to form hydrates (salts). This lowers the amount of lime and other elemental components in the water and therefore the solution is no longer saturated. The particles of binder compounds can then start to dissolve once again until the solution again becomes saturated. The hydrates that have formed from the solution are relatively insoluble in comparison to the binder compounds.

The illustrations below show (in a significantly over simplified form) progressive stages in the hydration of belite (C_2S) to form calcium silicate hydrates (C-S-H) – the most important hydraulic component in hydraulic limes.

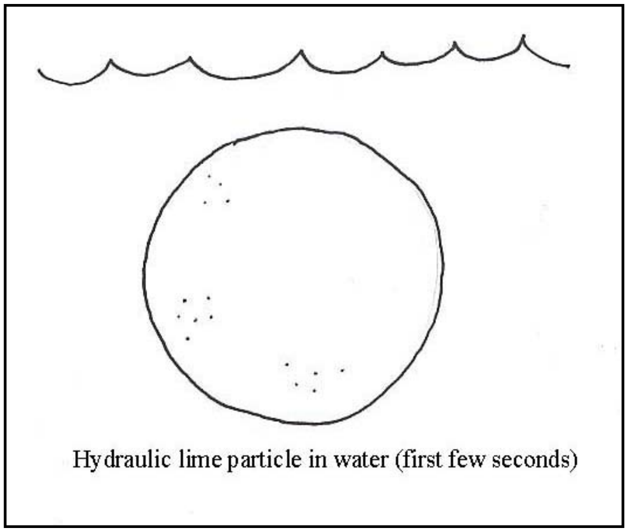

Figure 3: Stage 1 of hydration process – Hydraulic lime particle in water (Forster)

In stage 1 the hydraulic lime particle comes in contact with water with no loss of workability in the material and no signs of dissolution.

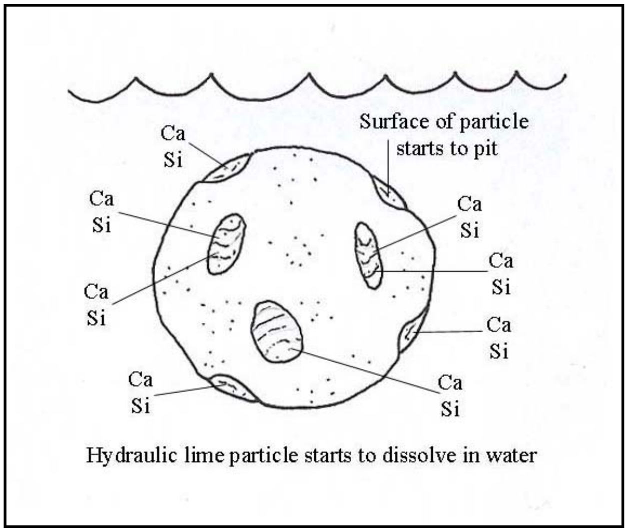

Figure 4: Stage 2 of hydration process – Hydraulic lime particle starts to dissolve (Forster)

In stage 2 as a result of its solubility the hydraulic lime particle starts to dissolve into parts, namely calcium and silica.

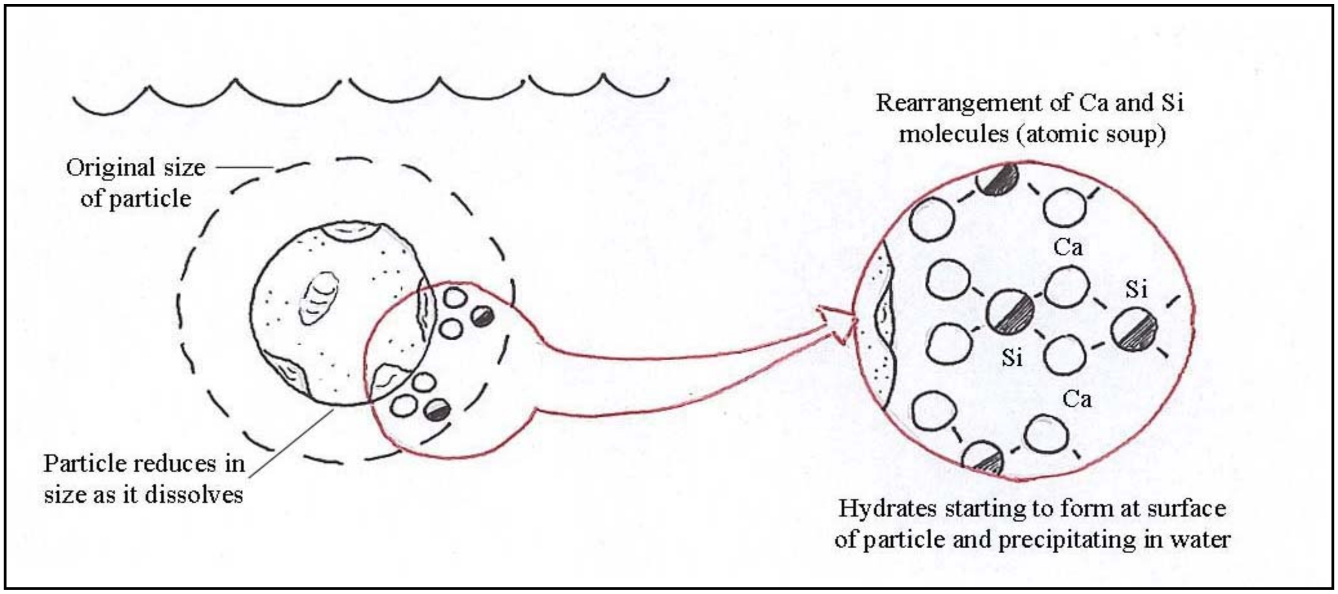

Figure 5: Stage 3 of hydration process – Ions start to rearrange in hydraulic reaction (Forster)

As the particle dissolves it reduces in size. The water of hydration starts to become increasingly filled with ions such as Ca and Si. As the concentration of ions increases and a supersaturated solution occurs, precipitation starts.

The Ca and Si have an affinity for each other and start to arrange in such a manner that they form complex micro-crystalline and amorphous C-S-H. The arrangement of these precipitated crystals follow blue prints. However sometimes, as with even the best construction project, unforeseen alterations do occur. The arrangement of the crystallites sometimes follows a regular crystal architecture but can also tend to develop in an amorphous manner (therefore seemingly featureless). This makes the identification of C-S-H somewhat difficult and things get worse when we consider that C-S-H changes throughout its life, especially throughout the first year.

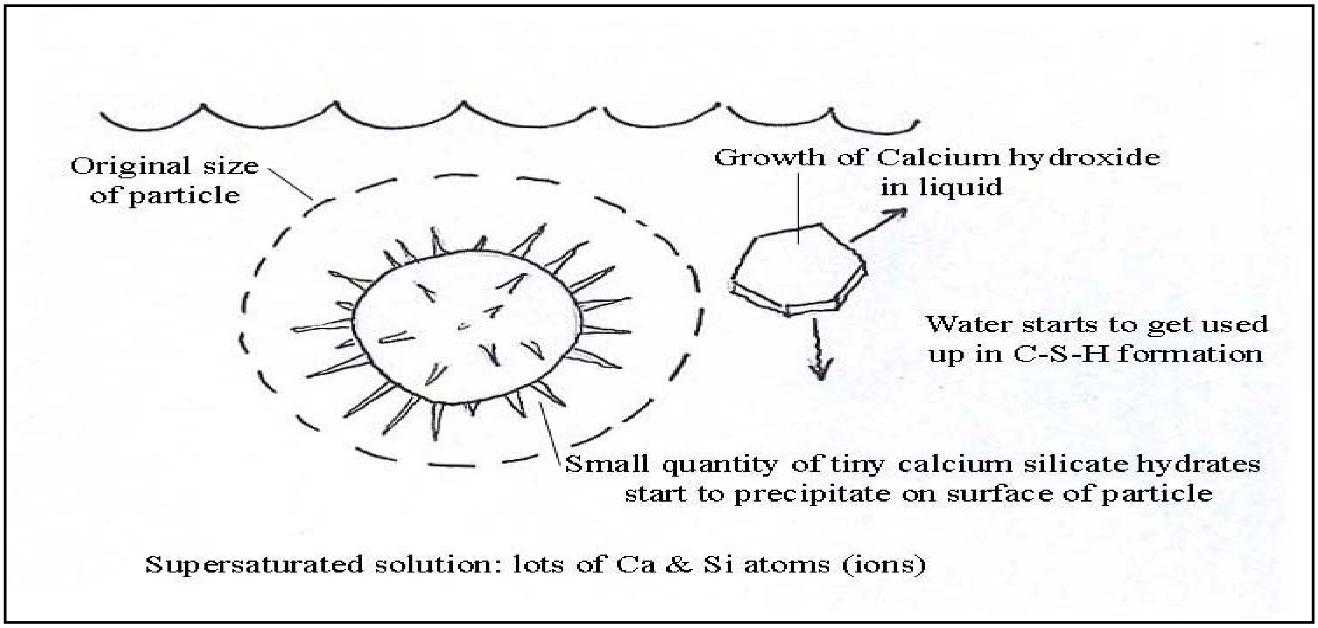

Figure 6: Stage 4 of hydration process – Low level precipitation of hydrates starts in the liquid and at the particle surface (Forster)

As the precipitated crystals develop the workability of the binder starts to reduce.

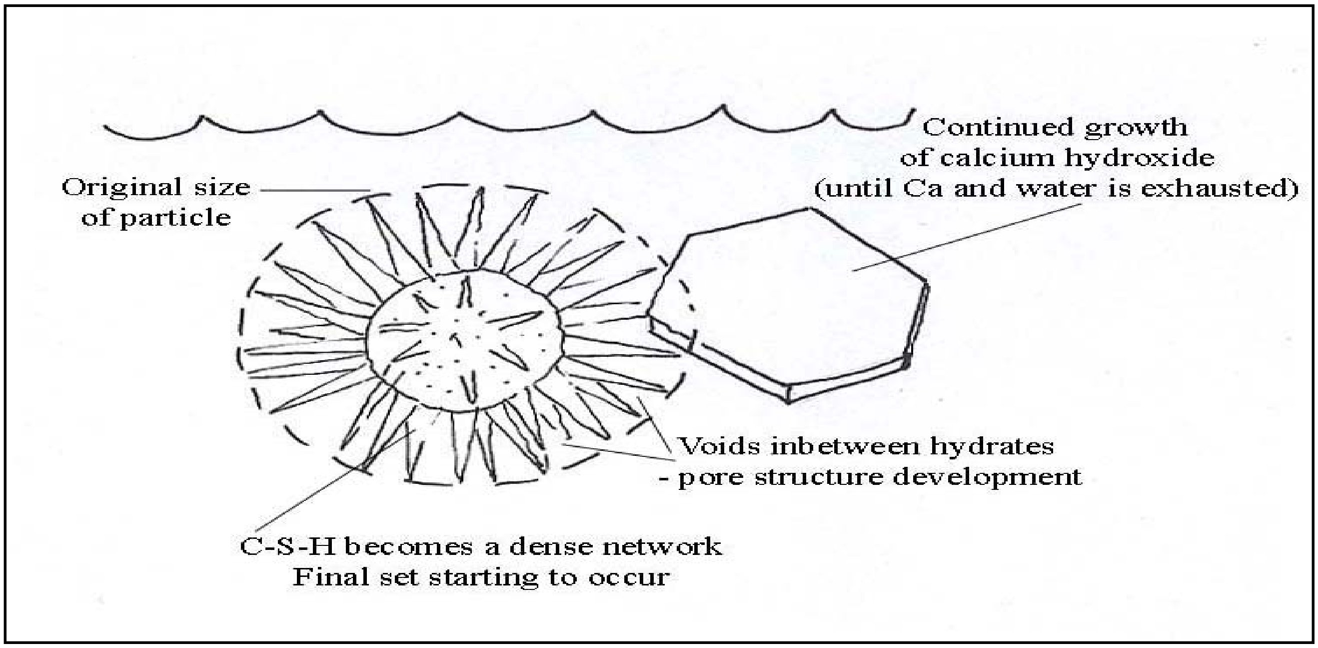

Figure 7: Stage 5 of hydration process – Precipitation of hydrates continue at an accelerated rate within the liquid and at the particle surface (Forster)

As the products of hydration develop into C-S-H, C-A-H and A-S-H (depending on the original composition of the binder compounds), they start to consume the water and also fill up the space where water once resided. This leads to increasing density of the material and causes the permeability to decrease.

'Initial set'. After several hours, the degree of hydration is such that the initial set takes place. Setting is synonymous with a rather sudden loss of plasticity in the material. It is not difficult to appreciate that our once relatively smooth and mobile hydraulic lime particles have now become rather spiky and with this change in shape comes a change in workability. It is important not to consider the particles in stage 5 in isolation – thousands of these hydraulic lime particles would be interacting and meshing together causing reduced workability. At this stage very little strength has been developed and the material would be still considered as being 'green' in building terms. When the initial set has occurred and the development of the final set is underway an increase in strength will be noted. At the same time the parallel process of carbonation will also contribute to the set and strength of the mortar.

It is important to emphasise that along side the hydraulic components the formation of relatively large $Ca(OH)_2$ (portlandite) crystals are forming simultaneously. They may range in size from approximately 1-2 nanometers to 2mm and may therefore engulf the C-S-H (or alternative products of hydration). Generally speaking this $Ca(OH)_2$ will carbonate when CO_2 enters the lime based material and complete the lime cycle. However, in general the denser the matrix the greater the difficulty the CO_2 may have in diffusing through the material.

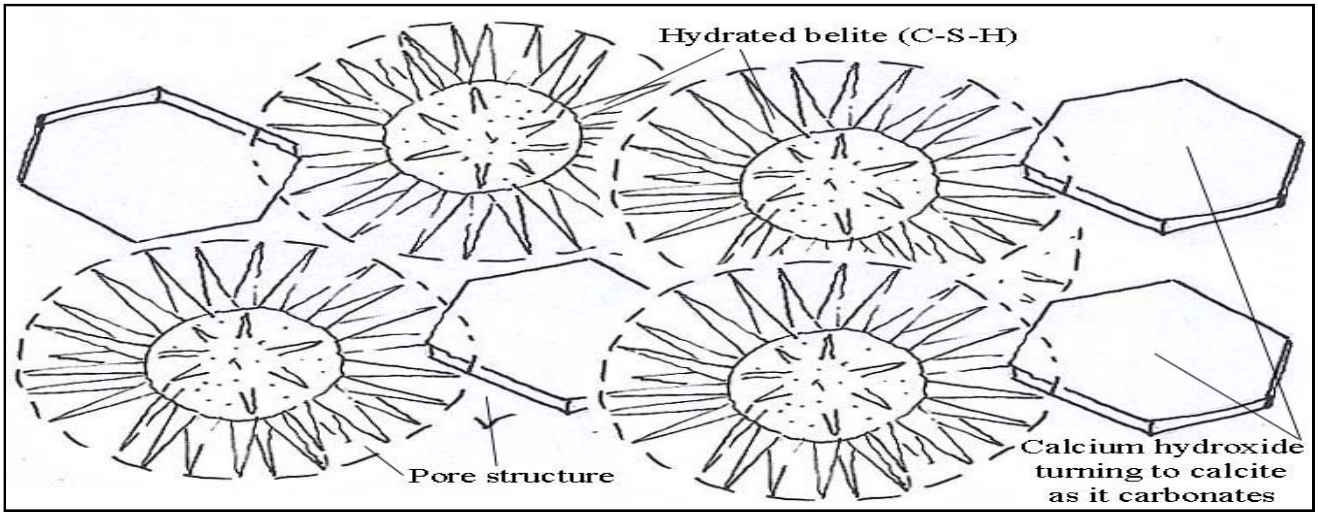

Figure 8: Stage 6 of hydration process – Final set of hydraulic lime particles showing the interlocking nature of the C-S-H and $Ca(OH)_2$ (portlandite) crystals (Forster)

'Final set'. This process of interacting and meshing together keeps repeating until

i) All of the water is used up, preventing further dissolution.
ii) The particle of lime or cement has been consumed in the reaction and total hydration has occurred.
iii) The particle has formed a very dense network of hydrates around the hydraulic lime or cement grain, too impenetrable for water to penetrate and cause further dissolution of the particle.

At this stage the 'final set' of the material is achieved, and any further disturbance of the particles will destroy the bond between them, resulting in failure of the mortar.

7.4 Free lime

Free lime is a major component of hydraulic limes (see table 1). Once the C_2S has hydrated to form C-S-H the majority of the binder is still calcium hydroxide. Hence, the lower the hydraulicity, the higher the free lime content will be, and the higher the carbonation requirement will be.

In cements, in addition to the free lime which is not involved in the hydraulic reaction, further free lime is generated by the hydration of alite (C_3S) into C-S-H. The reaction is described by: $C_3S + H_2O \Rightarrow CSH + Ca(OH)_2$.

In building conservation, free lime is generally considered as a good thing as it is associated with the flexibility and autogenous healing properties of lime mortars. However, free lime in cement is considered detrimental as it may carbonate, leading to volumetric change, instability and loss of alkaline environment (this is especially significant in reinforced concrete).

Free lime (even when carbonated) has a greater ability to migrate and although this is a very slow process it may result in migration and loss of binder. This phenomena generally only occurs if water can percolate continuously through the structure, and may take many, if not hundreds, of years (think of how long it takes to form stalagmites and stalactites). However, open wall heads and unprotected bridges may be susceptible.

8 Physical characteristics

8.1 Setting and the development of strength

As we have seen, the setting process of hydraulic limes is based on their reaction with water. When a hydraulic compound hydrates (reacts with water) to form a hydrate (salt) it changes in form. The hydrates that form, whether amorphous or crystalline, generally have a high surface area (reported to be up to a thousand times greater than the unhydrated material in the case of cement hydration) [iv]. Increased surface area for a given mass of hydrate may be correlated with increased strength development in hardened material.

Calcite (carbonated $Ca(OH)_2$), the main component of non-hydraulic limes, is also present in hydraulic limes. It is rather chunky in nature when compared with C-S-H and therefore has a low surface area. This characteristic may be observed in the relatively weak relationship between calcite – calcite, and calcite – aggregate in non-hydraulic lime mortars

This phenomena is noted in plate 1 which shows a non-hydraulic lime mortar. The calcite may be seen sporadically bound to the surface of the aggregate (centre).

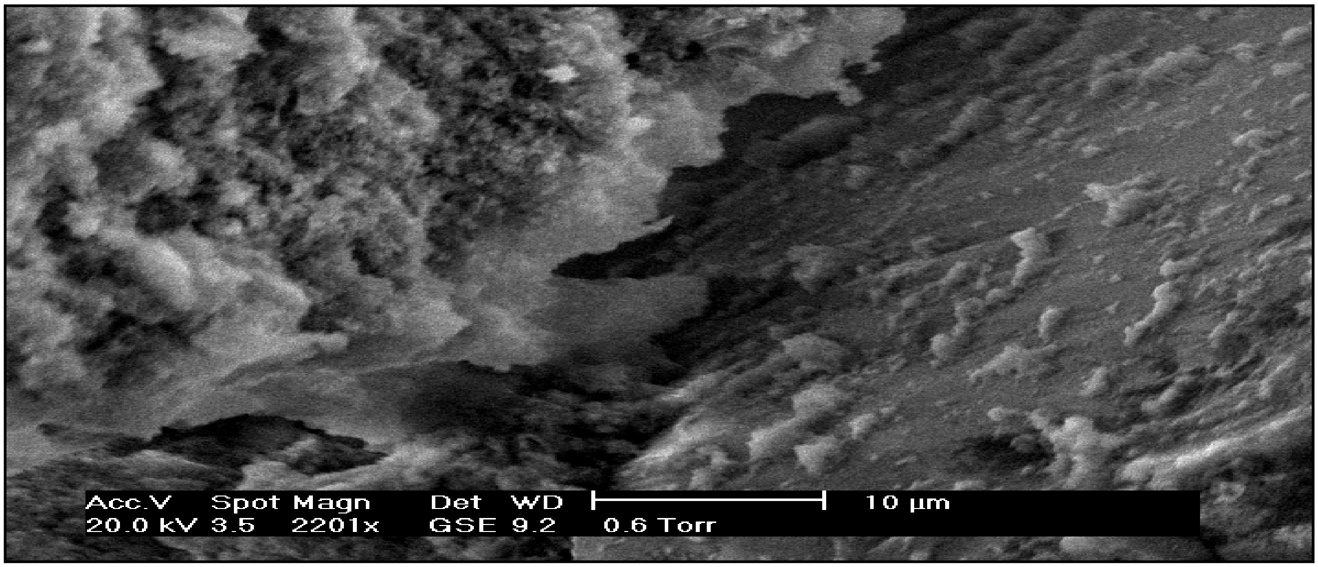

Plate1: Non-hydraulic lime mortar (Environmental Scanning Electron Microscope) [v]

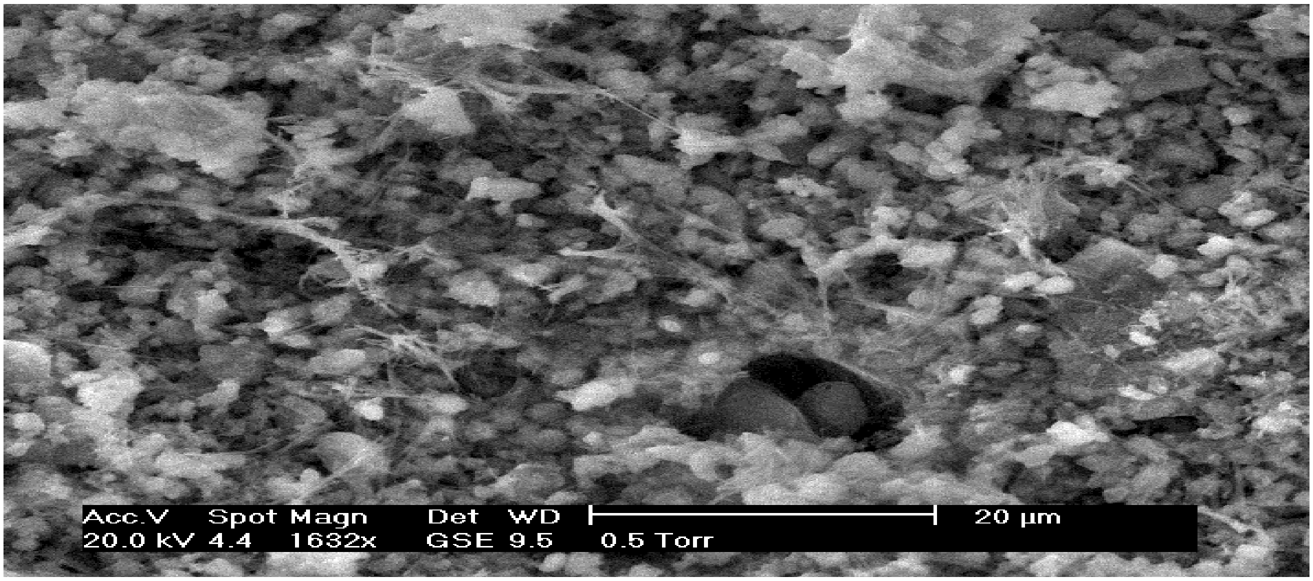

Plate 2: Hydraulic lime mortar NHL2 (Environmental Scanning Electron Microscope) [vi]

Plate 2 indicates a feebly hydraulic lime with a substrate of calcite and C-S-H seen throughout in the form of rod like crystallites. The darker regions are pores.

The relationship between soluble silica and setting times may be seen in table 3. The proportion of soluble silica present is considered by the producers of St Astier limes to be one of the most important and reliable factors when assessing the hydraulicity of a lime.

Binder	Setting time	Soluble silica concentration	Compressive strength at 28 days
Lime Putty	several days +	1-4%	<1 N/mm^2
NHL 2	6-10 hours	4-8%	2-7 N/mm^2
NHL 3.5	4-6 hours	8-12%	3.5-10 N/mm^2
NHL 5	2-4 hours	12-16%	5-15 N/mm^2
Natural Cements	1-2 hours	16-20%	≈20 N/mm^2
OPC	1 hour or less	>20%	>20 N/mm^2

Table 3: Percentage of combined silica in binders and its relationship to setting time and compressive strength (St Astier)

8.2 Longer term performance

It is current practice to assess the performance of mortars in terms of compressive strength; however it appears that stability of the binder (and aggregates) is of the utmost importance and may well be more important to long term performance than is compressive strength. The differing characteristics of C-S-H in hydraulic limes and cements appear to influence the longer-term stability of the materials. C_3S hydrates into a form of C-S-H traditionally known as tobermorite, whereas C_2S hydrates into jennite, a different type of C-S-H. Both of these are stable under normal conditions. However, certain other hydrated forms may be susceptible to instability (i.e. certain C-A-H)

This is reinforced by Bonen [vii] who believes that *'the outstanding performance of ancient* (hydraulic lime) *concrete structures implies that thermodynamic stability rather than mechanical strength is a key point for long-term durabilty ..……. to what extent is Portland cement durable? Or in other words, is the main hydrated product of Portland cement, the C-S-H, capable of withstanding the test of time? This question becomes relevant in the light of outstanding performance of a few ancient structures, some of which are continuously subjected to sequences of drying and wetting and salt attack*'.

9 Factors that may affect hydration and setting

The hydration and associated setting process of hydraulic limes and cements involves dissolving and precipitation reactions. By understanding the factors that may influence these reactions (such as drying out etc) it is hoped that we can better understand the processes and therefore develop better working practice.

9.1 Solubility of silica and particle size (fineness of binder)

Firing of certain clay minerals tends to increase their solubility. The smaller the particle size the higher the total surface area, and therefore the greater the degree of contact with the water. This increases the rate of dissolution and therefore the hydraulic reaction.

9.2 The mixing regime

In order for the hydration process to occur within the wet mortar it is essential to ensure that sufficient water is present in the mix. A correct water : lime (or cement) ratio for the mix must be maintained. Clearly correct and accurate proportioning are also critical and thorough mixing of the materials, to ensure all binder particles are wetted and well distributed throughout the wet mix. Overmixing, once the initial set has started, will generally result in damage to the bond which develops between the hydrating particles. Because the hydration process, and associated intermeshing of the crystals, generally takes place more slowly in hydraulic limes than in cements the mixing time can be longer without damage to the bond.

9.3 Curing conditions – moisture and temperature

Because the setting process relies on repeated dissolving and precipitation of minerals within the wet mortar it is essential to ensure that sufficient water is also present for a long enough period to allow the hydraulic reaction to continue after the mortar has been placed. If the water evaporates too quickly then only partial hydration will occur and the material will be prone to failure. This is one of the reasons why it is essential to cure materials correctly.

There is also a relationship between the temperature of the environment and the rate of hydration. Generally, the higher the temperature the faster the hydraulic reaction. If the temperature falls below 5°C the hydration almost stops. However, more importantly in practice, the risk of frost damage increases. Ice crystals forming in the matrix of the mortar disrupt the bond which is forming between particles. Therefore work should never proceed with lime or cement mortars in temperatures below 5°C.

9.4 Additional factors affecting hydration

Other technical factors may play a part in the hydration mechanisms, although generally these do not directly affect us on a practical level. These include the rate of dissolution of the involved phases; the rate of nucleation and crystal growth of the hydrates to be formed; the rate of diffusion of water and dissolved ions through the hydrated materials that have already formed; the processing history of the clinker, including the heating rate, maximum burning temperature and cooling rate (therefore, holistic calcination has an integral role to play in hydration kinetics); the fineness of the cement or lime particles; and the hydration temperature.

10 The hydrate families

As we have seen, the nature of the clinker / fired material formed in the kiln (see figure 1) will obviously control the type of hydration products produced when water is added to the mix. These hydrates lead to the formation of amorphous and crystalline components that are sometimes difficult to identify individually (even via complex analytical tools such as ESEM [Environmental Scanning Electron Microscopy]) and are commonly grouped generically. The main hydrated forms associated with OPC and hydraulic limes are shown in the following table.

Numerous other hydrates may be formed, but they all may be placed into primary families – calcium silicate hydrates (C-S-H) and calcium aluminate hydrates (C-A-H) – or smaller families, including calcium alumino-silicates (C-A-S [H]). These designations are generic for the collective hydrated products. The dashes denote unknown composition.

clinker / compound	reaction product	normally present in
Alite (C_3S)	C-S-H	cement
Belite (C_2S)	C-S-H	hydraulic lime & cement
Ettringite (C_3A)	C-A-H	Some hydraulic limes & cement
Brownmillerite (C_4AF)	C-A-H	Some hydraulic limes & cement
Gehlenite (C_2AS)	C-A-S	hydraulic lime
Portlandite [$Ca(OH)_2$] (anhydrous)	Calcite [$CaCO_3$] – on carbonation	hydraulic lime
Calcium Oxide CaO – Portlandite [$Ca(OH)_2$]	$Ca(OH)_2$	Cement

Table 4: Common compounds in hydraulic lime and OPC

11 Meet the family!

The reactive hydraulic compounds found in hydraulic limes and in cements form two main interrelated family groups – the ***calcium silicate hydrate*** family (C-S-H) and the ***calcium aluminate, alumino-ferrite hydrate*** family (C-A-H). Both family groups work in the wider family business of creating set in mortar materials, some will normally be found only in hydraulic lime *or* cement materials, others will be found in both. Just like any other family, the members all have different characteristics.

- Each anhydrous calcined compounded particle has its own name based on its respective compounds (ie C_2S, C_3S etc).
- Each have different characteristics, i.e. some are fast reacting, some are slow, some are stable, some less so, some are introduced to help with the manufacture of the binder and some affect colour.
- Each hydrate can be put into a family (or umbrella classification).
- Each may have different size and shape of crystallites.

These characteristics are reflected in the way that they hydrate and their influence within the mortar materials.

11.1 The calcium silicate hydrate family (C-S-H)

Within this family live cementing compounds, belite (C_2S) and alite (C_3S).
The most influential members of this family are Belite (C_2S) and Alite (C_3S), although the family also includes minor components such as mono-calcium silicate (CS).

Alite (C_3S: tri-calcium silicate): Character name Albert

Figure 9: Albert is strong and slender in nature, and is an early riser getting up at 8am$^{\Phi}$ *and gets straight to work, however by 10 am he is generally tired and spends the rest of the day going at a much slower pace. He is generally calm and stable and takes a prominent role in the family and community as a whole.*

This description illustrates the early stage reaction of alite. Alite (C_3S) leads to the formation of C-S-H when given sufficient water. It is the component in cement that leads to early strength development and is relatively fast reacting. It has a high surface area when hydrated. 90% of alite (C_3S) is exhausted after 28 days of hydration and the hydrated form is very stable under normal conditions. This can be seen in table 5 below, in which early stage alite (C_3S) hydration is clearly seen occurring rapidly when compared with belite (C_2S).

Alite (C_3S) is not found in commercially produced hydraulic limes due to their lower firing temperatures. However, in traditional small-scale manufacture its presence cannot be ruled out.

Belite (C_2S: di-calcium silicate): Character name Belinda

Figure 10: Belinda is also strong and slender in nature. She is a slow riser (not good in the mornings) and doesn't really get out of bed until 10 am, however once she is up and running she picks up pace quickly and is a real hard worker, generally putting in long working hours. She is very important for the long term well being of the family and without her the family would generally break down. She is similar to her brother Albert (alite - C_3S) in so much as she doesn't get flustered, is generally calm and is a pillar of the community.

As before, this description neatly illustrates the early stage reaction of belite. Belite (C_2S) leads to the formation of C-S-H (in the form of jennite), when in the presence of water.

It is the most important component in hydraulic lime, and a secondary (yet still important) component in OPC. It is responsible for long term strength development in cement and hydraulic limes. It is slow in terms of rate of reaction, with only 10% of belite (C_2S) consumed after 28 days. (This is reflected in table 5). As a hydrate it is very stable under normal conditions.

	7 days	**28 days**	**180 days**	**365 days**
Alite C3S	322	466	512	584
Belite β-C2S	24	42	194	325

Table 5: The hardening of both belite (C_2S) and alite (C_3S), determined by strength development (Kg/cm^2) of pure compounds [After Hewlett viii]

11.2 The calcium aluminate, alumino-ferrite hydrate family (C-A-H)

Within this family live C_3A and C_4AF.
C_3A leads to the formation of ettringite.
Small quantities of other components, such as gehlenite (C_2AS) and di-calcium alumino ferrite (C_2AF) may also be present, but little is presently known about the characteristics of these materials.

Ettringite (C_3A: tri-calcium aluminate): Character name Ernie

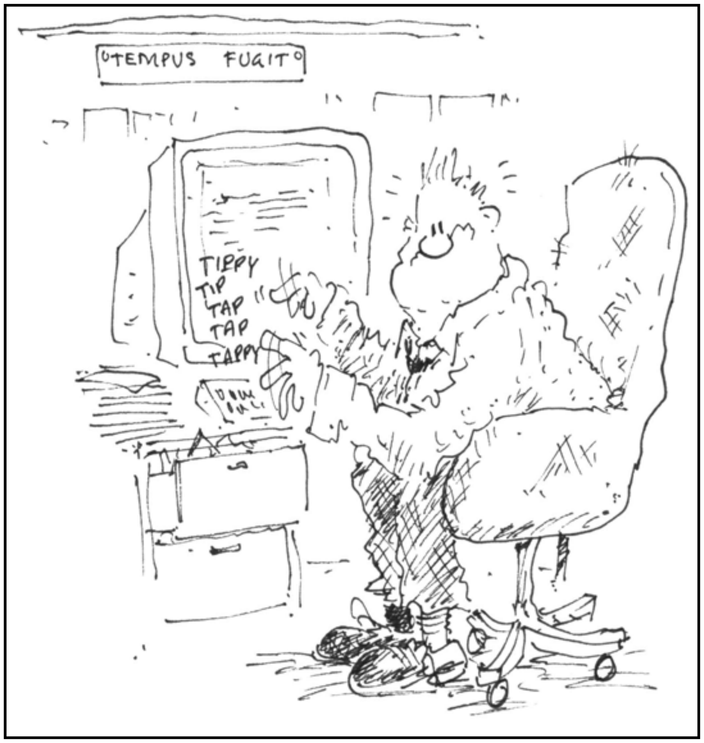

Figure 11: Ernie is relatively chunky and weak in nature, he hardly sleeps and is somewhat hyperactive. He sleeps in his clothes and is at work at 8am. He works so fast that he requires a sedative to slow him down (i.e. gypsum in cement). Without this he can run out of steam prematurely (i.e. flash set). He gets very hot under the collar and may over heat from time to time, causing trouble for others around him.

Again, this description illustrates the early stage reaction of ettringite (C_3A). Ettringite leads to the formation of C-A-H, when in the presence of water. It is a secondary component in OPC and varies in concentration in hydraulic limes depending on the concentration of aluminium present and the calcination processes to which it is subjected. Generally, ettringite (C_3A) is considered undesirable in OPC and hydraulic limes. It contributes little in the way of strength development except in the very early stages.

Ettringite (C_3A) hydrates rapidly, leading to early strength development and generates a great deal of heat via this process. If this heat generation is not checked then thermal fracturing may be seen (especially in mass concrete structures such as dams etc, and this is one of the primary reasons for the use of reinforcing in concrete). Low heat Portland cement is manufactured with a reduced amount of C_3A (and C_3S). Generally gypsum is added to the cement to retard this set, otherwise a flash set may occur and loss of workability would be very apparent.

Ettringite (C_3A) is stable in most environments, however when in the presence of water and sulphates (SO_3) (commonly present in by-products of fuel combustion or in ground water in some areas) it will break down, leading to sulphate attack (e.g. in unlined chimneys).

Ettringite (C_3A) has one perceived benefit in that it facilitates the combination of lime and silica to form calcium silicate hydrates.

Brownmillerite (C_4AF: tetra-calcium alumino ferrite): Character name Billy

Figure 12: Billy is relatively low-key and weak, as a sun worshiper he may be often found sunning himself on the beach and doing little work. He does, however, encourage Ernie and Belinda to work harder and is well known for his motivational management skills.

Billy personifies the early stage reaction of C_4AF. Brownmillerite (C_4AF) leads to the formation of calcium alumino-ferrites when in the presence of water. It is a secondary component in OPC and has very little effect on strength development and performance of the material. It is however, responsible for the rather blue / grey colour in OPC. White Portland cement is simply OPC with the Brownmillerite removed. However, it is important to realise that when it is removed it leaves a higher proportion of other components such as alite (C_3S) etc, and white cement is therefore generally stronger than OPC.

One benefit of C_4AF is that it may act as an accelerator to the formation of calcium silicate hydrates.

12 Suggestions for best practice

The document has discussed the main physical and chemical processes which have an effect on the final performance of the binder and / or mortar. It is the aim of this final section to relate the information to site practice.

12.1 Storage

As we have seen, a hydraulic set occurs when water comes in contact with the binder. This has a significant bearing on the way that the binder should be stored and the shelf life of the product. If the binder is stored in an atmosphere with a high humidity, moisture from the air will initiate the hydraulic reaction. When this occurs the binder is said to be 'blown'. Hydraulic limes and cements are nornally packaged in an outer paper bag with an internal plastic lining, if this gets damaged the binder must be used immediately.

12.2 Mixing

The process of mixing up a hydraulic lime mortar should follow basic good practice in order to attain batch consistency. Binder and sand should be mixed dry before the addition of water. Enough water should be added to give workability for the desired building operation. Accurate gauging and thorough mixing are essential to ensure even distribution of the particles and consistent wetting. Particles which are allowed to clump together will be unable to fully hydrate.

12.3 Reworking

It is important to realise that once the hydraulic lime particles come in contact with water the reaction starts. Despite this it is apparent that both NHL2 and NHL3.5 can often be reworked for up to 12 hours. This phenomena is not fully understood, but may be associated with the following:

- The set in NHL2 and NHL3.5 limes is relatively slow, with most hydrated forms not achieving a sufficient degree of set to cause a great loss of workability.
- Any loss of workability in the binder is compensated by an increase in the non-hydraulic (free lime) component within the binder as it matures.
- The development of the hydrates that have occurred in the early stages will be theoretically broken when reworking occurs, thereby the ultimate strength of the mortar cannot be ascertained or guaranteed. This requires a great deal more investigation.

12.4 Application

When a mortar, plaster or render is applied to any substrate it is imperative to take into consideration the amount of water that will be drawn from the binder. If a high suction background is not dampened down sufficiently then some of the water required for full hydration will be lost to the porous substrate, resulting in only partial hydration of the binder and may potentially lead to a friable and low strength material. The presence of excessive surface water will reduce adhesion between the mortar and the substrate.

12.5 Curing

Early loss of water resulting from too rapid a drying process will prevent full hydration of the hydraulic components, leaving the mortar weak and friable.

Frost forming at or below the surface of the mortar has the potential to break the bonds forming between the hydrate crystals (see figure 8) as ice grains develop and expand within the mortar, and this too will result in a friable and low strength material.

12.6 Further information

These brief notes in relation to site practice are not intended to provide a complete guide to the topic. Further information is included in the publications listed below.

13 Additional reading

Allen, A. Elton, J. Elton, N. Farey, M. Holmes, S. Livesey, P. & Radonjic, M. *'Hydraulic lime mortar for stone, brick and block masonry'* Donhead publications (2003)
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ii Bryson B (2003) 'A short history of nearly everything' Black Swan Press p327
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iv Illston JM and Domone PLJ (2001) 'Construction materials - their nature and behaviour' 3rd Edition, Spon Press
v Forster AM (2002) 'A correlation between water vapour permeability and hydraulicity of lime based mortars with particular reference to building conservation materials science' PhD Thesis, Heriot Watt University
vi Forster AM (2002) 'A correlation between water vapour permeability and hydraulicity of lime based mortars with particular reference to building conservation materials science' PhD Thesis, Heriot Watt University
vii Bonen et al (1995) 'The evolution of cementitious materials through history' Materials Symposium Proceeds Vol 370
viii Hewlett, P.C. and Lea, F. (Eds.) (1998) *Lea's Chemistry of Cement and Concrete*, 4th ed., Arnold, London

Φ The time frame used relates to a 12 month period, with every 2 hours relating to a 1 month period