PART 1

Cements

1

Cements

Graeme Moir

1.1 Introduction

The aims and objectives of this chapter are to:

- describe the nature of Portland (calcium-silicate-based) cements
- outline the manufacturing process and the quality control procedures employed
- review the cement hydration processes and the development of hydrated structures
- outline the influence of differences in cement chemistry and compound composition on the setting and strength development of concrete
- review cement types (including composite and masonry cements) and the nature of their constituents
- review the standards with which cements must comply and the applications for different cement types
- describe in outline methods used for chemical analysis and to study the hydration of cement
- briefly outline some health and safety aspects related to cement use

1.2 History of Portland cement manufacture

Portland cement is essentially a calcium silicate cement, which is produced by firing to partial fusion, at a temperature of approximately 1500°C, a well-homogenized and finely ground mixture of limestone or chalk (calcium carbonate) and an appropriate quantity of clay or shale. The composition is commonly fine tuned by the addition of sand and/or iron oxide.

The first calcium silicate cements were produced by the Greeks and Romans, who discovered that volcanic ash, if finely ground and mixed with lime and water, produced a hardened mortar, which was resistant to weathering. The reaction is known as the pozzolanic reaction and it is the basis of the contribution made to strength and concrete performance by materials such as fly ash, microsilica and metakaolin in modern concrete.

In the mid eighteenth century John Smeaton discovered that certain impure limes (these contained appropriate levels of silica and alumina) had hydraulic properties. That is, they contained reactive silicates and aluminates, which could react with water to yield durable hydrates, which resisted the action of water. Smeaton used this material in the mortar used to construct the Eddystone Lighthouse in 1759.

The term 'Portland cement' was first applied by Joseph Aspdin in his British Patent No. 5022 (1824), which describes a process for making artificial stone by mixing lime with clay in the form of a slurry and calcining (heating to drive off carbon dioxide and water) the dried lumps of material in a shaft kiln. The calcined material (clinker) was ground to produce cement. The term 'Portland' was used because of the similarity of the hardened product to that of Portland stone from Dorset and also because this stone had an excellent reputation for performance.

Joseph Aspdin was not the first to produce a calcium silicate cement but his patent gave him the priority for the use of the term 'Portland cement'. Other workers were active at the same time or earlier, most notably Louis Vicat in France. Blezard (1998) gives a comprehensive review of the history of the development of calcareous (lime-based) cements.

The cements produced in the first half of the nineteenth century did not have the same compound composition as modern Portland cements as the temperature achieved was not high enough for the main constituent mineral of modern cements, tricalcium silicate (C_3S), to be formed. The only silicate present was the less reactive dicalcium silicate (C_2S). The sequences of reactions, which take place during clinker production, are discussed in section 1.3.3.

The main technical innovations in cement manufacture which have taken place over approximately the last 150 years are summarized in Figure 1.1.

It was the introduction of the rotary kiln at the end of the nineteenth century that enabled a homogeneous product to be manufactured, which had experienced a consistently high enough temperature to ensure C_3S formation. During the twentieth century the nature of the product changed relatively little in terms of its overall chemistry and mineral composition but there have been considerable advances in production technology resulting in improved energy efficiency, improved quality control, reduced environmental impact and lower labour intensity.

It should be noted that the introduction of rotary kiln technology in the early twentieth century coincided with the publication of cement standards in the UK and the USA. Both standards required the strength of a briquette of cement paste to reach minimum values at 7 and 28 days.

The control of clinker composition has advanced from the volume proportions arrived at by trial and error in the late nineteenth century to precise control using rapid X-ray fluorescence techniques. The continuous improvements in manufacturing methods and quality control combined with market competitive pressures have resulted in a fourfold increase in the 28-day strength given by a typical European Portland cement at 28 days since the late nineteenth century. (Blezard, 1998). In Europe, this strength escalation has effectively been controlled by the introduction of cement standards with upper as well as

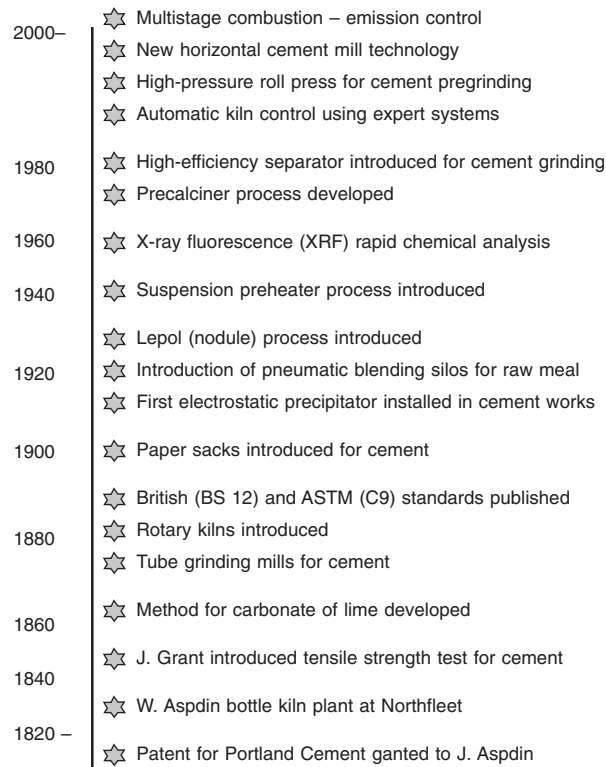lower strength limits. The European Standard for Common Cements (EN 197-1) is outlined in section 1.6.3.

Figure 1.1 Landmarks in Portland cement production.

1.3 Chemistry of clinker manufacture

1.3.1 Raw materials

Cement making is essentially a chemical process industry and has much in common with the manufacture of so-called heavy chemicals such as sodium hydroxide and calcium chloride. Close control of the chemistry of the product is essential if cement with consistent properties is to be produced. This control applies not only to the principal oxides which are present but also to impurities, which can have a marked influence on both the manufacturing process and cement properties.

As illustrated in Figure 1.2, a chemical analysis of Portland cement clinker shows it to consist mainly of four oxides: CaO (lime), SiO_2 (silica), Al_2O_3 (alumina) and Fe_2O_3 (iron oxide). In order to simplify the description of chemical composition, a form of shorthand is used by cement chemists in which the four oxides are referred to respectively as C, S, A and F.

Expressing the chemical analysis in the form of oxides, rather than the individual elements of silicon (Si), calcium (Ca) etc., has the advantage that the analysis total should
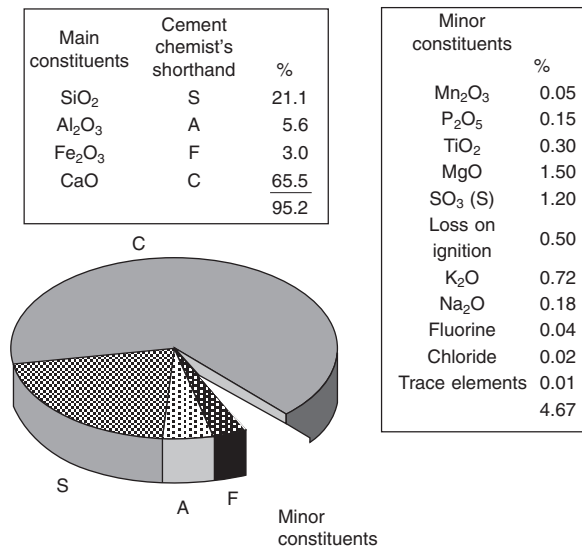
Main constituents	Cement chemist's shorthand	%
SiO$_2$	S	21.1
Al$_2$O$_3$	A	5.6
Fe$_2$O$_3$	F	3.0
CaO	C	65.5
		95.2

Minor constituents	%
Mn$_2$O$_3$	0.05
P$_2$O$_5$	0.15
TiO$_2$	0.30
MgO	1.50
SO$_3$ (S)	1.20
Loss on ignition	0.50
K$_2$O	0.72
Na$_2$O	0.18
Fluorine	0.04
Chloride	0.02
Trace elements	0.01
	4.67

Figure 1.2 Typical chemical composition of Portland cement clinker.

come close to 100, and this provides a useful check for errors. Oxidizing conditions are maintained during the burning process and this ensures that the metallic elements present are effectively present as oxides although combined in the clinker as minerals.

The source of lime for cement making is usually limestone or chalk. As typically 80% of the raw mix consists of limestone, it is referred to as the primary raw material. The secondary raw material, which provides the necessary silica, alumina and iron oxide, is normally shale or clay. Small quantities of sand or iron oxide may be added to adjust the levels of silica and iron oxide in the mix. When proportioning the raw materials, an allowance must be made for ash incorporated into the clinker from the fuel that fires the kiln. Most cement plants worldwide use finely ground (pulverized) coal as the primary fuel. Increasingly, by-product fuels such as the residue from oil refining (petroleum coke) and vehicle tyres are being used to partially replace some of the coal.

Typical contents of the four principal oxides in a simplified cement making operation utilizing only two raw materials are given in Figure 1.3.

Note that the ratio of CaO to the other oxides is lower in the clinker than in the raw mix. This is a result of the incorporation of shale from the coal ash. The levels of the oxides are also increased as a result of decarbonation (removal of CO$_2$).

1.3.2 The modern rotary kiln

The rotary kilns used in the first half of the twentieth century were wet process kilns which were fed with raw mix in the form of a slurry. Moisture contents were typically 40% by mass and although the wet process enabled the raw mix to be homogenized easily, it carried a very heavy fuel penalty as the water present had to be driven off in the kiln.

In the second half of the twentieth century significant advances were made which have culminated in the development of the precalciner dry process kiln. In this type of kiln, the
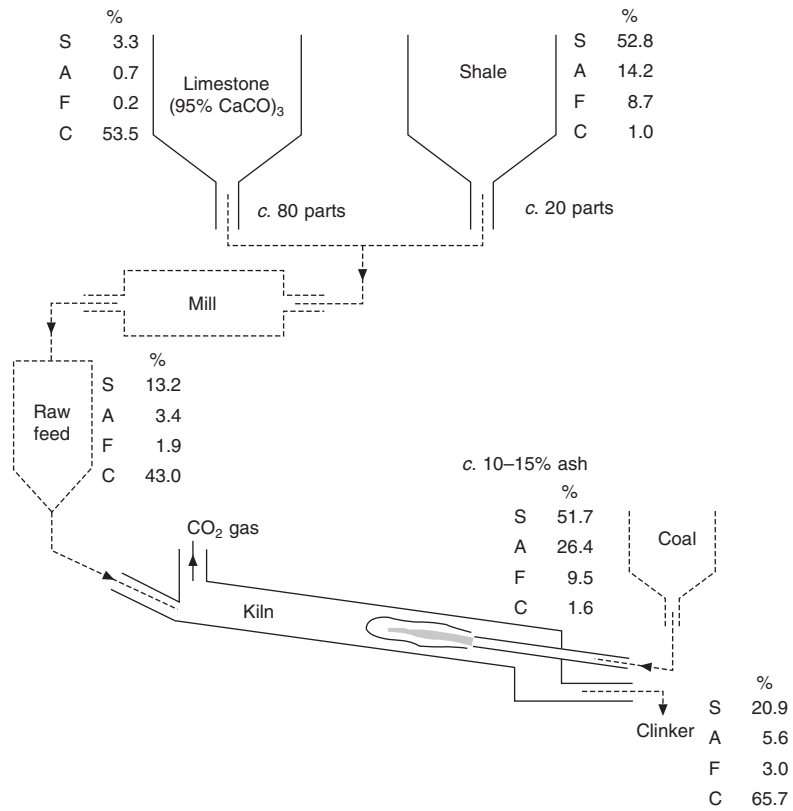
%
S 3.3
A 0.7
F 0.2
C 53.5

Limestone
(95% CaCO$_3$)

Shale

%
S 52.8
A 14.2
F 8.7
C 1.0

c. 80 parts

c. 20 parts

Mill

%
S 13.2
A 3.4
F 1.9
C 43.0

Raw
feed

CO$_2$ gas

c. 10–15% ash

%
S 51.7
A 26.4
F 9.5
C 1.6

Coal

Kiln

%
S 20.9
A 5.6
F 3.0
C 65.7

Clinker

Figure 1.3 Typical chemical analyses of materials.

Raw feed

Cyclones

Precalciner vessel

Back-end fuel

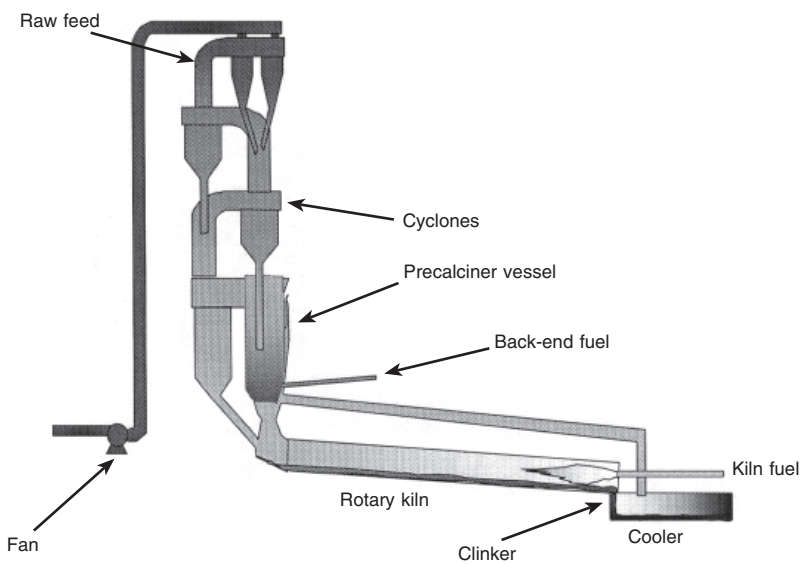Kiln fuel

Rotary kiln

Cooler

Clinker

Fan

Figure 1.4 The modern precalciner kiln.

energy-consuming stage of decarbonating the limestone present in the raw mix is completed before the feed enters the rotary kiln. The precalcination of the feed brings many advantages, the most important of which is high kiln output from a relatively short and small-diameter rotary kiln. Almost all new kilns installed since 1980 have been of this type. Figure 1.4 illustrates the main features of a precalciner kiln.

The raw materials are ground to a fineness, which will enable satisfactory combination to be achieved under normal operating conditions. The required fineness depends on the nature of the raw materials but is typically in the range 10–30% retained on a 90 micron sieve. The homogenized raw meal is introduced into the top of the preheater tower and passes downwards through a series of cyclones to the precalciner vessel. The raw meal is suspended in the gas stream and heat exchange is rapid. In the precalciner vessel the meal is flash heated to ~900°C and although the material residence time in the vessel is only a few seconds, approximately 90% of limestone in the meal is decarbonated before entering the rotary kiln. In the rotary kiln the feed is heated to ~1500°C and as a result of the tumbling action and the partial melting it is converted into the granular material known as clinker. Material residence time in the rotary kiln of a precalciner process is typically 30 minutes. The clinker exits the rotary kiln at ~1200°C and is cooled to ~60°C in the cooler before going to storage and then being ground with gypsum (calcium sulfate) to produce cement. The air which cools the clinker is used as preheated combustion air thus improving the thermal efficiency of the process. As will be discussed in section 1.5, the calcium sulfate is added to control the initial hydration reactions of the cement and prevent rapid, or flash, setting.

If coal is the sole fuel in use then a modern kiln will consume approximately 12 tonnes of coal for every 100 tonnes of clinker produced. Approximately 60% of the fuel input will be burned in the precalciner vessel. The high fuel loading in the static precalciner vessel reduces the size of rotary kiln required for a given output and also reduces the consumption of refractories. A wider range of fuel types (for example, tyre chips) can be burnt in the precalciner vessel than is possible in the rotary kiln.

Although kilns with daily clinker outputs of ~9000 tonnes are in production in Asia most modern precalciner kilns in operation in Europe have a production capability of between 3000 and 5000 tonnes per day.

1.3.3 Clinkering reactions and the minerals present in Portland cement clinker

Portland cement clinker contains four principal chemical compounds, which are normally referred to as the clinker minerals. The composition of the minerals and their normal range of levels in current UK and European Portland cement clinkers are summarized in Table 1.1.

It is the two calcium silicate minerals, C_3S and C_2S, which are largely responsible for the strength development and the long-term structural and durability properties of Portland cement. However, the reaction between CaO (lime from limestone) and SiO_2 (silica from sand) is very difficult to achieve, even at high firing temperatures. Chemical combination is greatly facilitated if small quantities of alumina and iron oxide are present (typically 5% Al_2O_3 and 3% Fe_2O_3), as these help to form a molten flux through which the lime and silica are able to partially dissolve, and then react to yield C_3S and C_2S.

Table 1.1 Ranges of principal minerals in European clinkers

Shorthand nomenclature	Chemical formula	Mineral name	Typical level (mass %)	Typical range (mass %)
C_3S	$3CaO \cdot SiO_2$ or Ca_3SiO_5	Alite	57	45–65
C_2S	$2CaO \cdot SiO_2$ or Ca_2SiO_4	Belite	16	10–30
C_3A	$3CaO \cdot Al_2O_3$ or $Ca_3Al_2O_6$	Aluminate	9	5–12
C_4AF	$4CaO \cdot Al_2O_3 \cdot Fe_2O_3$ or $Ca_4Al_2Fe_2O_{10}$	Ferrite	10	6–12

The sequence of reactions, which take place in the kiln, is illustrated in Figure 1.5.
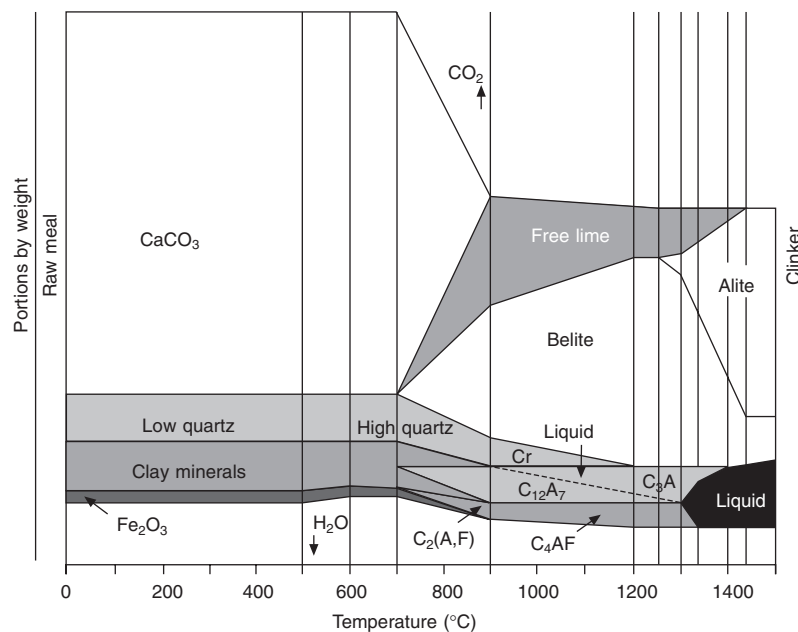

Figure 1.5 Sequence of reactions taking place during the formation of Portland cement clinker. (*Source:* Reproduced by courtesy of KHD Humbolt Wedag AG.)

The reaction requiring the greatest energy input is the decarbonation of $CaCO_3$, which takes place mainly in the temperature range 700–1000°C. For a typical mix containing 80% limestone the energy input to decarbonate the $CaCO_3$ is approximately 400 kCal/kg of clinker, which is approximately half of the total energy requirement of a modern dry process kiln.

When decarbonation is complete at about 1100°C, the feed temperature rises more rapidly. Lime reacts with silica to form belite (C_2S) but the level of unreacted lime remains high until a temperature of ~1250°C is reached. This is the lower limit of thermodynamic stability of alite (C_3S). At ~1300°C partial melting occurs, the liquid phase (or flux) being provided by the alumina and iron oxide present. The level of

unreacted lime reduces as C_2S is converted to C_3S. The process will be operated to ensure that the level of unreacted lime (free lime) is below 3%.

Normally, C_3S formation is effectively complete at a material temperature of about 1450°C, and the level of uncombined lime reduces only slowly with further residence time. The ease with which the clinker can be combined is strongly influenced by the mineralogy of the raw materials and, in particular, the level of coarse silica (quartz) present. The higher the level of coarse silica in the raw materials, the finer the raw mix will have to be ground to ensure satisfactory combination at acceptable kiln temperatures.

Coarse silica is also associated with the occurrence of clusters of relatively large belite crystals around the sites of the silica particles. Figures 1.6(a) and 1.6(b) are photomicrographs of a 'normal' clinker containing well-distributed alite and belite and clinker produced from a raw meal containing relatively coarse silica.
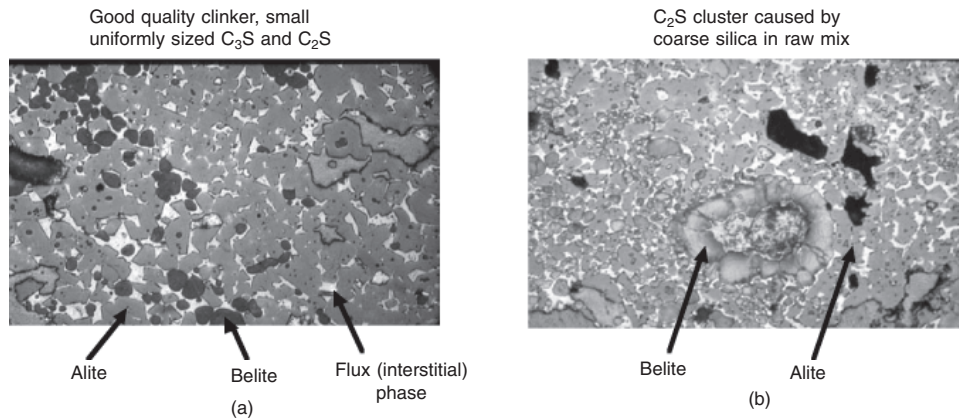

Good quality clinker, small uniformly sized C_3S and C_2S

C_2S cluster caused by coarse silica in raw mix

Alite   Belite   Flux (interstitial) phase   Belite   Alite
(a)   (b)

Figure 1.6 Reflected light photomicrographs of Portland cement clinker.

The belite present in the clusters is less reactive than small well-distributed belite and this has an adverse influence on cement strengths.

As the clinker passes under the flame it starts to cool and the molten C_3A and C_4AF, which constitute the flux phase, crystallize. This crystallization is normally complete by the time the clinker exits the rotary kiln and enters the cooler at a temperature of ~ 1200°C. Slow cooling should be avoided as this can result in an increase in the belite content at the expense of alite and also the formation of relatively large C_3A crystals which can result in unsatisfactory concrete rheology (water demand and stiffening).

1.3.4 The control ratios

The control of clinker composition, and optimization of plant performance is greatly assisted by the use of three ratios:

$$\text{Lime saturation factor LSF} = \frac{C}{2.8S + 1.2A + 0.65F} \times 100\%$$

$$\text{Silica ratio SR} = \frac{S}{A + F}$$

$$\text{Alumina ratio AR} = \frac{A}{F}$$

The most critical control ratio is the lime saturation factor, which is determined by the ratio of lime, to silica, alumina and iron oxide, and governs the relative proportions of C_3S and C_2S. The formula for LSF has been derived from high-temperature phase equilibria studies. When the LSF is above 100% there is an excess of lime, which cannot be combined no matter how long the clinker is fired, and this remains as free lime in the clinker. As a low level of uncombined lime must be achieved (~ 3% maximum and preferably below 2%), clinker LSFs normally lie in the range 95–98%. Figure 1.7 illustrates the influence of LSF on the content of C_3S and C_2S, and the firing temperature required to maintain clinker-free lime below 2% (normally referred to as the combinability temperature). The contents of C_3S and C_2S have been calculated by the so-called Bogue method. This procedure is discussed further in section 1.3.5. Normally, if the LSF is increased at a particular cement plant, the raw mix must be ground finer, i.e. the percentage of particles coarser than 90 microns is reduced.
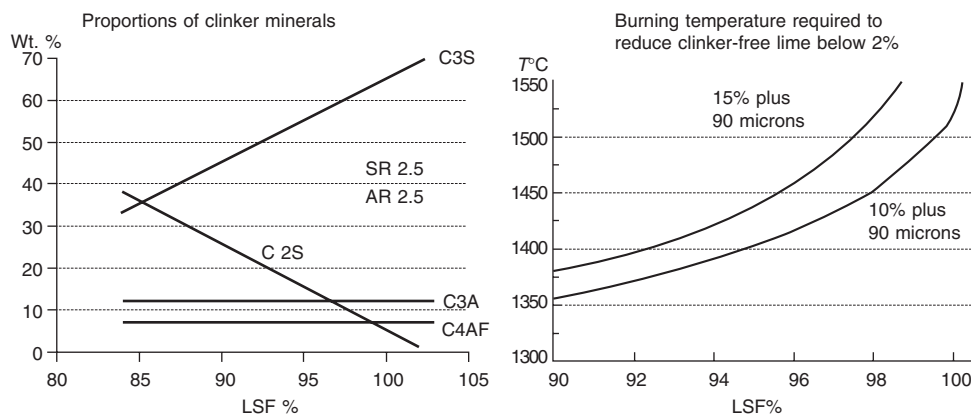

Figure 1.7 Influence of clinker LSF on compound composition and ease of combination.

In order to ensure optimum kiln performance and uniform cement quality it is essential that the LSF of the raw mix LSF is maintained within a narrow band, ideally ±2% or, more precisely, with a standard deviation of better than 1%, determined on hourly samples. As a change in LSF of 1% (at constant free lime) corresponds to a change in C_3S of ~2% the C_3S variability range is approximately double that of the LSF range.

The silica ratio, SR, is the ratio of silica to alumina and iron oxide. For a given LSF, the higher the silica ratio, the more C_3S and the less C_3A and C_4AF will be produced. Of greater significance, with regard to clinker manufacture, is that the higher the SR, the less molten liquid, or flux, is formed. This makes clinker combination more difficult unless the LSF is reduced to compensate. The flux phase facilitates the coalescence of the clinker into nodules and also the formation of a protective coating on the refractory kiln lining. Both are more difficult to achieve as the SR increases.

The alumina ratio, AR, is normally the third ratio to be considered. An AR of ~1.4 is normally optimum for clinker burning, as at this value the quantity of liquid phase formed when partial melting first occurs at ~1300°C is maximized. High AR cements will have

a high C_3A content, and this can be disadvantageous in certain cement applications, for example where it is desired to minimize the concrete temperature rise. Fortunately, the AR ratio is relatively easy to control by means of a small addition of iron oxide to the mix.

As a result of market requirements for cements from different sources to have similar properties and also to optimize clinker production there has been a trend to converge on a 'standard' clinker chemistry of

LSF   95 – 97%
SR   2.4 – 2.6
AR   1.5 – 1.8

At most plants the achievement of this ideal chemistry will require the use of corrective materials such as sand and iron oxide.

1.3.5 Calculation of clinker compound composition

The levels of the four clinker minerals can be estimated using a method of calculation first proposed by Bogue in 1929 (see Bogue, 1955). The method involves the following assumptions:

- all the Fe_2O_3 is combined as C_4AF
- the remaining Al_2O_3 (i.e. after deducting that combined in C_4AF) is combined as C_3A

The CaO combined in the calculated levels of C_3A and C_4AF and any free lime are deducted from the total CaO and the level of SiO_2 determines the proportions of C_3S and C_2S. The procedure can be expressed mathematically (in mass%) as follows:

$$C_3S = 4.071(\text{total CaO} - \text{free lime}) - 7.600SiO_2 - 6.718Al_2O_3 - 1.430Fe_2O_3$$

$$C_2S = 2.867SiO_2 - 0.7544C_3S$$

$$C_3A = 2.65Al_2O_3 - 1.692Fe_2O_3$$

$$C_4AF = 3.043Fe_2O_3$$

The calculated figures may not agree exactly with the proportions of the clinker minerals determined by quantitative X-ray diffraction or by microscopic point counting. However, they give a good guide to cement properties in terms of strength development, heat of hydration and sulfate resistance.

When calculating the compound composition of cements (rather than clinkers) the normal convention is to assume that all the SO_3 present is combined with Ca (i.e. is present as calcium sulfate). The total CaO is thus reduced by the free lime level and by $0.7 \times SO_3$. Examples of the calculation for cements are given in Table 1.7 later in this chapter.

1.3.6 Influence of minor constituents

As illustrated in Figure 1.2, approximately 95% of clinker consists of the oxides of CaO, SiO_2, Al_2O_3 and Fe_2O_3 (but present in combined form as the clinker minerals) and the

remainder consists of the so-called minor constituents. The influence of minor constituents on cement manufacture and cement properties has been reviewed (Moir and Glasser, 1992; Bhatty, 1995).

Table 1.2 indicates the typical UK levels of the most commonly encountered minor constituents and summarizes their impact on the cement manufacturing process. The inputs of alkali metal oxides (Na_2O and K_2O), SO_3 and chloride have to be closely controlled because they are volatilized in the kiln and can cause severe operational problems associated with their condensation and the formation of build-ups in the kiln 'back end' and preheater.

Table 1.2 Influence of most commonly encountered minor constituents on manufacturing process

Minor constituent	Typical range of levels in UK clinkers	Influence on process
Na_2O	0.07 – 0.22	Alkali sulfates are volatilized in the kiln and condense in lower-temperature regions resulting in build-ups and blockages
K_2O	0.52 – 1.0	
SO_3	0.5 – 1.5	
Fluorine	0.01 – 0.20	Greatly assists combination by virtue of mineralizing action
Chloride	0.005 – 0.05	Alkali chlorides are highly volatile and cause build-ups and blockages
MgO	0.8 – 2.5	Slight fluxing action
Trace metals	5–100ppm	Slight – but some (e.g. thallium) have to be minimized to limit emissions to the environment

The alkali metals Na_2O and K_2O have a very strong affinity for SO_3 and a liquid phase containing Na^+, K^+, Ca^{2+} and SO_4^{2-} ions is formed which is immiscible with the main clinker liquid (molten C_3A and C_4AF). On cooling this crystallizes to yield alkali sulfates such as K_2SO_4, aphthitalite ($3K_2SO_4 \cdot Na_2SO_4$) and calcium langbeinite ($K_2SO_4 \cdot 2CaSO_4$). The crystallization products depend on the relative levels of the two alkali oxides and the level of SO_3. If there is insufficient SO_3 to combine with the alkali metal oxides then these may enter into solid solution in the aluminate and silicate phases. C_2S can be stabilized at temperatures above 1250°C thus impeding the formation of C_3S. A similar stabilization of C_2S, requiring 'hard burning' to lower the free lime level to an acceptable level, can occur if there is a large excess of SO_3 over alkalis.

A deficiency of SO_3 in the clinker is associated with enhanced C_3A activity and difficulties in achieving satisfactory early age concrete rheology.

Fluorine occurs naturally in some limestone deposits, for example in the Pennines in England, and has a beneficial effect on clinker combination. It acts as both a flux and mineralizer, increasing the quantity of liquid formed at a given temperature and stabilizing C_3S below 1250°C. The level in the clinker, however, must be controlled below ~0.25% in order to avoid a marked reduction in the early reactivity of cement.

Minor constituents also have to be controlled on account of their impact on cement properties and also concrete durability. Related to this, the levels of alkalis, SO_3, chloride and MgO are also limited by national cement standards or codes of practice. These aspects are reviewed in section 1.6.

1.4 Cement grinding

The clinker is normally conveyed to a covered store where, provided stocks are adequate, it will cool from the cooler discharge temperature of 50–80°C to a temperature approaching ambient. If clinker stocks are low then the clinker may be ground to cement without the opportunity to cool further during storage. The clinker is ground to a fine powder with approximately 5% calcium sulfate, which is added to control the early reactions of the aluminate phase. These reactions are considered in detail in section 1.5. The European standard for common cements also permits the addition of up to 5% of a minor additional constituent (mac), which, in practice, is normally limestone. Macs can he helpful in optimizing cement rheological properties.

The vast majority of cement produced throughout the world is ground in ball mills, which are rotating tubes containing a range of sizes of steel balls. A closed-circuit milling installation is illustrated in Figure 1.8.
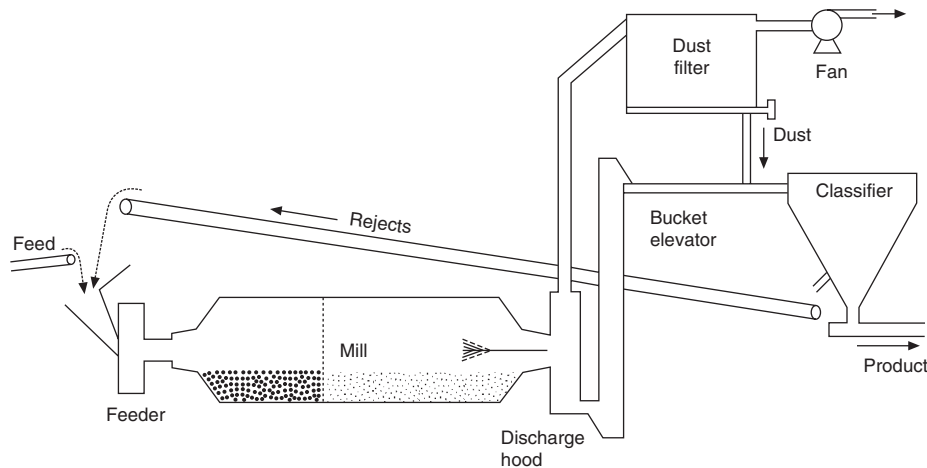

Figure 1.8 Schematic diagram of closed-circuit grinding mill.

Closed-circuit mills normally have two chambers separated by a slotted diaphragm, which allows the partially ground cement to pass through but retains the grinding balls. The first chamber contains large steel balls (60–90 mm in diameter), which crush the clinker. Ball sizes in the second chamber are normally in the range 19–38 mm.

The mill operates in a closed circuit in which the mill product passes to a separating device where coarse particles are rejected and returned to the mill for further grinding. The final product can thus be significantly finer than the material that exits the mill. Mills which do not have this separating stage are known as open-circuit mills and they are less efficient particularly at high cement finenesses (above 350 m^2/kg).

The efficiency of the clinker grinding process is very low. Less than 2% of the electrical energy consumed is used in actually fracturing the particles; the rest is converted to heat. Modern mills are equipped with internal water sprays, which cool the process by evaporation. Cement mill temperatures are typically in the range 110–130°C and at this temperature the hydrated form of calcium sulfate (gypsum, $CaSO_4 \cdot 2H_2O$) added to control the initial

hydration reactions undergoes dehydration. This has some advantages but the level of dehydrated calcium sulfate has to be controlled to optimise the water demand properties of the cement. This aspect is discussed in section 1.5.5.

The low efficiency of the grinding process has resulted in considerable effort being directed to find more efficient processes. Some of these developments are listed in Figure 1.1. As a general rule the more efficient the grinding process, the steeper the particle size grading. The range of particle sizes is smaller and this can result in increased water demand of the cement, at least in pastes and rich concrete mixes. This is because with a narrow size distribution there are insufficient fine particles to fill the voids between the larger particles and these voids must be filled by water. Concerns over product performance in the market and also mechanical/maintenance problems with some of the new milling technologies have resulted in the ball mill retaining its dominant position. One compromise, which lowers grinding power requirement without prejudicing product quality, is the installation of a pre-grinder, such as a high-pressure roll press, to finely crush the clinker obviating the need for large grinding media in the first chamber of the ball mill.

1.5 Portland cement hydration

1.5.1 Introduction

The hydration of Portland cement involves the reaction of the anhydrous calcium silicate and aluminate phases with water to form hydrated phases. These solid hydrates occupy more space than the anhydrous particles and the result is a rigid interlocking mass whose porosity is a function of the ratio of water to cement (w/c) in the original mix. Provided the mix has sufficient plasticity to be fully compacted, the lower the w/c, the higher will be the compressive strength of the hydrated cement paste/mortar/concrete and the higher the resistance to penetration by potentially deleterious substances from the environment.

Cement hydration is complex and it is appropriate to consider the reactions of the silicate phases (C_3S and C_2S) and the aluminate phases (C_3A and C_4AF) separately. The hydration process has been comprehensively reviewed (Taylor, 1997).

1.5.2 Hydration of silicates

Both C_3S and C_2S react with water to produce an amorphous calcium silicate hydrate known as C–S–H gel which is the main 'glue' which binds the sand and aggregate particles together in concrete. The reactions are summarised in Table 1.3. C_3S is much more reactive than C_2S and under 'standard' temperature conditions of 20°C approximately half of the C_3S present in a typical cement will be hydrated by 3 days and 80% by 28 days. In contrast, the hydration of C_2S does not normally proceed to a significant extent until ~14 days.

The C–S–H produced by both C_3S and C_2S has a typical Ca to Si ratio of approximately 1.7. This is considerably lower than the 3:1 ratio in C_3S and the excess Ca is precipitated as calcium hydroxide (CH) crystals. C_2S hydration also results in some CH formation. The following equations approximately summarize the hydration reactions:

Table 1.3 Hydration of calcium silicates

Mineral	Reaction rate	Products of reaction
C_3S	Moderate	C–S–H with Ca:Si ratio ~1.7 CH (calcium hydroxide)
C_2S	Slow	C–S–H with Ca:Si ratio ~1.7 Small quantity of CH

$$C_3S + 4.3H \Rightarrow C_{1.7}SH_3 + 1.3CH$$

$$C_2S + 3.3H \Rightarrow C_{1.7}SH_3 + 0.3CH$$

An important characteristic of C_3S hydration is that after an initial burst of reaction with water on first mixing it passes through a dormant, or induction, period where reaction appears to be suspended. This is of practical significance because it allows concrete to be placed and compacted before setting and hardening commences.

Several theories have been developed to explain this dormant period. The most favoured is that the initial reaction forms a protective layer of C–S–H on the surface of the C_3S and the dormant period ends when this is destroyed or rendered more permeable by ageing or a change in structure. Reaction may also be inhibited by the time taken for nucleation of the C–S–H main product once water regains access to the C_3S crystals.

1.5.3 Hydration of C_3A and C_4AF

The reactions of laboratory-prepared C_3A and C_4AF with water, alone or in the presence of calcium sulfate and calcium hydroxide have been extensively studied (Odler,1998). However, the findings should be interpreted with caution as the composition of the aluminate phases in industrial clinker differs considerably from that in synthetic preparations and hydration in cements is strongly influenced by the much larger quantity of silicates reacting and also by the presence of alkalis.

In the absence of soluble calcium sulfate C_3A reacts rapidly to form the phases C_2AH_8 and C_4AH_{19}, which subsequently convert to C_2AH_6. This is a rapid and highly exothermic reaction.

If finely ground gypsum ($CaSO_4 \cdot 2H_2O$) or hemihydrate ($CaSO_4 \cdot 0.5H_2O$) is blended with the C_3A prior to mixing with water then the initial reactions are controlled by the formation of a protective layer of ettringite on the surface of the C_3A crystals. The reaction can be summarized as:

$$C_3A + 3C + 3\blacksquare + 32H \Rightarrow C_3A.3C\blacksquare. 32H$$

where in cement chemists' notation $\blacksquare$ represents SO_3 and H represents H_2O, i.e.

$$C_3A + \text{dissolved calcium } (Ca^{2+}) + \text{dissolved sulfate } (SO_4^{2-}) + \text{water} \Rightarrow \text{ettringite}$$

The more rapid dissolution of dehydrated forms of gypsum ensures an adequate supply of dissolved calcium and sulfate ions and will be more effective in controlling the reaction of finely divided or highly reactive forms of C_3A. The role of gypsum dehydration is considered further in section 1.5.5.

In most commercial Portland cements there will be insufficient sulfate available to

sustain the formation of ettringite. When the available sulfate has been consumed the ettringite reacts with C_3A to form a phase with a lower SO_3 content known as monosulfate. The reaction can be summarized as:

$$C_3A.3C■.32H + 2C_3A + 4H \Rightarrow 3(C_3A.C■.12H)$$
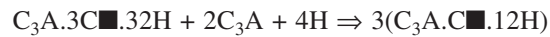
Many studies have shown that the hydration of C_4AF (or more correctly the $C_2A – C_2F$ solid solution) is analogous to that of C_3A but proceeds more slowly (Taylor, 1997). The iron enters into solid solution in the crystal structures of ettringite and monosulfate substituting for aluminium. In order to reflect the variable composition of ettringite and monosulfate formed by mixtures of C_3A and C_4AF they are referred to respectively as AFt (alumino-ferrite trisulfate hydrate)and AFm (alumino-ferrite monosulfate hydrate) phases. The hydration reactions of C_3A and C_4AF are summarized in Table 1.4.

Table 1.4 Hydration of aluminates

Mineral	Soluble calcium sulfate present	Reaction rate	Products of reaction
C_3A	No	Very rapid with release of heat	Hydrates of type C_2AH_8 and C_4AH_{19} which subsequently convert to C_2AH_6
C_3A	Yes	Initially rapid	Ettringite $C_3A3C■32H$ which subsequently reacts to form monosulfate $3(C_3A.C■.12H)$
C_4AF	No	Variable (depends on Al/Fe ratio)	Hydrates of type $C_2(A,F)H_8$ and $C_4(A,F) H_x$ which subsequently convert to $C_3(A,F)H_6$ (hydrogarnet)
C_4AF	Yes	Variable but generally slow	Iron substituted ettringite (AFt) and subsequently iron substituted monosulfate (AFm)

1.5.4 Hydration of Portland cement

The hydration of Portland cement is rather more complex than that of the individual constituent minerals described above. A simplified illustration of the development of hydrate structure in cement paste is given in Figure 1.9.

When cement is first mixed with water some of the added calcium sulfate (particularly if dehydrated forms are present, and most of the alkali sulfates present (see section 1.3.5), dissolve rapidly. If calcium langbeinite is present then it will provide both calcium and sulfate ions in solution, which are available for ettringite formation.

The supply of soluble calcium sulfate controls the C_3A hydration, thus preventing a flash set. Ground clinker mixed with water without added calcium sulfate sets rapidly with heat evolution as a result of the uncontrolled hydration of C_3A. The cement then enters a dormant period when the rate of loss of workability is relatively slow. It will be more rapid, however, at high ambient temperatures (above 25°C).

Setting time is a function of clinker mineralogy (particularly free lime level), clinker chemistry and fineness. The finer the cement and the higher the free lime level, the shorter the setting time in general. Cement paste setting time is arbitrarily defined as the time when a pat of cement paste offers a certain resistance to penetration by a probe of
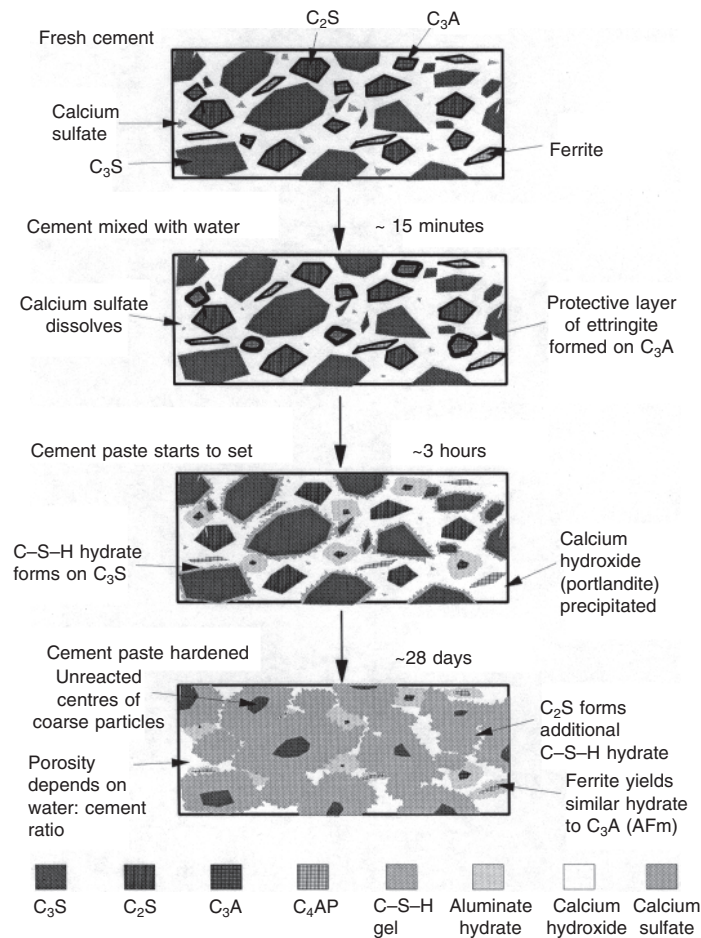
Figure 1.9 Simplified illustration of hydration of cement paste.

standard cross-section and weight (see section 1.7). Setting is largely due to the hydration of C_3S and it represents the development of hydrate structure, which eventually results in compressive strength.

The C–S–H gel which forms around the larger C_3S and C_2S grains is formed *in situ* and has a rather dense and featureless appearance when viewed using an electron microscope. This material is formed initially as reaction rims on the unhydrated material but as hydration progresses the anhydrous material is progressively replaced and only the largest particles (larger than ~30 microns) will retain an unreacted core after several years, hydration. This dense hydrate is referred to as the 'inner product'.

The 'outer hydration product' is formed in what was originally water-filled space and also space occupied by the smaller cement grains and by interstitial material (C_3A and C_4AF). When viewed using an electron microscope this material can be seen to contain crystals of $Ca(OH)_2$, AFm/AFt and also C–S–H with a foil-or sheet-like morphology. The structure of the outer product is strongly influenced by the initial water-to-cement ratio, which in turn determines paste porosity and consequently strength development.

The hydration of Portland cement involves exothermic reactions, i.e. they release heat. The progress of the reactions can be monitored using the technique of isothermal conduction calorimetry (Killoh, 1988).
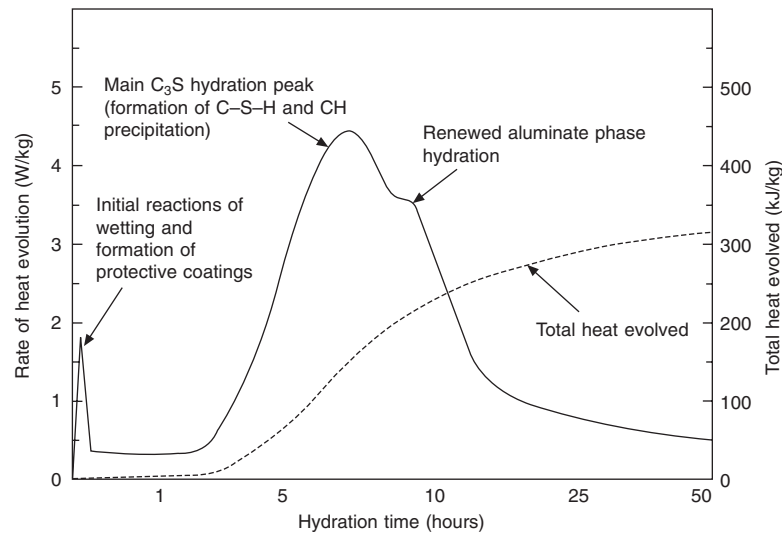

Figure 1.10 Heat of hydration of a cement paste determined by conduction calorimetry at 20°C.

The shoulder on the main hydration peak which is often seen at ~16 hours is associated with renewed ettringite formation which is believed to occur as a result of instability of the ettringite protective layer. In some cements with a low ratio of SO_3 to C_3A it may be associated with the formation of monosulfate.

The heat release is advantageous in cold weather and in precast operations where the temperature rise accelerates strength development and speeds up the production process. However, in large concrete pours the temperature rise, and in particular the temperature difference between the concrete core and the surface can generate stresses which result in 'thermal cracking. Figure 1.11 illustrates the influence of concrete pour size on concrete temperature for a typical UK Portland cement. The data were obtained using the equipment described by Coole (1988).

The temperature rise experienced depends on a number of factors, which include:

- concrete placing temperature
- cement content
- minimum pour dimensions
- type of formwork
- cement type (fineness, C_3S and C_3A contents)

Cement heat of hydration (during the first ~48 hours) is highest for finely ground cements with a high C_3S content (>60%) and a high C_3A content (>10%).

By 28 days a typical Portland cement cured at 20°C can be expected to be ~90% hydrated. The extent of hydration is strongly influenced by cement fineness and in particular the proportions of coarse particles in the cement. Cement grains which are coarser than ~30 microns will probably never fully hydrate. Thus, cement particle size distribution has
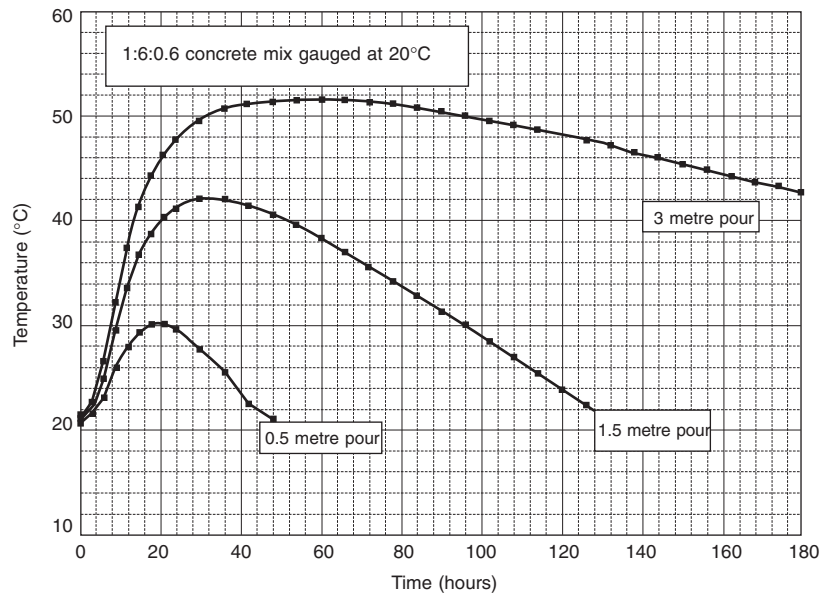
Figure 1.11 Influence of pour size (minimum dimensions) on concrete temperature.

a strong influence on long-term compressive strength. Cement produced in an open-circuit mill with a 45 micron sieve residue of 20% may give a 28-day strength ~10% lower than that of a cement produced from the same clinker but ground in a closed-circuit mill with a 45 micron sieve residue of 3% (Moir, 1994).

Elevated temperature curing, arising from either the semi-adiabatic conditions existing in large pours or from externally applied heat, is associated with reduced ultimate strength. This is believed to be due to a combination of microcracks induced by thermal stresses but also a less dense and 'well-formed' microstructure.

1.5.5 Optimization of level of rapidly soluble calcium sulfate

As described in section 1.3 cement mill temperatures normally lie in the range 100–130°C. Under these conditions the calcium sulfate dihydrate (gypsum) added to the mill undergoes dehydration first to hemihydrate ($CaSO4·0.5H_2O$) and then to soluble anhydrite ($CaSO_4$). These dehydrated forms of gypsum are present in commercial plasters and it is the formation of an interlocking mass of gypsum crystals which is responsible for the hardening of plaster once mixed with water.

The dehydrated forms of gypsum dissolve more rapidly than gypsum and this is beneficial in ensuring that sufficient Ca^{2+} and SO_4^{2-} ions are available in solution to control the initial reactivity of C_3A by forming a protective layer of ettringite. An inadequate supply of soluble calcium sulfate can result in a rapid loss of workability known as flash set. This is accompanied by the release of heat and is irreversible.

However, if too high a level of dehydrated gypsum is present, then crystals of gypsum crystallize from solution and cause a plaster or false set. This is known as false set because if mixing continues, or is resumed, the initial level of workability is restored.