

ACI Education Bulletin E3-13

Cementitious Materials for Concrete

Developed by ACI Committee E-701



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Cementitious Materials for Concrete

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CEMENTITIOUS MATERIALS FOR CONCRETE

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This document discusses commonly used cementitious materials for concrete and describes the basic use of these materials. It is targeted at those in the concrete industry not involved in determining the specific mixture proportions of concrete or in measuring the properties of the concrete. Students, craftsmen, inspectors, and contractors may find this a valuable introduction to a complex topic. The document is not intended to be a state-of-the-art report, user's guide, or a technical discussion of past and present research findings. More detailed information is available in ACI 225R-99, "Guide to the Selection and Use of Hydraulic Cements," ACI 232.2R-03, "Use of Fly Ash in Concrete," ACI 233R-03, "Slag Cement in Concrete and Mortar," and ACI 234R-06, "Guide for the Use of Silica Fume in Concrete."

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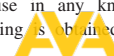
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CHAPTER 1—INTRODUCTION

Concrete is made from a properly proportioned mixture of hydraulic cement, water, fine and coarse aggregates and, often, chemical admixtures and supplementary cementitious materials (SCMs). The most common hydraulic cement used in construction today is portland cement. Although other types exist, portland cement is the most widely manufactured and the focus of this document. Exceptions are noted otherwise. The successful use of concrete in construction depends on the correct selection of the appropriate materials necessary and the proper proportioning of those materials. This requires knowledge of the material properties and the tests used to measure those properties.

The selection and characterization of hydraulic cement and SCMs are the subjects of this bulletin, while aggregates, admixtures, and concrete characteristics are discussed in companion volumes. There are several varieties of hydraulic portland cement, as recognized by **ASTM International**, which vary in their properties. Hydraulic cement is defined as cement that sets and hardens by chemical reaction with water and is capable of doing so underwater. The following chapters review the composition and properties of the various portland cements and SCMs, discuss the tests used to evaluate a cement, and consider how cement properties influence the performance of the concrete.

1.1—History of portland cement

The name “portland” originates from a trade name used by Joseph Aspdin in 1824 to describe the new cement he patented that year in England. He claimed that the artificial stone (concrete) made with his cement was similar in appearance to portland stone, a high-quality limestone used in construction during that time period. Although the term “portland cement” dates from Aspdin’s patent in 1824, hydraulic cement as a material can be traced back to ancient times, where several famous landmarks of the Roman era owe their survival to the cementitious qualities of the forerunner to portland cement.

The portland cement industry quickly spread in England. By 1890, there was a flourishing export business to the United States. The fledgling U.S. industry founded by David Saylor at Coplay, PA, in 1871, soon captured the domestic market. U.S. production rose from 54,000 metric tons (60,000 tons) per year in 1890 to 1.5 million metric tons (1.7 million tons) in 1900, and by 1915 had increased to 14.1 million metric tons (15.5 million tons). Early cement production was measured on the basis of a barrel. One barrel of cement was equivalent to 374 lb (170 kg) of cement. One-quarter barrel of cement was then equivalent to 94 lb (43 kg), which quickly became the accepted basis for the quantity of cement in a bag or sack. Today, more than 121 million metric tons (133 million tons) of portland cement are used each year in the United States. The worldwide consumption of cement is more than 2160 million metric tons (2376 million tons). In the past, cement production was measured in tons (2000 lb) and now it is measured in metric tons (1000 kg). A metric ton, or megagram (Mg), is equal to 1 million grams and is approximately 10% more than a U.S. ton.

1.2—Sustainability

The sustainable attributes of concrete are strongly tied to the service life and performance of the cementitious binder system used. Conventional systems based on portland cement have an unparalleled record of performance under a wide range of conditions. However, as is the case with manufacturing processes used in the production of other building materials, production of portland cement requires a significant amount of energy and inherently produces greenhouse gases. Given this fact, engineers have developed approaches to improving the sustainability of concrete by an increased use of cementitious materials that rely less on portland cement and more on alternative materials (for example, coal fly ash, silica fume, slag cement, and natural pozzolans). Through the use of alternative materials, the ability to accomplish significant reductions in the embodied energy and greenhouse gas emissions associated with portland cement production has served to significantly improve the overall sustainability of concrete. In the future, the use of alternatives to portland cement will only increase. However, any changes in the binder system used in concrete must be accomplished without sacrificing the service life and performance attributes that have made concrete the most widely used construction material on the planet.

When examining the sustainability of concrete, and specifically the role of the hydraulic cement binder system in achieving sustainability goals, it is important to consider those areas where portland cement contributes. Portland cement provides a low-cost, effective binder system, whether used alone or in combination with alternative materials. As a result, society has reaped the benefits, enabling the construction of bridges, roads, dams, and buildings that simply cannot be constructed with other materials. Importantly, the most critical infrastructure systems of our society are built with concrete that uses a portland-cement-based binder system. The societal benefits of concrete, and in particular the societal benefits of portland cement, cannot be overstated.

and must be considered when evaluating the sustainability of both materials.

It is equally important to identify those areas where improvements in the sustainability of all cementitious materials need to occur, including portland cement. Relative to the latter point, it is also important to recognize the progress of the portland cement industry toward reducing the embodied energy and greenhouse gas emissions associated with cement production. These improvements are striking when compared to almost any other industry; yet, there is more to accomplish. The portland-cement concrete industry is committed to achieving universal recognition as being a sustainable choice by continuing to improve and innovate the processes of cement production, as well as all other aspects of concrete production and use.

When measuring the sustainability of a construction material, it is necessary to assess the environmental impact of the material over the entire life cycle of the structure. The embodied energy and greenhouse gas emissions associated with portland-cement-based construction are largely associated with the material manufacture and initial construction phases of a structure's life cycle. After this initial phase, the durability and inherent long service life of concrete results in structures that require little to no additional energy expenditures associated with materials-related maintenance or rework. Also, buildings constructed using concrete are more thermally efficient, resulting in a reduced carbon footprint associated with the operation phase. When the structure has reached the end of its service life, the concrete material can be entirely recycled and reused without requiring disposal in landfills. This cradle-to-cradle life cycle for concrete materials must be considered when comparing the sustainability associated with different construction options.

1.2.1 Increased use of alternative cementitious materials—Alternative cementitious materials can be broadly grouped as SCMs, blended cements, and non-portland-cement-based cementitious systems.

Generally speaking, SCMs are materials added to a concrete mixture as a partial replacement for portland cement. A number of materials have been used for this purpose, including, but not limited to, coal fly ash, slag cement, silica fume, metakaolin, pumice pozzolan, and rice husk ash. Blended cements often use the same SCMs, but rather than being blended into the concrete at the time of mixing, the materials are added to the portland cement as an additional production step. A key benefit of blended cement is that the resulting cementitious material tends to be more consistent relative to that achieved by mixing at the point of concrete production. In addition, blended cement can be optimized for fineness and chemistry of the finished product. In comparison, the key benefit of adding an SCM directly to the concrete mixture is more freedom to develop custom mixtures that use a higher replacement of portland cement than may be available in blended products. Regardless of the mixing method or the specific SCM used, partial replacement of portland cement with an SCM reduces the greenhouse gas emissions and embodied energy associated with the portland cement fraction of concrete.

Non-portland-cement-based cementitious systems are emerging technologies that are increasingly being accepted for concrete production. These cementitious systems include alkali-activated slag cements, alkali-activated fly ash, calcium aluminate cements, calcium sulfoaluminate cements, and recycled-glass-based cements. They share the commonality that no portland cement is used in the binder system. These binder systems have been used for specific applications across the world for several decades but have not gained wide acceptance. However, as the construction industry develops a broader awareness of sustainability, it is expected that the use of these materials will increase in the future.

1.2.2 Portland cement industry sustainability goals—Any enhancement in sustainability will be partially the result of improving how portland cement is produced but also the result of diversifying the combinations of cementitious materials used in the hydraulic cement binder system.

With respect to cement production, the U.S. cement industry has committed to four major goals to further improve its environmental impact (**Portland Cement Association 2008b**):

- Carbon dioxide (CO₂)—The U.S. cement industry has adopted a 2020 voluntary target of reducing CO₂ emissions by 10% (from a 1990 baseline) per ton of cementitious product produced or sold.
- Cement kiln dust (CKD)—The U.S. cement industry has adopted a 2020 voluntary target of a 60% reduction (from a 1990 baseline) in the amount of CKD landfilled per ton of clinker produced.
- Environmental management systems (EMSs)—The U.S. cement industry has adopted a voluntary target of at least 90% of U.S. cement plants having implemented an auditable and verifiable EMS by 2020. As of 2010, 68% of U.S. plants had implemented these systems.
- Energy efficiency—The U.S. cement industry has adopted a 2020 voluntary target of 20% improvement (from a 1990 baseline) in energy efficiency as measured by total Btu-equivalent per unit of cementitious product.

1.2.3 Reduction in embodied energy—For decades, the cement industry has been steadily improving the environmental footprint of portland cement by reducing the energy consumption it takes to make clinker—the material produced in the kiln that is later ground with gypsum to make portland cement. Figure 1.1 shows the energy required to produce a ton of clinker and how process improvements have led to a 13% drop since 1988. Since 1972, the energy used has dropped by approximately 37% (**Portland Cement Association 2008a**).

1.2.4 Beneficial reuse of materials—Concerning the selection and use of raw materials, the cement industry has historically been a leader in the beneficial reuse of industrial by-products or waste materials. As an example, waste oils and scrap tires are commonly used as fuels in cement manufacture, and coal fly ash, blast-furnace slag, and CKD are commonly used as raw materials in clinker production in addition to their use as ingredients in concrete. Other materials used in cement manufacture include copper

slag, foundry sand, mill scale, sandblasting grit, synthetic gypsum, and tire-derived fuels. The high volumes of raw materials used to make cement and the detailed chemical analysis of raw materials allows for the chemically efficient and beneficial use of large volumes of industrial by-products. These materials would otherwise be landfilled and thus their beneficial use in cement manufacturing reduces the volume of these waste streams in addition to reducing the use of virgin materials.

1.2.5 Reduction in clinker factor—Recent changes to cement specifications have provided opportunities to use beneficial supplements to portland cement clinker in cement production. **ASTM C150/C150M-12 (AASHTO M 85-12)** now permits the use of up to 5% by mass of limestone and up to 5% by mass of inorganic processing additions, often coal fly ash or slag cement. Both of these changes reduce the amount of clinker in portland cement, which lowers the embodied energy and reduces the greenhouse gas emissions related to cement manufacture. Although chemical and physical requirements in the specifications limit the amount of these nonclinker materials to less than 10%, estimates for the reductions are significant nonetheless (Nisbet 1996). Extensive data were developed to demonstrate that equivalent performance was achievable with these changes (for example, Hawkins et al. 2005). Further reductions to the environmental impacts of cement production are possible through the use of blended cements (**ASTM C595/C595M-12e1 [AASHTO M 240-12]**) or performance-based cements (**ASTM C1157/C1157M-11**). In these cements, higher amounts of slag cement, fly ash, and natural pozzolans are used; thus, the amount of pyroprocessed materials in cement is reduced, as is the amount of calcined limestone.

1.2.6 Closing—When discussing the sustainability of concrete, it is important to recognize that concrete is more than cement. It is an engineered system that can be designed or optimized for any number of properties. In that design process, a number of decisions must occur that can have a profound effect on sustainability. Among these are the design of the binder system, the use of SCMs, adoption of hydraulic cements with a lower clinker factor, and optimization of the mixture proportions to minimize the total cementitious content. All of these are significant contributors to the overall sustainability of concrete.

CHAPTER 2—MANUFACTURE OF PORTLAND CEMENT

Portland cement is a finely ground gray powder chemically formed by combining raw materials containing calcium oxide (CaO), silica (SiO₂), alumina (Al₂O₃), and iron oxide (Fe₂O₃); heating this mixture to a high temperature; and then grinding the resulting material—called clinker—with a small quantity of calcium sulfate (CaSO₄).

In principle, the manufacture of portland cement is simple. It is made from abundant raw materials such as limestone, clay, sand, fly ash, and mill scale, to name a few. Intimately blended raw materials are heated in a kiln to 1400 to 1600°C (2550 to 2900°F)—the temperature at which these materials chemically interact to form the cementitious minerals in

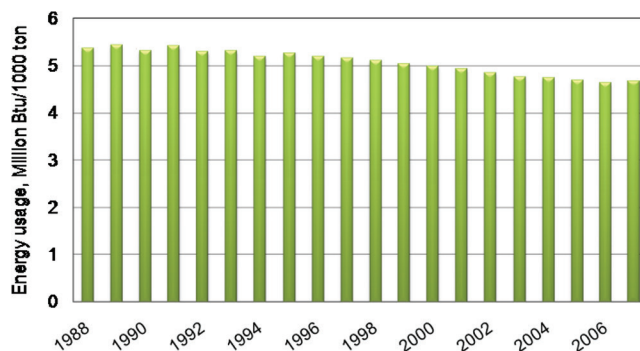


Fig. 1.1—Energy consumption data (1988 through 2007) for U.S. cement industry (Portland Cement Association 2008a) (reproduced by permission from Portland Cement Association, Skokie, IL).

portland cement. Considerable attention is paid to the various stages of processing to maintain good quality control. This processing requires 60 to 80 separate and continuous operations, the use of a great deal of heavy machinery and equipment, and the consumption of large amounts of fuel and electrical energy.

Typical steps in the manufacture of portland cement are illustrated in Fig. 2.1. Each manufacturer of portland cement uses a trade or brand name under which it is sold, but the material is made by the same general processes to conform to the applicable requirements for the type of cement.

2.1—Raw material preparation

The manufacture of portland cement requires blending raw materials to obtain appropriate proportions of lime (CaO), silica (SiO₂), alumina (Al₂O₃), and iron oxide (Fe₂O₃). High-quality cements require raw materials of proper chemical composition proportioned to precise quantities. Limestone, which consists primarily of calcium carbonate, is the most common source of lime, although other raw materials such as dolomite, chalk, shell deposits, and calcareous muds are used for this purpose. The location of cement plants is most often determined by the occurrence of suitable calcareous (lime-rich) deposits, as lime represents the largest portion of the raw mixture. Proximity to the market area is also an important factor. A suitable source of silica can usually be obtained close at hand. Iron-bearing aluminosilicates are often used as the primary source of silica. Clays or silts are preferred because they are already in a finely divided state, but shales, schists, and other argillaceous rocks are also used. Typical sources of these materials and their chemical compounds are given in Table 2.1.

A nearby quarry is the source of the basic material. The raw material is transported to the primary crusher by truck or rail. Upon leaving the primary crusher, the material is then conveyed to a secondary crusher system, where it is reduced to a maximum size of usually less than 25 mm (1 in.). The crushed material is then stored in a raw material storage facility.

Raw materials are carefully proportioned and ground in roller presses (vertical mills) or ball mills to a fineness

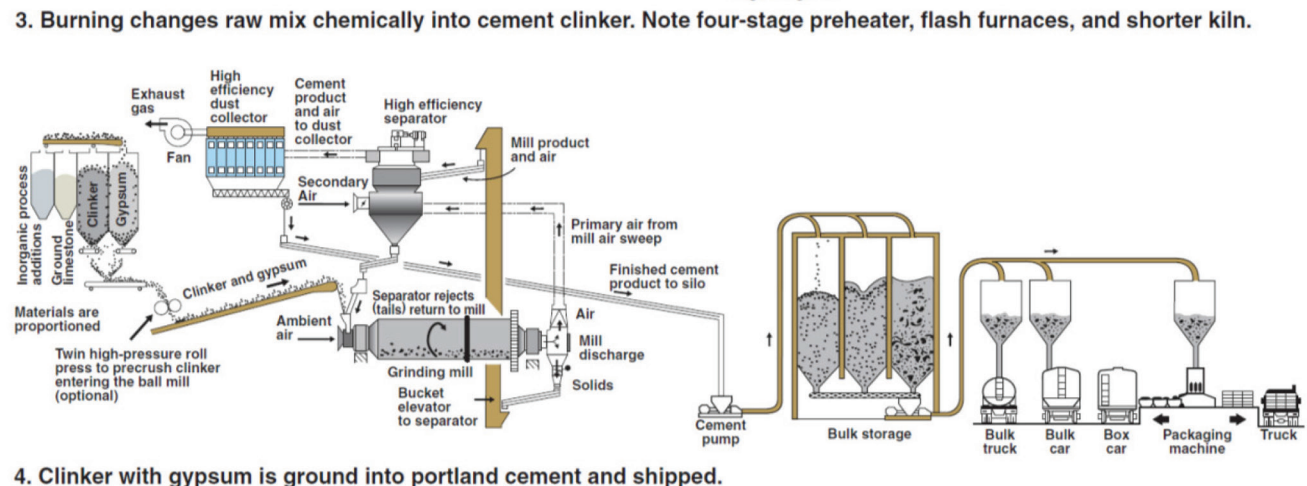
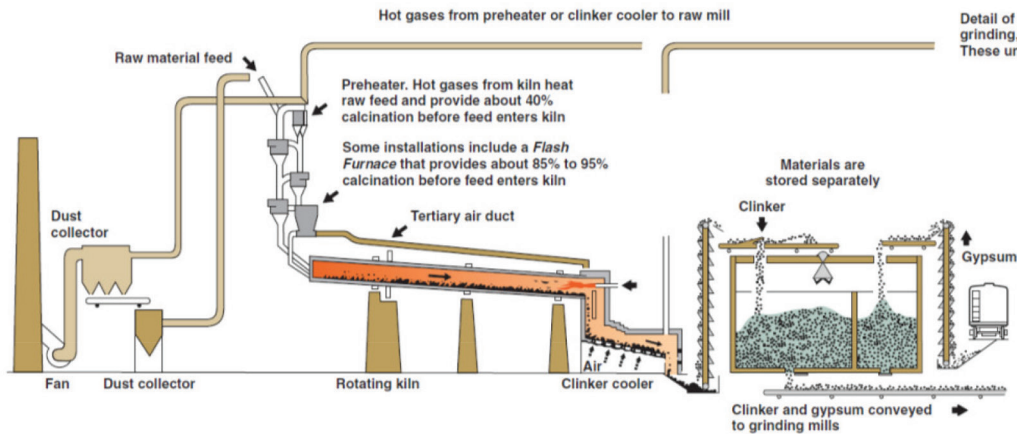
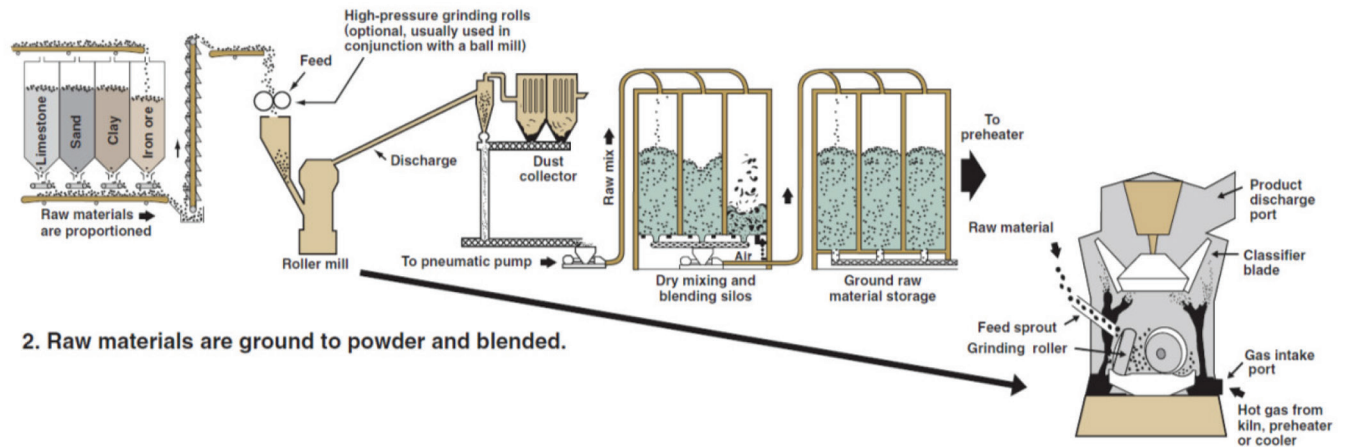
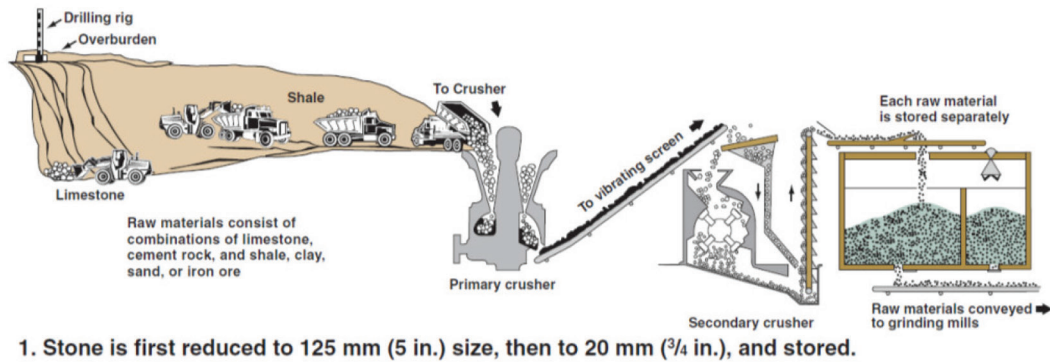


Fig. 2.1—Steps in manufacturing cement (Kosmatka and Wilson 2011).

similar to face powder. The ground material is then transported by pneumatic means through a pipeline to storage and blending silos. The material is constantly blended and checked for uniform chemical composition. The object of processing the raw materials is to ensure that the raw feed entering the kilns is of constant composition, finely divided, and chemically well-balanced. This results in a cement of uniform composition and predictable properties. A uniform mixture also ensures that the kiln temperature can be kept fairly constant near the optimum burning temperature.

2.2—Pyroprocessing

Once the raw feed has been satisfactorily ground and blended, it is ready to enter the kiln system, where pyroprocessing (burning) occurs. The rotary kiln is a long steel cylinder inclined a few degrees from the horizontal and rotated at 6 to 20 rpm about its axis. Modern kilns are up to 6 m (20 ft) in diameter and over 180 m (600 ft) long, with a production capacity exceeding 4500 metric tonnes/day (5000 tons/day).

There are three phases in clinker manufacture, the first being dehydration, where water is driven off of the incoming raw materials. Second is calcination, where carbon dioxide is driven off (from the conversion of calcium carbonate to calcium oxide). The final step is sintering (or clinkering), which occurs in the hottest part of the kiln and recombines the oxides in the raw materials into the desired clinker minerals.

In the typical modern kiln system, the raw feed enters the top of the preheater tower, where the dehydration step occurs and calcination begins. The material then enters the kiln, where the combination of rotation and inclination slowly moves the material the length of the kiln. Burning fuel, consisting of powdered coal, fuel oil, or gas, is forced into the lower end of the kiln, producing temperatures of 1400 to 1600°C (2550 to 2900°F) in the hottest part of the kiln. As the feed moves through the kiln, the calcination step is completed and the material enters the clinkering zone, where new chemical compounds are formed. Heating to these high temperatures consumes large quantities of energy, much of which is lost with the exiting gases. Often, the heated exhaust gases are used to raise the temperature of the incoming feed in special heat exchangers called preheaters.

2.3—Final processing

Material exiting the kiln is known as clinker—dark gray, porous nodules (13 to 50 mm [0.5 to 2 in.] in diameter) that are still hot. The clinker is cooled by forced air and then conveyed to storage or immediately to ball mills, where it is ground to a fine gray powder. A small amount of gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$), anhydrite (CaSO_4), or both is interground with the clinker to control setting behavior, strength development, and volume stability of the cement. The ball mills used for finish grinding are similar to the mills used to grind the raw materials. They are equipped with air separators that remove the fine particles and return the coarse material to the mills for further grinding. The final cement is so fine that 90% or more passes through a sieve having 60 openings per

square millimeter (40,000 openings per square inch). The cement is stored in large silos until it is ready for distribution. Cement is typically shipped in bulk by truck, train, or barge, although most plants also have equipment for bagging cement into bags typically weighing 42 kg (94 lb).

2.4—Quality control

The manufacture of portland cement involves complex chemical reactions, and all stages of production require close monitoring and control. Plant chemists analyze the raw materials from the quarry, the blending of materials, and the finished products using online automated analytical controls.

Cement is regularly sampled and tested by the producer. Tests include both chemical analysis and physical tests such as strength, fineness, and setting behavior. Tests on cement are done for quality control and to verify that the cement meets the requirements of standards such as **ASTM C150/C150M-12** or **C1157-11**. The cement manufacturer is able to supply these data on request in the form of a mill-test report that serves as a manufacturer certification that the cement meets the requirements of the standard. Requests for these data should be made when required by the project specifications.

CHAPTER 3—PROPERTIES AND CHARACTERISTICS OF CEMENTS

3.1—Compound composition

As the raw materials are processed into portland cement, the chemical constituents of these materials combine at the high temperatures of the kiln to form new compound phases. Portland cement may be considered to consist of four primary chemical compounds (or phases), as listed in **Table 3.1**. These compounds are sometimes referred to by the chemical shorthand notation.

3.2—Types of portland cement

The four main compounds, together with sources of calcium sulfate, may be present in different proportions and ground to different finenesses, resulting in slightly different chemical and physical properties for portland cements. Five principal types of portland cement are listed in **ASTM C150/C150M-12**. The typical compound composition of these cements is given in **Table 3.2**. It can be seen that the sum of C_3S and C_2S is approximately 75% by mass for each of the five types, so portland cements could be called calcium-silicate-based cements.

ASTM C150/C150M-12 is a combination prescriptive- and performance-based specification for portland cement. This means that the specification spells out the (maximum or minimum) chemical compound composition, like a recipe, while also having requirements for performance characteristics such as strength and setting time.

Although many manufacturers and specifiers still rely on **ASTM C150/C150M-12**, other types of specifications—namely, performance specifications—are also available. Rather than prescribe what the cement must be, these specifications measure conformance through the cement's

Table 2.1—Typical sources of raw materials used in portland cement manufacture

Lime (CaO)	Iron (Fe ₂ O ₃)	Silica (SiO ₂)	Alumina (Al ₂ O ₃)	Calcium sulfate
Alkali waste	Blast-furnace flue dust	Calcium silicate	Aluminum ore refuse	Anhydrite (CaSO ₄)
Calcite	Clay	Cement rock	Bauxite	Hemihydrate* (CaSO ₄ ·1/2H ₂ O)
Cement rock	Iron ore	Clay	Cement rock	Gypsum (CaSO ₄ ·2H ₂ O)
Chalk	Mill scale	Fly ash	Clay	—
Clay	Ore washings	Fuller's earth	Copper slag	—
Dolomite	Pyrite cinders	Limestone	Fly ash	—
Limestone	Shale	Loess	Fuller's earth	—
Marble	Fly ash	Marl	Granodiorite	—
Marl	—	Ore washings	Limestone	—
Seashells	—	Quartzite	Loess	—
Shale	—	Rice husk ash	Ore washings	—
Slag	—	Sand	Shale	—
—	—	Sandstone	Slag	—
—	—	Shale	Staurolite	—
—	—	Slag	—	—
—	—	Trap rock	—	—

*Produced as result of dehydration of gypsum in mill.

Note: As a generalization, probably 50% of all industrial by-products have potential as raw materials for portland cement manufacture.

ability to meet certain physical test parameters such as strength, setting time, and expansion. Performance specifications are well-suited to blended cements. They allow creative and efficient use of other resources, such as limestone, fly ash, slag cement, and other industrial by-products. ASTM has one performance specification for cement: **ASTM C1157/C1157M-11**. These cements are not classified as Types I through V but follow letter designations.

3.3—Hydration of portland cements

The differences in composition of the five **ASTM C150/C150M-12** cement types are used to achieve the special properties desired. The properties of hydraulic cement are primarily determined by the way each cement compound reacts with water, a process known as hydration. Hydration causes portland cement (and hence the concrete made with it) to harden and develop strength. It can be seen in **Fig. 3.1** that C₃S gains most of the strength developed in the first 2 to 3 weeks. C₂S contributes to long-term strength, whereas C₃A and C₄AF primarily contribute to early stiffening.

It can be seen in **Fig. 3.2** that the early strength development of the five types of portland cement is approximately proportional to their C₃S content. The early strength development of Type III cement is generally due to its greater fineness. Long-term strengths are more nearly the same.

C₃A is much more reactive than C₃S and can lead to premature and irreversible stiffening (flash set) if the reaction is not moderated. The addition of calcium sulfate (in the form of gypsum or anhydrite) is used to control the setting characteristics of C₃A and prevent flash set. The production of hemihydrate by the dehydration of gypsum in the mill can result in a condition called false set, which is premature stiffening, but the mixture can be returned to its plastic state with additional mixing. When the C₃A hydration is properly controlled, setting of hydraulic cement is determined by the hydration behavior of C₃S. The period during which

Table 3.1—Chemical compounds formed in cement kiln

Name	Chemical formula	Shorthand notation*
Tricalcium silicate (alite)	3CaO·SiO ₂	C ₃ S
Dicalcium silicate (belite)	2CaO·SiO ₂	C ₂ S
Tricalcium aluminate	3CaO·Al ₂ O ₃	C ₃ A
Tetracalcium aluminoferrite (ferrite phase)	4CaO·Al ₂ O ₃ ·Fe ₂ O ₃	C ₄ AF

*Shorthand notation routinely used by cement chemists using abbreviations for oxides: CaO is C; SiO₂ is S; Al₂O₃ is A; Fe₂O₃ is F. Also, SO₃ is S and H₂O is H.

concrete remains workable is due to the fact that C₃S only starts to react rapidly after a few hours of contact with water. This is a fortunate occurrence because it allows the handling and placing of concrete in the field.

The chemical reaction between cement and water (known as hydration) generates heat. This heat raises the temperature of the concrete. For large masses of concrete, such as dams, large foundations, and large bridge abutments, it is necessary to control the rate of temperature rise in the structure to prevent cracking due to thermal stress. This can be accomplished by selecting a type of cement with a low or moderate rate of heat generation; by the addition of chemical admixtures, pozzolans, and slags; and through proper construction practices. The contribution of each compound to this temperature rise depends on the amount of heat it liberates and its rate of hydration. C₃A and C₃S hydration produce the most heat and hence contribute to most of the temperature rise in concrete during hydration. The temperature rise in concretes is approximately proportional to the sum of C₃A + C₃S.

The behavior of the four compounds during hydration and their contribution to concrete performance can be conveniently summarized, as shown in **Table 3.2**. The setting time of portland cement depends a great deal on the amount of