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Guide to the Selection and Use of Hydraulic Cements

Reported by ACI Committee 225

ACI PRC-225-23



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Guide to the Selection and Use of Hydraulic Cements

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38800 Country Club Drive
Farmington Hills, MI 48331
Phone: +1.248.848.3700
Fax: +1.248.848.3701

Guide to the Selection and Use of Hydraulic Cements

Reported by ACI Committee 225

Kenneth G. Kazanis, Chair

Mark R. Lukkarila, Secretary

Michael M. Chehab
Marwan A. Daye
Jonathan E. Dongell
Brett A. Harris
Geoffrey Hichborn
R. Doug Hooton

Eric P. Koehler
Kimberly E. Kurtis
Kirk L. McDonald
Moncef L. Nehdi
James S. Pierce
Nicholas J. Popoff

Chengqing Qi
Oscar Tavares
Paul D. Tennis
James I. Turici Jr.
Jay E. Whitt
Matthew D. Wilbanks

Stephen D. Wilcox

Consulting Members

Glen E. Bollin
Larry Rowland
Bryce P. Simons

*The committee acknowledges B. Blair and M. D. A. Thomas for their contributions in the development of this guide.

The update to this guide includes a statement on life-cycle analysis (LCA), environmental product declarations (EPDs), and a new section on carbonation (10.6). This guide covers the influence of cement on the properties of concrete, summarizing the composition and availability of commercial hydraulic cements and the factors affecting their performance in concrete. Cement is the most active component of concrete and usually has the greatest unit cost; therefore, its selection and proper use is imperative to attaining the desired balance of properties and cost for a particular concrete mixture. Selection should include consideration of the cement properties in relation to the required performance of the concrete. It includes a discussion of cement types, a brief review of cement chemistry, the influences of chemical admixtures and supplementary cementitious materials, as well as the effects of the environment on cement performance and reviews of the sustainability aspects for the use and manufacture of portland cement. Cement storage, delivery, sampling, and testing of hydraulic cements for conformance to specifications are addressed. Users will learn to recognize when a readily available, general-purpose cement will perform satisfactorily or when conditions require selection of a cement that meets additional requirements.

Keywords: admixture; blended cement; calcium-aluminate cement; cement storage; cement types; chemical analysis; hydraulic cement; physical properties; portland cement; pozzolan; slag cement; supplementary cementitious materials; sustainability.

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ACI PRC-225-23 supersedes ACI 225R-19 and was published November 2023. This guide was first published in 1985 and revised in 1996, 2001, and 2019.

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CHAPTER 1—INTRODUCTION AND SCOPE

1.1—Introduction

This guide assists specifiers and designers in choosing appropriate cement for specified concrete applications. Although hydraulic cements are only one ingredient of a concrete mixture, they are the active ingredient and, therefore, play a key role in the long-term viability of the structure, floor, or pavement. Cement choice depends on many variables, such as the service conditions for which the concrete is designed, properties of other materials used in the mixture, or the performance characteristics of the concrete required during or shortly after placement.

Cement paste is the binder in concrete or mortar that holds the fine aggregate, coarse aggregate, or other constituents together in a hardened mass. The term “hydraulic” in this guide refers to the basic mechanism by which the hardening of the cement takes place—a chemical reaction between the cement and water. The term also differentiates hydraulic cement from binder systems that are based on other hardening mechanisms, as hydraulic cements can harden underwater.

Concrete properties depend on the quantities and qualities of its constituents. Because cement is the most active component of concrete and usually has the greatest unit cost, its selection and proper use are fundamental in obtaining the most economical balance of properties desired for a particular concrete mixture. Most cements will provide adequate levels of strength and durability for general use. Some provide higher levels of certain properties than are needed in specific applications.

Although not discussed in this document, there are non-hydraulic alternative cements commercially available, though generally not used as widely as hydraulic cements. For example, carbonated calcium silicate cement hardens through the absorption of CO₂, magnesium oxychloride cement hardens through the result of acid/base reactions in an aqueous environment, and alkali-activated fly ash and alkali-activated slag cements harden when the alkali activators dissolve the fly ash or slag particles and initiate the precipitation of reaction products. For more information, refer to ACI ITG-10R.

1.2—Scope

This guide summarizes information about the composition, availability, and factors affecting the performance of commercial hydraulic cements. For more information regarding:



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- Cement selection, whether a cement is readily available, and if conditions require a general-purpose cement or a special cement
- How the chemical and physical characteristics of a cement can affect certain properties of concrete
- How interaction of cements with various additives, admixtures, and mixture designs can affect concrete

This guide deals with hydraulic cements manufactured in conformance with ASTM International, American Association of State Highway and Transportation Officials (AASHTO), and Canadian Standards Association (CSA) standards. For information on other hydraulic cement standards, the user is directed to local specifications and building codes.

CHAPTER 2—NOTATION AND DEFINITIONS

2.1—Notation

Cement phases referred to throughout this guide follow the cement chemists' notation as follows:

A = Al_2O_3

C = CaO

$\bar{\text{C}}$ = CO_2

F = Fe_2O_3

H = H_2O

M = MgO

S = SiO_2

$\bar{\text{S}}$ = SO_3

Equivalent alkalies, $\text{Na}_2\text{O}_{\text{eq}} = \text{Na}_2\text{O} + 0.658 \cdot \text{K}_2\text{O}$

tricalcium silicate*: $3\text{CaO} \cdot \text{SiO}_2 = \text{C}_3\text{S}$

dicalcium silicate: $2\text{CaO} \cdot \text{SiO}_2 = \text{C}_2\text{S}$

tricalcium aluminate: $3\text{CaO} \cdot \text{Al}_2\text{O}_3 = \text{C}_3\text{A}$

tetracalcium aluminoferrite: $4\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{Fe}_2\text{O}_3 = \text{C}_4\text{AF}$

2.2—Definitions

Please refer to the latest version of ACI Concrete Terminology for a comprehensive list of definitions.

CHAPTER 3—CEMENT TYPES, AVAILABILITY, AND SELECTION

Cement selection is an important consideration when proportioning mixtures for specific project requirements and intended use. It is important that the specification for hydraulic cements be appropriate for the project and the hydraulic cements available in the area. Factors such as exposure conditions and desired properties can often require specific cement types based on the chemistry or physical properties. Specific cements may be available that are designed for applications where performance requirements cannot be achieved with ordinary portland cement.

3.1—Portland and blended hydraulic cements

A majority of the cement used for concrete construction in the United States is either portland cement, manufactured to meet the requirements of **ASTM C150/C150M**, blended hydraulic cement manufactured to meet the requirements of **ASTM C595/C595M**, or performance-

based hydraulic cement manufactured to meet the requirements of **ASTM C1157/C1157M**. Tables 3.1a and 3.1b include basic characteristics of these cements as listed in ASTM. Other portland cement specifications can be found in **AASHTO M 85** or, for Canada, in **CSA A3001**. Blended cements are also specified under the **AASHTO M 240** requirements. For more on hydraulic cement specifications and selection, refer to 3.4 of this guide.

Portland cements are manufactured by a process that begins by combining a source of lime such as limestone, a source of silica and alumina such as clay, and a source of iron oxide such as iron ore. The properly proportioned mixture of the raw materials is finely ground and then heated to approximately 2700°F (1480°C) for the reactions that form cement phases to take place. The product of a cement kiln is portland cement clinker. After cooling, the clinker is ground with calcium sulfate (gypsum), processing additions, and, in most cases, limestone to form a portland cement. Processing additions are organic or inorganic materials used in the manufacture of cements that are added at the finish mill. Their use is governed by **ASTM C465**. Processing addition rates for portland cements are specified in ASTM C150/C150M. The specific gravity of portland cement will vary slightly depending on the amounts of limestone, gypsum, and inorganic processing addition added to the clinker. For more reference on inorganic process addition, refer to **Taylor (2008)**. Most of these additions are less dense than clinker and tend to reduce the specific gravity of the portland cement. When proportioning concrete mixtures, unless an actual measurement of the specific gravity of the cement

Table 3.1a—Characteristics of portland cements*

Type*	Description
I	General use
II	General use; moderate sulfate resistance
II (MH)	General use; moderate heat of hydration, and moderate sulfate resistance
III	High-early-strength
IV	Low heat of hydration (LH)
V	High sulfate resistance

*For cements specified in ASTM C150/C150M and AASHTO M 85.

Table 3.1b—Blended hydraulic cements

ASTM C595/C595M Type	Name	Blended ingredients range, percent by mass		
		Pozzolan	Slag cement	Limestone
IP	Portland-pozzolan cement	1 to 40	—	—
IS	Portland blast-furnace slag cement	—	1 to 95	—
IL	Portland-limestone cement	—	—	5 to 15
IT	Ternary blended cement†	1 to 40	1 to 95	5 to 15

*Tricalcium silicate, Ca_3SiO_5 , in conventional notation becomes $3\text{CaO} \cdot \text{SiO}_2$ in oxide notation, or C_3S in cement chemists' notation. Simple oxides, such as CaO or SiO_2 , are often written in full.

†Ternary blended cements include clinker or portland cement, in addition to blended with two different pozzolans: slag and a pozzolan, a pozzolan and a limestone, or a slag and a limestone. Refer to ASTM C595/C595M.

has been made, 3.15 has been used for portland cements (Kosmatka and Wilson 2011). As the amount of processing additions increase, the specific gravity value has been found to decrease.

Blended hydraulic cements are usually made by intergrinding portland cement clinker with calcium sulfate (gypsum); processing additions; and a quantity of a suitable material such as slag cement, fly ash, limestone, silica fume, or raw or calcined natural pozzolans. They may also be made by blending the finely ground ingredients, or by a combination of blending and intergrinding. The specific gravity of a blended cement will vary with the type and amount of material(s) that is (are) interground or blended.

For specification purposes, portland and blended hydraulic cements are designated by type depending on their chemical composition and properties. The availability of a given type of cement can vary widely among geographical regions. Commonly used descriptions of portland and blended cements are given in Tables 3.1a for portland cement, Table 3.1b for blended hydraulic cements, and Table 3.1c for performance-based hydraulic cements. The use of blended cements is growing in response to the demand for concrete

requiring special properties, energy conservation, and raw materials.

3.2—Special-purpose cement

In addition to portland and blended cements, other hydraulic cements are available for specialized uses (Table 3.2). Other cement types are only briefly addressed, as their availability is limited in some regions.

3.2.1 Masonry cements—Masonry cements are used in masonry mortars. They are specified in **ASTM C91/C91M** and their use is covered by **ASTM C270** and **ACI 530/530.1**. Plastic and mortar cements are also used in mortars and specified in **ASTM C1328/C1328M** and **ASTM C1329/C1329M**, respectively. In Canada, masonry and mortar cements are specified in **CSA A3002**.

3.2.2 Special colored cements—Certain portland cements can give the finished product special colors, such as white or buff, which are used for architectural purposes. White and buff cements are usually furnished to meet **ASTM C150/C150M** specifications.

3.2.3 Modified portland cements—Modified portland cements as described in **ASTM C90**, which are sometimes referred to as block cements, are manufactured to meet the needs of the concrete masonry unit manufacturing industry.

3.2.4 Expansive or shrinkage-compensating cements—These are designed to expand a small amount during the first few days of hydration to offset the effects of later drying shrinkage. Their purpose is to reduce cracking resulting from volume decrease due to shrinkage or to cause stressing of reinforcing steel (**ACI 223R**). Those manufactured in the U.S. depend on the formation of a higher-than-usual amount of ettringite during hydration of the cement to cause the expansion (**ASTM C845/C845M**). The expansive ingredient, an anhydrous calcium sulfoaluminate, can be

Table 3.1c—Performance-based hydraulic cements

ASTM C1157/C1157M Type	Name
GU	General use
HE	High early strength
MS	Moderate sulfate resistance
HS	High sulfate resistance
MH	Moderate heat of hydration
LH	Low heat of hydration

Table 3.2—Miscellaneous or special purpose cements

Type	Description or purpose	ASTM specification
White cement	White architectural cement	C150/C150M*, C595/C595M, C1157/C1157M
Buff cement	Buff architectural cement	C150/C150M*
Expansive cement, Type E-1†	Expansive hydraulic cement	C845/C845M‡
Regulated-set cement	For use where rapid setting and moderate early strength development is needed	None
Rapid-hardening hydraulic cements	For use where early strength development is needed	C1600/C1600M
Well cements: Classes A through H, J*	Hydraulic cements used for oil-well casings and linings	None‡
Masonry cements: Types M, S, and N	For use in mortar for masonry, brick and block construction, and stucco	C91/C91M
Plastic cement	For use in exterior stucco applications	C1328/C1328M
Mortar cements: Types M, S, and N	For use in mortar for masonry, brick, and block construction	C1329/C1329M
Calcium-aluminate cement§	For use in refractory, high-early-strength, and moderately acid-resistant concretes	None§
Block cement	For use in making concrete masonry units	C1157/C1157M, C595/C595M, C150/C150M
Magnesium phosphate cement	Nonportland cement for use where rapid hardening is needed	None

*Although white and buff cements are not listed specifically in ASTM C150/C150M, C595/C595M, and C1157/C1157M, they could meet the requirements of each, as indicated by the manufacturer.

†Three kinds are identified by letters K, M, and S.

‡These are covered by API 10A.

§These are covered by EN 14647:2005.

purchased separately. Magnesium or calcium oxide can also be used as expansive agents.

3.2.5 Rapid-hardening hydraulic cements—These are designed to give rapid strength gain during the first 24 hours of hydration. Four categories of performance are specified in **ASTM C1600/C1600M** with strength requirements from 1.5 to 24 hours. Rapid-hardening hydraulic cements can be used in the same application as portland and blended cements, and usually include processing or functional additions. They are typically used for repair applications or where very rapid strength gain is needed.

3.2.6 Regulated-set cements—Regulated-set cements are similar in composition to portland cements, except that the clinker from which they are made contains a small quantity of fluorine. They are formulated to have unusually short setting times followed by development of a moderate early strength.

3.2.7 Well cements—Well cements are manufactured specifically for use in sealing spaces between well casings and linings, and the surrounding geological formations. They are usually required to comply with **API 10A**. These cements specified in API 10A can also meet ASTM specifications—for example, Class G well cements meeting API 10A often meet the requirements of **ASTM C150/C150M** Type II or V. For very-high-temperature wells, less-reactive cements are sometimes used, such as mixtures of dicalcium silicate and finely ground silica. Refer to API 10A for more detailed information regarding well cement classes.

3.2.8 Calcium-aluminate cements—Calcium-aluminate cements (**Appendix A**) are intended primarily for refractory applications and are designated as being of low, intermediate, or high purity. The purity level of the calcium-aluminate cement is based on iron content in the low-purity cement and free alumina content in the high-purity cement. Low-purity calcium aluminate cements are also used for concretes that are to be exposed to mild acids and certain industrial wastes. Other possible applications are self-leveling floors, and patching and repair when very high early strengths are needed.

3.2.9 Plastic cements—Plastic cements (**ASTM C1328/C1328M**) are formulated for use in mortars for stucco. They are portland cements modified by small amounts of additives that cause the mortars made from them to have flow properties that aid stucco applications.

3.2.10 Waterproof cements—These are portland cements interground with stearic acid or other water repellents with the objective of imparting water repellency to concrete containing them.

3.2.11 Ultrafine cements—These are of fine particle size with a 50 percent by mass distribution of the particles having a mean diameter of less than 0.0002 in. (5 μm) and are usually composed of blends of portland and slag cements. These small-sized particle systems are required in geotechnical applications and repairing relatively large cracks and other concrete applications where permeation grouting of fine sands, underground strength, or water control in finely fractured rock formations is needed.

3.2.12 Photocatalytic cements—These contain photocatalysts, often as engineered nanoparticles, which in the presence of water, oxygen, and ultraviolet light, and visible

light, produce strong oxidizing agents. The net effect of the surface-initiated reactions can impart new functionality to cement-based materials, including self-cleaning, biocidal, hydrophobicity, hydrophilicity, and smog-abatement functionality (**Giannantonio et al. 2009**; **Husken et al. 2009**; **Bowering et al. 2006**; **Kawakami et al. 2007**; **Diamanti et al. 2008**).

3.3—Research and development

Given the broad use of cement worldwide and the ever-increasing demands for enhancements in properties and performance, research and development has produced continued innovations in cements. For example, over the past decade, many innovations increasing the sustainability of cement have been introduced (**Chapter 10**). Another key area of innovation is the exploration of the potential for nanotechnology to improve cement and concrete performance. Some research has explored the incorporation of nanosized materials (**Sobolev et al. 2012**). These nanoparticles—for example, nanotubes—can graft molecules onto cement particles or cement phases to promote specific interfacial interactions and provide surface functionality. These composites can have a range of novel properties, such as low electrical resistivity, self-sensing capabilities, self-cleaning, self-healing, high ductility, and self-control of cracks.

3.4—Rational approach to selection

The goal of the specifier is to provide specifications that ensure that proper amounts and types of cement are used to meet the structural and durability requirements of the project. The cement choice for a particular concrete application should be assessed through a combination of these requirements related to the project. Imposing unnecessary requirements is not only economically wasteful but could compromise other principal performance characteristics. For example, moderate sulfate resistance can be specified for certain structural elements that also require accelerated strength gain in the production process. However, compositional variations that impart sulfate resistance tend to reduce the rate of strength gain, potentially requiring some form of compromise. Nevertheless, some projects entail special performance characteristics be implemented into the specifications. Another example, depending on the intended application, is that it might be necessary to design for various factors, including increased resistance to sulfate attack, reduced heat evolution, or use with aggregates susceptible to alkali-aggregate reaction (AAR) (refer to **Chapter 7**). Failure to impose these requirements may have serious consequences to the service life of the structure.

3.4.1 United States and Canadian standards—There are multiple standards for hydraulic cements for use in concrete in the U.S. and Canada. The two primary specifying agencies in the U.S. are ASTM International and the American Association of State Highway and Transportation Officials (AASHTO). Within ASTM and AASHTO, there are separate standards: **ASTM C150/C150M** and **AASHTO M 85**, and **ASTM C595/C595M** and **AASHTO M 309**. **ASTM** has one standard—**ASTM C1157/C1157M**—that does not have

Table 3.4.1a—Comparison of cement types and exposure conditions (ASTM and AASHTO)

Exposure condition	ASTM C150/ C150M or AASHTO M 85*	ASTM C595/ C595M or AASHTO M 240	ASTM C1157/ C1157M
General use	I	IL, IP, IS(<70), IT(S<70)	GU
Moderate sulfate resistance	II, II(MH)	IL(MS), IP(MS), IS(<70)(MS), IT(MS)	MS
Moderate heat of hydration	II (MH)	IL(MH), IP(MH), IS(<70)(MH), IT(S<70) (MH)	MH
High early strength	III	—	HE
Low heat of hydration	IV	IL(LH), IP(LH), IS(<70)(LH), IT(<70)(LH)	LH
High sulfate resistance	V	IL(HS), IP(HS), IS(<70)(HS), IT(<70)(HS)	HS

*Cements specified in ASTM C150/C150M or AASHTO M 85 can be air-entrained, in which case the Roman numeral designation is followed by the letter A. Example Type IIA indicates cement that meets the requirements for Type II, but in addition contains an air-entraining agent.

Table 3.4.1b—Comparison of cement and blended cement types (CSA A3001)

Exposure condition	Portland cement	Portland-limestone cement	Blended cement* using portland or portland-limestone cement
General use	GU	GUL	GUb-S, GUb-C, GUb-CI, GUb-F, GUb-N, GUb-SF, GULb-S, GULb-C, GULb-CI, GULb-F, GULb-N, GULb-SF
Moderate sulfate resistance	MS	—	MSLb, MSb-S, MSb-C, MSb-CI, MSb-F, MSb-N, MSb-SF
High early strength	HE	HEL	HEb-S, HEb-C, HEb-CI, HEb-F, HEb-N, HEb-SF, HELb-S, HELb-C, HELb-CI, HELb-F, HELb-N, HELb-SF
High sulfate resistance	HS	—	HSLb, HSb-S, HSb-C, HSb-CI, HSb-F, HSb-N, HSb-SF

*Ternary blends are also all owed (refer to 4.2 of this guide for designations).

an equivalent standard in AASHTO. Refer to Tables 3.1a and 3.1b for characteristics of ASTM and AASHTO portland and blended hydraulic cements.

In Canada, the Canadian Standard Association (CSA) is the specifying agency for hydraulic cements, and **CSA A3001** is the standard for portland cements, portland-limestone cements, blended hydraulic cements, and supplementary cementitious materials (SCMs). In CSA A3001, portland cements are designated as Types GU (general use), MS (moderate-sulfate-resistant), HE (high-early strength), and HS (high sulfate resistance), and correspond in intended use to ASTM C150/C150M cement Types I, II, III, or V, respectively. CSA A3001 also covers blended hydraulic cements

that are designated GUb, MSb, HEb, or HSb; portland-limestone cements with up to 15 percent interground limestone designated as GUL, MSL, HEL, or HSL; and portland-limestone blended cements designated as GULb, MHLb, HELb, or HSLb. Note that in the 2021 Amendment to CSA A3001-18, moderate and low-heat types of cements were removed. Refer to Tables 3.4.1a and 3.4.1b for comparisons of the cement types.

3.4.2 Supplementary cementitious materials—Supplementary cementitious materials standards in the U.S. are **ASTM C989/C989M** and **AASHTO M 302**, **ASTM C618** and **AASHTO M 295**, **ASTM C1240** and **AASHTO M 307**, and ASTM C1697 (AASHTO does not have an equivalent standard, but **AASHTO M 321** can be referenced). In Canada, SCMs are included in CSA A3001.

3.4.3 General-use cements—Using a general-purpose cement that is locally available is advised as long as the special properties of the other cement types is not required. General-purpose cements are described in **ASTM C150/C150M** as Type I, II, or II(MH); in **ASTM C595/C595M** as Type IL, IP, IT, or IS(<70); and in **ASTM C1157/C1157M** as Type GU. Although obtaining a special cement type could result in some improved performance characteristics, it could be detrimental to others. For this reason, justification is generally recommended before specifying a cement other than the commonly available ASTM C150/C150M Type I or Type II portland cement, or a corresponding blended cement.

In ASTM C150/C150M, although the term “Type I/II portland cement” is frequently used to describe some portland cements, it is not a standard ASTM designation. Type I/II does, however, denote that the cement being represented has a C₃A content of 8 percent or less and meets all the requirements of both ASTM C150/C150M Type I and Type II. This is particularly helpful to the concrete producer who has limited silo storage capacity, and for whom the ability to inventory a single cement that meets both ASTM C150/C150M Type I and Type II specifications in one silo is a convenience. Other combined descriptive terms for cements are possible; for example, Type II/V indicates that a cement meets all ASTM C150/C150M requirements for both Type II and Type V.

A technology that could reduce the environmental impact of cement production is the use of limestone as an ingredient in hydraulic cements in amounts up to 15 percent by mass. Environmental benefits could result from less energy required for pyroprocessing, a reduction in related greenhouse gases, and less raw materials used. This technology has been adopted by **CSA A3001** and used for several decades in Europe (Hooton et al. 2007) and other countries. Cements using this technology in the U.S. are manufactured under ASTM C1157/C1157M, ASTM C595/C595M, and **AASHTO M 240**. ASTM C595/C595M and AASHTO M 240 designate portland-limestone blended cements (PLC) as Type IL. Similar strength gain and other properties can be achieved in optimized systems. For more information, refer to Tennis et al. (2011) and Thomas and Hooton (2010).

3.4.4 Cements used in various exposure conditions—The requirements for concrete vary with the exposure conditions.

Table 3.4.4—ACI 318 exposure categories for concrete (ACI 318-19)

Exposure category	Severity	Class
Freezing and thawing (F)	Not applicable	F0
	Moderate	F1
	Severe	F2
	Very severe	F3
Sulfate (S)	Not applicable	S0
	Moderate	S1
	Severe	S2
	Very severe	S3
In contact with water (W)	Not applicable	W0
	Required low permeability	W1
Corrosion protection reinforcement (C)	Not applicable	C0
	Moderate	C1
	Severe	C2

ACI 318-19 Chapter 19 contains concrete specifications and hydraulic cement and SCM requirements for four exposure categories. These categories, as indicated in Table 3.4.4, are freezing-and-thawing exposures, sulfate exposures, water exposure, and corrosion protection of reinforcement. Each category contains multiple levels of severity that leads the designer toward the appropriate requirements for concrete and the choices available for hydraulic cements and SCMs. Table 3.4.4 shows the exposure categories and their different levels of severity. Table 3.4.1a compares the cement types used with varying exposure conditions according to ASTM C150/C150M, C595/C595M, ASTM C1157/C1157M, **AASHTO M 85**, and **AASHTO M 240**. Note that Table 3.4.1a excludes products that are generally used in combination with portland cements. These include slag cement, fly ash, silica fume, or blended SCM. ASTM C595/C595M, covering blended cements, prescribes ingredients and proportions, as well as some performance requirements, whereas ASTM C1157/C1157M, with which blended cements can also be specified, is a performance specification in which performance criteria alone govern the products and their acceptance.

Blended hydraulic cements under **ASTM C595/C595M** and **CSA A3001** are prescribed by ingredients, proportions, and performance characteristics. **ASTM C1157/C1157M** is based on performance characteristics alone.

3.4.5 Summary—As seen from Tables 3.4.1a, 3.4.1b, and 3.4.4, there is often more than one option for hydraulic binders for each exposure condition. A question might arise regarding the propriety of a cementitious blend containing a specific SCM that is locally available instead of portland cement only. When ACI-accepted concrete practices are followed, slag cement, some fly ashes, and silica fume batched in concrete at the appropriate rates can impart advantageous performance characteristics including improved mitigation of alkali-silica reaction (ASR), more resistance to sulfate attack, higher ultimate strengths, and lower permeability. Many SCMs are recycled or processed by-products

of other industries, and using them improves sustainability of the concrete mixture. Contrarily, the use of some SCMs can perform differently than ordinary portland cement mixtures, such as longer set times, lower early strengths, and more sensitivity to cold weather temperatures in the field during placement. Many of these aspects can be minimized or eliminated through adjustment of the concrete mixture design proportions and judicious use of chemical admixtures. Deciding on the correct blend for a particular hydraulic cement depends on the materials available in the local market and local experience with them. Input from local cement suppliers, concrete labs, concrete producers, and contractors can be helpful when deciding on mixture proportions.

In the U.S. and Canada, many producers of concrete have multiple storage silos on site so that more than one hydraulic cement can be used in concrete. In this case, the concrete producer is able to batch multiple cements as required by mixture design. Some concrete producers, however, may only have one or two storage silos, limiting the number of hydraulic cements specified. For producers who are limited by silo space, blends manufactured and sold by a local cement manufacturer might be available. Designers and specifiers should be aware that some hydraulic cements and SCMs, such as slag cement and Class C or Class F fly ash, may not be available in some markets.

CHAPTER 4—CEMENT CHEMISTRY

The principal constituents of cements, pozzolans, and slag cements, or their hydration or reaction products, are phases containing calcium, silicon, aluminum, iron, oxygen, sulfur, and hydrogen. Chemical analyses of these materials usually express the amounts of these elements present as percentages of the oxides CaO, SiO₂, Al₂O₃, Fe₂O₃, SO₃, and H₂O. The oxides are, with few exceptions, not actually present as such, but the elements are in the forms of more complex phases. More complete descriptions of the chemistry of cements can be found in **Lea (1998)** and **Taylor (1997)**.

4.1—Portland cement

The main phases present in portland cements are listed in Table 4.1a. The chemical phase or family of phases identified as tricalcium silicate (C₃S) exists in clinker in an impure form known as alite. Alite is complex and may take on six or seven crystal forms and contain sulfur, sodium, potassium, iron, magnesium, and fluorine as trace elements. Dicalcium silicate (C₂S) exists as belite. Belite has at least five crystal forms; the different forms of belite, unlike those of alite, differ greatly in performance.

Both the tricalcium-aluminate phase(s), C₃A, and the ferrite phase, C₄AF, also exist in several different crystal forms with some variation in properties. The ferrite phase can vary widely in composition. When the alumina to iron oxide mass (Al₂O₃/Fe₂O₃) ratio is less than 0.64, a ferrite solid solution of C₄AF and C₂F is formed. The ferrites are of less importance than C₃A in cements because of slower hydration of the latter.

The percentages of the phases in a portland cement, such as those given in Table 4.1b, can be calculated from

Table 4.1a—Common phases* in portland cements

Name (common name)	Cement chemists' notation	Oxide notation	Conventional notation
Tricalcium silicate (or alite)	C ₃ S	3CaO·SiO ₂	Ca ₃ SiO ₅
Dicalcium silicate (or belite)	C ₂ S	2CaO·SiO ₂	Ca ₂ SiO ₄
Tricalcium aluminate (or aluminite)	C ₃ A	3CaO·Al ₂ O ₃	Ca ₃ Al ₂ SiO ₆
Tetracalcium aluminoferrite (or ferrite)	C ₄ AF	4CaO·Al ₂ O ₃ ·Fe ₂ O ₃	Ca ₄ Al ₂ Fe ₂ O ₁₀
Calcium sulfate anhydrite (or anhydrite)	C $\overline{\text{S}}$ S	CaO·SO ₃	CaSO ₄
Calcium sulfate dehydrate (or gypsum)	C $\overline{\text{S}}$ H ₂	CaO·SO ₃ ·2H ₂ O	CaSO ₄ ·2H ₂ O
Calcium sulfate hemihydrate (hemihydrate or bassanite)	C $\overline{\text{S}}$ H _{1/2}	CaO·SO ₃ ·1/2H ₂ O	CaSO ₄ ·1/2H ₂ O
Calcium carbonate (or limestone)	C $\overline{\text{C}}$	CaO·CO ₂	CaCO ₃

*Ideal compositions; other elements are present in commercial cements.

Table 4.1b—Chemical and phase composition of portland cements in the U.S. in 2014 (Tennis 2016)

Cement type	Statistic*	Oxide composition						Loss on ignition	Insoluble residue	Na ₂ O _{eq}	Acid-soluble chloride	Potential phase composition			
		SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	SO ₃					C ₃ S	C ₂ S	C ₃ A	C ₄ AF
Type I	Mean	19.81	5.13	2.50	63.27	2.32	3.33	2.15	0.44	0.62	0.020	57.5	13.0	9.3	7.6
	Standard deviation	0.70	0.42	0.72	1.22	0.80	0.60	0.35	0.13	0.28	0.016	3.58	2.44	1.41	2.19
	Maximum	20.60	5.67	3.61	64.60	3.04	4.07	2.68	0.64	1.04	0.037	62	16	11	11
	Minimum	18.83	4.42	1.28	60.74	0.80	2.51	1.45	0.24	0.26	0.005	49	9	7	4
	<i>n</i>	10	10	10	10	10	10	10	10	10	3	10	10	10	10
Type II†	Mean	20.10	4.59	3.39	63.59	1.95	3.05	2.18	0.34	0.55	0.014	59.1	12.7	6.4	10.3
	Standard deviation	0.49	0.38	0.42	0.98	0.99	0.29	0.37	0.12	0.15	0.013	3.98	3.01	1.30	1.26
	Maximum	21.70	5.43	4.46	65.31	4.40	3.81	2.75	0.65	1.03	0.050	68	20	8	13
	Minimum	18.90	2.80	2.45	60.86	0.70	2.48	1.00	0.17	0.20	0.003	51	7	0	7
	<i>n</i>	56	56	56	56	56	56	56	53	56	20	56	55	56	56
Type III	Mean	20.05	4.71	3.06	63.32	2.12	3.56	1.83	0.31	0.56	0.014	58.0	13.6	7.3	9.2
	Standard deviation	0.60	0.51	0.62	1.05	1.03	0.49	0.54	0.14	0.19	0.011	3.66	2.58	2.04	2.05
	Maximum	21.24	6.17	3.92	65.17	4.48	5.20	2.77	0.67	1.04	0.045	66	20	14	12
	Minimum	18.68	3.73	1.20	60.62	0.71	2.82	0.89	0.09	0.29	0.003	49	7	4	4
	<i>n</i>	47	47	47	47	47	47	47	44	47	12	47	47	47	47
Type V*	Mean	20.83	3.99	3.83	63.74	2.24	2.63	1.76	0.36	0.45	0.008	59.2	14.6	4.1	11.6
	Standard deviation	0.53	0.23	0.42	0.61	0.97	0.39	0.61	0.13	0.08	0.007	2.81	3.68	0.66	1.30
	Maximum	21.98	4.44	5.03	64.56	4.47	3.40	2.73	0.58	0.57	0.019	63	22	5	15
	Minimum	19.71	3.51	3.11	62.75	1.14	2.08	0.57	0.10	0.29	0.002	52	8	2	9
	<i>n</i>	19	19	19	19	19	19	19	19	19	5	19	19	19	19

*Includes 12 cements marketed as Type II/V, 6 as Type V, and 1 as Type I/II/V.

†Includes 37 cements marketed as Type I/II, 10 as Type II, 8 as Type I/II(MH), and 1 as Type II(MH).

an oxide analysis of the cement using certain simplifying assumptions. Such calculated potential phase compositions of a cement only approximate the percentages actually present. The calculation procedure, which was developed by Bogue (1955), is given in ASTM C150/C150M. This procedure assumes that chemical equilibrium is attained in the burning zone of the kiln, where, in fact, equilibrium may not be reached. X-ray diffraction analysis (ASTM C1365) provides a more accurate representation of phases present. Small but significant quantities of other elements such as sodium, potassium, magnesium, phosphorus, and titanium are usually present in cements and may substitute for the

various principal elements or form other phases and solid solutions. Bhatti (1995) details the effects of over 50 trace elements on the manufacture and performance of cement.

The manufacturing process can be controlled to vary the relative proportions of the phases in cements and produce cements with different characteristics. This is recognized in ASTM C150/C150M. Typical phase compositions of some commonly used ASTM types of portland cement are given in Table 4.1b. Typical strength, setting time, and fineness of ASTM types of portland cement are provided in Table 4.1c.

4.1.1 Reactions of portland cement with water When portland cement and water are mixed, a series of chemical

Table 4.1c—Physical characteristics of portland cements in the U.S. in 2014 (Tennis 2016)

Cement type	Statistic	Compressive strength, MPa (psi)				Setting time (Vicat), minutes		Fineness (Blaine), m ² /kg	Fineness 45 µm (No. 325) sieve, % passing
		1 day	3 days	7 days	28 days	Initial	Final		
I	Mean	16.0 (2320)	27.1 (3930)	34.0 (4930)	42.3 (6140)	121	229	397	95.1
	Standard deviation	3.23 (469)	2.08 (301)	2.10 (304)	3.29 (477)	21.6	23.9	20.4	2.2
	Maximum	20.6 (2980)	30.4 (4410)	38.3 (5560)	47.8 (6940)	163	252	440	97.9
	Minimum	11.7 (1700)	24.3 (3520)	31.1 (4500)	37.2 (5390)	90	190	375	91.2
	<i>n</i>	9	10	10	10	10	7	10	10
II*	Mean	16.1 (2330)	26.8 (3890)	33.3 (4830)	42.7 (6200)	116	223	393	96.4
	Standard deviation	2.35 (341)	2.86 (415)	2.90 (420)	2.93 (425)	30.1	37.5	24.2	2.5
	Maximum	20.2 (2930)	31.8 (4610)	38.0 (5510)	48.6 (7050)	270	381	471	99.9
	Minimum	5.5 (800)	12.9 (1870)	19.7 (2850)	33.9 (4910)	74	178	305	85.7
	<i>n</i>	53	56	56	56	56	53	56	55
III	Mean	24.8 (3600)	34.9 (5060)	41.0 (5950)	48.8 (7080)	87	178	561	99.0
	Standard deviation	3.04 (441)	2.81 (408)	3.00 (436)	3.37 (488)	20.0	33.0	60.0	1.0
	Maximum	30.9 (4480)	40.9 (5930)	47.5 (6890)	54.1 (7850)	126	245	723	99.9
	Minimum	16.4 (2380)	26.7 (3870)	32.8 (4760)	41.0 (5950)	49	115	365	95.1
	<i>n</i>	45	46	45	45	46	39	45	45
V†	Mean	14.3 (2080)	25.3 (3670)	32.0 (4640)	42.7 (6190)	126	224	401	95.9
	Standard deviation	3.24 (470)	4.68 (678)	4.95 (718)	4.32 (626)	30.7	37.2	54.1	5.0
	Maximum	21.9 (3180)	33.4 (4850)	39.6 (5750)	47.9 (6950)	176	280	551	99.8
	Minimum	8.6 (1250)	15.9 (2310)	21.6 (3140)	32.1 (4660)	70	161	302	81.0
	<i>n</i>	19	19	19	19	19	16	19	19

*Includes 37 cements marketed as Type I/II, 10 as Type II, 8 as Type I/II(MH), and 1 as Type II(MH).

†Includes 12 cements marketed as Type II/V, 6 as Type V, and 1 as Type I/II/V.

Table 4.1.1—Primary phases formed by reactions of portland cements with water*

Name (common name)	Cement chemists' notation	Oxide notation	Conventional notation
Calcium silicate hydrate	C-S-H	3.4CaO·2SiO ₂ ·8H ₂ O	C _{3.4} Si ₂ O ₇ ·8H ₂ O
Calcium hydroxide	CH	CaO·H ₂ O	Ca(OH) ₂
Trisulfoaluminate hydrate (or ettringite or Aft)	C ₆ A $\bar{S}$ ₃ H ₃₂	6CaO·Al ₂ O ₃ ·3SO ₃ ·32H ₂ O	Ca ₆ Al ₂ S ₃ O ₁₈ ·32H ₂ O
Monosulfoaluminate hydrate (or monosulfate or AFm)	C ₄ A $\bar{S}$ H ₁₂	4CaO·Al ₂ O ₃ ·SO ₃ ·12H ₂ O	Ca ₄ Al ₂ SO ₁₀ ·12H ₂ O
Tetracalcium aluminate hydrate	C ₄ AH ₁₃	4CaO·Al ₂ O ₃ ·13H ₂ O	Ca ₄ Al ₂ O ₇ ·13H ₂ O
Calcium aluminoferrite hydrate	C ₆ (A,F)H ₁₂	6CaO·Al ₂ O ₃ ·Fe ₂ O ₃ ·12H ₂ O	Ca ₆ Al ₂ Fe ₂ O ₇ ·12H ₂ O
Water	H	H ₂ O	H ₂ O

*Major hydrated phases are shown in ideal compositions. Other phases also are present in hydrated cement pastes. Other elements are present in most phases and several phases have a range of composition.

reactions begin that result in slump loss, setting, hardening, evolution of the heat of hydration, and strength development. The overall process is referred to as cement hydration because it involves formation of water-containing hydrated phases. The primary phases that form are listed in Table 4.1.1. The gypsum, or other form of calcium sulfate, that is usually interground with the cement clinker is used to prevent flash setting and control the setting and early hardening process primarily by regulating the early hydration reactions of the C₃A (Tang 1992). It is thought to function, in part, by dissolving rapidly and causing a protective coating of ettringite to form on the C₃A surfaces. A side

effect of gypsum is accelerating the hydration of the silicates. Information on the relative differences in hydration rates of hydraulic cementitious materials and mixtures can be obtained by using isothermal calorimetry to track the heat evolution (for example, ASTM C1679 or C1702).

The ions or water-soluble compounds dissolved in the water are believed to affect the behavior of cements and their interactions with other concrete materials such as aggregates and admixtures. Figure 4.1.1a is a representation of how the quantities of some of the significant ions in solution might change with time. Figure 4.1.1b (Soroka 1980) indicates how the quantities of important cement reaction

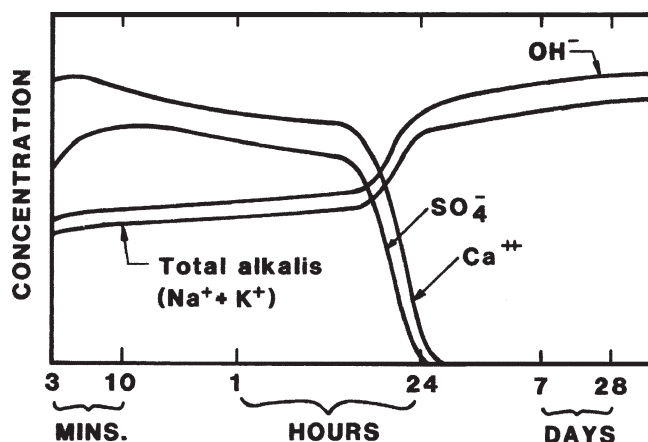


Fig. 4.1.1a—Diagram illustrating changes with time of concentrations of ions in solution in the pore water of a portland cement paste (adapted from Mindess et al. [2003]).

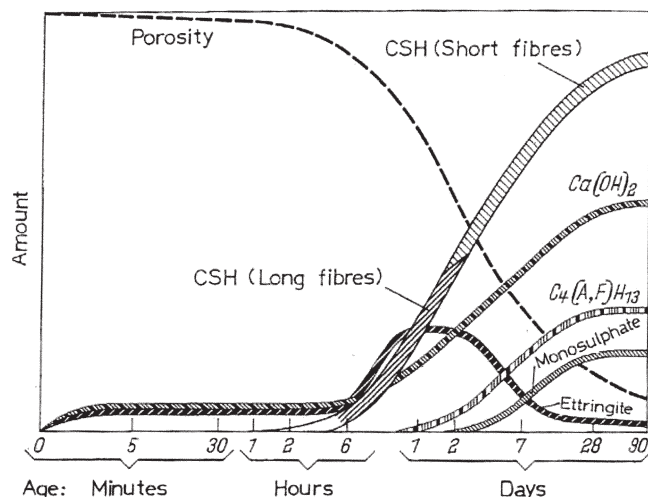


Fig. 4.1.1b—Diagram illustrating formation of portland cement reaction products and reduction with time of the volume of pore space in a portland cement paste (adapted from Locher et al. [1976]).

phases might change with time. It also indicates that a reduction in the volume of the originally water-filled pores takes place as the reactions proceed. The actual rates of reactions and nature and amounts of the phases formed depend on the specific compositions and fineness of the cements; they also depend on temperature, nature, and quantities of admixtures present (Helmuth et al. 1995).

ASTM C150/C150M establishes default maximum SO_3 contents ranging from 2.3 percent for Type V to 4.5 percent for Type III. The SO_3 content for Type I cements typically ranges from 2.0 to 4.4 percent (Bhatty and Tennis 2008). Generally, the maximum permissible amount of SO_3 is a function of the C_3A content and the fineness. The SO_3 not consumed in the first few days might combine with unreacted C_3A at later ages to produce ettringite, resulting in destructive long-term expansion. Sulfate content exceeding the default maximum is permitted if tests demonstrate that the expansion in water at 14 days (ASTM C1038/C1038M)

is not excessive for ASTM C150/C150M, ASTM C595/C595M, and ASTM C1157/C1157M cements.

The SO_3 present in cement comes principally from one or more forms of calcium sulfate added during grinding, but significant amounts may also come from the clinker if high-sulfur fuel is used in the clinker burning process. The combustion of sulfur compounds in the fuel often forms sulfites and sulfates that are less effective than the inter-ground gypsum in controlling the setting. The amount of SO_3 added is established by the cement producer primarily to optimize strength and time of set. The SO_3 content will also influence, among other properties, drying shrinkage and slump loss in concrete.

4.2—Blended hydraulic cement

The overall chemistry of blended hydraulic cements is similar to that of portland cements. They contain portland cement blended with such materials as slag cements, fly ashes, silica fumes, limestone, raw or calcined natural pozzolans, or combinations of two of these, if producing a ternary blend. Chemical requirements, physical requirements, or both, of the slag cements, pozzolans, or limestone to be used in blended hydraulic cement are described in ASTM C595/C595M. Products specified under ASTM C1157/C1157M can consist of blends of various cementitious materials as well. Detwiler et al. (1996) discusses the use of these materials in blended hydraulic cement. Table 4.2a provides chemical data for U.S. blended cements and Table 4.2b provides physical characteristics. Table 4.2c provides the compressive strengths, setting time, and fineness of ASTM C1157 Type GU cements.

4.2.1 Blast-furnace slags—Blast-furnace slags are by-products of the manufacture of iron. The molten slag leaves the blast furnace as a liquid. There are primarily two methods of rapidly cooling the molten slag: 1) water granulation, which involves quenching with water; and 2) pelletization, which includes a combination of both air and water spray. These methods form glassy nodules that can be ground to form a cementitious powder called slag cement. If the molten slag is cooled slowly, it forms a much less reactive crystalline product called air-cooled slag that is frequently crushed and used as aggregate. For additional information, refer to ACI 233R. In the U.S., Type IS cements typically include between 20 and 40 percent by mass blast-furnace slag (slag cements), averaging about 30 percent (Tennis 2016).

4.2.2 Fly ashes—Fly ashes are the finely-divided residues from the combustion of powdered coal. Large quantities are obtained from coal-burning power plants. Fly ashes contain small, spherical particles of glassy material with pozzolanic properties. In addition, crystalline components are also present. For additional information, refer to ACI 232.2R.

4.2.3 Limestone—Limestone is a rock consisting mainly of calcium carbonate that can be finely ground and used as an ingredient in portland and blended cements. Limestone can contribute beneficially to the performance of cements through physical effect, such as improved particle size distribution, acting as nucleation sites for cement hydration, and by providing a minor amount of chemical reaction.

Table 4.2a—Chemical composition of blended cements in the U.S. in 2014 (Tennis 2016), percent by mass

Cement type	Statistic	MgO	SO ₃	Loss on ignition	Insoluble residue
IL	Mean	2.08	3.16	5.40	0.55
	Standard deviation	0.88	0.42	0.79	0.32
	Maximum	3.44	3.60	7.20	1.29
	Minimum	0.84	2.09	4.28	0.16
	<i>n</i>	12	12	12	9
IP	Mean	1.90	3.08	1.81	—
	Standard deviation	0.71	0.44	0.42	—
	Maximum	2.60	3.53	2.59	—
	Minimum	0.83	2.40	1.40	—
	<i>n</i>	8	8	8	—
IS	Mean	3.98	3.08	1.59	0.38
	Standard deviation	0.96	0.43	0.60	0.15
	Maximum	5.30	3.78	2.40	0.63
	Minimum	2.31	2.39	0.69	0.22
	<i>n</i>	8	8	8	8

Portland-limestone cements or ternary cements with up to 15 percent limestone can be produced to have strength and performance characteristics comparable to portland and other blended cements. For additional information, refer to [Tennis et al. \(2011\)](#). In 2014, the average limestone content of Type IL blended cements in the U.S. was 11.1 percent (Tennis 2016).

4.2.4 Natural pozzolans—Natural pozzolans are naturally occurring siliceous, or siliceous and aluminous, minerals. Although they are usually not cementitious by themselves, pozzolans in finely divided form will react with the calcium hydroxide produced by cement hydration to form the same compounds as are formed by the hydration of portland cements. Most natural materials require heat treatment, grinding, or both, to make them useful as pozzolans. They include materials such as opaline cherts and shales, volcanic ashes, other noncrystalline materials such as diatomaceous earths, calcined clays ([Hooton et al. 1997](#)), and sometimes metastable crystalline materials such as tridymite. For additional information, refer to [ACI 232.1R](#).

4.2.5 Silica fume—Silica fume is a finely divided silica-bearing residue of the silicon metal manufacturing process that possesses pozzolanic properties. This material is added

Table 4.2b—Physical characteristics of blended cements in the U.S. in 2014 (Tennis 2016)

Cement type	Statistic	Compressive strength, MPa (psi)			Setting time (Vicat), minutes		Blaine fineness, m ² /kg	Fineness, 45 µm (No. 325) sieve, % passing
		3 days	7 days	28 days	Initial	Final		
IL	Mean	28.9 (4190)	34.8 (5050)	42.9 (6230)	117	218	479	97.4
	Standard deviation	2.88 (418)	3.43 (498)	3.85 (559)	19.3	30.3	68.6	1.35
	Maximum	31.7 (4600)	38.2 (5550)	47.8 (6930)	150	269	660	99.1
	Minimum	21.4 (3110)	26.2 (3800)	33.8 (4900)	80	178	409	95.4
	<i>n</i>	12	12	12	12	11	12	12
IP	Mean	25.1 (3640)	31.4 (4560)	45.1 (6550)	135	251	524	96.7
	Standard deviation	3.66 (531)	4.12 (597)	5.21 (756)	35.7	39.0	155.5	2.64
	Maximum	29.7 (4310)	37.9 (5500)	54.6 (7920)	205	311	850	98.6
	Minimum	19.0 (2760)	24.5 (3550)	37.8 (5480)	87	196	397	91.3
	<i>n</i>	8	8	8	8	8	8	7
IS	Mean	22.2 (3220)	31.1 (4520)	45.9 (6660)	132	223	475	97.0
	Standard deviation	2.88 (418)	2.69 (390)	4.11 (596)	30.7	71.5	41.2	1.85
	Maximum	28.6 (4140)	35.6 (5160)	51.0 (7400)	191	280	539	99.2
	Minimum	19.7 (2850)	27.5 (3990)	37.7 (5470)	90	143	391	93.6
	<i>n</i>	8	8	8	8	3	8	8

Table 4.2c—Compressive strengths, setting time, and fineness of ASTM C1157/C1157M Type GU cements in the U.S. in 2014 (Tennis 2016)

Cement type	Statistic	Compressive strength, MPa (psi)				Setting time (Vicat), minutes		Fineness (Blaine), m ² /kg	Fineness 45 µm (No. 325) sieve, % passing
		1 day	3 days	7 days	28 days	Initial	Final		
GU	Mean	19.1 (2780)	29.3 (4250)	34.9 (5070)	43.4 (6300)	106	199	514	97.5
	Standard deviation	3.71 (538)	4.16 (604)	3.76 (546)	3.35 (487)	19.9	39.7	51.7	1.99
	Maximum	25.9 (3760)	34.0 (4930)	39.1 (5680)	48.2 (6990)	122	262	619	99.2
	Minimum	13.0 (1880)	22.4 (3250)	28.9 (4190)	37.9 (5490)	59	131	452	94.9
	<i>n</i>	10	10	10	10	10	9	10	10

as a separate ingredient to concrete mixtures or as a component in blended cement to produce a cementitious system for concrete. Silica fume is often used in conjunction with fly ash or slag in concrete mixtures. For additional information, refer to [ACI 234R](#).

4.2.6 Reactions of blended hydraulic cements with water—

The blended ingredients all react with water, or with water and calcium hydroxide, to form the major phases of calcium silicate hydrates and calcium aluminate hydrates, similar to those produced by the reactions of portland cement with water. The rates of reaction of the materials blended with the portland cement tend to be lower than those of portland cement, but allowance for this can be made in the manufacture of the cement and curing of the concrete to ensure suitable performance in concrete, including strength development. Specially activated, blended hydraulic cements are available to provide very early high strength.

4.3—Shrinkage-compensating expansive cement

Shrinkage-compensating expansive cements are designed to expand a small amount during the first few days of hydration. The amount of expansion is intended to approximately offset the amount of drying shrinkage anticipated in the concrete. The expansion is brought about by incorporating specific compounds such as calcium sulfoaluminate, calcium aluminate, calcium sulfate ($C_4A_3\bar{S}$, CA, and $C\bar{S}$), or other phases that, in the presence of water, react to produce a larger quantity of ettringite than is normally produced by portland cements. The production of the ettringite in the hardened concrete causes the concrete to expand. This expansive reaction occurs during the first few days and is essentially complete after 7 days. ASTM C845/C845M, which describes the three cements of this type, limits the increase in expansion between 7 and 28 days to 15 percent of the 7-day expansion.

To achieve the proper performance of shrinkage-compensating expansive cements, the inclusion of the appropriate amounts of reinforcing steel in the concrete is necessary. For maximum expansion, additional moisture beyond that added as mixing water should be supplied during curing of the concrete to ensure that the desired amount of ettringite will be produced. The use of shrinkage-compensating expansive cements is described in detail in [ACI 223R](#).

4.4—Calcium-aluminate cement

Calcium-aluminate cements are primarily used for high heat refractory applications. Other uses include moderate acid-resistant applications, high-early-strength and quick-setting mixtures, and as part of the expansive component in some shrinkage-compensating cements. They are produced by pulverizing a solidified melt or clinker that consists predominantly of hydraulic calcium aluminates formed from proportioned mixtures of aluminous and calcareous materials. These cements are typically designed to gain strength much faster than ordinary portland cements and predominantly consist of calcium aluminate that can produce large amounts of heat during the first 24 hours. The cement

phase ratios (CA or CA_2) are proportioned according to the intended application performance characteristics ([Lea 1998](#); [Robson 1962](#)).

Potential users of calcium-aluminate cements should be aware that conversion of the hydration products from metastable hexagonal hydrates (CAH_{10}) to stable cubic hydrates (C_3AH_6) of lower volume can reduce strength ([Robson 1962](#)). Primary causes of the conversion from metastable to stable hydrates, with resulting loss of strength, are high water-cement ratios (w/c), high curing and ambient temperatures, and high ambient humidity. Conversion can be delayed by keeping the concrete cool and dry and by using a low w/c , but it will eventually occur. Therefore, concrete structures using this cement should be designed for converted strengths. In most refractory applications, strength is not a major concern and, therefore, conversion is not normally a major factor. The conversion of hydrates can increase permeability and result in acceleration of the corrosion of embedded steel in structures ([Odler 2000](#)). These cements are discussed further in [Appendix A](#) and [Lankard \(1978\)](#).

CHAPTER 5—INFLUENCE OF CHEMICAL ADMIXTURES, POZZOLANS, AND SLAG CEMENTS ON CEMENTITIOUS SYSTEMS

Chemical admixtures, pozzolans, and slag cements have become essential parts of concrete technology. The effects of admixtures on the performance of concrete are usually intricately linked to the particular cement-admixture combinations used. Although they may not be fully understood, it is helpful to recognize the types of effects that may result from changes in cement composition. This chapter is intended to provide a brief introduction to this subject.

[ACI 212.3R](#) contains extensive information on admixtures and their use. Slag cement, silica fume, raw and calcined natural pozzolan, and fly ash are discussed in [ACI 233R](#), [234R](#), [232.1R](#), and [232.2R](#), respectively. The primary purpose of this discussion is to highlight those characteristics of chemical admixtures, slag cements, and pozzolans that influence cement performance. Only air-entraining, accelerating, retarding, and water-reducing chemical admixtures are discussed in this chapter.

Pozzolans and slag cements are finely divided inorganic materials that can be added to concrete to enhance its performance and possibly reduce the overall cost. Specifications for fly ash and natural pozzolans are given in [ASTM C618](#). Slag cement specifications are given in [ASTM C989/C989M](#) and silica fume specifications are given in [ASTM C1240](#). Canadian specifications for slag cement and pozzolans are included in [CSA A3000](#). Pozzolans and slag cements can improve the workability and flow properties of fresh concrete, reduce shrinkage, and improve the strength and other properties of hardened concrete. Some can diminish the likelihood of sulfate attack and alkali-aggregate reaction (AAR) expansion. Additional guidance is given on natural pozzolans in [ACI 232.1R](#), fly ash in [ACI 232.2R](#), silica fume in [ACI 234R](#), and slag cement in [ACI 233R](#).