Cementitious Materials for Concrete

Developed by ACI Committee E-701
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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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 fore-runner to portland cement.

The portland cement industry quickly spread in England. By 1890, there was a flourishing export business to the United States. The fledging 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 indirectly 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 blended cements. 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 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 limestone 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 (CaSO₄·2H₂O), anhydrite (CaSO₄), 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). 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 C₃S and C₅S 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 contain, these specifications measure conformance through the cement’s
Table 2.1—Typical sources of raw materials used in portland cement manufacture

<table>
<thead>
<tr>
<th></th>
<th>Lime (CaO)</th>
<th>Iron (Fe₂O₃)</th>
<th>Silica (SiO₂)</th>
<th>Alumina (Al₂O₃)</th>
<th>Calcium sulfate</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alkali waste</td>
<td>Blast-furnace flue dust</td>
<td>Calcium silicate</td>
<td>Aluminum ore refuse</td>
<td>Hemihydrate (CaSO₄·1/2H₂O)</td>
<td></td>
</tr>
<tr>
<td>Calcite</td>
<td>Clay</td>
<td>Cement rock</td>
<td>Bauxite</td>
<td>—</td>
<td></td>
</tr>
<tr>
<td>Cement rock</td>
<td>Iron ore</td>
<td>Clay</td>
<td>Cement rock</td>
<td>Gypsum (CaSO₄·2H₂O)</td>
<td></td>
</tr>
<tr>
<td>Chalk</td>
<td>Mill scale</td>
<td>Fly ash</td>
<td>Clay</td>
<td>—</td>
<td></td>
</tr>
<tr>
<td>Clay</td>
<td>Ore washings</td>
<td>Fuller’s earth</td>
<td>Copper slag</td>
<td>—</td>
<td></td>
</tr>
<tr>
<td>Dolomite</td>
<td>Pyrite cinders</td>
<td>Limestone</td>
<td>Fly ash</td>
<td>—</td>
<td></td>
</tr>
<tr>
<td>Limestone</td>
<td>Shale</td>
<td>Loess</td>
<td>Fuller’s earth</td>
<td>—</td>
<td></td>
</tr>
<tr>
<td>Marble</td>
<td>Fly ash</td>
<td>Marl</td>
<td>Granodiorite</td>
<td>—</td>
<td></td>
</tr>
<tr>
<td>Marl</td>
<td>—</td>
<td>Ore washings</td>
<td>Limestone</td>
<td>—</td>
<td></td>
</tr>
<tr>
<td>Seashells</td>
<td>—</td>
<td>Quartzite</td>
<td>Loess</td>
<td>—</td>
<td></td>
</tr>
<tr>
<td>Shale</td>
<td>—</td>
<td>Rice husk ash</td>
<td>Ore washings</td>
<td>—</td>
<td></td>
</tr>
<tr>
<td>Slag</td>
<td>—</td>
<td>Sand</td>
<td>Slag</td>
<td>—</td>
<td></td>
</tr>
<tr>
<td>—</td>
<td>—</td>
<td>Sandstone</td>
<td>—</td>
<td>—</td>
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<tr>
<td>—</td>
<td>—</td>
<td>Shale</td>
<td>Staurolite</td>
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<tr>
<td>—</td>
<td>—</td>
<td>Slag</td>
<td>—</td>
<td>—</td>
<td></td>
</tr>
<tr>
<td>—</td>
<td>—</td>
<td>Trap rock</td>
<td>—</td>
<td>—</td>
<td></td>
</tr>
</tbody>
</table>

*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.

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 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 3.3. The gray color of portland cement depends a great deal on the amount of

Table 3.1—Chemical compounds formed in cement kiln

<table>
<thead>
<tr>
<th>Name</th>
<th>Chemical formula</th>
<th>Shorthand notation*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tricalcium silicate (alite)</td>
<td>3CaO·SiO₂</td>
<td>C₃S</td>
</tr>
<tr>
<td>Dicalcium silicate (belite)</td>
<td>2CaO·SiO₂</td>
<td>C₂S</td>
</tr>
<tr>
<td>Tricalcium aluminate</td>
<td>3CaO·Al₂O₃</td>
<td>C₃A</td>
</tr>
<tr>
<td>Tetracalcium alumino-ferrite (ferrite phase)</td>
<td>4CaO·Al₂O₃·Fe₂O₃</td>
<td>C₄AF</td>
</tr>
</tbody>
</table>

*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.
Fe₂O₃ present in the cement. Iron acts as a fluxing agent and is added to the raw materials to aid in the pyroprocessing (burning) of the raw materials in the kiln. In general, the higher the iron content of the cement, the darker gray the cement will appear. White portland cement contains very little iron (refer to Section 4.1.4.1).

In addition to the behavior of the cement compounds, some of the minor constituents may play a significant role throughout the chemical hydration process. Because the reactions that involve compound formation seldom go to completion during the clinkering operation, there are usually small amounts (less than 1% by mass) of uncombined CaO (referred to as free lime) present in the cement. If present in a sufficiently large amount, the expansion of free lime during hydration can cause cracking and strength loss (unsoundness) in concrete due to internal expansion. Unsoundness in concrete may also result if there are excessive amounts or certain forms of magnesium oxide (MgO) in the cement. MgO occurs in most raw materials and, when present above approximately 2% by mass, will crystallize as free MgO, which may also expand during the hydration of the cement. The reaction of MgO takes place very slowly, so unsoundness may only appear after many months, or even years. An autoclave soundness test is required in ASTM C150/C150M-12 to detect cements with excessive amounts of CaO or MgO. Hydrated lime (Ca(OH)₂) and MgO quenched in a glassy form will not expand.

Both sodium (Na) and potassium (K) (alkalies) are present in cement clinker in varying amounts up to approximately 1% by mass when expressed as equivalent sodium oxide (Na₂O eqv). The alkalies exist either as oxides dissolved in the major cement compounds or separately as sulfates. The alkali sulfates act as accelerators—they can increase early strength gain but can also marginally reduce strengths at later ages. Alkalies may also affect the performance of chemical admixtures in concrete.

Other minor constituents in hydraulic cement—totaling less than 1%—may include titanium, phosphorous, manganese, and strontium. In small amounts, these materials appear to have little effect on the behavior of the cement. Titanium, manganese, and iron do, however, have an effect on cement color.

### 3.4—Cement fineness

The fineness of cement has a direct effect on the rate at which cement hydrates. Finer cements hydrate more quickly and thus cause a more rapid generation of heat and greater strength gain, particularly during the early period of hydration. Coarser ground cement (250 to 280 m²/kg, Blaine) tends to produce lower early strength than conventionally ground cement (320 to 400 m²/kg, Blaine) and may affect the workability and bleeding of the concrete. Higher fineness (exceeding 400 m²/kg, Blaine) tends to increase early strength development and reduce bleeding. Type III cements are generally much more finely ground than other types, with fineness often exceeding 500 m²/kg.
The fineness of cement has increased over the years, primarily because of user demands for more rapid strength development in concrete. While cement fineness formerly averaged slightly more than 300 m\(^2\)/kg (Blaine) for Type I in the 1950s, similar cements today average approximately 370 m\(^2\)/kg (Blaine). By comparison, typical Blaine fineness for some SCMs is finer. Fly ash is roughly 420 m\(^2\)/kg, slag cement is approximately 400 m\(^2\)/kg, and silica fume is roughly 20,000 m\(^2\)/kg (Kosmatka and Wilson 2011). Concrete mixtures with high fineness cements will generally have a higher water demand for the required consistency and will bleed at a slower rate. Cements having fineness above 400 m\(^2\)/kg (Blaine) typically require higher dosages of air-entraining admixtures to achieve a given level of air entrainment in concrete.

### 3.5—Setting behavior

The setting characteristics of portland cement paste are defined by initial set and final set. Initial set indicates the approximate time at which the paste begins to stiffen considerably, while final set roughly indicates the time at which the paste has hardened and can support some load. These times of set are tested according to standardized procedures and have no special relationship to concrete setting behavior. Generally, initial set occurs within 1 to 4 hours and final set occurs within 3 to 6 hours. Setting times are affected by minor constituents in the cement (such as alkalies and sulfates) and by fineness, water-cement ratio (w/c), ambient temperature, and inclusion of SCMs and chemical admixtures. Concretes generally set more slowly than cement paste because of the higher w/c. There are two types of abnormal setting behavior that should be mentioned:

- **False set**—This refers to the rapid setting that occurs without the liberation of much heat and is caused by the production of too much hemihydrate in the cement. Plasticity can be regained by further mixing without the need to add more water and thus is not a problem when concrete is mixed for long periods (ready mixed concrete). Increasing mixing time when possible will help to reduce a false set problem.

- **Flash set (or quick set)**—This behavior is accompanied by the liberation of considerable heat and is caused by insufficient calcium sulfate to control the hydration of C\(_3\)A. The plasticity of the mixture cannot be regained with additional mixing or water.

### 3.6—Heat of hydration

Heat is liberated during the hydration reactions of the cement compounds. The amount of temperature rise in a concrete mass will depend on the cement content; the rate of hydration (determined by cement fineness, ambient temperature, and admixtures); the cement composition; the volume of aggregate; the thickness of the concrete member; and the rate at which heat is lost by the concrete to the surroundings. The heat of hydration may cause a considerable rise in concrete temperatures in the first few days of hydration, and temperature will continue to rise in mass concrete over longer periods. In cold weather, the heat of hydration may be used to help protect the concrete from freezing and increase the rate of hydration. Fly ash and other pozzolans or slag cement can be used as a partial replacement for portland cement to control the heat gain of mixtures during hot weather or in mass concrete.

Cement composition and fineness affect the rate of heat generation. C\(_3\)A and C\(_2\)S are primarily responsible for high early heat generation. The rate of hydration will be faster as the fineness of the cement grind increases, although the total heat of hydration over a long time will not be particularly affected. Concrete proportions influence the amount of generated heat primarily as a result of cement content, with higher cement contents raising the heat of hydration.

### 3.7—Strength development

As shown in Fig. 3.1, the rate of early strength development depends on cement composition. Other factors that affect strength gain are cement fineness, use of SCMs, curing temperature, chemical admixtures, mineral fillers, water-cementitious material ratio (w/cm), and curing conditions. The rate of early strength gain is directly correlated with the rate of hydration. The ultimate strength reached does depend, to some extent, on the initial rate of strength gain. The faster the early strength gain, the lower the ultimate strength, as can be seen in Fig. 3.2.

### 3.8—Sulfate resistance

Concrete can be attacked both by sulfates in soil or water or by weathering from salt crystallization. In the case of chemical sulfate attack, the concrete deteriorates as the sulfates penetrate the concrete and react with hydrated compounds in the hardened cement paste (refer to Fig. 3.3). These reactions weaken the cement paste and cause expansion. In the case of salt crystallization, the concrete deteriorates as the salts (while still in the solution) penetrate the concrete surface, crystallize, and expand.

Salt crystallization and chemical sulfate attack are sometimes, but not always, related. Sodium sulfate solutions, for example, can induce both salt crystallization and chemical sulfate attack. Sometimes one mechanism is the precursor to another; in other cases, the results of one mechanism make conditions much more favorable for the other mechanism. Additionally, mitigation of one mechanism may not mitigate the other.

Sulfate attack and salt crystallization tend to worsen when the concrete is exposed to cycles of wetting and drying. In the case of salt crystallization, cycles caused by changes in humidity and temperature may increase the potential for deterioration.
Because both mechanisms rely on penetration of the sulfate or salt into the concrete, it is critical that concretes exposed to sulfates or salt crystallization be designed with low permeability and preferably have a maximum w/cm of approximately 0.40 for severe conditions. The use of sulfate-resistant cements conforming to ASTM C150/C150M-12, C595-12e1, or C1157-11 also help control chemical sulfate attack, provided that a low w/cm concrete is used and good concreting practices are followed. Sulfate-resistant cements do not provide protection against salt crystallization. The best protection against salt crystallization is the use of a low w/cm concrete or providing a barrier preventing salts from contacting the concrete. More information can be found in ACI 201.2R-08 and ACI 318-11.

Seawater attack on concrete is generally thought to be of concern only in warm environments. Examinations of concrete in contact with cooler seawaters in San Francisco Bay and Puget Sound, however, reveal that concretes in cool environments are also attacked.

Seawater attack comes from components in salt water, such as sulfates and chlorides, as well as salt crystallization in concrete voids. Internal expansion then forces the concrete apart. Damage is usually most pronounced in the splash zone, where concrete alternates between wet and dry conditions. Submerged and dry portions typically do not experience as much deterioration.

CHAPTER 4—PORTLAND CEMENTS AND THEIR SPECIFICATIONS

4.1—Cement types

4.1.1 Portland cement—Portland cement is most often manufactured to conform to ASTM C150/C150M-12, which designates six basic types: I, II, II(MH), III, IV, and V. The standard chemical and physical requirements for Portland cement given in ASTM C150/C150M-12 are shown in Tables 4.1 and 4.2, respectively. The tests to determine whether a cement meets these requirements are described in Chapter 5.

4.1.1.1 Type I is a general-purpose cement suitable for all uses, except where special properties of the other types are required. It is used in most types of construction—for example, pavements, bridges, reinforced concrete buildings, culverts, reservoirs, masonry units, and water pipes.

4.1.1.2 Types II and II(MH) are used where moderate sulfate resistance is required, for drainage and structures exposed to environments in which sulfate concentration is higher than normal, or for concrete exposed to seawater. Type II(MH) can also be specified when moderate heat of hydration is desirable, as in mass concrete, dams, large piers, heavy retaining walls, and abutments. The lower heat of hydration option, Type II(MH), needs to be specified when cement is purchased. In some parts of the country, Type II serves as general-purpose cement. Some manufacturers produce cement that meets more than one specification—for example, a cement may meet both Type I and Type II requirements. These cements are often classified with a dual designation, such as Type I/II, but there are no separate ASTM requirements for dually designated cements. Most cement manufactured in the United States meets Type I or Type II specifications.

4.1.1.3 Type III is used when high early strength is desired. Examples are early removal of forms for cast-in-place concrete, precast concrete, and slipformed concrete. Under cold weather conditions, Type III is often beneficial because of its faster rate of hydration and hence higher initial heat of hydration and strength gain.

4.1.1.4 Type IV is used when the amount of heat of hydration must be minimized—for example, in massive structures such as gravity dams, where thermal cracking is likely to occur. Although concrete made with Type IV develops strength quite slowly, this is not a problem for such structures. Type IV is no longer commonly available in the United States because other methods of controlling temperature are available. Two of these other methods include the use of Type II cement with SCMs and removing heat with coolants.

4.1.1.5 Type V should be used when high sulfate resistance is required, such as when concrete is exposed to severe sulfate attack—for example, in structures exposed to soils or groundwaters having a high sulfate content. Type V cements generally develop strength at a slower rate than Type I cements and have lower heats of hydration. Other precautions should be taken in concrete exposed to sulfate attack, particularly using a low w/cm. The use of SCMs such as fly ash or slag cement may also be beneficial in these exposures. For more information on the use of these cements, refer to ACI 225R-99, “Guide to the Selection and Use of Hydraulic Cements.”

4.1.1.6 Air-entrained cements—ASTM C150/C150M-12 also specifies air-entraining versions of Types I, II, II(MH), and III and designates them as Types IA, IIA, II(MH)A, and IIIA, respectively. These cements are interground with an air-entraining addition at the cement manufacturing plant and may be used when air-entrained concrete is required. Air-entrained cements may not always be commercially available. When air-entrained cements are used, proper quality control of air contents should still be exercised at the job site. It is often easier to control entrained air content...
Table 4.1—ASTM C150/C150M-12 standard chemical requirements

<table>
<thead>
<tr>
<th>Cement type, †%</th>
<th>I and IA</th>
<th>II and IIA</th>
<th>II(MH) and IIIA</th>
<th>IV</th>
<th>V</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aluminum oxide (Al₂O₃), maximum</td>
<td>—</td>
<td>6.0</td>
<td>6.0</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Ferric oxide (Fe₂O₃), maximum, %</td>
<td>—</td>
<td>6.0</td>
<td>6.0</td>
<td>6.5</td>
<td>—</td>
</tr>
<tr>
<td>Magnesium oxide (CaO), maximum</td>
<td>6.0</td>
<td>6.0</td>
<td>6.0</td>
<td>6.0</td>
<td>6.0</td>
</tr>
<tr>
<td>Sulfur trioxide (SO₃), maximum, when (C₃A)³ is 8% or less</td>
<td>3.0</td>
<td>3.0</td>
<td>3.0</td>
<td>2.3</td>
<td>2.3</td>
</tr>
<tr>
<td>Sulfur trioxide (SO₃), maximum when (C₃A)³ is more than 8%</td>
<td>3.5</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>LOI, maximum</td>
<td>3.0</td>
<td>3.0</td>
<td>3.0</td>
<td>3.0</td>
<td>3.0</td>
</tr>
<tr>
<td>Insoluble residue, maximum</td>
<td>0.75</td>
<td>0.75</td>
<td>0.75</td>
<td>0.75</td>
<td>0.75</td>
</tr>
<tr>
<td>Tricalcium silicate (C₃S)³, maximum</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>35³</td>
<td>—</td>
</tr>
<tr>
<td>Dicalcium silicate (C₂S)³, minimum</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>40³</td>
<td>—</td>
</tr>
<tr>
<td>Tricalcium aluminate (C₃A)⁴, maximum</td>
<td>8</td>
<td>8</td>
<td>8</td>
<td>15</td>
<td>7³</td>
</tr>
<tr>
<td>Sum of C₃S + 4.75 C₆A⁴, maximum</td>
<td>100⁵</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Tetracalcium aluminoferrite plus twice tricalcium aluminate⁶ (C₆AF + 2(C₃A)) or solid solution (C₆AF + C₂F), as applicable, maximum</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
</tbody>
</table>

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Cements conforming to requirements for all types are not carried in stock in some areas. In advance of specifying use of cement other than Type I, determine whether proposed type of cement is, or can be made, available.

Does not apply when heat of hydration limit in Table 4 of ASTM C150/C150M-12 is specified.

Does not apply when sulfate resistance limit in Table 4 of ASTM C150/C150M-12 is specified.

Compliance with requirements of this specification does not necessarily ensure that desired air content will be obtained in concrete.

Table 4.2—ASTM C150/C150M-12 standard physical requirements

<table>
<thead>
<tr>
<th>Cement type, †%</th>
<th>I</th>
<th>II</th>
<th>IIIA</th>
<th>III</th>
<th>IV</th>
<th>V</th>
</tr>
</thead>
<tbody>
<tr>
<td>Air content of mortar, volume %</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Minimum</td>
<td>12</td>
<td>22</td>
<td>12</td>
<td>22</td>
<td>12</td>
<td>22</td>
</tr>
<tr>
<td>Maximum</td>
<td>260</td>
<td>260</td>
<td>260</td>
<td>260</td>
<td>260</td>
<td>260</td>
</tr>
<tr>
<td>Air permeability test</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Minimum</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>430⁷</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Maximum</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Autoclave expansion, maximum %</td>
<td>0.80</td>
<td>0.80</td>
<td>0.80</td>
<td>0.80</td>
<td>0.80</td>
<td>0.80</td>
</tr>
<tr>
<td>Compressive strength, not less than values shown for ages indicated as follows, MPa (psi)²</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1 day</td>
<td>12.0 (1740)</td>
<td>10.0 (1450)</td>
<td>10.0 (1450)</td>
<td>8.0 (1160)</td>
<td>10.0 (1450)</td>
<td>7.0 (1020)</td>
</tr>
<tr>
<td>3 days</td>
<td>19.0 (2760)</td>
<td>16.0 (2320)</td>
<td>17.0 (2470)</td>
<td>14.0 (2030)</td>
<td>17.0 (2470)</td>
<td>12.0 (1740)</td>
</tr>
<tr>
<td>7 days</td>
<td>19.0 (2760)</td>
<td>16.0 (2320)</td>
<td>17.0 (2470)</td>
<td>14.0 (2030)</td>
<td>17.0 (2470)</td>
<td>12.0 (1740)</td>
</tr>
<tr>
<td>28 days</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
</tbody>
</table>


†Compliance with requirements of this specification does not necessarily ensure that desired air content will be obtained in concrete.

Testing laboratory shall select fineness method to be used. However, when sample fails to meet requirements of air permeability test, turbidimeter test shall be used, and requirements in this table for turbidimeter method shall govern.

Maximunm fineness limits do not apply if sum of C₃S + 4.75C₆A is less than or equal to 90.

Strength at any specified test age shall be not less than that attained at any previous specified test age.

††Time of setting is that described as initial setting time in test method in ASTM C191-08.
in concrete by using non-air-entrained cement and a chemical air-entraining admixture conforming to ASTM C260/C260M-10a.

4.1.1.7 Other specifications—Some highway departments and other specifying agencies further modify ASTM C150/C150M-12 to meet their particular needs or use an alternate specification; the most well-known specification is the American Association of State Highway and Transportation Officials (AASHTO) M 85-12. While the provisions of AASHTO M 85-12 and ASTM C150/C150M-12 were generally consistent, there were also some substantive differences and, prior to 2003, the number of differences seemed to be increasing. After input from various private and governmental experts, AASHTO M 85-12 and ASTM C150/C150M-12 were harmonized in 2009.

The Canadian Standards Association (CSA) specifies portland cements as part of its A3001-08 compendium, with many similar requirements to ASTM C150/C150M-12.

Portland cements may also be specified under ASTM C1157/C1157M-11, a performance-based specification (refer to Section 4.1.3 of this document).

4.1.2 Blended cements—Portland cement or clinker can be blended or interground with other materials to achieve certain properties. Although blended cements are common in European countries and other parts of the world, they have not been used as extensively in the United States. However, they are gaining popularity because they require less energy to manufacture; can be made with by-product materials that would normally be disposed in a landfill, thus reducing solid waste; and offer performance benefits for certain applications. Standard requirements for these blended cements are given in Tables 4.3 and 4.4. Blended cements are specified under ASTM C595/C595M-12 or ASTM C1157/C1157M-11 (also refer to Section 4.1.3 in ASTM C1157/C1157M-11). There are four basic classes of blended cement in ASTM C595/C595M-12e1: portland blast-furnace slag cement (Type IS), portland-pozzolan cement (Type IP), portland-limestone cement (Type IL), and ternary blended cement (Type IT).

4.1.2.1 Portland blast-furnace slag cement—Portland blast-furnace slag cement is a blend of portland cement (usually Type I or II) and up to 95% by mass (weight) granulated (quenched) blast-furnace slag. Type IS(c<70) cement may be used for general concrete construction when the specific properties of other types are not required.

4.1.2.2 Portland-pozzolan cement—Portland-pozzolan cement Type IP may also be used for general concrete construction. Portland-pozzolan cements contain up to 40% by mass of pozzolan in the blended cement.

4.1.2.3 Portland-limestone cement—Portland-limestone cement contains between 5 and 15% by mass of fine limestone. Type IL cements may be used for general concrete construction.

4.1.2.4 Ternary blended cement—Ternary blended cements contain portland cement (or clinker) and two additional ingredients: either slag and pozzolan, slag and limestone, pozzolan and limestone, or two different pozzolans. Ternary blended cement Type IT(S≥70) has a maximum limestone content of 15% by mass. All other ternary blended cements have a maximum pozzolan content of 40% by mass; a maximum limestone content of 15% by mass; and the total content of pozzolan, limestone, and slag is less than 70% by mass.

4.1.2.5 Designation conventions—For Types IS, IP, and IL, a suffix in parentheses is added to designate the approximate amount of SCM in the material: Type IP(25) is a portland-pozzolan cement containing 25% pozzolan. In ternary blended cements, the letters for slag, pozzolan, or limestone contents are included in the parentheses to indicate the type of ingredients, and they are listed in decreasing order of abundance: Type IT(S25)(L10) describes a ternary blended cement with 25% slag and 10% limestone. When ASTM C595/C595M-12e1 cements meet special requirements for moderate sulfate resistance, high sulfate resistance, or moderate heat of hydration, the suffixes “(MS),” “(HS),” or “(MH),” respectively, may be added to the cement type designation. The suffix “A” is added to indicate air-entraining cement. Type IP cements may also optionally meet a low heat of hydration—(LH)—requirement. As an example, a blended cement with 35% slag cement that is air-entraining and moderately sulfate-resistant would be designated Type IS(35)(MS)A.

4.1.3 Performance specification for hydraulic cements—ASTM C1157/C1157M-11 is a performance specification that may be used for both portland and blended cements. This specification has primarily performance requirements, as measured by standard cement tests, and does not put restrictions on the cement composition. Often, ASTM C1157/C1157M-11 cements meet the requirements of either ASTM C150/C150M-12 or ASTM C595/C595M-12e1 as well. There are six designated types of cement: GU for

<table>
<thead>
<tr>
<th>Table 4.3—Compositional requirements of blended cements (ASTM C595/C595M-12e1)†</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cement type1, %</td>
</tr>
<tr>
<td>Magnesium oxide (MgO), maximum</td>
</tr>
<tr>
<td>Sulfur reported as sulfate (SO3), maximum</td>
</tr>
<tr>
<td>Sulfide sulfur (S), maximum</td>
</tr>
<tr>
<td>Insoluble residue3, maximum</td>
</tr>
<tr>
<td>LOI, maximum</td>
</tr>
</tbody>
</table>

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1Chemical requirements in this table are applicable to all air-entrained cement equivalents.

It is permissible to exceed values in table for SO3 content, provided it has been demonstrated by test method in ASTM C1038/C1038M-10 that cement with increased SO3 will not develop expansion exceeding 0.020% at 14 days. When manufacturer supplies cement under this provision, supporting data shall be supplied to purchaser.

2Insoluble residue maximum limit does not apply to ternary blended cements.

*For ternary blended cements with limestone, LOI is maximum of 10.0% by mass.

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Table 4.4—Physical requirements of blended cements (ASTM C595/C595M-12e1)

<table>
<thead>
<tr>
<th>Cement type</th>
<th>IS(&lt;70), IP, IL, IT(P≤S), IT(L≤S), IT(P&gt;S&lt;70), IT(L&gt;S&lt;70)</th>
<th>IS(&lt;70)(MS), IP(MS), IT(P≤S)(MS), IT(P&gt;S&lt;70)(MS)</th>
<th>IS(&lt;70)(HS), IP(HS), IT(P≤S)(HS), IT(P&gt;S&lt;70)(HS)</th>
<th>IS(≥70), IT(S≥70)</th>
<th>IP(LH)§, IL(LH)‡‡, IT(P≥S)(LH)††, IT(P≤L)(LH)‡‡, IT(L≥S)(LH)‡‡, IT(L≤P)(LH)††, IT(P&gt;S&lt;70)(LH)‡‡, IT(P&lt;L&gt;S&lt;70)(LH)‡‡</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fineness</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Autoclave expansion maximum, %</td>
<td>0.80</td>
<td>0.80</td>
<td>0.80</td>
<td>0.80</td>
<td>0.80</td>
</tr>
<tr>
<td>Autoclave contraction maximum, %‡‡</td>
<td>0.20</td>
<td>0.20</td>
<td>0.20</td>
<td>0.20</td>
<td>0.20</td>
</tr>
</tbody>
</table>

Time of setting, Vicat test§

<table>
<thead>
<tr>
<th></th>
<th>minutes, not less than</th>
<th>minutes, not more than</th>
</tr>
</thead>
<tbody>
<tr>
<td>Set,</td>
<td>45</td>
<td>45</td>
</tr>
<tr>
<td>Set,</td>
<td>7</td>
<td>7</td>
</tr>
</tbody>
</table>

Air content of mortar (test method in ASTM C185-08), maximum volume, %

|                        | 12                     | 12                     |

Compressive strength, minimum, MPa (psi)

<table>
<thead>
<tr>
<th></th>
<th>3 days</th>
<th>7 days</th>
<th>28 days</th>
</tr>
</thead>
<tbody>
<tr>
<td>3 days</td>
<td>13.0 (1890)</td>
<td>20.0 (2900)</td>
<td>25.0 (3620)</td>
</tr>
<tr>
<td>7 days</td>
<td>11.0 (1600)</td>
<td>18.0 (2610)</td>
<td>25.0 (3620)</td>
</tr>
<tr>
<td>28 days</td>
<td>11.0 (1600)</td>
<td>20.0 (2900)</td>
<td>25.0 (3620)</td>
</tr>
</tbody>
</table>

Heat of hydration‡

<table>
<thead>
<tr>
<th></th>
<th>7 days maximum, kJ/kg (cal/g)</th>
<th>28 days maximum, kJ/kg (cal/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>7 days maximum</td>
<td>290 (70)</td>
<td>330 (80)</td>
</tr>
<tr>
<td>28 days maximum</td>
<td>290 (70)</td>
<td>330 (80)</td>
</tr>
</tbody>
</table>

Water requirement, maximum, %

<table>
<thead>
<tr>
<th></th>
<th>of cement</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.020</td>
<td>0.020</td>
<td>0.020</td>
</tr>
</tbody>
</table>

Drying shrinkage, maximum, %

<p>| | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>64</td>
<td></td>
</tr>
</tbody>
</table>

Mortar expansion††

<table>
<thead>
<tr>
<th></th>
<th>180 days maximum, %</th>
<th>1 year maximum, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>180 days maximum</td>
<td>0.10</td>
<td>0.10</td>
</tr>
<tr>
<td>1 year maximum</td>
<td>0.05</td>
<td>0.10</td>
</tr>
</tbody>
</table>

Sulfate resistance††, expansion at

<table>
<thead>
<tr>
<th></th>
<th>180 days maximum, %</th>
<th>1 year maximum, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>180 days maximum</td>
<td>0.020</td>
<td>0.020</td>
</tr>
<tr>
<td>1 year maximum</td>
<td>0.060</td>
<td>0.060</td>
</tr>
</tbody>
</table>

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§Air-entrained cements shall have mortar air content of 19 ± 3% by volume and minimum compressive strength shall be no less than 80% of comparable non-air-entrained cement type.

‡Applicable only when higher strengths at early ages are not required or when low heat is required.

§§Both amount retained when wet sieved on 45 μm (No. 325) sieve and specific surface by air permeability apparatus, m²/kg, shall be reported on all mill test reports requested under Section 14.4.

†Specimens shall remain firm and hard and show no signs of distortion, cracking, checking, pitting, or disintegration when subjected to autoclave expansion test.

‡‡Time of setting refers to initial setting time in test method in ASTM C191-08. Time of setting of cements containing user-requested accelerating or retarding functional addition need not meet limits of this table but shall be stated by manufacturer.

§§Applicable only when moderate heat of hydration (MH) is specified, in which case strength requirements shall be 80% of values shown in table.

††Test for mortar expansion is optional requirement to be applied only at purchaser’s request and should not be requested unless cement will be used with alkali-reactive aggregate.

‡‡In testing of high-sulfate (HS) cement, testing at 1 year shall not be required when cement meets 180-day limit. HS cement failing 180-day limit shall not be rejected unless it also fails 1-year limit.

4.1.4 Other special cements—In addition to the cements described in the previous sections, there are several cements available for special applications, not all of which are covered by ASTM specifications. It should be emphasized that these cements are not typically used in general concrete work, but they may occasionally be encountered. Therefore, the more common classes are described in the following sections.

4.1.4.1 White cement—White cement is a portland cement made with similar raw materials, but the amount of iron oxide is kept low. White cement should conform to ASTM C150/C150M-12 and thus may be used for a wide range of applications. It tends to be used mainly for architectural purposes—for example, in the fabrication of precast panels, stucco, terrazzo surfaces, and decorative concrete. It is often recommended for use in colored concrete or mortar.

4.1.4.2 Masonry cement—These are factory-prepared (cement plant) mixtures of portland cement, air-entraining additions, and finely divided material, such as ground limestone, hydrated or hydraulic lime, ground shale, or fly ash, that are selected to improve one or more properties...
shrinkage cracking are undesirable—for example, floors and slabs. Proper pre-job planning and on-site supervision, accompanied by good quality control throughout construction, are essential elements to a successful job. If adequate moist curing is not maintained, the desired expansion may not occur. Expansive cements should not be used in concrete subjected to sulfate attack unless prior testing indicates satisfactory resistance to the levels of exposure expected in service.

4.1.4.6 Water-repellent cement—The addition of certain chemicals to regular portland cements can impart some water repellency to concrete. Water-repellent cement (sometimes incorrectly called waterproof cement) is commonly used for the construction of walls or other structures that are subjected to hydrostatic pressure or used to resist the penetration of water or other liquids in basement walls and containment vessels. Agents intended to provide water repellency are frequently adversely affected by cement alkalis. Water-repellent cements will not completely prevent water seepage under hydrostatic pressure. In addition, water repellents are more effective in concrete that is of high quality. There is no ASTM test for water repellency of cements.

4.1.4.7 Well cement—Well cements are manufactured in accordance with American Petroleum Institute Specification (API) Spec 10A. Well cements are designated by eight classes, of which Classes G and H are the most common. The classification system is based on the pressure-temperature thickening-time encountered at specified depths in the primary cementing of casing in wells. Well cement slurries may often be exposed to bottom-hole pressures in excess of 140 MPa (20,000 psi) and temperatures approaching 120°C (250°F). Well cements are made from the same basic ingredients as regular cements; however, certain properties are altered so the cements can perform as intended at the higher temperatures and pressures encountered in deep wells. Admixtures and other ingredients, such as sand, bentonite, pozzolan, and diatomaceous earth, are incorporated into the mixture for the purpose of controlling its fluid properties. Organic compounds are added to control its setting time.

4.1.4.8 Rapid-setting cements—Some concrete applications, such as repair and fast-track pavement construction, require concrete with high initial rates of strength gain. A number of techniques have proven successful in providing specified strengths in 4 hours or less. These techniques include high portland cement contents, Type III portland cements, low w/c, accelerating admixtures, and higher curing temperatures. Attempts to achieve more rapid strength gain have resulted in the development of a number of fast-setting hydraulic cement products.

Regulated-set cement is calcium fluoroaluminate hydraulic cement formulated to produce concrete with setting times from a few minutes to an hour accompanied by rapid early strength development. These cement products are portland-cement-based with functional additions that provide the accelerated set and strength gain.

Rapid-hardening cements (ASTM C1600/C1600M-11) are used in construction applications such as pavement patching and fast-track paving, where load-carrying strength must
Another fast-setting cement is calcium-aluminate-based. This type of cement is capable of attaining design strengths in 1 day. It has been used in applications requiring chemical-resistant concrete or high corrosion resistance. Calcium aluminate can develop an unstable paste structure that results in loss of strength over time. For this reason, calcium aluminate cements should not be used in structural applications.

Fast-setting hydraulic cements, when available, are generally more expensive than ordinary portland cement. Because of their rapid setting characteristics, concrete containing these cement products is often more difficult to control at the job site and is prone to cracking.

### Table 4.5—ASTM C1157/C1157M-11 standard physical requirements

<table>
<thead>
<tr>
<th>Cement type</th>
<th>GU</th>
<th>HE</th>
<th>MS</th>
<th>HS</th>
<th>MH</th>
<th>LH</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fineness</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Autoclave length change, maximum, %</td>
<td>0.80</td>
<td>0.80</td>
<td>0.80</td>
<td>0.80</td>
<td>0.80</td>
<td>0.80</td>
</tr>
</tbody>
</table>

**Time of setting, Vicat test**

| Initial, not less than, minimum | 45 | 45 | 45 | 45 | 45 | 45 |
| Initial, not more than, minimum | 420 | 420 | 420 | 420 | 420 | 420 |
| Air content of mortar volume, maximum, % | 12 | 12 | 12 | 12 | 12 | 12 |

**Compressive strength, minimum, MPa (psi)**

| 1 day | — | 12.0 (1740) | — | — | — | — |
| 3 days | 13.0 (1890) | 24.0 (3480) | 11.0 (1600) | 11.0 (1600) | 5.0 (725) | — |
| 7 days | 20.0 (2900) | — | 18.0 (2610) | 18.0 (2610) | 11.0 (1600) | 11.0 (1600) |
| 28 days | 28.0 (4060) | — | — | 25.0 (3620) | — | 21.0 (3050) |

**Heat of hydration**

| 7 days, maximum, kJ/kg (kcal/kg) | — | — | — | — | 290 (70) | 250 (60) |
| 28 days, maximum, kJ/kg (kcal/kg) | — | — | — | — | — | 290 (70) |

**Mortar bar expansion**

| 14 days, maximum, % | 0.020 | 0.020 | 0.020 | 0.020 | 0.020 | 0.020 |

**Sulfate expansion (sulfate resistance)**

| 6 months, maximum, % | — | — | 0.10 | 0.05 | — | — |
| 1 year, maximum, % | — | — | — | 0.10 | — | — |

**Optional physical requirements**

**Option A—air-entraining**

| Air content of mortar volume, maximum, % | 16 | 16 | 16 | 16 | 16 | 16 |

**Option R—low reactivity with alkali-reactive aggregates**

| Expansion | 0.020 | 0.020 | 0.020 | 0.020 | 0.020 | 0.020 |
| 56 days, maximum, % | 0.060 | 0.060 | 0.060 | 0.060 | 0.060 | 0.060 |
| Early stiffening, final penetration, minimum, % | 50 | 50 | 50 | 50 | 50 | 50 |
| Compressive strength, minimum, MPa (psi), 28 days | — | — | 28.0 (4060) | — | 22.0 (3190) | — |

**Drying shrinkage**, %

| — | — | — | — | — | — |

---

2. Both amount retained when wet sieved on 45 μm (No. 325) sieve and specific surface area by air permeability apparatus in m²/kg shall be reported on all certificates of test results requested from manufacturer.
3. Time of setting refers to initial setting time in test method in ASTM C191-08.
4. Cements may be shipped prior to later-age test data being available. In such cases, test value may be left blank. Alternatively, manufacturer can generally provide estimates based on historical production data. Report shall indicate if such estimates are provided.
5. Given value in mortar does not necessarily ensure that desired air content will be obtained in concrete.
6. In testing of high-sulfate (HS) cement, testing at 1 year shall not be required when cement meets 6-month limit. HS cement failing 6-month limit shall not be rejected unless it also fails 1-year limit.
7. Primarily air-entraining cements shall be developed in less than 4 hours to allow early opening of the roadway. These hydraulic cements are typically calcium sulfoaluminate combinations.
8. Another fast-setting cement is calcium-aluminate-based.

**CHAPTER 5—STANDARD TESTS FOR PORTLAND CEMENTS**

The production of portland cement requires strict quality control to comply with established specifications for chemical and physical requirements. Over the years, a number of standard tests have been developed that can be carried out relatively easily and rapidly to ensure that the cement conforms to the desired standard. In the United States,
testing standards developed by ASTM are used to determine if the cement complies with specifications. Similar tests are used in Canada for evaluating conformance to CSA standards. It should be noted that these tests do not measure concrete behavior in the field. Cement passing these standards should be evaluated in concrete with local materials to ensure that the desired fresh and hardened concrete properties are obtained.

5.1—Chemical tests

Chemical analysis of portland cements is covered by ASTM C114-11b. This standard provides referee, optional, and rapid techniques for measuring a variety of elements or compounds that can be found in cement. The referee method is used primarily to resolve disputes where chemical test results are being questioned, as in the case of two laboratories testing the same cement with the same methods but obtaining different results. No rejections of cement failing to meet chemical requirements may be made until the test is conducted using the referee method. Optional and rapid test methods are provided for those who need shorter or more convenient methods for routine testing.

Laboratories involved in testing cement generally verify their testing procedures and results by testing standard cement samples, and they participate in reference sample testing programs conducted by the Cement and Concrete Reference Laboratory (CCRL) at the National Institute of Standards and Technology (NIST). CCRL also conducts regular inspections of cement testing laboratories to ensure that equipment and testing techniques comply with current ASTM methods. In addition, CCRL conducts a semi-annual survey wherein approximately 400 laboratories test two samples of cement for interlaboratory comparison on a wide range of characteristics. This program enables a laboratory to statistically compare its results with averages from other laboratories.

For many years, wet chemistry was the primary technique of chemical analysis, although today instrumental analysis with atomic adsorption and X-ray fluorescence is more widely used. Chemical analysis, either by wet chemistry or instrumental analysis, is used to determine the oxide composition (CaO, SiO$_2$, Al$_2$O$_3$, Fe$_2$O$_3$, MgO, SO$_3$) of cements. By using the formulas contained in the annexes of ASTM C150/C150M-12, the potential phase composition of the cement is calculated. The value of chemical test results is of importance to the user in determining which type of cement to use, as in the case of heat of hydration or sulfate resistance. Chemistry alone cannot be used to predict performance in concrete, and the cement producer will normally vary both chemical and physical characteristics to obtain the required performance characteristics for the cement. As an example, early-age strength is affected by fineness and chemistry.

Two other chemical characteristics of interest are loss on ignition (LOI) and insoluble residue. LOI is an indication of prehydration or carbonation of the cement that can occur during storage of clinker at the cement plant. It is also influenced by the calcium sulfate and limestone added to the cement during final grinding. High ignition loss can potentially reduce strengths. Insoluble residue is a means of detecting contamination that can occur at a cement plant or when storing clinker. Tables 4.1 and 4.3 show limits for LOI and insoluble residue in ASTM C150/C150M-12 and ASTM C595/C595M-12e1, respectively.

5.2—Physical tests

ASTM requirements for physical tests include air content, fineness, soundness, time of set, false set, heat of hydration, sulfate expansion, and strength. Physical tests are more aligned to the characteristics of concrete.

5.2.1 Fineness—For specification purposes, fineness is usually described by a single parameter: the specific surface area, typically determined by the Blaine air permeameter. Because cement particles are irregularly shaped, the measurement of fineness is approximate. The real use is to allow a relative comparison between cement from the same source and different cements. ASTM C204-11 details the test method for determining Blaine fineness, which is based on measuring the time required to pass a given volume of air through a porous bed of cement. The device is calibrated with a standard cement sample issued by NIST, which has a known specific surface area. The specific surface area of the unknown sample can then be calculated because it is proportional to the square root of the time. A less common test, the Wagner turbidimeter, is detailed in ASTM C115-10. In this method, fineness is measured with a suspension of cement in kerosene through which light is passed. The cross-sectional area of the particles intersecting the beam can be determined by measuring the light intensity. From these data, specific surface area and a particle size distribution can be obtained.

Both the Wagner and Blaine methods provide an acceptable way of determining relative fineness. The Blaine numerical value is generally approximately 1.8 times the Wagner value because of the different approaches involved.

Finesness was originally specified as a minimum value to ensure strength development and minimize bleeding in concrete. The trend has been toward more finely ground cements because they produce higher strengths at early ages. This is due to the fact that finer cements have a higher surface area exposed to water and hence a greater rate of hydration in the first few days. Some portland cement types now also have a maximum limit on cement fineness to control water requirements and drying shrinkage of concrete.

5.2.2 Setting behavior—There are two commonly accepted test methods for determining the setting time of cement. They are both carried out on cement paste samples prepared by standard methods. Setting times determined by the two different methods will have different numerical values and the method used should be indicated when reporting setting times.
Setting time by the Vicat Method (ASTM C191-08) is measured on a standard molded specimen with a depth of 30 mm using a 1 mm diameter needle weighing 300 g. At regular intervals, the needle is placed on the specimen surface and allowed to settle for 30 seconds. The elapsed time between mixing the cement and water and the time when the weighted needle penetrates 25 mm is the initial setting time. When no penetration is observed, the elapsed time from molding to that point is the final setting time. There is no final setting time requirement in ASTM C150/C150M-12 when testing by the Vicat Method.

Setting time can also be defined using the Gillmore Method (ASTM C266-08e1), which uses a standard specimen called a pat and measures initial set by penetration of a 2.12 mm (0.084 in.) diameter needle weighing 113.4 g (0.250 lb) and final set by penetration of a 1.06 mm (0.042 in.) diameter needle weighing 453.6 g (1.000 lb). In each case, the setting time is the measured time when the needle will not make an appreciable indentation in the surface of the pat specimen. The Gillmore test is an optional test in ASTM C150/C150M-12, as the Vicat Method is generally preferred.

These tests are used to determine if a cement sets according to the time limits specified by cement specifications. The purpose of these limits is to help ensure that the user will have sufficient time to place and finish concrete after mixing. The final set limits are used to ensure that the cement is setting in a normal fashion that will result in normal early strength gain.

5.2.3 False set—The test for abnormal early stiffening is described in ASTM C451-08 (paste method) using the Vicat apparatus. This test is used to determine whether the cement complies with optional requirements in ASTM C150/C150M-12 and C1157-11 when these are specified. It provides information as to whether the cement is likely to exhibit false set and make handling and placing the concrete difficult. False set is generally not a problem with transit mixing, where the concrete is continuously agitated before placing, or where the concrete is remixed prior to placement. The consequences of flash set are more severe, with complete loss of workability that cannot be regained. Another test for false set is ASTM C359-08 (mortar method). This test method uses a mortar mixture and measures stiffness of the mortar at specified time intervals, followed by remixing and remeasuring. A false-setting mortar will develop early stiffness that will return to the original consistency after remixing.

5.2.4 Soundness—Soundness in cement paste is the absence of excessive volume change after setting. Unsoundness can result from the hydration of MgO or unreacted CaO. Because some of the reactions are very slow, unsoundness may take months to develop. Thus, it is necessary to use some form of accelerated test so that tendencies toward unsoundness can be detected as a quality control measure during manufacture. The autoclave expansion test (ASTM C151/C151M-09) is designed to detect unsoundness due to both free lime and crystalline MgO. This method measures expansion of a standard mortar bar after it has been subjected to accelerated curing with steam at elevated temperature and pressure. Cement specifications require that expansion must be less than 0.80% of the original length. ASTM C595/C595M-12e1 also limits contraction to a maximum of 0.20%. ASTM C151/C151M-09 is an accelerated test that does not clearly simulate service conditions, although it will detect unsound cement that would cause concrete to crack. It does provide a valuable quality control measure because changes in the expansion test results would indicate some irregularity in the cement manufacturing process.

5.2.5 Heat of hydration—The heat of hydration varies greatly with the cement composition, fineness, and concrete proportions, with C3A and C3S being primarily responsible for high heat evolution. Finely ground cements increase the hydration rate, but the total heat of hydration over a long time is not particularly affected. The heat of hydration may be defined as the amount of heat liberated (in cal/g or kJ/kg of unhydrated cement) during the setting and hardening of portland cement at a given temperature. This is measured by ASTM C186-05. Types II and IV cements have optional heat-of-hydration requirements, while Types MH and LH cements have mandatory requirements. ASTM C595/C595M-12e1 cements are required to meet the heat-of-hydration limit when the MH or LH options are requested. In addition to the optional requirements, Type II cements are required to meet a limit on the sum of 4.75 times C3A content and the C3S content (% by mass) of less than or equal to 100 as one way of controlling the heat of hydration.

Heat of hydration is particularly important in any massive concrete placement, such as gravity dams, mass foundations, and relatively thick concrete sections with high cement content mixtures (some high-performance and high-strength concretes). As cement hydrates, it gives off heat, but in most cases the heat is dissipated without detrimental effects. In mass concrete or thick sections, however, heat dissipation is restricted and internal temperatures can exceed exterior temperatures to the extent of developing thermal stresses sufficient to crack the concrete upon cooling. Numerous methods are available to alleviate potential problems arising from heat gain: partial replacement of cement with a pozzolan or slag, use of a cement meeting the low heat-of-hydration option of ASTM C150/C150M-12 (although Type IV is rarely available), control of concrete temperature, or cooling of the concrete mixture or structure.

5.2.6 Strength tests—Because concrete is used primarily in load-bearing applications, it follows that cement strength properties are important. The test for compressive strength prescribed in ASTM C109/C109M-11b uses a 50 mm (2 in.) mortar cube as the test specimen. The sand-cement ratio is 2.75:1 by weight, using standard sand (ASTM C778-12), while the w/c is 0.485 for all portland cements and 0.460 for air-entraining portland cements. The specimens are moist-cured until they are tested. Mortars for blended cements in ASTM C595/C595M-12e1 and C1157-11 are mixed with variable w/c to a constant flow—a measure of consistency.

Because cement strength increases with time, it is also necessary to specify the age at which tests should be carried out. Normally, minimum strengths are specified for 3, 7, and 28 days. In addition, high-early-strength cements (Types III
or HE) have a 1-day requirement. At any given age, the cement strength should be higher than at a previous age. For specification purposes, cement strength is only measured in compression. Flexural or tensile strengths are not specified in cement standards, although ASTM test methods for these strengths in concrete are still recognized.

It is important to note that the strengths of mortar as determined by these tests cannot be related directly to the strengths of concrete made with the same cements. Only a general relationship exists. Thus, the strength tests on standard mortars serve primarily as quality control tests in cement manufacturing to determine compliance with specifications and as an aid for comparing cements from different sources. The strength of concrete can only be determined from tests done on the concrete itself. In practice, however, cement sold in the United States exceeds ASTM C150/C150M-12 strength limits by a wide margin. Normally, the level of strengths in a geographic area is controlled by the market demands and limitations of raw materials. The user should also be concerned with how much the strength level varies. A mill test report represents the average properties from a defined production period resulting in average values and has the prime objective of showing that the cement meets the strength requirements of the cement standard.

5.2.7 Air content of mortar—ASTM C185-08 is used to determine the air content of a standard mortar. For cement without air-entraining additions, the purpose is to ensure that the cement will not entrain undesired air; for air-entraining cement, the purpose is to ensure that the additions are present in the correct quantity. ASTM C150/C150M-12 and C595-12e1 specify maximum and minimum air contents of the mortar for air-entraining cement and maximum air contents for non-air-entraining cements. ASTM C1157/C1157M-11 requires the air content to be reported but has no limits.

In ASTM C185-08, mortar is made with cement, standard sand, and enough water for a required consistency. The mortar is placed in a standard container and the weight of mortar is determined. The air content is calculated from the measured density and the calculated density of the air-free mixture. The calculated air-free density is determined from the mixture proportions and the separate densities of the constituents. Measuring air content of mortar should result in values of less than 12% for non-air-entraining cements and 16 to 22% for air-entraining cements. The air content of air-entrained concrete is typically in the range of 5 to 8% and is not related to this test of standard mortar.

5.2.8 Sulfate expansion—ASTM C452/C452M-10 can provide useful information relating to sulfate resistance of portland cements and is an optional requirement for Type V cements. This test measures the expansion of mortar bars made from a mixture of cement and gypsum such that the total $\text{SO}_4$ content is 7.0% by mass. After casting, the specimens are stored in water at 23°C (73°F), and the length is determined at different times. The expansion is then a measure of the sulfate resistance of the cement and should not exceed 0.040% after 14 days. This test is seldom used in purchase specifications because the values obtained may not correlate with sulfate expansions measured in concrete using the same cement. However, it is useful as a warning to prompt further investigation. Because ASTM C452/C452M-10 is not suitable for testing cements with SCMs, ASTM C1012/C1012M-12 is used to test ASTM C595/C595M-12e1 and C1157-11 cements to demonstrate that these cements meet sulfate resistance requirements. Mortar bars are prepared, cured, and exposed to a standard sulfate solution, and their lengths are measured periodically. For moderate sulfate resistance, specifications limit expansion to 0.10% at 6 months. For high sulfate resistance, a maximum of 0.05% expansion at 6 months or 0.10% at 1 year is required (refer to Tables 4.4 and 4.5). A drawback of ASTM C1012/C1012M-12 is the long time required to obtain a result.

CHAPTER 6—FLY ASH AND NATURAL POZZOLANS

The cementitious materials of today were among the chief cementitious components of concretes produced many centuries ago. Commonly termed “pozzolans,” these materials are capable of forming a durable binder. A pozzolan is defined in ASTM C125-11b as “a siliceous or siliceous and aluminous material, which in itself possesses little or no cementitious value but which will, in finely divided form and in the presence of moisture, chemically react with calcium hydroxide at ordinary temperatures to form compounds possessing cementitious properties.” These characteristics make pozzolans ideal additions to portland-cement concrete mixtures. They are composed of similar materials and react with the products of hydrating cement to create additional cementitious binder. Pozzolanic material can be used to modify and improve plastic and hardened properties of concrete.

6.1—Classification of pozzolans

ASTM C618-12 outlines the physical and chemical requirements of pozzolanic materials. Pozzolanic materials include natural pozzolans (Class N) and by-product materials. Natural pozzolans are notably volcanic ashes, diatomaceous earth, calcined clay, metakaolin clay, and rice husk ash. By-product material is most typically fly ash, classified as either Class F or Class C, reflecting a difference in chemical composition. Class F fly ashes possess largely pozzolanic properties. Class C fly ashes generally possess cementitious and pozzolanic properties. ASTM C618-12 differentiates Class C and Class F fly ashes based on the sums of the $\text{SiO}_2$, $\text{Al}_2\text{O}_3$, and $\text{Fe}_2\text{O}_3$. For Class C fly ash, $\text{SiO}_2 + \text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3$ must be greater than or equal to 50%. For Class F fly ash, $\text{SiO}_2 + \text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3$ must be greater than or equal to 70%. Class C fly ashes essentially contain 15 to 25% calcium, which makes their performance characteristics different from a low-calcium Class F fly ash.

Some fly ash distributors are blending fly ashes from different sources to meet the chemical and physical properties of ASTM C618-12. Certain fly ashes may also be processed by grinding or through a centrifugal classifier to increase the fineness and reactivity of the fly ash.
6.2—Fly ash as cementitious material

Fly ash is a fine residue resulting from the burning of powdered coal at high temperatures. The most common sources of fly ash are electric power-generating stations. Fly ash has become the predominant pozzolan in use throughout the world due to performance and economic factors. Extensive literature is available on the effects of fly ash in both fresh and hardened concrete.

Development of fly ash as a constituent of portland cement concrete was initiated in the United States during the early 1930s. Work at the University of California published in 1937 served as the foundation for specifications, methods of testing, and use of fly ash for this application. This work concluded “that where available, fly ashes of suitable fineness and composition can be used with technical benefit and economy to replace 20 to 50% of the amount of portland cement that otherwise would be required to produce concrete of specific strength and durability.” If the concrete is exposed to a moist freezing-and-thawing environment and deicing salts are anticipated, 25% by mass of cementitious materials is suggested as the upper limit to prevent deicer salt scaling. Applications using up to 70% fly ash as a substitution for portland cement have been successful (Davis et al. 1937).

The main constituent of fly ash is silica. Glassy noncrystalline forms of silica, alumina, and iron are principally responsible for the pozzolanic reaction with calcium hydroxide (lime). In concrete, lime results from the hydration of portland cement. Other components of fly ash are calcium, magnesium, sulfur, potassium, and sodium. Class C fly ashes contain less silica, alumina, and iron than the Class F fly ashes, and Class C fly ashes usually have elevated levels of calcium.

Although the constituents are not necessarily present in the oxide form, it is customary to express chemical analysis results in terms of the oxides of the elements: SiO₂, Al₂O₃, Fe₂O₃, CaO, and SO₃. Carbon is seldom determined directly but is often assumed to be approximately equal to the LOI.

6.3—Effect of fly ash on fresh concrete

According to ACI 232.2R-03, fly ash can have the following effects on fresh or plastic concrete:

• Improve workability;
• Lower water demand;
• Change air-entraining admixture dosage;
• Improve pumpability;
• Extend time of set;
• Decrease bleeding;
• Improve consolidation in forms; and
• Reduce heat evolution.

6.3.1 Workability—Workability in fresh concrete is governed by such factors as the age of the fresh concrete; volume of paste; \( \text{w/cm} \); chemical admixtures and SCMs; and the proportion, grading, amount, shape, and porosity of aggregates. One benefit of the use of fly ash is the increase in paste volume. Fly ash (specific gravity of 1.9 to 2.8) occupies approximately 25% greater volume than an equal mass of portland cement (specific gravity of 3.15). When fly ash is substituted for cement on a one-to-one basis by mass, the additional volume of fly ash replaces part of the fine aggregate and fills aggregate voids with paste, providing more cohesion and plasticity. A common explanation for the improved workability is that the spherical shape of fly ash particles provides a ball-bearing effect (Fig. 6.1).

6.3.2 Water demand—The use of fly ash as a partial replacement for portland cement will usually reduce water demand for equivalent slump compared to the portland-cement-only mixture. The degree of water reduction will depend on the mixture proportions, shape, and fineness of fly ash particles, as well as the characteristics of the aggregates.

6.3.3 Effect on entrained air content—ASTM C618-12 sets a 6% limit for the maximum allowable LOI. The LOI is an indirect measure of the quantity of unburned carbon remaining in the fly ash. Excessive amounts of carbon act as an adsorbent and will affect the dosage of air-entraining admixture required in concrete. Limiting LOI to 6% helps control performance of air-entraining admixtures in concrete. If a fly ash contains an appreciable amount of carbon, it may be difficult to control the air content. Presently, there are a number of technologies available to reduce the impact unburned carbon particles have on the ability to reliably entrain air in concrete. One technology uses the principle of turbo-electric charging and electrostatic separation to separate and remove excess carbon particles. Another technology uses a liquid reagent to coat unburned carbon particles. Other technologies include burning out unused carbon and froth flotation, which separates carbon from fly ash by introducing it into a slurry. The effects of fly ash and other pozzolans on air content are summarized in Table 6.1.

6.3.4 Pumping—The use of fly ash in pumped mixtures can be beneficial, as it reduces segregation and increases cohesiveness. Fly ash helps fill voids between aggregates, and its spherical particle shape acts as a lubricant in the pump line. This lubrication can be used to an advantage in one of two ways: if the same flow rate is maintained, the pressure in the pump line will decrease, or if the same line pressure is maintained, flow rates will increase, allowing a greater amount of material to pass through the pipe in a given time (faster placement).

6.3.5 Time of set—The setting time of a concrete mixture is influenced by the temperature; water content; portland cement characteristics; type and dosage of chemical admixtures; and the type, source, and amount of fly ash. Fly ash chemistry may influence setting times. When portland cement is replaced by Class F fly ash, concrete setting times may be extended. The chemical action from Class C fly ash can lead to reduced or extended setting times. The longer setting times of concrete mixtures containing fly ash may be shortened by the proper use of an accelerating admixture or may be used to an advantage in hot weather concreting. Setting times of concrete mixtures can be tested using the method in ASTM C403/C403M-08.

6.3.6 Bleeding—The use of fly ash in concrete mixtures generally reduces the rate and amount of bleed water appearing on the surface of the concrete. This is the result of
6.4—Effect of fly ash on hardened concrete

Fly ash can modify hardened concrete properties in the following ways:

- Increase strength (long-term);
- Decrease permeability;
- Improve durability; and
- Reduce alkali-aggregate expansion (must be investigated by testing).

6.4.1 Strength—The strength of a concrete mixture containing fly ash may be higher or lower than a similar concrete mixture containing portland cement only (Fig. 6.2). In general, concrete mixtures that contain fly ash as a partial replacement for portland cement will have lower strengths at early ages but usually higher strengths at later ages when compared to similar concrete mixtures containing portland cement only.

The rate of strength gain is dependent on the cement, fly ash, and water contents. Concrete mixtures proportioned using fly ash as a partial replacement for portland cement can be expected to experience slower strength development at early ages due to the reduced portland cement content. Concrete mixtures proportioned for performance at 28 days of age can use partial cement replacements from 15 to 25% Class F fly ash, depending on the characteristics of the materials and proportioning. With strength requirement delayed to 56 days, 90 days, or later, dosage rates can be increased to 30 to 50% or more. Many concretes containing Class C fly ash up to 35% have similar 28-day strength gain characteristics as plain cement concrete. Where early-age strengths are needed, it is also possible to use other ingredients, such as chemical accelerators, silica fume, or a lower w/cm coupled with a high-range water-reducing admixture, to improve the rate of strength gain of the mixture at early ages.

Properly designed concrete mixtures containing fly ash can exhibit higher ultimate compressive strengths than portland-cement-only mixtures.

While portland cement continues to hydrate and generate additional strength for many years, the rate of strength gain typically slows down after approximately 28 days. Fly ash concretes, however, continue to gain strength beyond 28 days at a rate greater than plain portland-cement concrete as a result of continued pozzolanic reaction with available calcium hydroxide inside the concrete. Using 28-day strengths for comparison, over time, plain portland-cement concretes, fly ashes, and ground granulated blast-furnace slag 

**Table 6.1—Effects of supplementary cementitious material on air content**

<table>
<thead>
<tr>
<th>Material</th>
<th>Effects</th>
<th>Guidance</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fly ash</td>
<td>Air content decreases with increased LOI</td>
<td>Changes in LOI or fly ash source require that</td>
</tr>
<tr>
<td></td>
<td>(carbon content).</td>
<td>air-entaining agent dosage be adjusted.</td>
</tr>
<tr>
<td></td>
<td>Air void system may be more unstable with</td>
<td>Perform foam index test to estimate</td>
</tr>
<tr>
<td></td>
<td>some combinations of fly ash/cement/air-</td>
<td>increase in dosage.</td>
</tr>
<tr>
<td></td>
<td>entraining agents.</td>
<td></td>
</tr>
<tr>
<td>Ground granulated</td>
<td>Decrease in air content with increased</td>
<td>Use up to 100% more air-entaining agent for</td>
</tr>
<tr>
<td>blast-furnace slag</td>
<td>fineness of GGBFS.</td>
<td>finely ground slags.</td>
</tr>
<tr>
<td>(GGBFS)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Silica fume</td>
<td>Decrease in air content with increase in</td>
<td>Increase air-entaining admixture dosage up to</td>
</tr>
<tr>
<td></td>
<td>silica fume content.</td>
<td>100% for fume contents up to 10%.</td>
</tr>
<tr>
<td>Metakaolin</td>
<td>No apparent effect.</td>
<td>Adjust air-entaining agent dosage if needed.</td>
</tr>
</tbody>
</table>

Whiting and Nagi 1998.

*Fig. 6.1—Fly ash particles viewed at 1000× magnification (Helmuth 1987).*

the higher surface area of the fly ash particles and the lower water content of concrete mixtures containing fly ash.

6.3.7 Consolidation—Consolidation energy is the amount of effort required to consolidate concrete in formwork and is influenced by both concrete ingredients and proportioning. Concrete mixtures made with fly ash may be easier to consolidate than those made without. The fineness, void-filling ability, and spherical particle shape all assist in increased response to vibratory energy.

6.3.8 Heat evolution—The hydration of portland cement with water is a reaction that liberates considerable heat. The pozzolanic reaction of Class F fly ash also gives off heat but to a lesser extent than portland cement. Evolution of heat during hydration is of primary concern in thick or massive concrete sections or for mixtures with high cement contents where the likelihood of differential temperatures from the concrete surface to the center is great enough to result in thermal cracking. Minimizing the heat liberated during the hydration of cementitious materials is the major method of reducing thermal cracking. Class F fly ash and natural pozzolans have been used historically for this purpose. Class C fly ash may behave differently from Class F fly ash in that pozzolanic reaction of Class F fly ash also gives off heat but with water is a reaction that liberates considerable heat. The water content of concrete mixtures containing fly ash.

Consolidation energy is the amount of effort required to consolidate concrete in formwork and is influenced by both concrete ingredients and proportioning. With strength requirement delayed to 56 days, 90 days, or later, dosage rates can be increased to 30 to 50% or more. Many concretes containing Class C fly ash up to 35% have similar 28-day strength gain characteristics as plain cement concrete. Where early-age strengths are needed, it is also possible to use other ingredients, such as chemical accelerators, silica fume, or a lower w/cm coupled with a high-range water-reducing admixture, to improve the rate of strength gain of the mixture at early ages.

Properly designed concrete mixtures containing fly ash can exhibit higher ultimate compressive strengths than portland-cement-only mixtures.
concrete generally gains approximately 30% additional strength, whereas portland cement/fly ash concrete can gain 50 to 100% additional strength. If 28-day strengths are similar, the ultimate strength of fly ash concrete may be greater. Generally, the higher the fly ash content, the greater the potential long-term strength gain. The exact increases will depend on the characteristics of materials used, the proportioning of the mixture, and the curing conditions of the concrete.

Flexural strength of fly ash concrete measured at ages as early as 7 days can be expected to be equivalent to a plain portland-cement mixture. As a result, the use of fly ash concrete has become widespread in paving applications.

6.4.2 Permeability—Permeability of concrete is affected by cementitious materials content, w/cm, aggregate characteristics, water content, curing conditions, air content, and extent of consolidation. Studies have shown that permeability of fly ash concrete is substantially lower than plain portland-cement concrete. This effect is due to the pore refinement that occurs as a result of the long-term pozzolanic action of fly ash. Reduced permeability of fly ash concrete can decrease the rates of water, corrosive chemicals, oxygen, and carbon dioxide entry into concrete.

6.4.3 Durability—Durability of concrete refers to its ability to resist either physical forces, such as repetitive loading, freezing and thawing, and abrasion, or chemical attack such as soluble sulfates. Addition of fly ash may improve concrete performance against the various forms of chemical and physical attack.

6.4.4 Sulfate attack—The use of Class F fly ash decreases the amount of tricalcium aluminate in the concrete cementitious system and makes the concrete more resistant to sulfate ions. Class F ashes generally improve sulfate resistance more efficiently than Class C ashes, although both classes of fly ash help to lower the permeability of concrete, improving the resistance to sulfate damage. Some Class C fly ashes may increase the amount of C₃A in the system and could lower the resistance to sulfates. Generally, fly ashes containing less than 15% CaO will improve the resistance of concrete to sulfate attack. Other fly ashes may also improve sulfate resistance, but they should be tested using test methods such as ASTM C1012/C1012M-12.

6.4.5 Acid resistance—Some acids attack concrete by dissolving the cementitious paste and certain aggregates. Fly ash concrete may slow down the rate of attack from acids because permeability is reduced. The only known way to protect concrete from aggressive acids, however, is to provide a barrier between the acid and the concrete.

6.4.6 Corrosion resistance—Generally, reinforcing steel is protected against corrosion by the concrete cover and the natural alkalinity of the concrete. Corrosion of reinforcing steel embedded in concrete is accelerated by intrusion of chlorides. Because the permeability of fly ash concrete is reduced, the ingress of chlorides into the concrete will also be reduced and the onset of corrosion may be delayed.

6.4.7 Reduction of expansion caused by alkali-silica reactivity—Class F fly ash and some Class N pozzolans have been shown to be effective in reducing expansion from alkali-silica reaction (ASR). Class C fly ashes may or may not improve the performance of concrete susceptible to ASR. When fly ash or natural pozzolans react with calcium hydroxide, alkalies are consumed and held in the cementitious phase, where they are kept from the aggregate. Any pozzolanic material should be investigated for its effectiveness in controlling expansion (Fig. 6.3). This can be done by following the methods described in ASTM C311-11b. Requirements based on this test are listed in the supplementary optional requirements of ASTM C618-12.

Another option to test the effectiveness of a fly ash to reduce ASR is described in ASTM C1567-11.

6.4.8 Resistance to freezing and thawing—The resistance to damage from freezing and thawing of concrete made with or without fly ash depends on the adequacy of the air-void system, soundness of the aggregates, age, maturity of the cement paste, and moisture condition of the concrete (Larson et al. 1964). Care should be exercised in proportioning mixtures to ensure that the concrete has adequate strength when first exposed to cyclic freezing and thawing.

ACI 301-10, “Specifications for Structural Concrete,” places a maximum limit of 25% fly ash and natural pozzolans in concrete that will be exposed to deicing chemicals. Abrasion resistance of concrete is related to the compressive strength, quality of aggregate, proportioning of the concrete mixture, and quality of the finishing. Fly ash does not directly influence abrasion resistance but may lead to increased ultimate strength of concrete and thus indirectly improve abrasion resistance.

6.5—Concrete mixture considerations with fly ash

As is true for all materials specified for use in portland-cement concrete, different fly ashes may perform differently while meeting the quality requirements of ASTM specifications. It is therefore advisable that actual performance in concrete be determined by testing with trial batches.
Fly ash performance in concrete depends on the quality and performance of the other constituents of the mixture. If other mixture components change, the fly ash in question should be re-evaluated with trial batches before implementing the change in commercial production.

Fly ash should be used as a partial replacement for or an addition to the Portland cement fraction in the mixture. In the mixture proportions, some quantity of Portland cement should be maintained to ensure that early strengths, setting times, resistance to freezing and thawing, and deicer salt scaling resistance obligations are met. Additionally, fly ash can be used to improve the workability, strength, and durability of concrete.

Whereas Portland cement reacts quickly with water, Class F fly ash remains basically inert in plastic concrete. Some Class C fly ashes can react quickly with water and may affect water demand, slump loss, and other fresh concrete properties. Most fly ashes do not interfere with the activity of chemical admixtures. The exception would be when an air-entraining admixture can be adsorbed by excessive carbon in the fly ash. Fly ash is considered compatible with most chemical admixtures.

For more detailed information on the use of fly ash in Portland-cement concrete, refer to ACI 232.2R-03.

CHAPTER 7—SLAG CEMENT

The term “slag cement” had been used in the past to identify an ASTM C595/C595M-12e1 blended cement containing more than 70% slag. ASTM has since combined the three categories of slag blended cements into one category: IS—Portland Blast-Furnace Slag Cement, with the percentage of slag stated. Subsequently, the slag industry has elected to use slag cement rather than the traditional ground-granulated blast-furnace slag (GGBFS) or ground iron blast-furnace slag to identify their product. This change is reflected in the latest version of ACI 233R-03, “Slag Cement in Concrete and Mortar.”

7.1—Classification of blast-furnace slag

In the production of iron, a blast furnace is typically charged with iron ore, flux stone (limestone or dolomite), and coke for fuel. The two products obtained from the furnace are molten iron and slag.

Consisting primarily of silica and alumina from the iron ore combined with calcium from the flux stone, slag contains the same major elements as Portland cement but in different proportions (refer to Table 7.1).

Granulated blast-furnace slag (GBFS), however, is comprised essentially of glasses. GBFS, when ground, exhibits cementitious properties by itself and is referred to as an SCM in this document. The various other slag products listed in Table 7.1 are generally not used as SCMs.

The physical properties of iron blast-furnace slag depend on how the molten slag is cooled. The four methods of processing the molten slag are as follows:

- Air-cooled—The molten slag is allowed to cool in pits and then crushed for use principally as aggregate or railroad ballast. Air-cooled slag has no significant value as a cementitious material.
- Expanded—The molten slag is treated with controlled quantities of water. This makes a cellular lightweight product. Finely ground expanded slag may have some cementitious value, but its principal use is as a lightweight aggregate in a concrete block.
- Pelletized—The molten slag is sprayed with water as it falls on a rapidly rotating drum. This breaks up the slag and flips the pieces into the air, forming pellets. If cooling is sufficiently rapid, some glassy material may be made; this material, when finely ground, may exhibit significant cementitious properties.
- Granulated—The molten slag is very rapidly cooled by quenching in water, which results in a glassy, granular product. It is this glassy material that is the main source of the cementitious properties of the granulated slag. Finely ground granulated blast-furnace slag cement is a hydraulic cementitious material commonly used in conjunction with Portland cement.

Because approximately 85 to 90% of the 24 million metric tons (26 million tons) of blast-furnace slag produced in the United States is processed as an air-cooled product, only a small percentage of total slag produced currently is being used for its cementitious properties. However, in today’s energy-conscious environment, it is expected that more blast-furnace slag will be processed, either by granulating or pelletizing, for its potential cementitious properties. The cost of energy to produce slag cement is lower than that of cements made from clinker, like Portland cement.

In the United States, ASTM C989/C989M-12, “Standard Specification for Slag Cement for Use in Concrete and Mortars,” is the principal specification for slag cement. ASTM C989/C989M-12 identifies three grades of slag cement: 120, 100, and 80. These grades represent roughly the average strength of a standard mortar mixture containing 50% slag cement relative to a plain Portland-cement standard mixture.

ASTM C595/C595M-12e1 covers the use of slag cement in blended cements. Types of blended cements that contain...
slag cement are described in ASTM C595/C595M-12e1 and are given in Table 7.2.

**ASTM C595/C595M-12e1** blended cements use slag cement that has been either interground with portland cement clinker or blended intimately with separately ground material. Slag cement can be used as an ingredient in hydraulic cements covered by ASTM C1157/C1157M-11, a performance specification for hydraulic cements.

Slag cement has been used for many years. Even though it has a long, credible service record, less than 1% of the cement being produced in the United States today contains slag cement.

### 7.2—Slag cement as supplementary cementitious material

Recently, attention has been focused on the production of slag cement that is marketed separately to the ready mix producer and used as a partial replacement for portland cement. The optimum replacement dosage depends on the cementitious activity of the slag cement and the properties desired in the concrete. In many cases, replacement dosages between 25 and 65% are seen. Fineness, glass content, and mineral constituents are generally considered to be important factors regarding the cementitious activity of slag cement. Studies have indicated that the composition of the portland cement is also a factor in the strength development of concrete containing slag cement.

### 7.3—Effects of slag cement on fresh and hardened properties of concrete

Chemical and physical characteristics of the slag and portland cements, slag cement dosage, temperature, curing, and other factors affect the concrete properties. Generally, the comparison with portland-cement concrete can be summarized as follows:

- If the slag cement component is finer than portland cement, greater amounts of air-entraining admixture may be required to achieve a specific air content.
- Concretes containing slag cement may show a somewhat longer time of setting than straight portland-cement mixtures, particularly for moderate and higher dosages.
- Concrete with slag cement added at the mixer will usually have lower heat of hydration and is recommended for mass concrete applications.
- Concrete with slag cement added to the mixer gains strength more slowly, tending to have lower strength at early ages and equal or higher strength at later ages.

Slag cement has been used successfully in many high-strength applications:

- The degree of curing has a similar effect on both types of concrete.
- Increasing slag cement dosage is associated with lower permeability and reduced electrical conductivity.
- Specific slag cement mixtures have demonstrated an improvement in the resistance to sulfate attack and prevention of alkali-aggregate expansion.
- There is no significant difference in the shrinkage characteristics of concrete with and without slag cement as part of the cementitious materials.
- The resistance to damage from cycles of freezing and thawing for air-entrained concrete with and without slag cement is similar.
- The color of concrete containing slag cement is lighter than normal portland-cement concretes.

Slag cement can be used in conjunction with other cementitious materials, such as fly ash and silica fume.

## CHAPTER 8—SILICA FUME

### 8.1—Silica fume production

Silica fume is a highly reactive pozzolan material that is used in relatively small amounts to improve or enhance the properties of concrete. Silica fume is captured smoke, a by-product of producing silicon and ferrosilicon metal in open-arc electric furnaces, where quartz, coal, wood chips, and other furnace burden materials are reduced to extract the silicon products from the quartz. This finely divided, gray-colored, glassy powder results from the condensation of silicon oxide gas into noncrystalline silica dioxide. Silica fume is composed primarily of amorphous SiO$_2$. Particles are approximately 100 times smaller than the typical particles of portland cement. The chemical composition and size of silica fume make it a very reactive pozzolanic material. Silica fume is frequently referred to by other names, including condensed silica fume, microsilica, and volatilized silica.

There are several materials similar to silica fume in chemical and physical properties.

The following materials may contain silica in crystalline form and may or may not perform well in concrete: precipitated silica, fumed silica, silica gel, colloidal silica, silica flour, and silica dust.

In North America, silica fume is transported, stored, and used as a dry powder in two forms: as-produced powder and a dry, densified powder. The as-produced powder has a light bulk density (128 to 433 kg/m$^3$ [8 to 27 lb/ft$^3$]), is difficult to transport and handle pneumatically, and can create a severe dust problem; therefore, it is used in bag form only.
The more commonly used dry, densified form of silica has been processed to increase the bulk density to approximately 560 to 720 kg/m³ (35 to 45 lb/ft³). This form is shipped and handled by bulk pneumatic transports, similar to portland cement or fly ash. Testing has shown no significant differences in the performance of the various forms of silica fume.

A third, slurried form is not available in all parts of the world and consists of silica fume and water, usually in equal amounts by mass. Some slurry products may contain chemical admixtures, such as water-reducing admixtures or high-range water-reducing admixtures. Slurries should be kept agitated prior to batching in concrete. Due to the large volume of slurry commonly used—50 L/m³ (10 gal./yd³) or more—special dispensing equipment is required. Because water is a main ingredient of the slurry, it is necessary to subtract an equal amount of water from the mixing water to maintain the same w/cm.

8.2—Silica fume as cementitious material

Silica fume is typically used in quantities ranging from 5 to 15% of the mass of the cementitious material. The amount used depends on the desired concrete property. Small amounts of silica fume can decrease concrete permeability, while higher amounts are typically used to produce high-strength concretes. There may be an opportunity to reduce cement contents when producing low-permeability, conventional-strength concretes that contain silica fume. The concrete producer may use the strength contribution from the addition of silica fume to offset the amount of cement needed to produce the specified strength or performance. Silica fume should conform to the requirements of ASTM C1240-11.

8.3—Effects of silica fume on properties of fresh and hardened concrete

Silica fume addition benefits concrete in two ways. First, the minute particles physically decrease the void space in the cement matrix—this phenomenon is known as “packing.” Second, silica fume is chemically an extremely reactive pozzolan.

Silica fume is added to concrete to increase compressive strength or improve durability. Properly proportioned silica fume concrete can achieve very-high-early and ultimate compressive strengths. Ready mixed concretes with a compressive strength of 135 MPa (20,000 psi) have been produced in the United States using silica fume combined with other admixtures. Silica fume enhances durability by decreasing the permeability while increasing the electrical resistance of concrete. With its reduced permeability, silica fume concrete has been extensively used in applications where limiting the entry of chlorides is essential, such as in bridge decks, parking structures, and marine structures. The increase in electrical resistivity of the concrete will restrict current flow necessary for macrocell corrosion of reinforcing steel.

The fineness of silica fume will increase the water demand of a concrete mixture. The increase in water demand will be proportional to the amount of silica fume being used. It is common to use a high-range, water-reducing admixture to control workability and slump while maintaining the desired w/cm.

Fresh concrete made with silica fume is more cohesive and therefore less prone to segregation than concrete without silica fume. Because of the lack of segregation, silica fume concrete is readily pumped with the silica fume, allowing an increase in slump. Silica fume concretes typically used for flatwork applications show little, if any, bleeding. Bleed-water channels can serve as shortcuts for chloride ions from deicing salt or seawater to get back into the concrete. The onset of bleeding may lead to plastic shrinkage cracking if precautions are not taken in the finishing operations to prevent moisture evaporation from the surface of the concrete. Finishers must be prepared to prevent plastic shrinkage cracking or crusting by following the guidelines in ACI 305R-10, “Guide to Hot Weather Concreting,” or by using a fast-track finishing process, whereby the concrete is placed and finished followed by immediate curing to reduce the evaporation exposure time necessary to develop plastic shrinkage. Project specifications should require trial placements for inexperienced finishing crews using the concrete mixture proportions that will be used for the actual structure. Once finishers have been properly trained, silica fume concrete is no more difficult to finish than any other type of concrete. For more information, refer to ACI 234R-06, “Guide for the Use of Silica Fume in Concrete.”

CHAPTER 9—ADDITIONAL FACTORS IN SELECTION AND USE OF PORTLAND CEMENT

The previous chapters have covered the basic information to assist in the selection of cementitious materials for a particular application and the testing and evaluation of these materials. There are, however, a number of miscellaneous topics that should be considered, and these are discussed in this chapter.

9.1—Uniformity

Cement is an inherently variable material. Cements supplied from the same mill can have different characteristics from lot to lot. Minor fluctuations in raw material compositions and burning conditions are the main cause of this variability. Some differences persist even after fluctuations have been smoothed out by blending in the storage silos.

9.1.1 Strength variations—ASTM C150/C150M-12 only sets a minimum strength requirement that is exceeded by most manufacturers. However, the concrete producer is often concerned with minimizing strength variations in concrete, and this is somewhat influenced by the variability of the cement manufacturing process. Testing data acquired in accordance with ASTM C917-05(2011) enable the cement consumer to make such an estimate of the statistical history of strength variations for use in controlling the strength of concrete mixtures.

9.1.2 Color variations—There can be considerable color variations between different brands of the same type of cement. This depends on the amount of Fe₂O₃ and MgO (both affecting the amount and color of the ferrite phase,
which is responsible for cements’ gray color). When patching and repair work are being carried out on new structures, cement from a single source should be used to minimize color variations. On old concrete structures, an acceptable match of color should be sought. However, it is important to remember that color variations in concrete depend not only on the cement but also on many other factors, such as the amount of admixtures (especially calcium chloride), type and amount of curing, contamination on the form face, texture or finish technique, w/cm, and color of the sand.

9.2—Handling and storage of cement

Today, cement is most often transported in bulk and transferred pneumatically from the carrier to the storage silo. Cement should normally flow well if it is kept free of moisture, and flow is generally improved by the use of processing additions during manufacturing. Bag cement should be stored so that it is protected from direct contact with moisture or other contamination from the environment (preferably in well-ventilated surroundings). If hard lumps are found (warehouse set) in either bulk or bag cement, it is likely that the cement has been in contact with moisture and its quality may be impaired. Standard tests to determine its strength gain characteristics and setting times should be carried out.

9.2.1 Cement temperature—Cement can be at very high temperatures when it is placed in the storage silos at the plant, and this heat dissipates slowly. Therefore, in the summer months when demand is high, cement may still be warm when it is delivered to the concrete plant or job site. The cement should be satisfactory even if the temperature is as high as 77°C (170°F). A problem of early stiffening and increased water demand may develop in very hot weather if the concrete temperatures become too high, but this can be controlled by lowering the temperature of the other ingredients. For each 5.6°C (10°F) increase in cement temperature, the temperature of the concrete will increase approximately 0.6°C (1°F). Therefore, only in those cases where the concrete temperature is near an upper control or specification limit might an increase in cement temperature cause problems.

9.3—Availability

Although ASTM C150/C150M-12 recognizes five types of portland cement, not every type is available in all parts of the United States. Types I and II are readily available in most areas, but other types may not be available within a reasonable shipping distance. A recent trend has been the identification of cements using the nomenclature of Type I/II. This designation is an indication that the cement meets the requirements specified for both Types I and II cement. Type III is generally used for special applications requiring high early strengths. Type IV is no longer routinely made in the United States, and Type V may be made only on request in some areas. The availability of blended cements and other specialty cements is even more limited. The user should investigate other available options, such as the use of admixtures and different cement contents, to determine the most economical and reliable means of achieving the desired result.

CHAPTER 10—REFERENCES

Committee documents are listed first by document number and year of publication followed by authored documents listed alphabetically.

American Association of State Highway and Transportation Officials
AASHTO M 85-12—Standard Specification for Portland Cement
AASHTO M 240-12—Standard Specification for Blended Hydraulic Cement

American Concrete Institute
ACI 201.2R-08—Guide to Durable Concrete
ACI 207.1R-05—Guide to Mass Concrete
ACI 223R-10—Guide for the Use of Shrinkage-Compensating Concrete
ACI 225R-99—Guide to the Selection and Use of Hydraulic Cements (Reapproved 2009)
ACI 232.2R-03—Use of Fly Ash in Concrete
ACI 233R-03—Slag Cement in Concrete and Mortar
ACI 234R-06—Guide for the Use of Silica Fume in Concrete
ACI 301/301M-10—Specifications for Structural Concrete
ACI 305R-10—Guide to Hot Weather Concreting
ACI 318/318M-11—Building Code Requirements for Structural Concrete and Commentary

American Petroleum Institute
API Spec 10A—Specification for Cements and Materials for Well Cementing

ASTM International
ASTM C91/C91M-12—Standard Specification for Masonry Cement
ASTM C115-10—Standard Test Method for Fineness of Portland Cement by the Turbidimeter
ASTM C125-11b—Standard Terminology Relating to Concrete and Concrete Aggregates
ASTM C150/C150M-12—Standard Specification for Portland Cement
ASTM C151/C151M-09—Standard Test Method for Autoclave Expansion of Hydraulic Cement
ASTM C185-08—Standard Test Method for Air Content of Hydraulic Cement Mortar

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ASTM C204-11—Standard Test Methods for Fineness of Hydraulic Cement by Air-Permeability Apparatus
ASTM C266-08e1—Standard Test Method for Time of Setting of Hydraulic-Cement Paste by Gillmore Needles
ASTM C311-11b—Standard Test Methods for Sampling and Testing Fly Ash or Natural Pozzolans for Use in Portland-Cement Concrete
ASTM C359-08—Standard Test Method for Early Stiffening of Hydraulic Cement (Mortar Method)
ASTM C403/C403M-08—Standard Test Method for Time of Setting of Concrete Mixtures by Penetration Resistance
ASTM C452/C452M-10—Standard Test Method for Potential Expansion of Portland-Cement Mortars Exposed to Sulfate
ASTM C595/C595M-12e1—Standard Specification for Blended Hydraulic Cements
ASTM C618-12—Standard Specification for Coal Fly Ash and Raw or Calcined Natural Pozzolan for Use in Concrete
ASTM C778-12—Standard Specification for Standard Sand
ASTM C939/C939M-12—Standard Specification for Slag Cement for Use in Concrete and Mortars
ASTM C1012/C1012M-12—Standard Test Method for Length Change of Hydraulic-Cement Mortars Exposed to a Sulfate Solution
ASTM C1038/C1038M-10—Standard Test Method for Expansion of Hydraulic Cement Mortar Bars Stored in Water
ASTM C1072-11—Standard Test Methods for Measurement of Masonry Flexural Bond Strength
ASTM C1240-11—Standard Specification for Silica Fume Used in Cementitious Mixtures
ASTM C1328/C1328M-12—Standard Specification for Plastic (Stucco) Cement
ASTM C1329/C1329M-12—Standard Specification for Mortar Cement

ASTM C1600/C1600M-11—Standard Specification for Rapid Hardening Hydraulic Cement

Canadian Standards Association
CSA A3001-08—Cementitious Materials for Use in Concrete

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