The manufacture of quicklime in limekilns
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These notes refer to calcareous quicklime. Manufacture and use of dolomitic lime is quite a different story.

1 Quicklime and lime mortar
If lumps of limestone are heated to a temperature in excess of about 800°C, carbon dioxide is driven off and what remains is quicklime, calcium oxide.

\[
\text{limestone decomposes into quicklime and carbon dioxide} \quad \text{CaCO}_3 \rightarrow \text{CaO} + \text{CO}_2
\]

by weight 100 \rightarrow 56 + 44

The process is called ‘calcination’. If calcination is carried out correctly the lumps of quicklime are approximately the same size as the original lumps of limestone but much less dense, because of the weight loss of 44% arising from the removal of carbon dioxide.

If a precisely controlled amount of water is added to quicklime, a (violent) chemical reaction ensues with much evolution of heat. In this reaction the lumps of quicklime break down to a dry fine white powder known as hydrated lime or lime hydrate.

\[
\text{quicklime} + \text{a controlled amount of water} \rightarrow \text{hydrated lime} \quad (\text{hydrated lime is also called lime hydrate})
\]

\[
\text{CaO} + \text{H}_2\text{O} \rightarrow \text{Ca(OH)}_2
\]

If excess water is added the lime is said to have been slaked and the outcome is a slurry or paste of hydrated lime, such as might be used for lime-washing a wall or for spreading on acid ground to reduce acidity and improve soil structure. Quicklime was also spread directly on the ground and in the eighteenth century its use was often a requirement set down in farm leases. It was also used for disposal of hanged bodies in gaols. Modern uses of quicklime and hydrated lime are outlined in section 5.

Lime mortar consists of a mixture of hydrated lime, sand (and/or other fine grained material such as coal ash) and sufficient water to make a workable paste. It hardens through the reaction of hydrated lime with atmospheric carbon dioxide.

\[
\text{hydrated lime} + \text{atmospheric carbon dioxide react together to produce calcite and water}
\]

\[
\text{Ca(OH)}_2 + \text{CO}_2 \rightarrow \text{CaCO}_3 + \text{H}_2\text{O}
\]

Calcite is the principal constituent of limestone. Hardened lime mortar can be considered to be man-made sandstone bound with calcite cement.

Without access to atmospheric carbon dioxide lime mortar paste will not harden. Lime mortar used in foundations would not have access to atmospheric carbon dioxide so, prior to the invention of Portland cement, foundations were built without a binder to hold the stones together. Lack of sound foundations has been the cause of structural problems in many medieval cathedrals. Portland cement, reinvented in the 19th century, is fundamentally different to quicklime as it achieves its strength through a chemical reaction with water and is eminently suitable for use in permanently damp conditions.
If you purchased ‘lime putty’ it would be in a sealed container or covered by water to prevent premature hardening by reaction with atmospheric carbon dioxide. Lime putty was used extensively for plastering, often mixed with dung and horse hair for added strength. Lime wash, which is slaked lime of paint consistency, is a very effective wall covering and can be coloured by the use of pigments. It is still used as paint, although only for specialist applications.

In the quicklime manufacturing industry the word ‘lime’ is used to mean quicklime, CaO. The word ‘lime’ is also used in the building trade to mean hydrated lime, Ca(OH)$_2$. You have to interpret what is meant by ‘lime’ from the context. Understanding is important, because quicklime is very much more hazardous than hydrated lime. In this account the word quicklime will not be abbreviated to ‘lime’.

2 Early kiln types
A field kiln, like that shown in Figure 1, would have been operated on a batch basis. Alternate layers of limestone and fuel would have been stacked in the kiln, with a fuel to limestone ratio of about 1:4, and the fuel ignited. After about 60 hours quicklime would be removed from the base of the kiln. It is likely that succeeding batches were produced with only a short pause between, as fuel would be wasted firing the kiln from cold on every occasion. Most of the quicklime produced from these early kilns was used locally. David Johnson, in his book on Limestone Industries of the Yorkshire Dales, describes how he has identified kilns of this type in the Craven area built between 1440 and 1700. (For details of this and other references see Section 8).

Field kilns were semi-permanent structures made entirely of stone. In a simple form they appeared in the north of England in the seventeenth century. Only in the mid to late nineteenth century did this design go out of use. Some may have been operated on a continuous basis, with new layers of limestone and fuel being added to the top as quicklime was withdrawn from the base.

It is difficult to assess the fuel efficiency of early kilns; a reasonable estimate would be that more than 250 kg of coal were required to produce 1000 kg of quicklime.

The inner shell of a field kiln was a separate construction from the outer ‘visible’ structure. This design improved insulation and reduced the opportunity for rain water ingress, which could have had disastrous consequences.
Figure 2 is a diagram of a field kiln. Figure 3 is a picture of a similar kiln near Horton-in-Ribblesdale.

Fig 2: Sketch by Titus Thornber of a field limekiln, about 3.5m diameter, based on what he found at Shedden Clough (near Burnley)

Another example of a field kiln is shown in Figure 4. The kiln is adjacent to the road. Like many such kilns, it was built into a slope so that the limestone could be transported downhill en route to the kiln. Cow Ark is in the Forest of Bowland, at NGR SD673454, about 7 miles NW of Clitheroe.

The arrangements at Shedden Clough, near Burnley, were unusual because of the source of the limestone, but they are of special interest and will be described in some detail.

In Shedden Clough are the remains of a large number of relatively primitive kilns. Kilns of various designs were operated over a period of hundreds of years. That is not to say that any of these kilns operated for more than a few months per year; some may have operated for one summer only. Local resident and historian Titus Thornber spent a great deal of time documenting the kilns in this locality; his work is preserved in the local history section of Burnley Public Library.

Fig 3: Field kiln near Horton-in-Ribblesdale
At first sight, Shedden Clough is a very unlikely location for limekilns. There is no bedrock exposure of limestone within many miles, so the limestone could not be won by conventional quarrying. At Shedden, a deposit of till contains boulders of Carboniferous limestone. The limestone was eroded by glaciers in upper Ribblesdale and the Yorkshire dales, transported within the ice to Shedden and deposited there as the ice sheet retreated between about 18,000 and 10,000 years ago. Separating boulders of limestone from the till must have involved considerable effort as they were separated by hushing, Figure 5.

**Fig 4: The well-preserved base of a field kiln at Cow Ark, probably of an early 19th century date**

**Fig 5: Hushing for limestone at Shedden Clough**

Hushing is the process in which a reservoir of water is held back by a dam at the top of a slope, the ground surface below the dam is broken up with picks and shovels and the dam broken. Whoosh! The resulting surge of water entrains the loose surface material and washes it down the slope. Hushing was not confined to Shedden. The process was extensively used for exposing veins of galena in Swaledale, for instance.

The Burnley Geological Memoir describes a four feet thick (1.2m) seam of the Gannister Coal cropping out in Shedden Clough so, although limestone extraction was not straightforward, a fuel supply was available close by.
Titus Thornber produced a detailed map of Shedden Clough, incorporating hushes, limekilns and pack horse tracks. Thornber’s map, reproduced in Figure 6 below, shows just how extensive operations were.

![Map of the area around Shedden Clough, reproduced from Thornber Note: quicklime makers built a mile long leat (goyt, goit) to bring water from Black Clough (top right)](image)

When the Leeds Liverpool canal reached Burnley in about 1800, five limekilns were built on one side of the canal and four on the other. When fired, they obliterated Burnley beneath a pall of smoke and acrid fumes. An Act of Parliament stated that chimneys had to be built up 90 ft. to get the fumes away from the town. The fumes from one bank of kilns were discharged up one tall chimney. Hushing and the manufacture of quicklime at Shedden soon ceased, because it was no longer economic.

3 The evolution of kiln design

The next step in the evolution of lime burning technology was the development of the continuously operated ‘industrial’ kiln, with its output destined for a wider market. Figure 7 shows the principles of operation of a continuous process limekiln. Modern versions are described as shaft kilns. The diagram shows a limekiln being loaded from ‘jubilee’ wagons.

The great benefit of the design of an industrial kiln was the considerable improvement in fuel efficiency. Air for combustion passed through the quicklime, cooling the quicklime and preheating the combustion air at the same time. Exhaust gas from combustion also dried and preheated the feed limestone.

Industrial scale limekilns were certainly in operation by the mid nineteenth century. The bank of kilns shown in Figures 8 to 10 is located on private land near Bellman Quarry, Clitheroe. The kilns were probably built very soon after the completion of the railway in 1850.

The Bellman limekilns, like many others, were designed so that quicklime could be loaded directly into full sized railway wagons.
Fig 7: Principles of operation of an early continuous process limekiln
In this diagram the fuel is described as coke; coal, wood and charcoal were also used.

Fig 8: Bank of four industrial scale limekilns near Bellman Quarry. Clitheroe

Fig 9: Photograph of the Bellman limekilns in operation. The long bridge-like structure supported an endless chain conveyor which carried limestone and fuel to the top of the bank of kilns (which is to the left of the chimney).
In the early design of continuous process kilns the fuel was fed into the top with the limestone. This may not have mattered much if the fuel was coke, but it did not make good use of coal. Coal typically contains between 20 and 30% by weight of volatile matter, consisting of methane and other combustible gases. Because the coal was heated slowly the volatile matter was evaporated before the temperature was high enough for it to burn. Consequently much of the heat value of the coal was wasted.

In 1802 Romford invented a more fuel-efficient kiln in which the fuel was introduced into the calcining zone, the hottest part of the kiln, Figure 11. Because of the difficulty of introducing coal into the centre of kilns of this design, the kilns were of limited diameter. All modern limekilns introduce fuel into the calcining zone.

The motive power for drawing air and gas through the kiln was initially provided by convection, sometimes supported in earlier designs by orientation of the quicklime withdrawal arch towards the prevailing wind. A chimney was sometimes used to maximise the benefit from convection, but then a gas tight seal was required at the limestone feed point. A kiln of this design is located at Toft Gate, near Greenhow in north Yorkshire, Figures 12 to 14. The chimney is on higher ground, connected to the limekiln by a flue. Gas flow control was achieved by restricting the fresh air input to the kiln.

Fig 10: Remains of the wooden chutes used to transfer quicklime directly from the Bellman kilns to railway trucks
In modern kilns the motive power for drawing gas through the kiln comes from an induced draught fan, the suction side of which is connected to the top of the kiln.

Fig 11: Limekiln with coal chutes

Fig 12: The remains of the flue and chimney stack at Toft Gate. Except when limestone was being loaded to the kiln an iron plate was used to seal the top of the kiln

Fig 13: The kiln with coal feeding ports at ground level
The quicklime withdrawal arch is lower down at the back
Figure 14: Inside Toft Gate kiln

Figure 14 shows the inside of the Toft Gate kiln. The rectangular coal feed ports can clearly be seen and the distorted lining shows the impact of high temperatures inside the kiln. Even today, refractory linings of limekilns require regular replacement.

A successful advance in kiln design was made by Hoffmann, who invented an annular (ring shaped) kiln. Variants of this design are still used today for brick manufacture.

In principle the Hoffmann kiln is a vertical shaft kiln placed on its side in a ring. Three zones, (i) limestone preheating, (ii) conversion to quicklime (calcining) and (iii) quicklime cooling, are located horizontally inside an annular tunnel. Although the design was efficient, it was very labour intensive because the stone had to be stacked and the quicklime removed by hand.

Consider the kiln in normal operation, as shown in Figure 15, sketch 1. All the arched access doors (wickets) between positions B and A are bricked up and sealed. One steel door near to the tunnel seal at position A is open and provides a route for exhaust gas to pass into the flue gas duct. All other steel doors around the whole kiln tunnel are closed so that gas is only drawn through the successive quicklime cooling, calcining and limestone preheating zones and ultimately up the stack. For that reason the tunnel seal at position A is a vitally important gas tight seal. The seal at A is made of paper (papier mâché) so that it can quickly be removed later. While operating in the condition shown in sketch 1 new stone lumps are piled up to fill the tunnel between position A and A1. The tunnel must be filled completely or the gas will pass around the pile of stone instead of through it. To avoid too much gas passing through the material near the top of the tunnel and too little lower down (because hot air rises) there are small apertures near the base of the stone pile and parallel to the tunnel, along which hot gas encounters reduced flow resistance.

When the stone in the red zone has been converted to quicklime, the operation is ready to move one chamber clockwise to the condition shown in Figure 15 sketch 2. A new paper seal is fitted at position A1 and the arched access doors between A and A1 are bricked up and sealed. The steel door to the flue gas duct near A1 is opened and that near to A closed. The old seal at position A would normally burn away, but if necessary was ripped out. The whole ‘lime burning’ operation that previously took place between B and A has now moved one step clockwise. The final action is to open the side door near to position B1 for fresh air input. The access doors between B and B1 are then opened up and the relatively cool quicklime located between points B and B1 is removed by hand without any interference with kiln operation.
For ease of explanation the three zones have been shown to be the same length. In practice each zone would consist of several chambers. In large kilns the active part of the process occupied rather less than half the length of the annular tunnel. Two separate lime burning operations could then be operated at the same time, 180° apart. Much maintenance could be carried out in the ‘empty’ section without interfering with kiln operation, so these kilns could operate for years without stopping.

Figure 15: Plan view of Hoffmann kiln showing principle of operation. The zones are located inside an annular tunnel. The exhaust gases leave via a chimney located above the central blue arrows on the diagram.

The base of a Hoffmann kiln at Langcliffe, near Settle, is well preserved but it lacks chimney and superstructure. The site is open to the public, but not well signed. There are explanation boards and a short trail. Also on the site are examples of industrial kilns and two, more modern, vertical steel-shelled Spencer kilns.

Figure 16 is a photograph taken in the straight tunnel at one side of the Langcliffe kiln. The apparent size of the person at the end of the tunnel gives some idea of its size. The complete annular tunnel consists of two straight sections, like the one shown, joined together at both ends by two semi-circular tunnels of the same size.
Fig 16: View down the tunnel on one side of the Hoffmann kiln at Langcliffe, near Settle

Figures 17 and 18 are pictures of the Hoffmann kiln, now demolished, at Harpur Hill Buxton. It is reported (Leach) that the kiln was lit in 1872 and the fire never went out until 1944 when the kiln was finally shut down. The picture has been reproduced by agreement with ‘Picture the Past’ with acknowledgements to Derbyshire County Council Environmental Services, see website: http://www.picturethepast.org.uk/frontend.php?keywords=Ref_No_increment;EQUALS;PTPD200949&pos=3&action=zoom&id=110212.

A Hoffmann kiln at Zehdenick was used for brick making. It has been very well preserved, see picture on website: http://en.wikipedia.org/wiki/File:Ringofen_Ansicht.jpg

Fig 17: Stone loading into the Hoffmann kiln at Harpur Hill, Buxton
Fig 18: Hoffmann kiln at Harpur Hill, Buxton, courtesy of ‘Picture the Past’ This kiln has now been demolished

Figure 19 is a diagram of the Hoffmann kiln at Llanymynech. In the foreground is the ramp for taking coal into the covered area, from which it is fed though vertical chutes into the calcining zones of the kiln. Alongside the ‘wicket’ arches, which give access to the kiln tunnel, are ‘jubilee’ wagons for transporting limestone to the kiln and taking away quicklime. The diagram was kindly provided by the Llanymynech Community Project, web address: http://www.llanymynech.org.uk/html/hoffman_kiln.html

Today most limekilns consist of one or more vertical steel tubes, lined with refractory brick. They are always fitted with induced draught fans to optimise gas flow through the kiln and maximise production. They operate on a similar principle to that shown in Fig 10.
Critical success factors in the manufacture of quicklime.

Much has to be ‘done right’ to make good quality quicklime. Today manufacture is controlled with the aid of a deeper scientific understanding of the process and high quality instrumentation. In earlier times the quality of the quicklime depended on the skill and experience of the ‘lime burner’.

The first important parameters are temperature and residence time. Certainly a temperature of between 800 and 900°C is a primary requirement and the residence time must be sufficient for that temperature to be reached in the centre of each lump of limestone. If the correct time temperature relationship is achieved then the lumps of quicklime will be about the same size as the limestone feed and the quicklime produced will be highly reactive. In modern production facilities quicklime reactivity is measured by dropping a prescribed weight of quicklime into a known volume of water and monitoring the temperature rise. In the old days it would have been sufficient to drop a lump of quicklime into water; the violent reaction accompanied by fizzing and even local boiling of the water. If limestone is heated to too high a temperature for too long the lumps of quicklime become compacted and partially fused. The resulting dense quicklime is described as ‘dead burnt’. If you drop a lump of dead burnt quicklime into water, no sign of a reaction can be seen. For most applications highly reactive quicklime is required.

The particle size distribution of the limestone feed is important. Modern vertical kilns used for the production of quicklime are fed with limestone lumps that typically would be small enough to pass through a sieve with a 100mm square mesh and large enough not to pass through a 50mm square one. The two to one ratio of stone size has historically been a ‘golden rule’ in the industry. In the kiln, the air for combustion and the resulting exhaust gases have to pass between the lumps of limestone and this stone size range provides sufficient gas permeability, as shown in Figure 19. Insufficient gas flow, insufficient air for combustion, insufficient heat, insufficient temperature, no quicklime!

The centre of a lump of limestone that is too large is not fully converted into quicklime in the kiln. A lump of quicklime withdrawn from the kiln but retaining a limestone core is known as a ‘bullhead’. Even in the 1980s the author can remember bullheads being removed by operators ‘picking’ from the moving belt conveyor which transported quicklime from kiln to storage. Removal of bullheads improved the quality of the quicklime despatched to customers.
For kilns that were loaded with alternate layers of limestone and fuel, the particle size range of the fuel was also important. Physically robust fuels such as coke presented no problems, but fine grained coal, peat, wood and bracken were also used and could restrict gas flow. High ash fuels would be avoided because the ash was likely to fuse and stick the lumps of quicklime together, causing blockages near the outlet from the kiln. Most lime burners would have had little choice; they would just have had to use what fuel was available and learn to deal with the consequences.

High purity limestone is the key to the manufacture of good quality quicklime. If the limestone contains silica rich impurities such as mudstone, quality problems are likely to arise. The raw material for Roman cement is a mixture of limestone and mudstone, which is a source of silica. At a temperature much the same as is required for lime burning, the mudstone and quicklime combine to form anhydrous calcium silicates. Anhydrous calcium silicates are the principal strength-forming minerals in cement. They undergo a chemical reaction with water and set hard. Roman cement is not quicklime!

The cost of supply of quicklime to customers includes manufacture and transport. Prior to canals and railways, pack horses would have been the principal means of transport. Quicklime was carried in sacks or boxes slung across the backs of the pack horses, see Figure 20. The animals were small Galloway ponies, known as lime-gals, but it likely that donkeys and mules were used too. A good supply of limestone near Clitheroe resulted in the construction of large numbers of limekilns. In 1773 between 500 and 1000 packhorse loads of quicklime per day passed through the town. Quicklime was carried because the addition of water, to convert it to hydrated lime, would have increased the load on the pack horses. However, if water penetrated into the quicklime, the boxes or sacks would set on fire; an unsettling experience for the pack horse!

5 Historical uses of quicklime
Quicklime mixed with just enough water to break down into a dry powder is known as hydrated lime. If more water is added the quicklime is described as slaked. Historically, for use inside buildings, the quicklime was slaked sufficiently to make a paste known as lime putty, of the consistency of whipped cream. Clearly that portion of quicklime which was dead burnt (overcooked) would take a long time to hydrate.

An architect, interviewed about the National Trust property Ightham Mote near Sevenoaks, said that the lime putty used for the restoration was stored in a sealed container for twelve months prior to use. It seems likely that in the past quicklime reactivity was not well controlled and in an attempt to convert large lumps of limestone to quicklime the small lumps were dead burnt. Dead burnt quicklime would hydrate long after the mortar had hardened and the expansion during hydration would damage the mortar. Today six months would be enough time to store lime putty prior to use.
In the recipe for wattle and daub the proportions used were 4 to 1.5 to 1, lime putty to sharp sand to cow dung with finely chopped straw, horse hair or sheep’s wool added as a binder. Thorough mixing was required either by use of a pug mill or by treading, chopping and treading again for at least 30 minutes.

A finishing coat without the fibrous binder was applied for the final finish and pigment could be mixed with this coat.

Lime plaster, which is how the finishing coat would normally be described, was used in Anatolia in about 7000 BC. From the time of the first Greek civilisation its use was commonplace.

It is possible that lime putty mixed with sand and/or coal ash and/or volcanic ash to produce a mortar was established before 2000BC. It is known, however, that the Egyptians used ‘gypsum mortar’ in the pyramids, probably because that raw material was readily available locally and required less heat in its manufacture.

In the early 16th century it was discovered that quicklime could be used to ‘improve’ acid peaty ground so that grass could be grown for sheep grazing. Slaked lime was widely used and many small clamp kilns were built, many of them producing a batch of quicklime only a few times a year. The fuels used included wood, bracken and peat, so the quicklime quality was probably poor. Limestone could be used instead of quicklime but only if ground very finely. Ground limestone is very much slower acting but is used today as it is cheaper than quicklime.

6 Modern uses of quicklime
Quicklime is more widely used than is generally recognised. The short list which follows gives some idea of the breadth of its application. Uses include:-

- purification of drinking water
- removal of silica, sulphur and carbon in the basic oxygen process used to treat molten iron discharged from a blast furnace
- lime mortar and associated products
- sewage treatment
- neutralisation of acid mine drainage
- flue gas desulphurisation
- manufacture of paper
- tanning
- manufacture of bleaching powder
- soap
- removing impurities in the manufacture of sugar

7 Portland cement and hydraulic lime
The familiar grey powder, Ordinary Portland Cement (OPC), is radically different from quicklime. OPC is made to a tightly controlled recipe consisting of about 80% limestone and 20% siliciclastics. The finely ground raw material is heated in a horizontal kiln to a temperature of close to 1400°C, under which conditions quicklime is combined with silica and the material agglomerates to a black bally material known as clinker. The cooled clinker is ground with about 5% gypsum to produce OPC. The active ingredients of OPC are anhydrous dicalcium and tricalcium silicates, \((\text{CaO})_2\text{SiO}_2\) and \((\text{CaO})_3\text{SiO}_2\) respectively. Quicklime hardens by reaction with \(\text{CO}_2\) but these silicates harden through a chemical reaction with water. OPC is therefore described as hydraulic and it is this property which has made OPC such a universal binder, ideal for use away from atmospheric \(\text{CO}_2\) such as in foundations,
harbour walls etc. Tricalcium silicate hydrates rapidly and it is this property which gives OPC a high strength after 24 hours, although its ultimate strength is only approached after about a month.

In the manufacture of early cements, such as Roman cement, a temperature of only 900°C or so was achieved, a temperature only sufficient for the formation of dicalcium silicate. Dicalcium silicate hydrates slowly, only developing significant strength after a week but ultimately achieving a similar strength to tricalcium silicate.

In between the extremes of OPC and quicklime are a range of compounds known as hydraulic limes. When lumps of impure limestone containing siliciclastics are heated in a lime kiln, hydraulic lime is produced, the hydraulicity dependent on the proportion of siliciclastics. Hydraulic lime hardens both through silicate hydration and carbonation of quicklime (in the form of hydrated lime). Both quicklime and hydraulic lime are widely used today in the repair of historic buildings which predate the invention of OPC in the mid nineteenth century.

If quicklime is hydrated in the presence of highly reactive and fine grained silicate, such as volcanic ash, some hydraulicity is achieved through a reaction between quicklime and silica at room temperature. The Romans used ash from Pozzuoli near Naples and even today materials which are used as a partial substitute for OPC are known as pozzalans.

8 References and bibliography


Thornber, T. Notes and informal publications by Titus Thornber with a map of Shedden Clough, all kept in Burnley Public Library local history section.

A film of his presentation about Shedden Clough has been preserved electronically in Clitheroe Sound Archive, located at Clitheroe Museum.