CHAPTER 12.30

Portland and Other Cements

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The Roman term *opus caementicium* describing a combination of volcanic ash or pulverized brick plus burnt lime as a binder is deemed to be the origin of the word *cement*. A general definition of cement may be "a substance used in construction that adheres to other materials, binding them together when it sets and hardens." Cement is usually mixed with fine aggregate to produce mortar for masonry, or mixed with sand and gravel aggregates to produce concrete. Cements can be classified as either hydraulic or non-hydraulic, depending upon the ability of the cement to set in the presence of water. Hydraulic cements (e.g., portland cement, or PC) set and become adhesive because of a chemical reaction between the dry ingredients and water, resulting in mineral hydrates with low solubility in water and resistance to chemical attack.

TRENDS IN CEMENT CONSUMPTION

Global cement production in 2015 was approximately 4 Bt/yr (billion metric tons per year; Beyond Zero Emissions 2017), making it the second most widely used commodity besides water. Global construction output is expected to exceed US$15 trillion by 2030, with China, the United States, and India accounting for 57% of all growth. Global construction growth is also expected to outpace that of global gross domestic product (GDP) by over one percentage point (Global Construction Perspectives and Oxford Economics 2015), so with construction contributing about 10% of global GDP, demand for cement will continue to grow.

As outlined later in this chapter, production of PC contributes about 8% of global carbon emissions—more than the total emissions from all global road transport. Even if the global cement industry achieves its own emissions targets, cement-related emissions will contribute an alarming 20%–26% of global carbon emissions by 2050 (Beyond Zero Emissions 2017). Clearly, there is a need to change cement production practice to reduce carbon emissions. This chapter aims to equip the mining professional with the ability to identify mineral deposits that will result in new opportunities for making cements and to reduce the consumption of PC.

CEMENTITIOUS MATERIALS

The main source materials used in the production of PC are limestone and clays. Supplementary cementitious materials (SCMs), such as fly ash, ground granulated blast-furnace slag (GGBS) from ironmaking, natural pozzolans, volcanic rock, calcined clays, fine limestone, and silica fume, are added to PC to reduce carbon emissions, reduce cost, and improve durability of the concrete. Figure 1 shows the compositional relationship between these materials. PC with addition of approximately 20–50 mass % SCMs are called "blended cements." It is possible to make a cement containing no PC from SCMs and an alkali activator, which is called "alkali-activated cement." These cements have been demonstrated in many projects but are not yet widely available commercially. In view of the dominance of portland and blended cements, and because most of the existing standards pertain to such cements, the following discussion focuses primarily on these cements.

CEMENT TERMINOLOGY

Before describing cement chemistry, it is necessary to introduce its terminology, aimed at simplifying compositions by leaving out the oxygen and abbreviating elemental symbols, as shown in Table 1. Examples of typical cement minerals and products are given in Table 2, with Figure 2 showing the compositional relationship between some of these binding phases.

About 90%–95% of PC is composed of four minerals (C_3S, C_2S, C_3A, and C_4AF), with the remainder consisting of calcium sulfate, alkali sulfates, unreacted (free) lime (CaO), magnesia (MgO), and other minor constituents. The C_3S and the C_2S contribute virtually all of the beneficial properties by generating the main hydration products C-S-H and CH. In blended PCs, the reaction of SCMs such as fly ash, GGBS, and calcined clay result in a higher aluminum content of the C-S-H gel, and often a decrease in the Ca/Si ratio, with these gels called C-A-S-H. In alkali-activated cements, some alkali cations like sodium are included in the gel, so that the gel is called C-(N,K)-A-S-H. A high alkali content in

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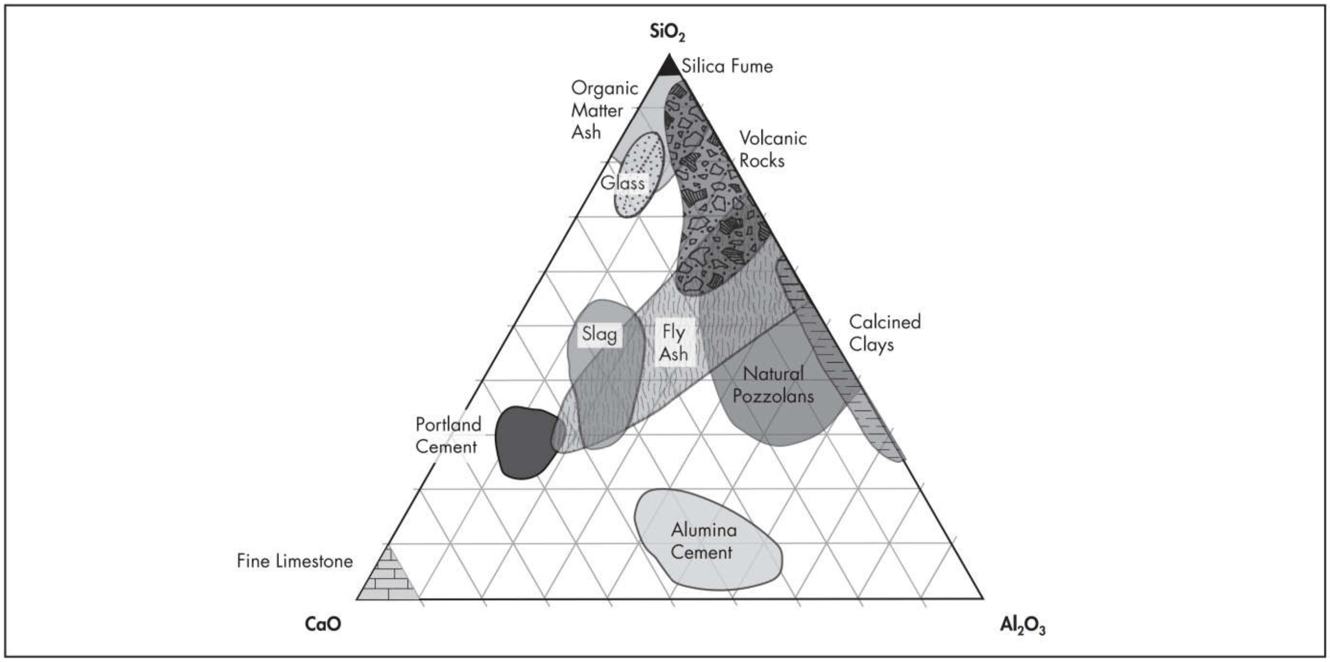


Adapted from Glasser et al. 1987, Lothenbach et al. 2011, Snellings et al. 2012, van Deventer et al. 2015

Figure 1 Ternary CaO–SiO$_2$–Al$_2$O$_3$ diagram (mass % based) depicting the chemical composition of major cementitious materials

Table 1 Cement chemistry notation based on oxide

Oxide Form	Notation	Oxide Form	Notation
CaO	C	SO_3	$\bar{S}$
SiO_2	S	H_2O	H
Al_2O_3	A	MgO	M
Fe_2O_3	F	Na_2O	N

alkali-activated cements may result in the formation of (N,K)-A-S-H gel as well.

TYPES OF PORTLAND CEMENT

There are five main types of PC in the United States, according to standard ASTM C150/C150M, with some of them subdivided, giving 10 types of cements (Table 3). These different types of PC need to satisfy many physical and chemical requirements given in ASTM C150/C150M. The differences between these cement types are rather subtle. All five types contain about 75 mass % calcium silicate minerals, and the properties of mature concretes made with all five are quite similar.

Type I cement is conventional PC. Types II and V PC are resistant to damaging sulfate attack resulting from expansive ettringite crystals formed by the reaction of hydration products of C_3A with sulfate ions entering the concrete pores. To control this reaction, Type II and Type V cements focus on keeping the C_3A content low. However, the most effective way to prevent sulfate attack is to prevent the sulfate ions from entering the concrete in the first place by using a low water/cement (w/c) ratio. Alkali-activated concrete has a lower susceptibility than PC to sulfate attack.

Type III cement develops early strength more quickly than Type I cement, which is useful for a rapid pace of construction, since it allows cast-in-place concrete to bear loads sooner. These advantages are important in cold weather, which reduces the rate of hydration. The disadvantage of rapid-reacting cements is a shorter period of workability, greater heat of hydration, and a slightly lower ultimate strength.

Type IV cement is designed to release heat more slowly than Type I cement, meaning that it also gains strength more slowly. A slower rate of heat release limits the increase in the core temperature of a concrete element. The maximum temperature scales with the size of the structure, and Type IV cement was developed to prevent excessive temperatures in large concrete structures such as dams. Type IV cement is rarely used today, because similar properties can be obtained by using a blended PC.

SOURCE MATERIALS

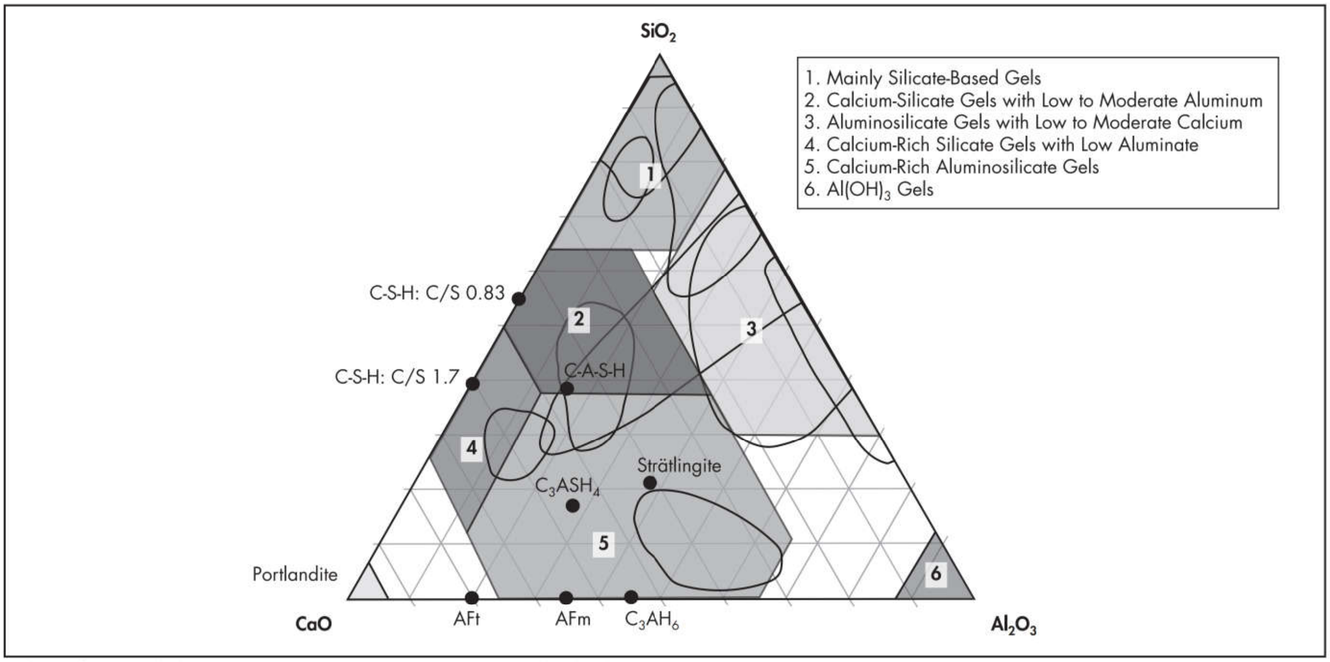
Cementitious materials comprise primarily of lime (CaO), silica (SiO_2), alumina (Al_2O_3), and ferrite (Fe_2O_3) sourced from a wide range of materials (Figure 1), including limestone, clays, metallurgical slags, and ashes. Small quantities of gypsum and other admixtures are added during clinker grinding to manipulate setting.

Limestone

Limestone ($CaCO_3$) for PC production is quarried and transported for crushing and grinding prior to delivery into a clinker plant. Frequently the limestone is impure and can contain as low as 80% $CaCO_3$ (Moir 2003). ASTM C1797 gives the requirements for the different types of limestone, which can be used for PC production, as SCM, interground with clinker and gypsum, or calcined to produce lime. Furthermore, alkali-activated binders based on limestone and slag (containing up to 68% granular limestone) have been reported (Moseson et al. 2012). Limestone can also be blended with calcined clays and used as an SCM, partially replacing PC clinker (limestone calcined clay cement, LC^3) (Sánchez Berriel et al. 2016; Cancio Díaz et al. 2017). With overall limestone sources widespread and abundant, future supply is secure.

Table 2 Examples of cement minerals and products

Chemical Name	Chemical Formula	Oxide Formula	Cement Notation	Mineral Name
Tricalcium silicate	Ca_3SiO_5	$3CaO{\cdot}SiO_2$	C_3S	Alite
Dicalcium silicate	Ca_2SiO_4	$2CaO{\cdot}SiO_2$	C_2S	Belite
Tricalcium aluminate	$Ca_3Al_2O_6$	$3CaO{\cdot}Al_2O_3$	C_3A	Aluminate
Tetracalcium aluminoferrite	Ca_2AlFeO_5	$4CaO{\cdot}Al_2O_3{\cdot}Fe_2O_3$	C_4AF	Ferrite
Calcium hydroxide	$Ca(OH)_2$	$CaO{\cdot}H_2O$	CH	Portlandite
Calcium sulfate dihydrate	$CaSO_4{\cdot}2H_2O$	$CaO{\cdot}SO_3{\cdot}2H_2O$	$C\,\bar{S}\,H_2$	Gypsum
Calcium oxide	CaO	CaO	C	Lime
Alumina, ferric oxide, trisulfate	—	$Ca_3(Al,Fe)(OH)_6{\cdot}12H_2O]_2{\cdot}X_3{\cdot}nH_2O$ where X = a doubly charged anion or, sometimes, two singly charged anions	AFt	Example: ettringite, where X = SO_4^{2-}
Alumina, ferric oxide, monosulfate	—	$Ca_2(Al,Fe)(OH)_6)]{\cdot}X{\cdot}nH_2O$ where X = a singly charged anion or "half" a doubly charged anion. X = OH^-, SO_4^{2-}, and CO_3^{2-}.	AFm	Examples: hemicarboaluminate, monocarboaluminate, monosulfoaluminate, gehlenite hydrate, strätlingite
Calcium-silicate-hydrate gel	—	$CaO–SiO_2–H_2O$ gel	C-S-H gel	Structural analogue: tobermorite or jennite
Calcium-alumina-silicate-hydrate gel	—	$CaO–Al_2O_3–SiO_2–H_2O$ gel	C-A-S-H gel	Structural analogue: tobermorite or jennite
Sodium-alumina-silicate gel	—	$Na_2O–Al_2O_3–SiO_2–H_2O$	N-A-S-H gel	Structural precursor to zeolites



Adapted from Durdiński et al. 2016, van Deventer et al. 2015, Lothenbach et al. 2011

Figure 2 Ternary $CaO–SiO_2–Al_2O_3$ diagram (mass % based) depicting the chemical composition of cementitious binders

Clays

Clay minerals used in cement are formed primarily by weathering of silicate minerals in rocks (e.g., feldspar, micas, amphiboles, and pyroxenes); however, clay minerals in waste products from sand quarries and clayey mines may also be used if calcined properly. Clays comprise silica tetrahedra and aluminum octahedral sheets arranged in layers that are stacked in a variety of arrangements. Clay minerals that are naturally abundant and of interest for cement production include kaolinite, illite, and montmorillonite.

Clays are not inherently cementitious and must be heated to remove structural water and to form a metastable/disordered structure with pozzolanic reactivity. Metakaolin exhibits the greatest degree of disorder after calcination at low temperatures (500°–800°C), while montmorillonite and illite retain their structure after calcination at these temperatures. Consequently, metakaolin exhibits the highest pozzolanic activity (Wild and Khatib 1997; Sabir et al. 2001). Calcined calcium-montmorillonite exhibits a slightly lower degree of pozzolanic reactivity than metakaolin, whereas illite and other thermally activated clay minerals exhibit relatively low pozzolanic reactivity.

Montmorillonite is the most abundant of these clay minerals and has much potential for use in cements; however,

Table 3 Types of portland cement according to ASTM C150/C150M

Types	Classification	General Characteristics	Applications
Type I and Type IA*	Special properties are not required	Fairly high C_3S content for good early-strength development	Most buildings, bridges, pavements, precast units, etc.
Type II and Type IIA*	Moderate sulfate resistance is desired	Low C_3A content (<8%)	Structures exposed to soil or water containing sulfate ions
Type II(MH†) and Type II(MH)A*	Moderate heat of hydration and moderate sulfate resistance are desired	Low C_3A content (<8%)	Structures exposed to soil or water containing sulfate ions
Type III and Type IIIA*	High early strength is desired	Ground more finely, may have slightly more C_3S	Rapid construction, cold-weather concreting
Type IV	Low heat of hydration is desired	Low content of C_3S (<50%) and C_3A	Massive structures such as dams (now rare)
Type V	High sulfate resistance is desired	Very low C_3A content (<5%)	Structures exposed to high levels of sulfate ions

Adapted from ASTM C150/C150M
*Air-entraining cement where air entrainment is desired.
†MH = Moderate heat.

there has been limited work done to enhance pozzolanic reactivity of this clay. Sodium-montmorillonite in particular has received limited attention due to the high sodium content being undesirable in PC, whereas in alkali-activated systems, a high sodium content can be accommodated. Metakaolin is the most widely used calcined clay in cementitious materials and exhibits pozzolanic reactivity when mixed with lime or PC (Ambroise et al. 1985; He et al. 1995) and drastically improves the mechanical properties and durability of concrete (Zhang and Malhotra 1995; Singh and Garg 2006).

Slags

Slag is a glassy by-product of both ferrous and nonferrous smelting processes, and comprises primarily metal oxides, silicon dioxide, and sulfides. The type of slag and its characteristics are dependent on processing conditions during production. Common examples are air-cooled blast-furnace slag, air-cooled basic oxygen steel slag, air-cooled high-alloy electric arc furnace slag, stainless-steel slag, electric arc furnace carbon steel slag, granulated blast-furnace slag, and GGBS.

GGBS is a latent hydraulic material consisting primarily of depolymerized calcium silicate glasses, as well as small amounts of poorly crystalline phases within the melilite group (Shi et al. 2006; Duxson and Provis 2008; Provis and van Deventer 2009; Le Saoût et al. 2011; Li et al. 2011). During granulation, slag obtained from blast-furnace smelting of iron ore is cooled quickly to facilitate the formation of glassy phases, enabling it to exhibit cementitious properties. This cooling process can cause GGBS to contain up to 30% water (particularly older slags produced in China and Russia) (Shi et al. 2006), although modern slags are almost completely dry. After granulation, the slag must be ground for use as a cementitious material. GGBS is particularly useful in cement because of its composition, which contains high levels of CaO, SiO_2, and Al_2O_3, and lower levels of Fe_2O_3, relative to other slags and exhibits high pozzolanic reactivity.

It is estimated that global iron slag production in 2016 was between 300 and 360 Mt (million metric tons) and global steel slag production in 2016 was 160–240 Mt (USGS 2017). It is estimated that global slag production is approximately one-half to two-thirds of coal fly ash production (Fernández-Jiménez and Palomo 2005) and far below that of the available natural clay mineral deposits. Consequently, the amount of GGBS available for use as a PC substitute is significantly reduced compared to that of fly ash. The composition of GGBS varies across different locations, with CaO, Al_2O_3, SiO_2, and MgO typically varying between 35 and 42 mass %, 7 and 13 mass %, 34 and 36 mass %, and 6 and 15 mass %, respectively (Shi et al. 2006; Duxson and Provis 2008; Provis and van Deventer 2009; Ben Haha et al. 2011, 2012; Bernal et al. 2014). The reactivity of GGBS is dependent on the level of depolymerization of the aluminosilicate framework and on the particle size distribution (PSD). The chemical requirements for slag used in cement are specified by ASTM C989. Other metallurgical slags can be modified while hot and in the liquid phase (hot-stage engineering) to tailor the properties of the final cooled slag for use in cement (Engström et al. 2011).

Ashes

About 80% of ash leaves the coal-fired boiler as fly ash entrained in the flue gas, while the remainder is collected as bottom ash. Bottom ash is cooled naturally and consequently is coarse, so size reduction is required if used in cement. Also, bottom ash often contains high levels of unburned carbon that must be removed. Fly ash particles are roughly spherical in shape and can be completely or partially hollow, containing primarily Al_2O_3, SiO_2, and Fe_2O_3.

Fly ash is collected by electrostatic precipitators, after which it is either collected dry and dispatched unclassified, or collected dry and classified with the fines (approximately one-third of the fly ash), then separated and dispatched for use in cement. If the fly ash is deemed to be unsuitable for use, it is collected wet and pumped into disposal ponds. In 2016, worldwide fly ash production was estimated to be 0.7–1.1 Bt/yr, with approximately 30% being utilized (Scrivener et al. 2016; Snellings 2016), which makes it a low-cost partial PC substitute.

The composition of fly ash varies significantly from one source to the next. The CaO content of fly ash can be as high as 15 mass %; however, many fly ashes contain less than 5% CaO. Fly ash is categorized based on the CaO content, with Class F fly ash specified to contain at least 70% combined silica, alumina, and iron oxide and exhibiting pozzolanic reactivity, and Class C fly ash typically containing more than 20 mass % CaO and exhibiting both pozzolanic reactivity and some self-cementing properties (ASTM C618). Fly ash also contains crystalline minerals such as quartz, mullite, and ferrite spinels; kaolinite and other layered silicates present in the coal melt upon combustion to form the glassy phase in fly ash, and consequently are mostly absent (Provis and van Deventer 2009). ASTM C618 details the chemical and physical requirements of coal fly ash for use in concrete.

Coal can also be burnt via fluidized-bed combustion (FBC), which enables high-efficiency combustion of low-grade fuels. Limestone is often added to react with SO_2 in high-sulfur coal to minimize SO_x (sulfur oxides) emissions; consequently, ashes from FBC can contain gypsum ($CaSO_4{\cdot}2H_2O$) and free lime (CaO). Currently, the vast majority of FBC ashes are deemed unsuitable for use as a pozzolanic material in blended cements and are disposed of in ponds; however, alkali-activated FBC ashes can exhibit mild strength development (Yliniemi et al. 2015, 2017; Pesonen et al. 2016).

Natural Pozzolans

Natural pozzolans and volcanic ashes can also be used in PC blends with up to 50 mass % replacement achievable (Celik et al. 2014), as well as in alkali-activated cements (Lemougna et al. 2011, 2013; Takeda et al. 2014). Volcanic ash is often a locally available material and comprises primarily silica at varying content, depending on the ash source, and lower amounts of Al_2O_3, Fe_2O_3, CaO, MgO, and sodium oxide (Na_2O). ASTM C618 details the chemical and physical requirements of natural pozzolans for use in concrete. They may need to be dried or calcined and ground prior to use in cement. In 2016, global annual production of natural pozzolans was estimated to be approximately 75 Mt (Snellings 2016).

Silica Fume

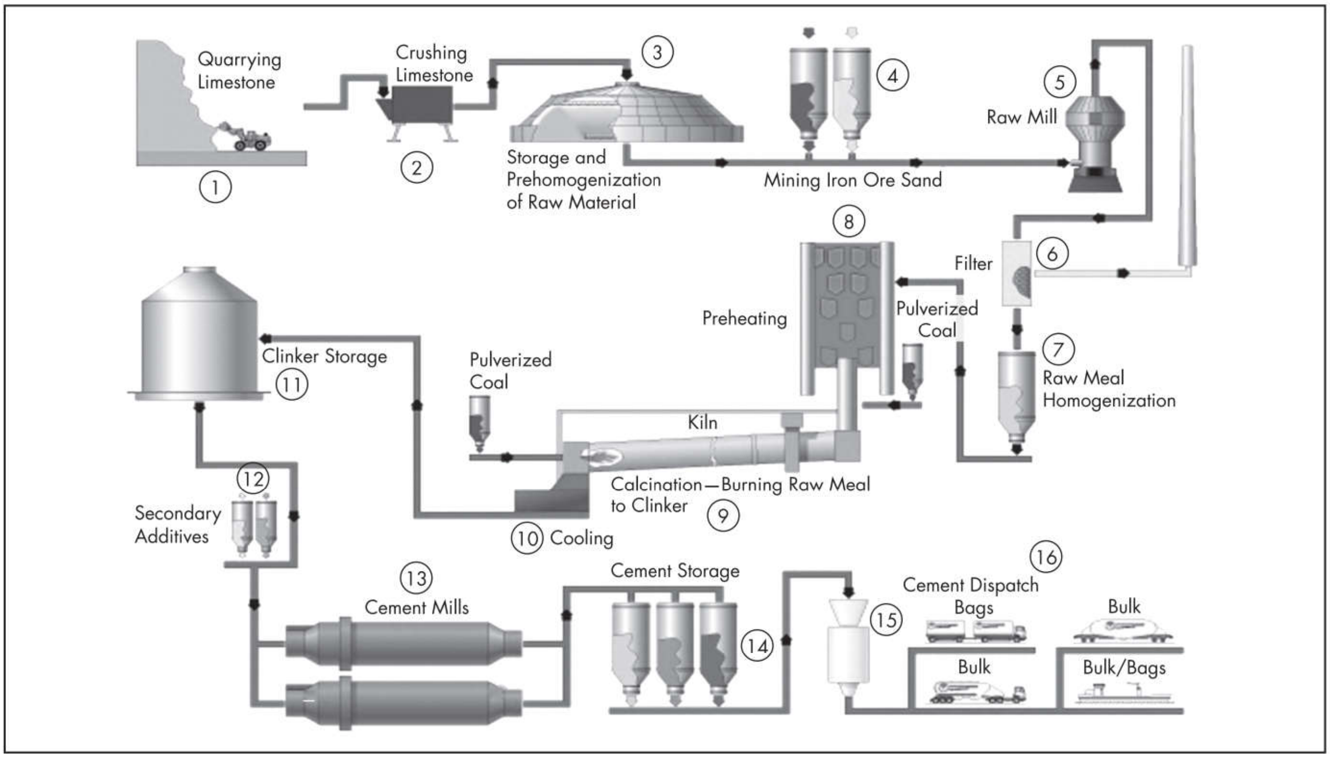
Silica fume (also referred to as condensed silica fume and microsilica) is an amorphous polymorph of silica (SiO_2) produced as a by-product in the production of silicon metal and ferrosilicon alloys. Silica fume particles are spherical and typically have a diameter of approximately 150 nm. In general, it comprises 85–99 mass % SiO_2, with oxides Fe_2O_3, Al_2O_3, CaO, MgO, Na_2O, and potassium oxide (K_2O) accounting for less than 1 mass % and loss on ignition approximately 1–2 mass % (Snellings et al. 2012). It is a commonly used supplementary cementitious material with high pozzolanic reactivity and consequent rapid rate of reaction when blended with PC and hydrated lime, due to the very small particle size and spherical morphology (Lothenbach et al. 2011). The chemical requirements for silica fume used in cement are specified by ASTM C1240. In 2016, global annual production of silica fume was estimated to be approximately 1–2.5 Mt (Snellings 2016).

TRANSFORMATIONS

Raw materials such as limestone, clays, sand, and aluminates have to be transformed to become cementitious materials. This section outlines the processing equipment, energy requirements, and physical and chemical processing steps required to transform raw materials into PC and calcined clay.

Manufacturing of Clinker and PC

Figure 3 depicts the general flow diagram of PC production. The first step in making PC is to combine a mixture of quarried materials (raw materials), composed mainly of limestone mixed in accurate proportions (step 7) with silica and alumina (from sands, clays, or shales), and iron (from iron ore or other iron-bearing minerals) to form a "raw mix." Limestone provides the required calcium oxide and some of the other oxides, whereas clay, shale, and other materials provide most of the silicon, aluminum, and iron oxides required for



Courtesy of Cement Plant Manufacturers, Ashoka Group

Figure 3 Flow diagram of the PC manufacturing process

the manufacture of PC. The raw mix is then ground to a fine powder called "raw meal" (steps 2 to 4). The size reduction of the raw mix can be done by the "dry process" or the "wet process," as explained below. The raw meal is then chemically transformed by intensive heating to form an intermediate product called clinker (steps 8 to 10), which is then ground with gypsum and small proportions of additional materials to produce PC (steps 12 and 13). This cement is often blended with SCMs such as fly ash, slag, metakaolin, fine limestone, and fillers to make blended cements (step 15). The following subsections provide a more detailed description of the processing steps to transform raw materials to PC.

Quarrying

PC plants usually operate their own quarries for limestone (step 1 in Figure 3), while other materials, such as clays, iron, and sand, may be sourced externally. More than 1.5 t of raw materials are required to produce 1 t of PC (Alsop 2007).

Crushing and Homogenization

The PSD of the kiln feed has a direct effect upon the burnability, time, and cost of the process. Hence, multiple screening steps are performed at different stages of the process and retained particles are recycled to the mill (step 6). The raw mix is reduced to a powder with sizes smaller than 100–150 µm.

The limestone is first crushed by a jaw crusher (step 2) and then fed into the second crusher, usually an impact crusher or gyratory jaw crusher to reduce particle size below 50 mm. The clay and sand portion of the raw mix can be reduced in size using the same principle. All the raw materials are then subjected to a second size reduction with rollers or hammer mills (step 5). This size reduction can be with the addition of water, called the wet process, or without water, called the dry process.

In the wet process, water is usually added to the limestone and the clay separately, because of differences in the handling of moist clay and limestone. The wet process was preferred in the 1950s because of its ease of use, but it requires a long wet kiln, which has a very poor fuel efficiency. In the wet process, once materials are milled and homogenized in the desired proportion of the raw mix (limestone 70%, clays 30%), the slurry is fed to the kiln. The slurry is fed into the kiln at the upper end and pulverized coal is blown in by an airblast at the lower end of kiln, where the temperature is about 1,450°C. This type of kiln has to operate continuously to ensure a steady regime. A large kiln in a wet process plant typically produces 3,600 t of clinker per day.

In the dry and semidry processes, the raw materials are crushed and fed in the correct proportions into a grinding mill, where the raw materials are dried and reduced in size to a fine powder. Although ball mills have been used in the past for raw meal grinding, vertical roller mills (VRMs) have become the industry standard in more than 80% of new plants (Harder 2010). These powdered minerals are mixed by compressed air to get the dry raw mix, which is then stored in silos before being sent into the rotary kiln.

In the semidry process, the blended raw meal is then sieved and fed into a rotating dish where water (about 12% of the meal) is added at the same time. In this manner, hard pellets about 15 mm in diameter are formed. This is necessary, as cold powder fed directly into kiln would not permit the airflow and exchange of heat necessary for the formation of clinker. The pellets are heated in a preheating grate by hot gases from the kiln and then enter the kiln heated at about 1,450°C. The dry material undergoes reactions in the hottest part of the kiln, with 20%–30% of the material becoming liquid. The consumption of coal in this dry method is only about 100 kg/t cement compared to about 220 kg/t cement in the wet process. The dry process uses smaller equipment, is more economical, and gives better control over clinker quality.

Preheating

Nearly all new kilns have precalciners or preheaters (step 8) in the dry process. If a long dry rotary kiln is used, the preheating step is not necessary. The long dry kiln is similar to the long wet kiln, however less fuel is consumed. Modern kilns contain ceramic heat exchangers, allowing the kiln to be split into three or four areas, dividing the feed and gas flow, improving heat transfer, and resulting in energy savings.

After preheating, the raw meal is fed to a shorter rotary kiln (length/diameter = 15) where it enters at approximately 800°C, so decarbonation is almost complete and only clinkerization occurs in the rotary kiln. Since the decarbonation reaction is highly endothermic (~1.88 MJ/kg), this involves introducing about 60% of the total fuel required by the kiln system into the preheater.

Calcination/Pyroprocessing

The burning process is carried out in the rotary kiln (step 9) while the raw materials are rotated at 1–2 rpm along the longitudinal axis of the kiln. The rotary kiln has a diameter of approximately 2.5–3.0 m and a length of 90–120 m and comprises steel tubes. The inside of the kiln is lined with refractory bricks. The kiln rests on roller bearings at a gradient of 1 in 25 to 1 in 30, with material moving at 15 m/h. The raw mix from the dry process or the slurry from the wet process is injected into the kiln from the upper end. The kiln is heated by powdered coal, oil, or hot gases from the lower end of the kiln so that a long, hot flame is produced.

Figure 4 shows the chemical changes as the raw mix is converted into clinker:

- Water is evaporated during a drying step below 750°C. Unbound water evaporates between 20°C and 100°C, adsorbed water evaporates between 100°C and 300°C, and chemically bound water evaporates between 400°C and 750°C. Clays are calcined during this stage (e.g., kaolinite is converted to metakaolin via $Al_4Si_4O_{10}(OH)_8 \rightarrow 2(Al_2O_3{\cdot}2SiO_2) + 4H_2O$).
- Decomposition reactions occur between 750°C and 950°C.
- Calcined clays are converted to aluminates and silica via $Al_2O_3{\cdot}2SiO_2 \rightarrow Al_2O_3 + 2SiO_2$.
- Limestone is converted to free lime, releasing carbon dioxide (CO_2), via $CaCO_3 \rightarrow CaO + (CO_2)_{gas}$.
- Between 950°C and 1,350°C, calcium, silicon, and aluminum oxides react to form calcium aluminates, or CA ($CaO{\cdot}Al_2O_3$), and calcium silicates, or CS ($CaO{\cdot}SiO_2$), via $3CaO + 2SiO_2 + Al_2O_3 \rightarrow 2(CaO{\cdot}SiO_2) + CaO{\cdot}Al_2O_3$.
- Lime reacts with CS to form belite (C_2S) via $CS + C \rightarrow C_2S$ as well as $2C + S \rightarrow C_2S$.
- Between 1,350°C and 1,450°C, lime reacts with belite (C_2S) to form alite (C_3S) in a process called *clinkerization* via $C_2S + C \rightarrow C_3S_{(solid)}$. Lime also reacts with CA and ferrite (F) to form tricalcium aluminate and tetracalcium

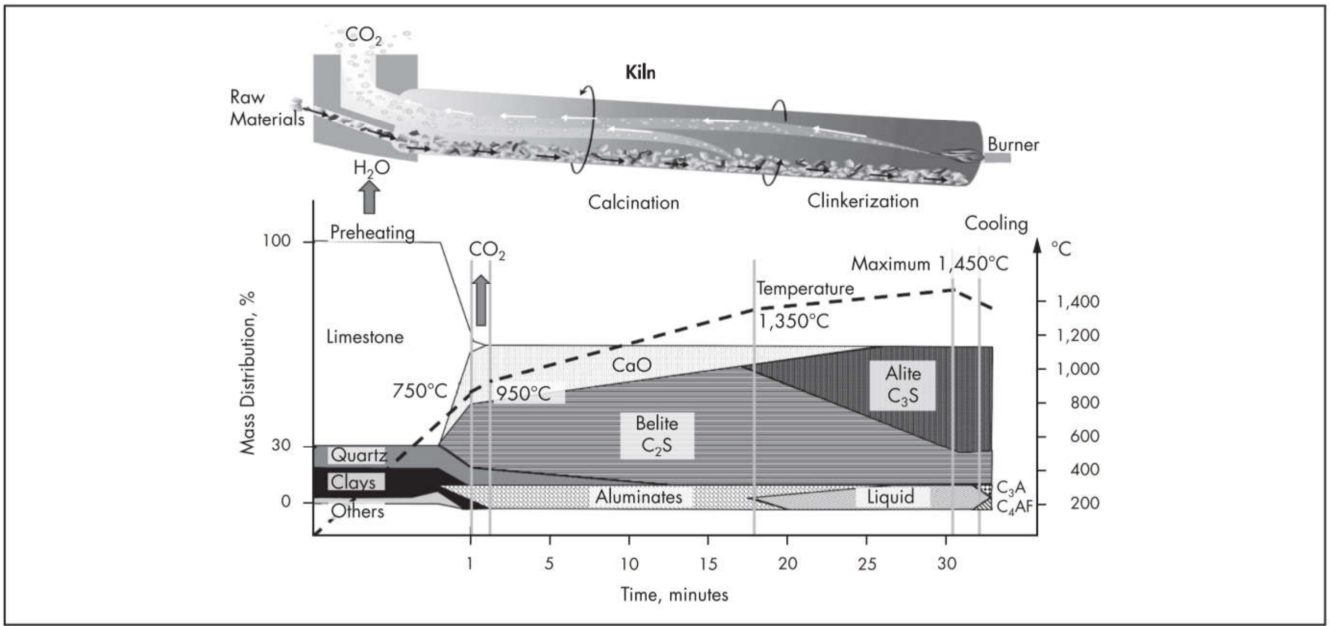


Figure 4 Chemical transformation of clinker

aluminoferrite via CA + 2C → $C_3A_{(liquid)}$ and CA + 3C + F → $C_4AF_{(liquid)}$.

- Cooling then occurs, resulting in solidification of tricalcium aluminate (C_3A) and tetracalcium aluminoferrite (C_4AF).

Cooling and Storage of Clinker

After exiting the kiln (steps 10 and 11), the clinker falls onto a grate and is cooled by large air fans. The heat recovered from the cooling process is recirculated back to the kiln or preheater. The cooling of clinker has a significant effect on the quality of cement, as quenching of the clinker (~50-mm diameter) preserves the reactive metastable high-temperature minerals and maximizes its strength potential.

Grinding of Clinker to Cement

Clinker is transported to the finishing mill (step 13) by a conveyor belt, where a small amount of gypsum is added to control setting of the cement. Blended cements and masonry cements may include large additions of natural pozzolans, fly ash, slag, limestone, silica fume, or metakaolin. The rate of the initial reaction of cement is dependent on the PSD; therefore, the grinding process is closely controlled to obtain a specific surface area, called the Blaine fineness, which usually ranges from 300 to 500 m^2/kg.

Traditionally, closed-circuit ball mills have been used for clinker grinding, as they are simple to operate and can deal with variations in mill feed quality and quantity. Harder (2010) stated that ball mills are used in <50% of plants, while VRMs are used in about 40% of plants for clinker grinding. The maintenance costs for a VRM and a ball mill are comparable; while the wear rates for a ball mill are higher than for a VRM, the cost of the replacement parts is lower. Because of its high internal circulation and high separation efficiency, a VRM tends to produce a narrow PSD, which is not always desirable in cement. Usually, a compromise is found between the PSD and energy consumption. Although the capital cost of an installed VRM may be 20% more than for a ball mill, the lower energy consumption of a VRM is a determining factor for increased use of VRMs.

Storage of Cement

The ground cement is conveyed by belt or powder pump into a silo for storage, where it is ready for bagging and/or shipping in bulk by trucks, rail, or barge. The capital necessary for cement storage represents usually about 10% of the total capital cost of the cement plant. The principal function of the cement storage silos is to provide surge capacity between the grinding mills and the shipping media. There are usually several separated storage silos for the different cements produced. The storage silos must be waterproof to prevent early hydration of the cement. Figure 5 depicts the complete flow sheet for a dry PC plant.

Metakaolin and Other Calcined Clays

Metakaolin and calcined clays are produced by burning kaolinite clay or other clays (e.g., montmorillonite or illite) at temperatures between 700°C and 850°C, which induces dehydroxylation and produces a disordered metastable state. Calcined clays can be used as SCMs and as precursors for alkali-activated cement. Unlike the kaolin used in paper and ceramics which require further processing, clay used as a SCM can contain up to 50% sand and 10% limestone.

Rotary Kiln Calcination

Clays are usually calcined in a rotary kiln by both dry and wet processes, similar to the kilns used for cement production. The dry process is simpler but produces a lower-quality product than the wet process. In the dry process, the raw material is crushed to the desired size, dried in rotary dryers, pulverized, air-floated to remove coarse grit, and then fed to the kiln. The calcination process, between 650°C and 700°C, which lasts about 3–5 hours, drives the particles of metakaolin to agglomerate in pellets of 5–10 cm in diameter, which are

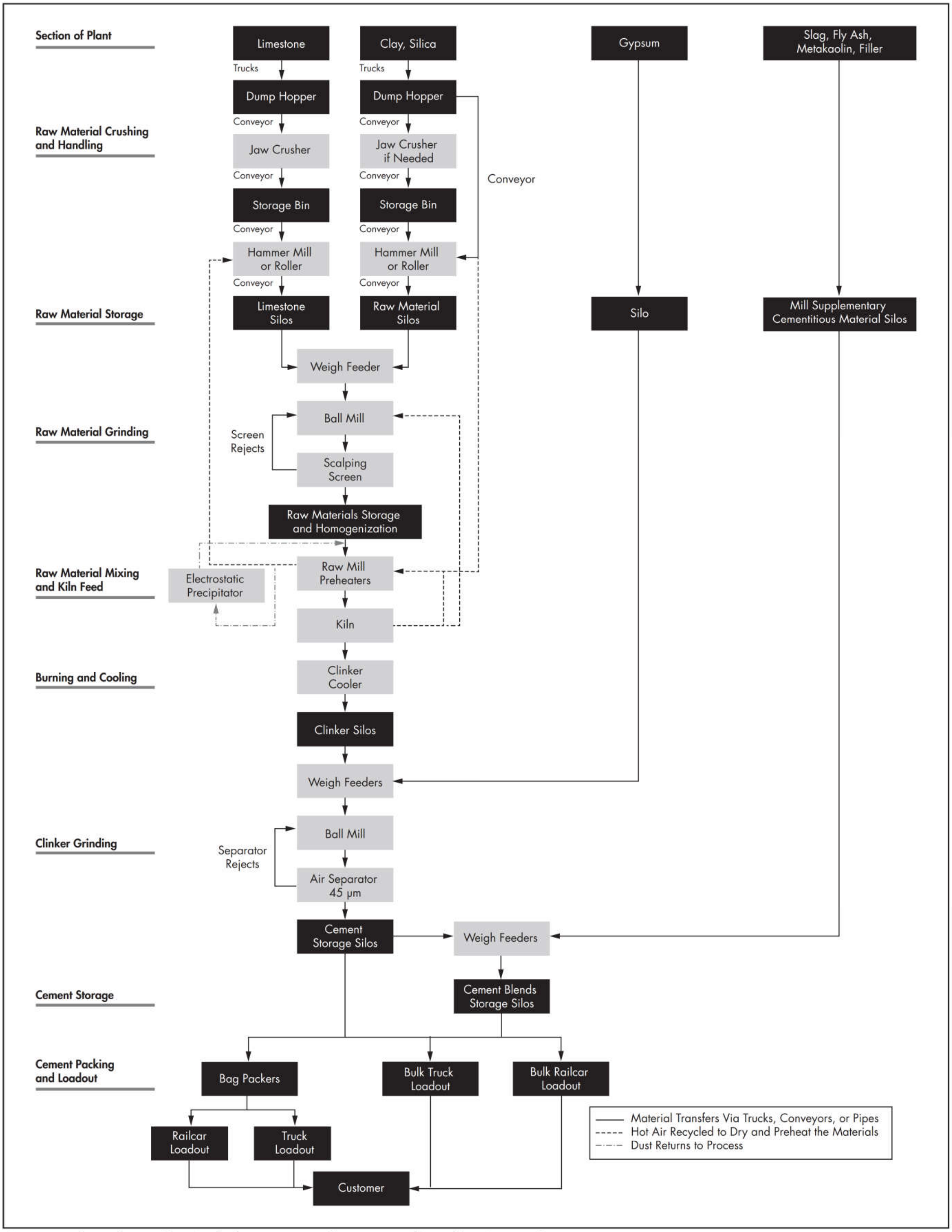


Figure 5 Flow sheet of typical dry process of cement with preheating cyclones

then ground by a ball mill to the desired fineness. This method results in flaky, irregular morphology and high specific surface area particles.

Flash Calcination

More recently, flash calcination has been used in metakaolin production, which involves rapid heating and calcining for a tenth of a second, then cooling at a rate of 103°–105°C/s, with insufficient time for agglomeration of the particles, so no subsequent grinding is required as in rotary calcination. This type of installation consumes 2.2 MJ/t of metakaolin, which is 80% less than the energy consumed during cement production (San Nicolas 2011). As such, flash-calcined metakaolin particles are usually spherical, whereas rotary kiln–calcined metakaolin particles are generally flat. Flash calcination therefore results in metakaolin with drastically improved workability, water demand, and reactivity when compared to rotary kiln–calcined metakaolin (San Nicolas et al. 2013).

BLENDED CEMENTS

The composition, structure, and performance of PC, blended cement consisting of PC and SCMs, and alkali-activated cements are discussed in this section.

PC Reactions

Only the principal reactions and phases in PC hydration are described here; the comprehensive texts by Hewlett (2018) and Taylor (1997) may be consulted for further details. PC hydration can be separated into five stages, as determined by calorimetry (Figure 6):

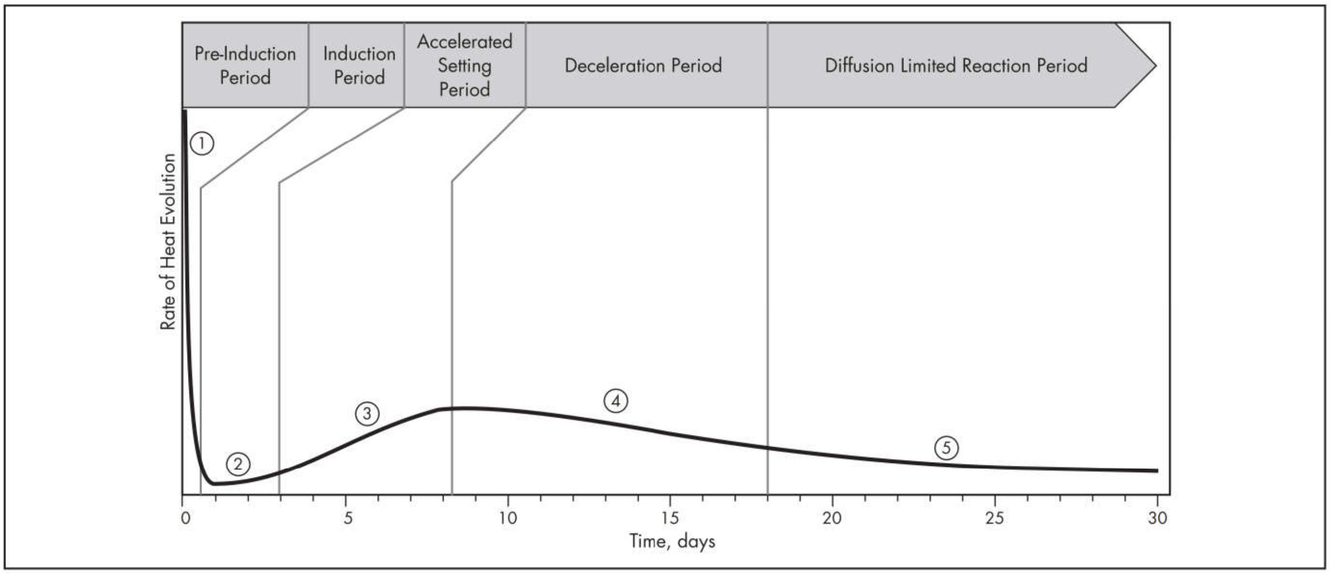
1. **Pre-induction period.** Immediately after contact with water, an intense, short hydration of PC occurs. The hydration rate increases rapidly and subsequently decreases rapidly to very low values (Taylor et al. 1984). An intense liberation of heat may be observed in this stage of hydration. The duration of this period is typically no more than a few minutes, represented by the first very sharp peak at the beginning of the curve in Figure 6.
2. **Induction period or dormant period.** The rate of reaction slows down significantly, while simultaneously the liberation of heat of hydration is also significantly reduced. This stage typically lasts a few hours. This stage is very important because it is the period over which concrete can be handled, transported, and placed with ease.
3. **Acceleration (post-induction) period.** After several hours, the rate of hydration accelerates suddenly, reaching a maximum within about 5 hours from the commencement of acceleration. This phenomenon is explained in detail in the literature (Regourd et al. 1980; Brown et al. 1984; Taylor et al. 1984; Jennings 1986; Grutzeck and Ramachandran 1987).
4. **Deceleration period.** After reaching a maximum, the rate of hydration starts to slow down gradually.
5. **Diffusion limited reaction period.** After the deceleration period, the hydration reactions continue, however at a greatly reduced rate, and are measurable after months of curing.

It is the combination of PC compounds that determines the shape of the reaction kinetic curves. Each of the four main components of PC (C_3S, C_2S, C_3A, C_4AF) dissolves and diffuses in water and then precipitates in different phases that form the binder; these reactions are described below in more detail.

Tricalcium silicate ($3CaO \cdot SiO_2$, abbreviated C_3S), called alite, is the main constituent of PC, and largely controls its setting and hardening (Figure 6). The hydration of C_3S at ambient temperature forms a calcium-silicate-hydrate (C-S-H) phase with a CaO/SiO_2 molar ratio of <3.0, and calcium hydroxide (CH). C_3S hydration is summarized by the following equation:

tricalcium silicate + water →
calcium-silicate-hydrate + lime + heat

$$2C_3S + 6H \rightarrow C_3S_2H_3 + 3CH \qquad \Delta H = 502.8 \text{ kJ/kg}$$



Adapted from Hewlett 2018

Figure 6 Rate of heat of hydration over time

Initially, the dissolution rate of C_3S is higher than the diffusion rate, which allows the movement of dissolved ions away from the surface. This results in a concentration gradient on the surface of C_3S particles; very close to the surface, the liquid phase becomes oversaturated with respect to calcium-silicate-hydrate and a layer of C-S-H precipitates. This precipitated C-S-H is responsible for the large reduction in hydration rate within the first few minutes of C_3S hydration and subsequent acceleration of the reaction after a dormant period. The hydration rate accelerates with increasing water/solid (w/s) ratio. The induction period becomes shortened and at very high w/s ratios may be absent altogether. Also, rapid cooling in the course of C_3S synthesis may increase the reactivity of C_3S.

Dicalcium silicate ($2CaO \cdot SiO_2$, abbreviated C_2S), called belite, is another important constituent of PC. Similar to C_3S, hydration of C_2S at ambient temperature forms an amorphous C-S-H phase and portlandite. The hydration of C_2S contributes to the strength of the cement paste (Figure 6) and can be summarized by the following equation:

dicalcium silicate + water →
calcium-silicate-hydrate + lime

$$C_2S + 4H \rightarrow C_3S_2H_3 + CH \qquad \Delta H = 259.4\ \text{kJ/kg}$$

This reaction generates less heat and proceeds at a slower rate, meaning that the contribution of C_2S to the strength of the cement paste will be slow initially. This compound is, however, responsible for the long-term strength of PC concrete. Similar to C_3S, hydration of C_2S may be accelerated by increasing the fineness of grinding, by increasing the temperature of hydration, or by increasing the w/s ratio.

Tricalcium aluminate ($3CaO \cdot Al_2O_3$, abbreviated C_3A) is usually present in PC in a much lower quantity than C_3S or C_2S. In the presence of calcium sulfate or gypsum, C_3A reacts according to the following equation:

tricalcium aluminate + gypsum + water →
ettringite + heat

$$C_3A + 3C\overline{S}H_2 + 26H \rightarrow C_6A\overline{S}_3H_{32}\ (\text{AFt}) \qquad \Delta H = 866.1\ \text{kJ/kg}$$

Ettringite (abbreviated AFt) consists of long crystals that are only stable in solution with gypsum and does not contribute to the strength of the cement. Hydration of C_3A and gypsum is accompanied by a significant liberation of heat. After a rapid initial reaction, the hydration rate slows down distinctly. The length of this dormant period may vary and escalates with increasing amounts of calcium sulfate in the original paste. A faster hydration, associated with a second heat release maximum, occurs after all the available calcium sulfate has been consumed. Under these conditions, the ettringite formed initially reacts with additional amounts of tricalcium aluminate, yielding calcium aluminate monosulfate hydrate (abbreviated AFm, often called monosulfate) as the product of the following reaction:

tricalcium aluminate + ettringite + water →
monosulfate aluminate hydrate

$$2C_3A + 3\ C_6A\overline{S}_3H_{32}\ (\text{or AFt}) + 22H \rightarrow 3C_4ASH_{18}\ (\text{AFm})$$

The monosulfate crystals are only stable in a sulfate-deficient solution. In the presence of sulfates, the monosulfate is converted to ettringite, whose crystals occupy 2.5 times the volume of those of monosulfate. In a paste hydration at ambient temperature, nearly complete hydration of C_3A is attained within several months. The actual reaction rate depends on a variety of factors, such as the w/s ratio and temperature. The kinetics of hydration of C_3A are also used to explain the induction period. The buildup of ettringite at the surface of C_3A may slow down hydration, but this has been disputed by Mehta and Monteiro (2006).

Calcium aluminoferrite (C_4AF) phases, usually present in PC in low amounts, react initially with gypsum and then with ettringite, according to the following equations:

ferrite + gypsum + water →
ettringite + ferric aluminum hydroxide + lime

$$C_4AF + 3C\overline{S}H_2 + 3H \rightarrow C_6(A,F)\overline{S}_3H_{32}\ (\text{or AFt}) + (A,F)H_3 + CH$$

ferrite + ettringite + lime + water → hydrogarnets

$$C_4AF + C_6(A,F)\overline{S}_3H_{32}\ (\text{or AFt}) + 2CH + 23H \rightarrow 3C_4(A,F)\overline{S}H_{18}\ (\text{AFm}) + (A,F)H_3$$

The hydrogarnets assume a space-filling role and do not contribute to the strength of the cement paste (Figure 6). The assemblage of these phases in concrete, dictating its strength and durability, depends on the composition of the PC and SCMs (Table 2 and Figure 2).

Blended Cements and Supplementary Cementitious Materials

Blended cements consist of PC blended with one or more SCMs, which contribute to the strength-gaining properties of the cement (ASTM C219). Blended cements account for the majority of cementitious binders (Schneider et al. 2011). The increased use of blended cement is due to the growing demand for concrete, the aim to reduce cost and CO_2 emissions, and to provide enhanced durability.

Most standards allow substitution of PC with different SCMs in specified proportions (ASTM C1697). All SCMs must also fulfill requirements of other relevant standards. For example, slag cement (Type S) needs to conform to ASTM C989/C989M, natural pozzolans (Type N) and coal fly ash (Types F and C) need to conform to ASTM C618, and silica fume (Type SF) to ASTM C1240. In Europe, limestone filler and calcined clays (such as metakaolin) are also considered SCM. There are no chemical requirements for final blended cement; however, there are composition requirements for the individual constituents. There are physical requirements for the final blended cement, with further optional requirements listed in ASTM C1697. ASTM standards specify the proportions of SCMs in blended cements. Ternary blended cement cannot have more than 15% by mass of limestone, no more than 40% of pozzolan content, and slag shall be less than 70% by mass of the blended cement. Selected blends are described in the following subsections.

Limestone Cement

In Europe, limestone content can be as high as 35%. Such practice is not permitted by ASTM standards; however, limestone is permitted in high–early strength cement (ASTM cement Type III). The limestone content allowed by ASTM standards is more than 5% but less than or equal to 15% by mass of the blended cement. Blending finely ground limestone to PC has several effects on the properties of concrete. The "filler effect" tends to accelerate PC hydration rates, as replacing PC by limestone increases the w/c ratio and surface area for nucleation, with increase in early strength (Gutteridge and Dalziel 1990; Berodier and Scrivener 2014).

Binders with limestone tend to be denser, which can result in improved durability properties, including enhanced sulfate resistance, and decreased drying shrinkage and carbonation depths (Baron 1988; Barker and Matthews 1994). Even if the limestone does not have pozzolanic properties, it reacts with the alumina phases (C_3A) of cement to form an AFm phase (calcium monocarboaluminate hydrate) with no significant changes in the strength of blended cement (Bonavetti et al. 1999).

Pozzolan Cements

According to ASTM C219, PC-pozzolan cement (Class N) consists of an intimate and uniform blend of PC or PC blast-furnace slag cement and fine pozzolan produced by blending PC or PC blast-furnace slag cement and finely divided pozzolans within specified limits. *PC-pozzolan cement* is defined as a hydraulic cement in which the pozzolan constituent is up to 40 mass %. Several materials qualify as pozzolans, including slag, calcined clay, fly ash, natural pozzolans (volcanic ash), silica fume, and rice husk ash. These materials all comprise amorphous silica to some extent. When a pozzolan is blended with PC and hydrated, the silica within the pozzolan reacts with CH and forms additional C-S-H. This C-S-H has a lower Ca/Si ratio (around 1.55, cf 1.7 for hydrated PC) and is consequently called secondary C-S-H, which fills up large capillary pores, thus improving the strength and decreasing the permeability of the system (Mehta and Monteiro 2006). The general pozzolanic reaction can by expressed as follows:

$$\text{silica component of pozzolan (S)} + \text{portlandite (CH)} \rightarrow \text{secondary C-S-H}$$

$$\mathrm{S} + 1.5\mathrm{CH} + y\mathrm{H} \rightarrow \mathrm{C}_{1.15}\text{-}\mathrm{S}\text{-}\mathrm{H}_{y+1.15}$$

Calcined clays do not have a specific ASTM standard specifying these requirements, so the chemistry of hydrated calcined clay/PC blends is discussed here. Following calcination, kaolin and some montmorillonites have the highest pozzolanic activity compared to other clays, as measured according to ASTM C311/C311M (He et al. 1995). Amorphous aluminosilicate phases (ASx) in calcined clays react with CH in the presence of water, producing a cementing compound like C-S-H, C-A-S-H, or C-A-H according to the following equations:

$$\mathrm{A} + 3\mathrm{CH} + 3\mathrm{H} \rightarrow \mathrm{C_3AH_6}$$
$$\mathrm{A} + \mathrm{S} + 2\mathrm{CH} + 6\mathrm{H} \rightarrow \mathrm{C_2ASH_8}$$
$$\mathrm{A} + x\mathrm{S} + 3\mathrm{CH} + (y - -3)\,\mathrm{H} \rightarrow \mathrm{C_3AS}_x\mathrm{H}_y$$

In PC-calcined clay blends, the clay content is often less than 40% due to strong reduction in the workability of the blended concrete, usually associated with higher water demand (Badogiannis et al. 2005). However, water demand can be reduced by use of flash calcination instead of rotary kiln calcination, allowing higher amounts of PC to be substituted. PC-calcined clay blends also exhibit enhanced mechanical properties. In the case of metakaolin, substitution between 10% and 20% seems to be optimal regarding mechanical properties (Badogiannis et al. 2002).

The pore size of PC-calcined clay cements is often reduced compared to PC due to formation of secondary C-S-H, C-A-H, and C-A-S-H, which reduces permeability and mass transfer (Sabir et al. 2001) and enhances the resistance to chloride migration, sulfate attack, and acid attack (Courard et al. 2003; Al-Akhras 2006). Accelerated carbonation tests, however, showed that increasing the metakaolin content tends to increase the carbonation depth of concretes due to the consumption of portlandite by the pozzolanic reaction (Courard et al. 2003; San Nicolas et al. 2014). However, the carbonation was predominantly within the range of carbonation depths found in commercially available blended cements with proven industrial performance. The combination of metakaolin and limestone filler behaves well with respect to carbonation, similarly to PC on its own. The modeling of CO_2 ingress into concrete shows that, although metakaolin increases carbonation, the carbonation depth does not exceed 30 mm after 5 years, which is acceptable.

Fly Ash Cements

Fly ashes are pozzolanic constituents that are used to partially substitute for PC in Class F and Class C cements. When PC-fly ash blends are hydrated, a pozzolanic reaction occurs, generating low Ca/Si C-S-H and increasing the density and durability of the concrete via two mechanisms:

1. Fly ash substitution for PC results in a binder with a higher w/c ratio, improving the hydration of PC grains (Xu et al. 1993).
2. Fly ash particles tend to absorb Ca^{2+} and provide precipitation sites that accelerate hydration (Lawrence et al. 2003; Cyr et al. 2005, 2006).

Because of the presence of significant quantities of aluminum and silicon in fly ash, additional reactions also occur (Marsh and Day 1988; Papadakis 1999; Zeng et al. 2012):

- $1.5\mathrm{CH} + \mathrm{S} \rightarrow \mathrm{C}_{1.5}\,\mathrm{SH}_{1.5}$
- $\mathrm{A} + 4\mathrm{CH} + 9\mathrm{H} \rightarrow \mathrm{C_4AH_{13}}$
- $\mathrm{A} + \mathrm{C\overline{S}H_2} + 3\mathrm{CH} + 7\mathrm{H} \rightarrow \mathrm{C_4A\overline{S}H_{12}}$

Fly ash reacts slower than other pozzolans, which explains the small increase in setting time for fly ash–based concretes compared with PC on its own, especially if Type III and not Type I is used (Carette et al. 1993; Bilodeau and MalhotraI 1995). Usually, even a high fly ash substitution shows acceptable setting time and adequate early strength (Dunstan and Hicks 2003). In the fresh state, the substitution of PC by fly ash increases the workability of the concrete at the same w/s ratio, resulting from the spherical shape of fly ash particles and the wider size distribution that decreases yield stress; consequently, the w/c ratio can be reduced. In general, the mechanical properties of fly ash concrete are excellent, due to lower water content and denser microstructure. High-volume fly ash concrete has low chloride penetration, low permeability, high sulfate resistance, and good freeze–thaw resistance, but it has inferior deicing salt scaling resistance compared with PC on its own (Bisaillon and Malhotra 1988).

Silica Fume Cements

Silica fume in Class SF cement is a highly reactive pozzolan, typically with a much smaller particle size than PC, which gives an added filler effect by accelerating the hydration of C_3S (Cheng-yi and Feldman 1985a, 1985b) and provides more nucleation sites. The hydrates obtained in this system are primarily C-S-H, ettringite, and AFm phases and a reduced quantity of portlandite. The blending of PC with ≥24 mass % silica fume results in complete consumption of portlandite after longer hydration times, with ettringite and C-S-H of a reduced Ca/Si ratio as the only hydrate phases (Cheng-yi and Feldman 1985a, 1985b; Calvo et al. 2010; Lothenbach 2010; Rossen et al. 2015). The substitution of PC in Class SF cements is usually between 5% and 10%, which gives reduced bleeding, enhances mechanical properties, and improves durability of the concrete. Higher additions of silica fume (up to 50%) can also be used for low-pH materials (Lothenbach et al. 2012).

Slag Cements

The use of GGBS as a PC replacement in Class S cements is widely practiced due to technological, economic, and environmental benefits. According to ASTM C219, slag cement is a uniform blend of PC and GGBS, where the content of GGBS has to be kept below 95% by mass of the blended cement. GGBS shows both cementitious behavior and some pozzolanic characteristics (reaction with portlandite). The main hydration products of the slag-cement are C-A-S-H, $Ca(OH)_2$, the sulfoaluminate hydrate phases AFt and AFm, and a Mg, Al-rich hydroxide phase. The phases formed are similar to those in a PC-only binder; however, the chemistry is somehow different. For example, the morphology and composition of the C-A-S-H gel may be modified by partial accommodation of Mg^{2+} and Al^{3+} within the micro- or nanostructure, and their Ca/Si ratio becomes lower (e.g., 1.55). A hydrotalcite-like phase with approximate composition $Mg_6Al_2(OH)_{16}(CO_3)\cdot 4H_2O$ is formed from the MgO content of the GGBS, typically 5%–9% (Chen 2006).

One of the principal reasons for the use of GGBS in blended cements is the reduction of the heat released during the hydration process, which reduces thermal stresses in concrete (Sakai et al. 1992; Binici et al. 2007) and improves long-term strength and modulus of elasticity, reduces its long-term shrinkage and creep, and significantly decreases its permeability at later ages. The long-term durability properties of PC-slag blends are enhanced compared with neat PC, which increases resistance to the penetration of chloride ions (Escalante et al. 2001; Kolani et al. 2012), with little impact on freeze–thaw resistance. Concrete incorporating GGBS can cost less than concrete made with PC only; costs are dependent on the availability of GGBS in a market, transportation and handling costs, and who controls that market.

Ternary Blended Cements

Ternary blended cements can be developed by combining the different positive attributes of SCMs with the PC system, such as the filler effect, pozzolanic effect, and chemical balancing. LC^3 (limestone calcined clay cement) has recently been promoted strongly in Europe and the United States and may meet ASTM guidelines. Parallel chemical reactions occur in these blends, with the cement reacting with water in the same way as in pure PC, and the limestone reacting with alumina from the metakaolin to form supplementary AFm phases and stabilized ettringite (Antoni et al. 2012). The pore size of LC^3 concrete appears to be smaller than in PC concrete, improving durability performance (e.g. reducing chloride migration; Antoni 2013).

Alkali-Activated Cements

It is possible to make a cement without PC, containing just SCMs and alkali activator, which is called alkali-activated cement. These cements have been demonstrated in many projects but are not yet widely available commercially. As more countries have standards based on performance instead of being prescriptive, these materials can be used and have been demonstrated to perform well. The following paragraphs describe the composition of the binder and general properties of concretes made from these alkali-activated binders. For further details, please see Pacheco-Torgal et al. (2014) and Provis and van Deventer (2014).

The main reaction product of alkali activation of silica-rich precursors such as fly ash or metakaolin is a three-dimensional alkali aluminosilicate hydrate gel network consisting of cross-linked AlO_4^- and SiO_4 tetrahedra linked via shared oxygen atoms denoted as "bridging oxygen," with terminal hydroxyl groups forming at the gel surface, or (N,K)-A-S-H (Davidovits 1994; Duxson et al. 2007; Bernal et al. 2013; Provis and van Deventer 2014). The level of network-modifying cations present affects the compressive strength of the geopolymer binder formed upon alkali activation, with strength generally increasing with increasing network-modifying cation content. Alkali activation of GGBS (generally with sodium silicate solution, although other alkali solutions can be used) produces an aluminum-substituted calcium-silicate-hydrate (C-(N)-A-S-H) gel plus possibly portlandite, calcium monosulfoaluminate (and similar hydrocalumite-like "alumina, ferric oxide, monosulfate [AFm]" phases with carbonate, aluminosilicate, or hydroxide anion substitution), the "third aluminate hydrate," Mg-Al layered double-hydroxide phases such as hydrotalcite and M_4AH_{13}, ettringite, and hydrogarnet. These additional reaction products are intimately mixed with the C-(N)-A-S-H gel framework because of differences in bulk composition stability (García-Lodeiro et al. 2011; Lothenbach et al. 2011) and can significantly influence gel-phase evolution and nanostructural development.

Coexistence of N-A-S-H and C-(N)-A-S-H gel frameworks has been observed in binders based on blends of low-calcium and high-calcium precursors (Yip et al. 2005; Bernal et al. 2011b, 2013; Ismail et al. 2014); however, the stability of the gel coexistence remains unclear. Blends of different precursors can often show advantages over pure systems (Bernal et al. 2011a).

ENERGY CONSUMPTION AND EMISSIONS

The manufacturing of PC is energy intensive, and with the associated emission of carbon dioxide resulting from the decomposition of limestone, the PC industry globally is one of the highest emitters of CO_2. This section analyzes the sources of energy consumption and emissions for PC and explains how CO_2 emissions can be reduced by blending with SCMs and/or alkali activation.

Energy Consumption of PC Manufacturing

The energy consumption in a PC plant is shared between thermal and electrical energy. Assessments of energy consumption conducted on more than 100 PC plants in Europe and the United States estimated the thermal energy share at around 90% against 10% for the electrical energy share. The kiln alone is responsible for 99% of this thermal energy consumption plus 25% of the electrical energy consumption (Schneider et al. 2011). The rest of the electrical energy is associated with grinding and drying of the raw mix (60%), and finally, 15% is associated with handling and carrying materials (Afkhami et al. 2015).

Much effort has been dedicated to reducing the energy consumption of PC plants. It has been demonstrated that if the efficiency of the kiln is low, the energy loss is around 40% (Atmaca and Yumrutaş 2014). To date, the most economical and practical option to improve the efficiency of the kiln is to add heat exchangers, which recycle heat at different stages of PC manufacturing. Improving the insulation and the combustion efficiency of the kiln also improves the general efficiency of the kiln system. The optimum size of kiln in regard to energy efficiency is dependent on the moisture content of the raw materials.

PC plants have actively reduced their energy consumption over the past 40 years, especially with the increased use of alternative and waste fuel such as tires, animal residues, sewage sludge, waste oil, and lumpy materials. In most plants, these alternative fuels are replacing all of the fuel used in the precalcination stage of the PC process; however, their use for clinker kilns is still progressing. Importantly, the combustion process needs to be adapted to the fuel employed; consequently, it is common to find modern multichannel burners designed for the use of alternative fuels and thermograph systems allowing control of the flame shape to optimize the burning behavior of the different fuels and burning conditions. The use of most alternative fuels does not have any effect on the final clinker. Nevertheless, phosphorous-rich fuel such as meat and bone meal or sewage sludge retards setting.

Emissions of PC

The CO_2 emissions associated with PC production can be classified into two groups: direct emissions as a result of the intrinsic chemical reaction occurring during thermal processing (calcination) of limestone ($CaCO_3$) to produce cement clinker (55%), and indirect emissions associated with energy requirements for thermal processing, crushing, grinding, and transport (45%).

The use of limestone as a raw feedstock for clinker production results in a total CO_2 embodiment of 0.73–0.99 t CO_2/t PC, with the variation primarily due to the kiln efficiency during PC clinker production (Bernstein et al. 2007). It has been estimated that by 2050, CO_2 emissions associated with PC production will account for 20%–26% of the total global anthropological CO_2 emissions (Beyond Zero Emissions 2017). Therefore, there is ample justification for seeking an alternative binder to high-PC blends.

The manufacturing of PC also causes emissions other than just CO_2 and has global environmental impacts, including abiotic depletion, ozone layer depletion, human toxicity, fresh-water aquatic effects, ecotoxicity, photochemical oxidation, acidification, and eutrophication (Oss and Padovani 2003; Kumar et al. 2008; Huntzinger and Eatmon 2009; Habert et al. 2011).

Reduction of Energy Consumption and Emissions of Cement by Blending and Alkali Activation

The energy consumption and emissions of PC can be reduced by blending with SCM. All the SCMs have a lower energy consumption compared to PC; hence, the more SCMs used in a blend, the lower the net energy consumption. The hierarchy of energy consumption of SCMs is: calcined clays > slag, limestone > fly ash, silica fume.

Clay calcined at about 700°C is the SCM with the highest energy consumption, even when its production uses 50%–80% less energy than PC production. Similar to clinker kilns, heat exchangers and plant modifications can reduce the energy needs of calciners. Rotary kiln calcining requires higher energy than flash calcining, not only regarding thermal energy used for calcination but also concerning the electrical energy required to grind the calcined product from a rotary kiln, which is not required in flash calcination (Salvador 1995; San Nicolas 2011; San Nicolas et al. 2013).

Slag and limestone as SCMs require less energy than calcined clay but still need to be ground finely. The power consumption for slag grinding in a VRM is about 30 kW·h/t compared with the 40 kW·h/t for a ball mill. Silica fume and fly ash (requires classification) do not need energy for grinding because they are both fine products and hence are the SCMs with the lowest energy consumption. Even when the processing of SCMs used in blended cement involves some energy consumption, it is much less than when only PC is used (Schneider et al. 2011). The embedded CO_2 emissions of the SCMs are very low, so the higher the SCM content of a blended cement, the lower its CO_2 emissions.

Many SCMs can be alkali activated, which gives further reduction in CO_2 emissions as a result of the elimination of PC with high CO_2 emissions. The production of alkali activators requires energy and generates CO_2 emissions, which vary vastly in intensity from one activator to the next. For example, some alkali activators may be waste products from other industries with no inherent emission penalty (Pacheco-Torgal et al. 2014; Phetchuay et al. 2014). A commonly used activator is sodium silicate, which has inherent emissions from the smelting of sodium carbonate with silica sand, where the emissions of sodium carbonate may vary vastly, depending on whether it is mined or chemically synthesized. Activators also have environmental impacts other than CO_2 emissions (Habert et al. 2011). Alkali-activation technology can reduce CO_2 emissions by about 80% in comparison with blended PC available in Australia (van Deventer et al. 2012).

TECHNO-ECONOMIC PERSPECTIVES

Cement production cost and market pricing are complex functions of the cost of raw material, energy, labor, transportation and capital, the scale of operations, market positioning, and competition. These factors are discussed with regard to changes in the market, partly due to climate change, and technological developments.

Production Costs and Cement Pricing

A survey of PC producers in the United States gives the following breakdown of production cost of PC as a percentage of the sales price (Pabon 2014):

- Power and fuel: 30%
- Limestone and other raw materials: 30%–40%
- Transportation: 10%
- Maintenance, labor, administration: 15%–20%

As explained earlier in this chapter, the production of clinker is energy intensive, so the cost of power and fuel (natural gas, fuel oil, coal, diesel, pet coke, lignite, used tires, and other waste) has a major impact on the operating expenditure of a PC plant. According to the survey by Pabon (2014), the energy consumption is 130–150 kW·h/t of clinker.

The location of a PC plant is largely dependent on the proximity of sources of raw materials and the market, and hence a function of the cost of transportation. A PC plant is usually located near a limestone quarry, but there are cases where low-cost water transport justifies a location closer to the market. Road and rail contribute more than 90% of the transportation of PC product.

Modern PC plants rarely have a capacity of less than 300,000 t clinker per year, whereas large plants in China frequently produce in excess of 10 Mt clinker per year. The capital and operating costs of clinker production are strongly dependent on scale, so there is a trend for clinker to be produced in very large plants close to limestone quarries, not just for the local market but also for export. Countries like China, Thailand, United Arab Emirates, Turkey, Vietnam, Japan, and India export a sizable portion of their PC production, usually at a lower landed cost than the production cost in the destination country. To protect local PC production, some countries impose tariffs on imported PC, but usually not on imported clinker. Therefore, clinker is often shipped from the low-cost countries to remote locations with smaller markets where it is ground to become PC. These grinding plants may also source slag granulates from remote suppliers and grind it to become GGBS, which they may blend with the PC. Similarly, fly ash from local coal-fired power stations may also be used for blending with PC.

Cement prices vary by a factor of 3 or more from one location to another. Evidently, large local markets near deposits of limestone result in low transportation costs and, associated with low labor costs, give low PC prices, especially in the presence of competitive market action. In contrast, locations where PC is most expensive are characterized by a small market size, a high cost of transportation, restricted access to importation infrastructure, and limited or ineffective competition.

The availability of local SCMs such as fly ash or slag that can be ground (to become GGBS) to blend with PC should, in theory, reduce the price of blended cement in the market. In practice, such price reduction does not always happen, especially when fly ash or GGBS is in short supply or when cement companies also control the supply chain of these SCMs. For example, unclassified ash may be more widely available, but cement companies may have exclusive supply arrangements with coal-fired power stations and control classification plants, and hence determine the price of classified fly ash. Unground slag granulates may be available in a market, but often there are only a few independent facilities for the grinding of slag, apart from the cement companies purchasing and grinding slag for blending with PC. The result is that the prices for GGBS and classified fly ash in a market may be on par with or slightly less than the PC price. In such markets there is little incentive for new entrants to introduce high-SCM-blended cement or alkali-activated cement, unless an independent supply chain can be established to reduce the cost of SCM.

Developments in Grinding Technology

Currently, cement and slag grinding plants are large ball mills or VRMs that are capital intensive and often located in association with PC operations. It is not practical to use such equipment in smaller markets to exploit waste streams such as metallurgical or steel slag, or virgin materials like volcanic ash or rock that can be used as SCM.

Loesche (2017) in Germany has recognized this limitation and now has a compact VRM available for remote locations where a customer will grind PC clinker and/or slag granules in smaller volumes. The Universal Vortex acoustic grinder produces a shock wave generated in a precisely designed geometry to shatter brittle materials and has been used at demonstration scale for clinker and slag granules (van Deventer 2017). The advantage of the Universal Vortex is that it fits into a shipping container, so it is mobile and can be deployed easily in remote locations for the grinding of smaller volumes of material and also for one-off construction projects.

Potential Impact of Alkali Activation and Modularized Grinding on Cement Value Chain

Alkali activation has the potential to expand the scope of SCMs used in cement, especially in hybrid cements incorporating clinker as a minor component. The result will be the valorization of waste streams currently not utilized as cementitious materials, which should reduce the cost of cement in remote locations or smaller markets. Mining often takes place in locations remote from established markets and PC supply chains. Consequently, PC used in either backfill or shotcrete may be a substantial part of the operating cost of a mine. If indigenous mine waste such as clays or volcanic material could be used as SCM, even when alkali activated, less PC will be required, with substantial savings in transportation cost. Usually, the beneficiation of mine waste as a SCM will require dry fine-grinding in addition to calcining if clays are used.

With the development of modularized grinding technology, it becomes possible to grind smaller amounts of SCMs and even clinker. The possibility to decentralize grinding gives a lower barrier of entry to the cement market that may change the cement value chain. An associated benefit of modularized grinding is that it becomes economical to transport smaller volumes of clinker or slag granulates in bulk carriers (shipping, road, or rail) to remote locations, which is cheaper than transporting cement powder in pneumatic tanks.

Performance-Based Versus Prescriptive Standards

The regulatory framework for cement and concrete in most jurisdictions has been prescriptive, even when it is claimed superficially that such standards are performance based. Standards frameworks often restrict the definition of SCMs to GGBS and fly ash, usually place an upper limit on the SCM content, and hence prescribe concrete compositions. To enable the wide adoption of advanced concrete technologies, including alkali activation, it is essential that performance-based standards be adopted instead of the current prescriptive system. There should be no restriction on the type of components used, either as cementitious material, aggregates, or admixtures/activators. The amount of cementitious material and the w/c ratio should also not be restricted.

It is important to decide which performance and durability testing methods should be used to specify performance criteria. In a critical review of performance-based approaches (Alexander and Thomas 2015), it was explained that it is possible to relate service-life prediction models to durability testing, even when it is known that the diffusion parameters in concrete are complicated by several factors, including interaction between the diffusing species and the matrix, and the reduction of diffusion coefficients with age.

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