

Guide to the Selection and Use of Hydraulic Cements

Reported by ACI Committee 225

Gregory S. Barger
Chair

Claude Bedard	Michael S. Hammer	Colin L. Lobo
Glen E. Bollin	Eugene D. Hill	Kenneth Mackenzie
Michael M. Chehab	R. Doug Hooton	Bryant Mather
James R. Clifton*	Kenneth G. Kazanis	Walter J. McCoy
Christopher Crouch	Paul Klieger	Leo M. Meyer, Jr.
Marwan A. Daye	Steven H. Kosmatka	James S. Pierce
George R. Dewey	Jim Kuykendall	Sandor Popovics
Richard D. Gaynor		Bryce P. Simons

*Deceased

Because cement is the most active component of concrete and usually has the greatest unit cost, its selection and proper use is important in obtaining the balance of properties and cost desired for a particular concrete mixture. Selection should take into account the properties of the available cements and the performance required of the concrete. This report summarizes information about the composition and availability of commercial hydraulic cements, and factors affecting their performance in concrete. Following a discussion of the types of cements and a brief review of cement chemistry, the influences of admixtures (both chemical and mineral) and the environment on cement performance are discussed. The largest part of this report covers the influence of cement on the properties of concrete. Cement storage and delivery, and the sampling and testing of hydraulic cements for conformance to specifications, are reviewed briefly.

This report will help users recognize when a readily available, general-purpose (ASTM C 150 Type I) cement will perform satisfactorily, or when conditions require selection of a cement that meets some additional requirements. It will also aid cement users by providing general information on the effects of cements on the properties of concrete. Some chemical and physical characteristics of cement affect certain properties of concrete in important ways. For other properties of concrete, the amount of cement is more important than its characteristics.

This report is not a treatise on cement chemistry or concrete. For those who need to know more, this report provides many references to the technical literature, including ACI documents.

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Appendix—Calcium-aluminate cements, p. 29**CHAPTER 1—INTRODUCTION****1.1—The need for a rational approach to selecting cements**

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 is associated with the word cement in this document to point out to the consumer that the basic mechanism by which the hardening of the concrete or mortar takes place is the reaction of the cement material with water. The word hydraulic also differentiates this type of cement from binder systems that are based on other hardening mechanisms.

The properties of concrete 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 important in obtaining most economically the 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. For some applications, such as those requiring increased resistance to sulfate attack, reduced heat evolution, or use with aggregates susceptible to alkali-aggregate reaction, special requirements should be imposed in the purchase specifications. While failure to impose these requirements

may have serious consequences, imposing these requirements unnecessarily is not only uneconomical but may degrade other more important performance characteristics. For example, moderate sulfate resistance may be specified for certain plant-manufactured structural elements that require strength gain in the production process. Because the compositional variations that impart sulfate resistance tend to reduce the rate of strength gain, some compromise must be made.

The goal of the specifier is to provide specifications that will ensure that the proper amounts and types of cement are obtained to meet the structural and durability requirements—no more, no less. Due to gaps in our knowledge, this goal is seldom, if ever, fully achieved; economies, however, can often be obtained with little or no decrease in performance in service, if specifications are aimed at this goal.

For a long time, there have been virtually no economic penalties to discourage users and others from overspecifying cement characteristics. For example, even though a fully satisfactory ASTM C 150 Type I cement has been available, users have often chosen to specify an ASTM C 150 Type II cement or a low-alkali cement on the basis that it could do no harm and its special characteristics might be beneficial. They have not had to worry about possible shortages of supply or increased cost. The effects of increased attention to pollution abatement and energy conservation, however, are changing the availability and comparative costs of all types of cement. This brings about a need for greater understanding of factors affecting cement performance than was previously necessary.

It is usually satisfactory and advisable to use a general-purpose cement that is readily obtainable locally. General-purpose cements are described in ASTM C 150 as Type I or Type II, in ASTM C 595 as Type IP or IS, and in ASTM C 1157 as Type GU. When such a cement is manufactured and used in large quantity, it is likely to be uniform and its performance under local conditions will be known. A decision to obtain a special type of cement may result in the improvement of one aspect of performance at the expense of others. For this reason, a strong justification is usually needed to seek a cement other than a commonly available ASTM C 150 Type I or Type II portland cement, or corresponding blended cement.

1.2—Purpose of the report

This report summarizes current information about the composition, availability, and factors affecting the performance of commercial hydraulic cements. Although the amount of information given may make it appear that selecting cement for a specific purpose is complicated, this is only true in unusual circumstances.

The purpose of this report is to provide users with general information on cements to help them recognize when a readily available general-purpose cement will perform satisfactorily or when conditions may require selection of a special cement. It will also aid the cement user by providing general information on the effects of cements on the properties of concrete. Some chemical and physical characteristics of a cement affect certain properties of concrete in important ways. For other properties, the amount of cement is more important

Table 2.1—Characteristics and consumption of portland cements*

Type*	Description	Optional characteristics	% of total† U.S. shipments (1995)
I	General use	1, 5	86.6
II	General use; moderate heat of hydration and moderate sulfate resistance	1, 4, 5	—
III	High-early-strength	1, 2, 3, 5	3.3
IV	Low heat of hydration	5	(Not available in U.S.)
V	High sulfate resistance	5, 6	2.1
Optional characteristics			

1. Air entraining (A).
2. Moderate sulfate resistance: C_3A maximum, 8%.
3. High sulfate resistance: C_3A maximum, 5%.
4. Moderate heat of hydration: maximum heat of 290 kJ/kg (70 cal/g) at 7 days, or sum of C_3S and C_3A , maximum 58%.
5. Low alkali: maximum of 0.60% alkalis, expressed as Na_2O equivalent.
6. Alternative limit of sulfate resistance is based on expansion tests of mortar bars.

*For cements specified in ASTM C 150.

†% of all cement types, including masonry cement.

Reference: *U.S. Cement Industry Fact Sheet*, PCA, 1995.

than its characteristics. The report is not a treatise on cement chemistry or concrete; for those who need to know more, however, it provides references to the technical literature, including many ACI documents.

CHAPTER 2—CEMENT TYPES AND AVAILABILITY

Before discussing the factors affecting cement performance, many types of inorganic cements will be mentioned. The purpose is to define the scope of this report by indicating those that will and will not be included, as well as indicating the relationships among various types of cement.

2.1—Portland and blended hydraulic cements

Perhaps 99% of the cement used for concrete construction in the U.S. is either a portland cement, as specified in ASTM C 150, or a blended cement, as specified in ASTM C 595 or C 1157. Similar specifications are published by the American Association of State Highway and Transportation Officials (AASHTO) such as M85 for portland cements and M240 for blended cements, and by the Canadian Standards Association (CSA). CAN/CSA 3—A5—M88 portland cements are designated as Types 10, 20, 30, 40, or 50 and correspond in intended use to ASTM C 150 cement Types I, II, III, IV, or V, whereas CAN/CSA—A362 covers blended hydraulic cements.

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 1500 C (2700 F) for the reactions that form cement phases to take place. The product of the cement kiln is known as portland-cement clinker. After cooling, the clinker

Table 2.2—Characteristics of blended hydraulic cements*

Type	Name	Blended ingredients† range		Optional characteristics	% of total U.S. cement shipments (1995)
		Pozzolan	Slag		
I (PM)	Pozzolan-modified portland cement	0 to 15	‡	1, 2, 3	—
IP	Portland-pozzolan cement	15 to 40	‡	1, 2, 3, 5	—
P	Portland-pozzolan	15 to 40	‡	1, 2, 4, 5	1.1
I (SM)	Slag-modified portland cement	—	0-25	1, 2, 3	—
IS	Portland-blast furnace slag	—	25-70	1, 2, 3, 5	—
S	Slag cement§	—	70-100	1, 5	—

Type	Name	Optional
GU	General use	6
HE	High early strength	6
MS	Moderate sulfate resistance	6
HS	High sulfate resistance	6
MH	Moderate heat of hydration	6
LH	Low heat of hydration	6

Optional characteristics

1. Air-entraining (A).
2. Moderate sulfate resistance (MS): must be made with Type II portland-cement clinker.
3. Moderate heat of hydration (MH): maximum heat of 290 kJ/kg (70 cal/g) at 7 days.
4. Low heat of hydration (LH): maximum heat of 249 kJ/kg (60 cal/g) at 7 days.
5. Suitability for use with alkali-silica reactive aggregate: mortar bar expansion less than 0.02% at 14 days, 0.06% at eight weeks.
6. Option R: mortar bar test for determining potential for alkali-silica reaction.

*For cements specified in ASTM C 595.

†Concretes comparable to blended cement concretes may be made at the batch plant by adding the individual components, i.e., portland cement and either or both of a pozzolan and slag, to the concrete mixture.

‡These cements may be blends of pozzolans with either portland or slag-containing cements. Certain combinations with slag cement will reduce alkali-silica reactions and sulfate attack.

§For use in combination with portland cement in making concrete and in combination with hydrated lime in making masonry mortar.

is ground with an addition of approximately 6% calcium sulfate (gypsum) to form a portland cement.

Blended hydraulic cements are usually made by grinding portland-cement clinker with calcium sulfate (gypsum) and a quantity of a suitable reactive material such as granulated blast-furnace slag fly ash, silica fume, or raw or calcined natural pozzolans. They may also be made by blending the finely ground ingredients.

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 may vary widely among geographical regions. An appreciation of the relative consumption percentages and commonly used descriptions of portland and blended cements can be gained from the information given in Tables 2.1 and 2.2. The use of blended cements, though

Table 2.3—Miscellaneous or special purpose cements

Type	Description or purpose	ASTM specification	% of total U.S. [†] cement shipments (1995)
White cement	White architectural cement	C 150 [†]	0.690
Buff cement	Buff architectural cement	C 150 [†]	0.008
Expansive cement, Type E-I [‡]	Expansive hydraulic cement	C 845	0.060
Regulated-set cement	For use where rapid setting and moderate-early-strength development is needed	None	—
Very-early-strength blended cements	For use where early strength development is needed	Some may meet specifications of other cements	
Oil-well cements, Types A through H, J [§]	Hydraulic cements used for oil-well casings and linings	None	0.940
Masonry cement, Types M, S, and N	For use in mortar for masonry, brick and block construction, and stucco	C 91	4.400
Plastic cement	For use in exterior stucco applications	C 1328	—
Mortar cements Types M, S, and N	For use in mortar for masonry, brick, and block construction	None	
Calcium-aluminate cement	For use in refractory, high-early-strength, and moderately acid-resistant concretes	None	0.090
Block cement	For use in making concrete masonry units	None	0.620
Magnesium phosphate cement	Nonportland cement for use where rapid hardening is needed	None	

[†]% of total of all types of cement.

[‡]Although white and buff cements are not listed specifically in C 150, they may meet the requirements of C 150 as indicated by the manufacturer.

[§]Three kinds are identified by letters K, M, and S.

[§]These are covered by API Specification 10 for Materials and Testing for Oil-Well Cements.

^{||}Very small.

presently small, is growing in response to needs for use in concrete requiring special properties, conservation of energy, and raw materials.

The term Type I/II portland cement is a frequently used and frequently misunderstood term. Type I/II is not an actual ASTM designation and should not be used by specifiers. Type I/II does, however, denote that the cement being represented has a C₃A content of 8% or less and meets all of the requirements of both ASTM C 150 Type I and Type II. This is particularly helpful to the ready-mixed concrete producer who has limited silo storage capacity, and for whom the ability to inventory a single cement that meets both ASTM C 150 Type I and Type II specifications in one silo is a convenience.

“Type II modified” is another term that is frequently misunderstood. The word “modified” can mean modified by such characteristics as lower alkali content, coarser fineness, or significantly lower C₃A content. When the term “Type II modified” is used, the purchaser should request that the manufacturer define the modification employed to ensure that the product is appropriate for the intended application.

2.2—Special-purpose cements

In addition to portland and blended cements, other cements may be available for specialized uses, as shown in Table 2.3. Other cement types will only be discussed briefly here.

Masonry cements for use in masonry mortars are specified in ASTM C 91, and their use is covered by ASTM C 270, ACI 530/ASCE 5/TMS 402, ACI 530R/ASCE 5/TMS 402, ACI 530.1/ASCE 6/TMS 602, and ACI 530.1R/ASCE 6/TMS 602. Plastic cements and mortar cements are also used in mortars and are specified in ASTM C 1328 and C 1329, respectively.

Block cements are modified portland cements manufactured to meet the needs of the concrete masonry-unit manufacturing industry.

Certain portland cements manufactured under carefully controlled conditions give special colors, such as white or buff, that are used for architectural purposes. White cements and buff cements are usually furnished to meet ASTM C 150 Type I or III specifications. Some other special cements, specifically oil-well and block cements, may also meet ASTM specifications; for example, Class G oil-well cements meeting API Specification 10 often meet the ASTM C 150 Type II specification.

Expansive or shrinkage-compensating cements are designed to expand a small amount during the first few days of hydration to offset the effects of later drying shrinkage. Their purposes are to reduce cracking resulting from drying shrinkage, or to cause stressing of reinforcing steel. 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. They are covered by ASTM C 845. The expansive ingredient, an anhydrous calcium sulfoaluminate, may be purchased separately. Magnesium oxide or calcium oxide may also be used as expansive agents, which are used in Europe and Japan.

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.

Very-early-strength blended cements are similar in composition to other ASTM C 595 and C 1157 blended cements, except that they are specially formulated with functional additions (such as accelerators and superplasticizers) to provide design strengths in approximately 3 to 12 h. Regular blended cements normally provide design strengths in 7 to 28 days. Very-early-strength blended cements can be used in the same application as portland and blended cement. They are usually used in applications where early-strength development is highly beneficial, such as in repair applications. These cements have been used in concrete for airports, industrial plants, highways, and bridges.

Portland oil-well cements are manufactured specifically for use in sealing spaces between oil-well casings and linings and the surrounding rock. They are usually required to comply with the requirements of specifications issued by the American Petroleum Institute (API). For very high-temperature

wells, less reactive, nonportland cements are sometimes used, such as mixtures of dicalcium silicate and finely ground silica.

Calcium-aluminate cements (see [Appendix](#)) 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 upon iron content (in the low purity) 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. ACI 547R and ACI 547.1R provide some additional information on these cements and their uses.

Plastic cements (ASTM C1328) 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.

So-called *waterproof cements* are portland cements interground with stearic acid, or other water repellent, with the objective of imparting water repellency to concrete containing them.

Magnesium phosphate cements are rapid-hardening, non-portland cements that are primarily used in highway and airport pavement repairs. They may be two-part cements consisting of a dry powder and a phosphoric acid liquid with which the powder must be mixed, or they may be one-component products to which only water is added.

Ultrafine cements are cements of fine particle size with the distribution (50% by mass) of the particles having a mean diameter of $<5 \mu\text{m}$ (2×10^{-4} in.) and are usually composed of blends of portland cement and ground blast-furnace slag. These small-sized particle systems are required in geotechnical applications and repairing relatively large cracks in this and other concrete applications where permeation grouting of fine sands, underground strength, or water control in finely fractured rock formations are needed. More information on these specialty systems should be obtained from the manufacturers of the products.

CHAPTER 3—CEMENT CHEMISTRY

Although this report is not intended to be a treatise on cement chemistry, it may help the reader to be reminded of some of the nomenclature and terminology used in later chapters. Also, the nature of the chemical differences between the cements is discussed. More complete descriptions of the chemistry of cements can be found in Lea (1970) and Taylor (1990).

The principal constituents of cements, pozzolans, and blast furnace slags (and/or their hydration or reaction products) are phases containing the elements calcium (Ca), silicon (Si), aluminum (Al), iron (Fe), oxygen (O), sulfur (S), and hydrogen (H). Chemical analyses of these materials usually express the amounts of these elements present as percentages of the oxides, CaO (lime), SiO₂ (silica), Al₂O₃ (alumina), Fe₂O₃ (ferric oxide), SO₃ (sulfur trioxide), and

Table 3.1—Phases^{*} assumed to occur in portland cements

Formula	Name	Cement abbreviation
3 CaO · SiO ₂	Tricalcium silicate	C ₃ S
2 CaO · SiO ₂	Dicalcium silicate	β-C ₂ S
3 CaO · Al ₂ O ₃	Tricalcium aluminate	C ₃ A
4 CaO · Al ₂ O ₃ · Fe ₂ O ₃	Tetracalcium aluminoferrite	C ₄ AF
2 CaO · Fe ₂ O ₃	Dicalcium ferrite	C ₂ F
MgO	Magnesium oxide	M
CaO	Calcium oxide	C
CaSO ₄ · 2H ₂ O	Calcium oxide Gypsum ^{†,‡}	CSH ₂

^{*}In commercial cements, the phases all contain significant quantities of impurities.

[†]Added to the clinker during grinding to control setting time.

[‡]Other forms of calcium sulfate, specifically hemihydrate, anhydrite (Hansen and Hunt 1949), and soluble anhydrite, are also added in some cases.

H₂O (water). To simplify the writing of formulas, these oxides are written frequently as C, S, A, F, S, and H, respectively. The oxides are, with few exceptions, not actually present as such, but the elements are in the forms of more complex phases.

3.1—Portland cements

The main phases present in portland cements are listed in Table 3.1. The chemical compound phase (or family of phases) identified as C₃S exists in clinker in the impure form known as alite. Alite is extremely complex and may take on six or seven crystal forms and contain the elements sulfur (S), sodium (Na), potassium (K), iron (Fe), magnesium (Mg), and fluorine (F) in addition as trace elements. 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 (phases), C₃A, and the ferrite phase, C₄F, also exist in several different crystal forms with some variation in properties. The ferrite phase can vary widely in composition. When the A/F 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.

Progress has been made in the understanding of the crystal structures of individual portland cement phases, their relative proportions, and grain shapes, sizes, and distributions. This knowledge has been applied to the control of cement manufacture and prediction of properties of the finished cement (Chatterjee 1979). Ono et al. (1969) and Fundal (1982) have developed systems for predicting strength or changes in strength from a microscopic determination of the size, shape, and abundance of alite and belite crystals in clinker, and the distinctness of their grain boundaries. These microscopic observations of clinker are used to control raw mixture composition and fineness, kiln conditions, and cooling rates.

The percentages of the phases in a portland cement, such as those given in [Table 3.2](#), are calculated from the oxide analysis of the cement using certain simplifying assumptions. Such calculated potential phase compositions of a cement only approximate the percentages actually present.

Table 3.2—Chemical and phases composition and fineness of 1990s cements* (PCA 1996)

Type of portland cement	Range of chemical composition, %						Loss on ignition	Na ₂ O Eq.	Range of potential phase composition, %				Blaine fineness, m ² /kg
	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	
I (min - max)	18.7 - 22.0	4.7 - 6.3	1.6 - 4.4	60.6 - 60.3	0.7 - 4.2	1.8 - 4.6	0.6 - 2.9	0.11 - 1.20	40 - 63	9 - 31	6 - 14	5 - 13	300 - 421
I (mean)	20.5	5.4	2.6	63.9	2.1	3.0	1.4	0.61	54	18	10	8	369
II (min - max)	20.0 - 23.2	3.4 - 5.5	2.4 - 4.8	60.2 - 65.9	0.6 - 4.3	2.1 - 4.0	0.0 - 3.1	0.05 - 1.12	37 - 68	6 - 32	2 - 8	7 - 15	318 - 480
II (mean)	21.2	4.6	3.5	63.8	2.1	2.7	1.2	0.51	55	19	6	11	377
III (min - max)	18.6 - 22.2	2.8 - 6.3	1.3 - 4.9	60.6 - 65.9	0.8 - 4.8	2.5 - 4.8	0.1 - 2.3	0.14 - 1.20	46 - 71	4 - 27	0 - 13	4 - 14	390 - 644
III (mean)	20.6	4.9	2.8	63.4	2.2	3.5	1.3	0.56	55	17	9	8	548
IV (min - max)	21.5 - 22.8	3.5 - 5.3	3.7 - 5.9	62.0 - 63.4	1.0 - 3.8	1.7 - 2.5	0.9 - 1.4	0.29 - 0.42	37 - 49	27 - 36	3 - 4	11 - 18	319 - 362
IV (mean)	22.2	4.6	5.0	62.5	1.9	2.2	1.2	0.36	42	32	4	15	340
V (min - max)	20.3 - 23.4	2.4 - 5.5	3.2 - 6.1	61.8 - 66.3	0.6 - 4.6	1.8 - 3.6	0.4 - 1.7	0.24 - 0.76	43 - 70	11 - 31	0 - 5	10 - 19	275 - 430
V (mean)	21.9	3.9	4.2	63.8	2.2	2.3	1.0	0.48	54	22	4	13	373

*Values represent a summary of combined statistics; air-entraining cements are not included. Adapted from Gebhardt (1995).

Table 3.3—Primary phases formed by reactions of portland cements with water

Approximate formula	Name	Common abbreviation
3CaO · 2SiO ₂ · xH ₂ O (x ≈ 3)	Calcium silicate hydrate	C-S-H
6CaO · Al ₂ O ₃ · 32H ₂ O	Ettringite	C ₆ A \overline{S} ₃ H ₃₂
6CaO · Fe ₂ O ₃ · 3SO ₃ · 32H ₂ O	Iron ettringite	C ₆ F \overline{S} ₃ H ₃₂
4CaO · Al ₂ O ₃ · SO ₃ · 12H ₂ O	Calcium monosulfoaluminate 12-hydrate	C ₄ A \overline{S} H ₁₂
Ca(OH) ₂	Calcium hydroxide	CH
Mg(OH) ₂	Magnesium hydroxide	MH

The calculation procedure, which was developed by Bogue (1955), is given in ASTM C 150. This procedure assumes that chemical equilibrium is attained in the burning zone of the kiln, whereas, in fact, equilibrium is not quite reached. X-ray diffraction analysis 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 C 150. Typical phase compositions and fineness of the five ASTM types of portland cements are given in Table 3.2.

3.1.1 Reactions of portland cements with water—When portland cement and water are mixed, a series of chemical reactions begins that results in slump loss, setting, hardening, evolution of the heat of hydration, and strength development. The overall process is referred to as cement hydration, as it involves formation of water-containing (hydrated) phases. The primary phases that form are listed in Table 3.3. 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 dis-

solving rapidly and causing a protective coating of ettringite to form on the C₃A surfaces. A side effect of the gypsum is to accelerate the hydration of the silicates.

The ions or water-soluble compounds dissolved in the water are believed to affect the behavior of cements and their reactions with other concrete materials such as aggregates and admixtures. Figure 3.1 is a representation of how the quantities of some of the important ions in solution might change with time. Figure 3.2 is a companion figure indicating how the quantities of important cement reaction 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 the reactions and the nature and amounts of the phases formed depend on the specific compositions and fineness of the cements; they also depend on the temperature, nature, and quantities of admixtures present (Helmuth et al. 1995).

To illustrate the relationships between cement chemistry and cement standards, ASTM C 150 establishes maximum SO₃ contents ranging from 2.3% for Type V to 4.5% for Type III. The SO₃ content for Type I cements may vary from 1.8 to 4.6% (Gebhardt 1995). Generally, the maximum permissible amount of SO₃ is a function of the C₃A content and the fineness. Additional SO₃ exceeding the stated maximum is permitted if tests demonstrate that the expansion in water at 14 days (ASTM C 1038) is not excessive, for C 150 and C 1157 cements, or that the amount of SO₃ remaining in solution after 24 h of hydration is suitably low (ASTM C 265), which is required for ASTM C 595 cements. Careful control is exercised because SO₃ not consumed in the first few days might react with any unreacted C₃A at later ages to produce ettringite and result in destructive long-term expansion.

The SO₃ present in a cement comes principally from the gypsum (CaSO₄ · 2H₂O) added during grinding, but significant amounts may also come from the clinker if high-sulfur fuel is used in the clinker burning process. SO₃, from the combustion of sulfur compounds in the fuel, often forms sulfites and sulfates that are less effective than the interground gypsum in controlling the setting. The amount of gypsum added is established by the cement producer to opti-

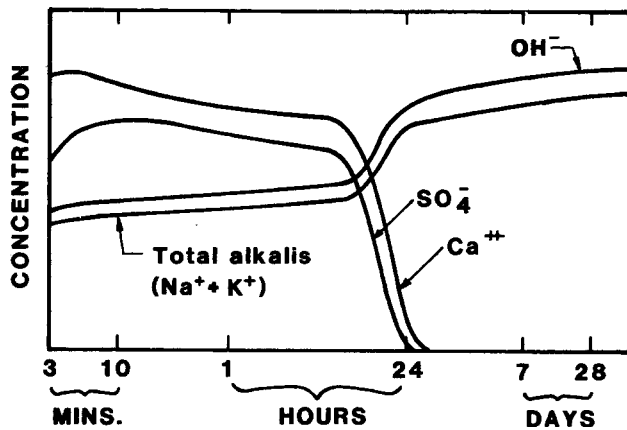


Fig. 3.1—Diagram illustrating changes with time of concentrations of ions in solution in the pore water of a portland cement paste.

mize strength, minimize drying shrinkage, and control time of setting and slump loss.

3.2—Blended hydraulic cements

The overall chemistry of blended hydraulic cements is similar to that of portland cements. Blended hydraulic cements usually contain portland cement; in addition, the blending ingredients contain the same major elements as portland cements, that is, calcium, silicon, aluminum, iron, and oxygen. Blending materials can be granulated blast-furnace slags, fly ashes, silica fumes, and raw or calcined natural pozzolans. Specification chemical and/or physical requirements of the slags or pozzolans to be used in blended hydraulic cement are described in ASTM C 595 and ASTM C 1157. Detwiler et al. (1996) discusses the use of supplementary cementing materials in blended hydraulic cement.

Blast-furnace slags—Blast-furnace slags are byproducts from the manufacture of iron. The molten slag leaves the blast furnace as a liquid. If the molten slag is cooled rapidly, as by quenching with water (water granulation) or with air and a water spray (pelletization), it forms glassy nodules that can be ground to form a cementitious powder. If the molten slag is cooled slowly, it forms a much less reactive, crystalline product (air-cooled slag) that is frequently crushed and used as aggregate. For additional information, see ACI 233R.

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; crystalline components are also present. For additional information, see ACI 232.2R.

Natural pozzolans—Natural pozzolans are naturally occurring siliceous (or siliceous and aluminous) rocks or minerals. Though 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. Natural pozzolans in their natural form are often not very active. They frequently require heat treat-

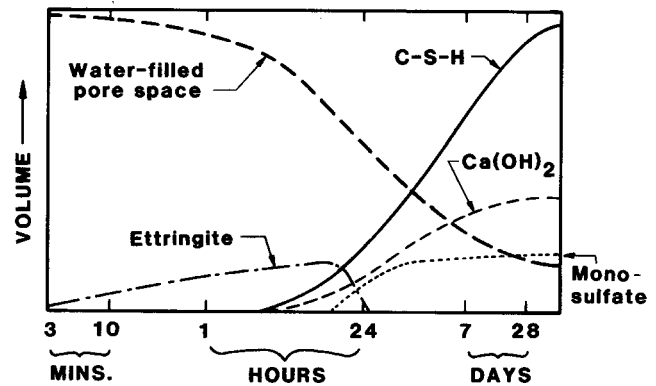


Fig. 3.2—Diagram illustrating formation of portland cement reaction products and reduction with time of the volume of pore space in a portland cement paste.

ment or 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, and sometimes metastable crystalline materials such as tridymite. For additional information, see ACI 232.1R.

Silica Fume—Finely divided silica-bearing residues of the silicon metal manufacturing process which possess pozzolanic properties when combined into hydrating hydraulic cement reactions. For additional information, see ACI 234R.

3.2.1 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 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.

3.3—Shrinkage-compensating expansive cements

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, and calcium sulfate ($\text{C}_4\text{A}_3\text{S}$, C_3A , CA , C , and CS), 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 C 845, which describes the three cements of this type, limits the increase in expansion between 7 and 28 days to 15% 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 must 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 223.

3.4—Calcium-aluminate cements

Calcium-aluminate cements are hydraulic cements that principally contain phases of such ratio (CA or CA₂) as to impart the necessary performance characteristics (Lea 1970; Robson 1962). These cements, which are discussed in the **Appendix**, are used primarily for refractory applications, but they also find use in moderate acid-resistant applications, high-early-strength and quick-setting mixtures, and as part of the expansive component in some shrinkage-compensating cements.

Potential users of calcium-aluminate cements should be aware that conversion of the hydration products from metastable hexagonal hydrates (CAH₁₀) to stable cubic hydrates (C₃AH₆) of lower volume may 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 (British Royal Commission Report).

CHAPTER 4—INFLUENCE OF CHEMICAL AND MINERAL ADMIXTURES AND SLAG ON THE PERFORMANCE OF CEMENTS

Chemical and mineral admixtures and ground slag 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 and 212.4R contain extensive information on admixtures and their use. Ground granulated blast-furnace slag, silica fume, raw and calcined natural pozzolans, and fly ash are discussed in ACI 233R, 234, 232.1R, and 232.2R, respectively. The primary purpose of this discussion is to highlight those characteristics of admixtures that influence cement performance or those characteristics of cements that influence admixture performance. Only a few categories of admixtures will be discussed: air-entraining; chemical (accelerating, retarding, and water-reducing); and mineral.

Air-entraining admixtures are necessary in all concrete that may freeze while critically saturated with water, but se-

rious problems still exist in obtaining consistent, high quality air-void systems in field concretes (Manning 1980).

Chemical admixtures, principally of the water-reducing and the water-reducing and retarding varieties, are used in perhaps 50% of the concrete in the United States. High-range water-reducing admixtures, although not presently used in a large proportion of the concrete, are experiencing steady growth. Mineral admixtures, principally fly ash, were estimated to have been used in a 55% of the ready-mixed concrete produced in 1989 (NRMCA 1991).

4.1—Air-entraining admixtures

Air-entraining admixtures are surface-active agents that form stable air bubbles with diameters less than 1 mm (0.04 in.) in concrete during mixing (Klieger 1994; Mielenz et al. 1958). The generally available admixtures are formulated to provide these small-sized bubbles rather than undesirable larger ones. A discussion of factors affecting the performance of air-entraining agents in concrete is given in ACI 212.3R and Whiting and Stark (1983).

Serious problems sometimes occur in obtaining consistent high-quality air-void systems in concrete under field conditions. Both the volume and the characteristics of the air voids are influenced by many factors, including water-cementitious material ratio (*w/cm*), aggregate grading, other admixtures, temperature, and, to some extent, the particular cement used. The ability to entrain air in concrete or mortar for a given admixture dosage is also affected by the slump or fluidity of the mixture, concrete temperature, and some properties of the aggregate, such as texture, angularity, and grading. During the many years of successful use of air entrainment, the specific influences of cements have not received as much attention as those of other factors. Recent trends toward concrete with lower *w/cm*, smaller coarse aggregate, and increased use of mineral and chemical admixtures are bringing about renewed study of air entrainment, including the influence of cement. Increasing the amount of cement or other finely divided material in concrete decreases the amount of air entrained by a given amount of admixture.

Two characteristics of portland cement are known to influence air entrainment. An increase in cement fineness or a decrease in cement alkali content generally increases the amount of admixture required for a given air content.

Blended hydraulic cements may require a greater quantity of air-entraining admixture than portland cements to produce a given air content. Further, if fly ash is used in a blended cement, there may be an increased tendency for loss of air during mixing, transit, and placement than when portland or blended cements that do not contain fly ash are used. Despite this loss in volume of air, the size and distribution of air voids remain relatively unaffected (Gebler and Klieger 1983). For additional information, see ACI 212.3R on air-entraining admixtures and ACI 232.2R on fly ash.

4.2—Chemical admixtures

ASTM C 494 defines the types of chemical admixtures and classifies them according to their effects on portland cement concrete as follows:

Type	Description
A	Water-reducing
B	Retarding
C	Accelerating
D	Water-reducing and retarding
E	Water-reducing and accelerating
F	Water-reducing, high-range
G	Water-reducing, high-range, and retarding

The most commonly used types are A, C, D, and E. Of these, Types A or E admixtures are generally made by the addition of an accelerator to a basic water-reducing and retarding material similar to a Type D admixture. Type G admixtures are generally made by the addition of a retarder to a Type F admixture.

The behavior of chemical admixtures with cements other than portland cements is difficult to predict. With blended cements, the behavior is determined primarily by the amount of portland cement present. Variations in the effectiveness of chemical admixtures frequently make it necessary to make trial mixtures simulating job materials, conditions, and procedures. Field experience with specific combinations is also valuable. A general discussion of the effects of admixtures with shrinkage-compensating expansive cements is given in ACI 223.

Accelerators—Calcium chloride is the most widely used inorganic accelerator. Several nonchloride accelerators (such as calcium formate, calcium nitrate, calcium nitrite, sodium thiocyanate, and combinations of these) are commercially available for all applications in which the chloride content of the concrete must be limited. Organic compounds, such as triethanolamine, are used in proprietary admixtures to offset retardation, but are not normally sold separately as accelerators.

Calcium chloride does react, to some extent, with the aluminate compounds in portland cements but, at the levels required to give significant acceleration, a considerable portion remains soluble and uncombined so that the potential for chloride-assisted corrosion of steel reinforcement remains.

Water-reducing retarders—ACI 212.3R lists a variety of materials that are marketed, singly or in combination, as water-reducing retarders. The composition of the cementitious material in concrete can have a significant influence on the behavior of all chemical admixtures. Inasmuch as these admixtures affect the early stages of hydration, and are at least partly removed from solution by the early reactions, the cement phases that react most rapidly have a large influence on their action. The early reacting compounds include C_3A and the alkali and calcium sulfates. For more information, see ACI 212.3R and Klieger (1994), Mather (1994), and Cain (1994) of ASTM STP-169C.

Polivka and Klein (1960) studied the effectiveness of water-reducing retarders. Their results showed that the quantity of admixture required to produce the desired results increases with increases in the C_3A , the alkali content, and the fineness of the cement. The alkali content of the cement, the amount

and form of SO_3 in the cement, the temperature, and the composition and amount of admixture, all affect the performance of the cement-admixture combination (Helmuth et al. 1995). In general, the cement has less effect on the reduction in mixing water than on the setting and strength gain of the cement-admixture combination. C_3A and alkali contents and the fineness vary not only among cements from different sources, but also, to a lesser degree, among samples of cement from the same source.

The amount and form of SO_3 in a cement affect the amount of a specific admixture required at the concrete temperature in use. Meyer and Perenchio (1979) concluded that the addition of a chemical admixture (by altering the rates of the reactions in the presence of water) can upset the balance between the soluble sulfate and the C_3A in a portland cement. This may result in rapid loss of slump or extended setting time.

To some extent, each cement-admixture combination is unique. The temperature and mixing time have a large effect on the early hydration reactions, and the specific results with different combinations are difficult to predict. The effects previously outlined, however, are the most significant effects of cement composition on the response of admixtures. Because the effects cannot be predicted with confidence, admixtures should be evaluated with job materials using temperatures, delivery times, and placing conditions expected on the job.

High-range water-reducing admixtures—For several years, high-range water-reducing admixtures (often referred to colloquially as superplasticizers) have been commercially available. They have been the subject of considerable discussion and study. Information concerning their use is contained in ACI SP-62, Whiting and Dziedzic (1992), ACI SP-119, and ACI SP-68. These admixtures permit considerably larger water reductions than Types A, D, and E, and can be used to produce very low w/c concretes at conventional slumps, or flowing concretes at conventional w/c . For further information on admixtures for flowing concrete, see ACI 212.4R and ASTM C 1017. Concretes containing these admixtures, particularly those with low slump and low w/c , may lose slump and stiffen rapidly.

The performance characteristics of high-range water-reducing admixtures, such as retention of slump, rate of setting, and strength gain, seem to be related to the same cement properties as those mentioned under water-reducing retarders, though not always in the same way as those that influence conventional water-reducing admixtures. These properties are cement SO_3 , C_3A , alkalies, and fineness. These properties can regulate the rate at which the early hydration reactions occur.

Most high-range water-reducing admixtures are typically dispersing surfactants. These chemicals adsorb onto the surface of cement particles and repel (disperse) other cement particles which also have dispersant molecules adsorbed onto their surfaces.

The practice of delaying the addition of the high-range water-reducing admixture allows for the early cement grain surface hydration to occur and the surfactant to adsorb onto

the top surface of the hydration products without being chemically absorbed, trapped, or hindered by the hydration products and kept from doing the dispersing function (Ramachandran 1984). The effect of temperature is also significant with high-range water reducers and generally similar to the effects observed with conventional water reducers.

4.3—Mineral admixtures

Mineral admixtures and slag are finely divided inorganic materials that may be added to concrete to modify its performance or cost. Specifications for fly ash and natural pozzolans are given in ASTM C 618. Slag specifications are given in ASTM C 989 and silica fume specifications are given in ASTM C 1240. Ground limestone is a permitted addition to portland cement during manufacture under Canadian and European specifications, (CAN/CSA3-A5-M88, and ENV 197, respectively). Mineral admixtures and slag 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 expansion. Pigments may also be used to change the color of concrete. Additional guidance on the use of mineral admixtures is given in ACI 232.1R (natural pozzolans), ACI 232.2R (fly ash), and ACI 234R (silica fume).

Fly ashes—Fly ashes are pozzolanic materials. Those with relatively high calcium contents are typically more reactive than those with lower calcium contents. Also, fly ashes with higher alkali contents are more reactive than those with lower alkali contents. Because the main elements in fly ashes are the same as those present in portland cements, fly ashes are generally compatible with portland cements. The amount of fly ash used in concrete may vary from less than 5 to more than 40% by mass of the cement plus fly ash. The percentage will depend on the properties of the fly ash and cement and the desired properties of the concrete.

When improved sulfate resistance is desired, the sulfate resistance of the combination of cement and fly ash should be tested before use. ASTM C 1012 is an appropriate test method and ASTM C 618, specifies the acceptable expansion limits. The alumina in the fly ash, as well as the C_3A in the cement, both contribute to susceptibility to sulfate deterioration. The minimum quantity of fly ash required for sulfate resistance is variable, but it is generally accepted that the addition rate used should be that which has been demonstrated to provide adequate sulfate resistance.

Some fly ashes are helpful in reducing the disruptive effects of the alkali-aggregate reactions of some siliceous aggregates. Mortar bar expansion tests in accordance with ASTM C 441, ASTM C 227, or concrete tests such as ASTM C 1293 should be made with the appropriate combinations of fly ash, the potentially reactive aggregates, and the cement under consideration to determine whether the expansion due to the alkali-aggregate reaction is adequately reduced.

Possible problems with fly ash are irregular performance, particularly in regard to air entrainment, lower early strength, longer setting time, and the need for longer curing

of the concrete. The lack of uniformity in response to air-entraining admixtures results from variations in the quantity of carbon in the ash and possibly other organic residues from the fuel. These problems can be largely alleviated by using a uniform, good-quality fly ash. ACI 232.2R provides additional information on the use of fly ash in concrete.

Natural pozzolans—Natural pozzolans can be incorporated in a concrete mixture to provide additional cementing value because of their reactions in the presence of cement and water. To increase their reactivity, natural pozzolans often need to be activated by heating for a short time at temperatures approaching 1000 C (1800 F) and by grinding. The main constituents of pozzolans are compounds of calcium, silicon, aluminum, iron, and oxygen. Benefits from the use of natural pozzolans in concrete can be increased strength at late ages, modified color, improved durability in sulfate environments, and inhibition of alkali-aggregate reaction. Disadvantages can be lower early strength, longer curing time, increased water requirement, and the problems of handling an additional material. As with fly ash, if sulfate resistance and reduction of expansion due to alkali-silica reaction are desired, tests should be made with project-specific materials. For more information, see ACI 232.1R.

Silica fume—Silica fume, as a pozzolan in concrete, is often used to reduce permeability and increase strength. Silica fume is a byproduct from the operation of electric arc furnaces used to reduce high-purity quartz in the production of elemental silicon and ferrosilicon alloys. Typically, silica fume consists of extremely fine, spherical particles of amorphous silicon dioxide. The average particle diameter may be 1/100 that of cement, and the specific surface, as determined by a method such as the nitrogen absorption technique, BET, may be 50 times that of typical cements.

Silica fume is extremely reactive with portland cements but, because of its high surface area, the amount used is generally less than approximately 10% by mass of cement. Silica fume has also been used to increase strength in calcium-aluminate cement systems. Usually, high-range water reducers are used with silica fume to maintain mixing water requirements at acceptably low levels to control drying shrinkage and improve workability.

Because of its reactivity, silica fume can generally replace three to four times its mass of portland cement and maintain equal compressive strength. For additional information, see ACI 234R.

4.4—Ground granulated blast-furnace slags

Ground granulated blast-furnace slags are used either as a separate cementing material added to the concrete batch, or as an ingredient of blended hydraulic cements. Ground granulated slag has been used extensively as a separate material in the South African ready-mixed concrete industry for many years, and it is available from at least three sources in North America. The main constituents of blast-furnace slags are composed of calcium, magnesium, silicon, aluminum, and oxygen. Slags are typically combined with portland cements over a wide range of proportions (approximately 25 to 70%).

The performance of a given ground granulated or pelletized slag depends greatly upon the characteristics of the cement with which it is used. Generally, improved strength performance is obtained with cements that have higher contents of alkali and C_3A and higher fineness (Schroder and Vinkeloe 1969, Detwiler et al. 1996).

The ASTM standard for ground granulated blast-furnace slags is ASTM C 989 and the Canadian standard for cementitious hydraulic slag is CSA—A 23.5. Refer to ACI 233R for additional information on the use of ground granulated blast-furnace slag in concrete.

CHAPTER 5—INFLUENCE OF ENVIRONMENTAL CONDITIONS ON THE BEHAVIOR OF CEMENTS

The behavior of a cement in concrete is affected by the environmental conditions to which the concrete is exposed, particularly during curing. Curing is the process of maintaining a satisfactory moisture content and a favorable temperature in concrete during its early ages so that the desired properties are developed. Curing methods and materials are discussed in ACI 308. The dependence of the behavior of a cement on temperature and relative humidity depends on the chemical and physical characteristics of the cement. These effects are reviewed briefly to provide background for the more extensive discussion of factors affecting cement performance given in Chapter 6.

Hydraulic cements require water for hydration. The quantity of mixing water required to completely hydrate portland cement is a w/c of approximately 0.4 by mass, of which approximately 0.2 is chemically combined and 0.2 fills the gel pores; the chemically combined water cannot form gel unless other water is available to fill the gel pores (Philleo 1986). Any loss of water by evaporation, however, will reduce the quantity of water available for hydration. Excessive loss of water during the early stages of hydration may result in premature termination of hydration. Such loss of water can also contribute to plastic- and drying-shrinkage cracking.

The rate of reaction between cement and water can be dramatically affected by temperature. Hydration of most cements proceeds very slowly below approximately 4 C (40 F), but the rate increases with the temperature. A useful rule of thumb is that the rate of reaction doubles for each 10 C (18 F) increase in temperature and, conversely, is halved for each 10 C (18 F) decrease. According to ACI 305R, placement temperatures in excess of 35 C (95 F) can reduce long-term strength gain. Lower temperatures produce higher ultimate strengths, but the rate of strength development is reduced. For a discussion of steam curing, see ACI 517.2R (available only as a separate). Another reference concerning high-temperature curing is Hanson (1963) and Hanson et al. (1963).

Fineness and chemical composition are the major characteristics of cement that influence its rate of reaction and strength development in concrete. Generally, the finer the portland cement, the higher its rate of reaction and early strength gain. Table 3.2 shows typical differences in fineness and composition between Type III (high-early-strength) cements and other portland cements. At standard

laboratory testing temperatures (23 C) and below, blended hydraulic cements may gain strength more slowly than portland cements of the same fineness and may require longer curing.

The hydration of hydraulic cements is an exothermic reaction and can offer the effects of temperature induced retardation when these hydration reactions are accelerated. Thus, the higher the rate of reaction of the cement, the more rapidly is heat produced. In thick sections of concrete, a condition can exist under which temperature-related cracking can occur. Surface cracks can develop from a steep temperature gradient between the exposed surface and interior concrete. Information on mass concreting is given in ACI 207.1R, and guidance on estimating the effects of heat generation and volume changes on the behavior of thick structures is given in ACI 207.2R.

CHAPTER 6—INFLUENCE OF CEMENT ON PROPERTIES OF CONCRETE

Cement should be characterized primarily on the basis of its effects on the performance of concrete and only secondarily on its chemical composition. For some performance-related properties, such as strength and volume stability, comparatively rapid and reliable test procedures are available. For other properties involving aspects of long-term durability, the time required for testing and the difficulties of duplicating specific environmental factors seem to require characterization by composition and prediction of potential long-term performance from the body of literature relating performance to composition. Therefore, proper selection of cement to provide specific properties or to meet special service requirements can only be made if the influence of cement upon individual properties of concrete is understood. These influences are discussed in the following sections.

6.1—Thermal cracking

Heat is liberated as cement hydrates and the amount and rate of heat liberation are functions of the composition and fineness of the cement (Lea 1970). In general, the rate of heat liberation parallels the rate of strength increase. In most concrete construction, the heat evolved is quickly dissipated and is of little concern. In structures such as large abutments, massive foundations, and dams, however, precautions may have to be taken to limit the temperature rise. If they are not taken, thermal expansion may be so great that cracking will occur later, either as the exterior of the mass cools and contracts before the interior does so, or as the whole structure cools, and cracks due to the restraint imposed. Information on estimating heat effects is given in ACI 207.2R, and guidance on thermal cracking is given in ACI 224R.

Information on concrete for mass structures is given in PCA (1987) and Bamforth (1984).

The principal phases in portland cements hydrate at different rates. They also yield considerably different amounts of heat per unit mass hydrated (see Table 6.1). Generally speaking, tricalcium aluminate (C_3A) releases most of its heat in the first day or so and tricalcium silicate (C_3S) in the first

Table 6.1—Heats of complete hydration of pure cement compounds

Compound	Heat of hydration, kJ/kg (cal/g)
C ₃ S	502 (120)
C ₂ S	259 (62)
C ₃ A	865 (207)
C ₄ AF	418 (100)
CaO (free lime)	1166 (279)

Table 6.2—Heats of hydration of different types of portland cement manufactured in the 1940s, as determined by ASTM C 186

ASTM cement type	Heat of hydration, kJ/kg (cal/g) 21 C (70 F) storage					
	3 days	7 days	28 days	3 months	1 year	6-1/2 years
Type I	225 (61)	334 (80)	401 (96)	435 (104)	456 (109)	489 (117)
Type II	196 (47)	255 (61)	334 (80)	368 (88)	397 (95)	410 (98)
Type III	314 (75)	385 (92)	422 (101)	447 (107)	477 (114)	506 (121)
Type IV	171 (41)	213 (51)	276 (66)	309 (74)	339 (81)	355 (85)
Type V	184 (44)	230 (55)	309 (74)	347 (83)	380 (91)	393 (94)

Table 6.3—ASTM C 186 heat of hydration for selected portland cements, cal/g

Type I cement			Type II cement			Type II (moderate heat) cement		Type III cement			Type IV cement			Type V cement								
No.	7 day	28 day	No.	7 day	28 day	No.	7 day	No.	7 day	28 day	No.	7 day	28 day	No.	7 day							
1	82.0	—	16	77.7	101.4	32	67.6	36	88.0	99.0	38	60.0	—	41	81.5							
2	85.6	—	17	82.6	88.8	33	65.0	37	89.0	95.0	39	57.3	—	42	66.5							
3	81.6	—	18	88.7	89.4	34	54.3				40	49.7	65.5	43	79.3							
4	80.2	—	19	88.0	—	35	64.7										44	80.4				
5	78.4	—	20	73.6	—															45	76.1	
6	88.3	90.2	21	88.5	—																	
7	88.2	106.1	22	77.1	89.7																	
8	87.7	93.5	23	87.3	—																	
9	88.9	97.7	24	81.9	100.3																	
10	76.4	91.7	25	88.3	99.4																	
11	84.4	91.7	26	86.5	96.8																	
12	84.4	98.5	27	79.5	—																	
13	83.5	—	28	79.4	—																	
14	79.5	—	29	80.0	—																	
15	83.0	—	30	80.0	—																	
—	—	—	31	77.6	—																	
Avg.	83.5	95.6	Avg.	82.3	95.1	Avg.	62.9	Avg.	88.5	97.0	Avg.	55.7	NM	Avg.	74.2							
Max.	88.9	106.1	Max.	88.7	101.4	Max.	67.6	Max.	NM	NM	Max.	60.0	NM	Max.	81.5							
Min.	76.4	90.2	Min.	73.6	88.8	Min.	54.3	Min.	NM	NM	Min.	49.7	NM	Min.	61.4							

week; dicalcium silicate (C₂S) and calcium aluminoferrite (C₄AF) hydrate more slowly.

The data shown in Table 6.1 are the heats evolved in the complete hydration of a unit mass of each of the pure phases. Although useful in indicating the orders of magnitude of the total contributions of the individual phases to the heats of complete hydration, the figures in Table 6.1 cannot be used for calculating heats of hydration of commercial portland cements for the following reasons:

1. The phases mixed together in a cement may hydrate at very different rates from phases hydrating alone, so that unless the rates are known, the contribution of each phase at a given time will not be known.
2. The phases in commercial cements are not pure; their crystal structures contain elements other than those indicated by the simple formulas.
3. The high temperature reactions in the clinker manufacture may not have gone to completion; if they did not, the potential phase composition of the cement will differ from its actual phase composition.

Fineness of cement is an important factor affecting rate of heat liberation, particularly at early ages. Table 6.2 gives heat of hydration values for batches of various types of portland cement manufactured many years ago (Verbeck and Foster 1950). More typical but less complete data for modern cements are given in Table 6.3. The comparison of data in Table 6.2 to Table 6.3 shows the trend towards an increase in heat of hydration for modern cement (example, Type II at 7 days = 61 cal/g in the 1940s data, while it developed approximately 82 cal/g for T-II cement or 62.9 cal/g for Type II moderate heat in modern cements [Kozmatka 1997]). The requirements in many construction specifications for higher early strengths has predominantly been met by higher cement finenesses or changes to cement composition.

The heat of hydration values for the different types of cement shown in Table 6.2 reflect the amounts of the various phases present and the fineness of the cements. Fineness is a major contributor to the differences between the characteristics for Type III and Type I cements. In all cases, including Type III, cements continue to hydrate even beyond the age of 1 year. The rate of heat liberation during hydration

is related to the rate of strength gain for each of the five types of cement.

The data in Table 6.3 depict data based on Kosmatka (1997).

It is often assumed that blended cements have lower heats of hydration than portland cements; depending, however, on the ingredients, they may have lower or roughly equal heats of hydration. The temperature-induced effects (expansion or contraction) in a structure also depend on the mass of the member and its age.

In general, the heat of hydration of shrinkage-compensating expansive cements, as stated in ACI 223, is within the range of variation of the heat of hydration of the particular portland cements used in their manufacture.

6.2—Placeability

Several characteristics of a cement may influence the placeability of the concrete in which the cement is used. The influence of the cement on placeability can be beneficial or detrimental. Some of the factors are discussed below or in this section.

Quantity of cement used in the concrete mixture—Cement is frequently the material in concrete having the smallest particle size (fly ashes and silica fume, when added, may be much smaller in particle size). The amount of cement in a concrete mixture has a large effect on the plasticity and placeability of the mixture. Mixtures containing small amounts of cement (lean mixtures less than 225 kg/m³ [380 lb/yd³]) tend to be harsh and difficult to work. They are, therefore, more difficult to place and finish. Mixtures containing large amounts of cement [rich mixtures of approximately 400 kg/m³ (670 lb/yd³)] tend to have more body and are more cohesive, fluid, and workable. Unusually rich concrete mixtures (more than 500 kg/m³ [840 lb/yd³]), however, tend to be undesirably cohesive or sticky and more difficult to place.

Cement fineness—Fineness of cement influences the placeability, workability, and water content of a concrete mixture in much the same way as the amount of cement used in the concrete. The overall importance of cement fineness, however, is only modest relative to the effect of the amount of cement used.

Low cement-content mixtures tend to lack cohesion, bleed excessively, and segregate. Use of a coarsely ground cement aggravates these tendencies. As fineness or amount of cement used increases, the mixture becomes more cohesive. At the same time, the amount of water required to produce a given slump may decrease and the tendency to bleed and segregate will be reduced. At some intermediate cement content, further increases in cement content make the mixture sticky and difficult to handle and place, and the required water content is increased. The cement content at which the minimum water requirement and optimum workability occur is reduced if the cement fineness is increased.

In concrete, other constituents such as entrained air, mineral and chemical admixtures, and the fine materials and clays in aggregates also affect workability, plasticity, and mixing-water requirements.

Cement-setting characteristics—The setting or stiffening characteristics of cement are transferred directly to the concrete mixture. A tendency for the mixture to stiffen prematurely or to rapidly lose slump directly affects placeability, consolidation, and finishability. The normal setting or stiffening characteristics will determine the time available for placement, consolidation, and finishing. Rich mixtures frequently set a little sooner than lean mixtures.

The temperature of the concrete has a significant effect on its rate of hardening. The temperature of the cement itself has very little influence on the temperature of the concrete and, consequently, on its hardening rate. Often, a rapid loss of slump or reduction in hardening time is considered to be caused by the use of “hot cement.” As cement clinker is ground into finished cement, energy, in the form of heat, is imparted to the finished ground cement. Dependent on the efficiency of the cooling system, the cement temperatures may range from a low of 32 C (90 F) to a high of 77 C (170 F). After the cement is put into the storage silo, it takes a considerable amount of time for the heat to dissipate. The thermal acceleration of the cement hydration, however, is controlled by the overall concrete temperature. ACI 305R (Appendix A) gives a formula for estimating the effect of cement temperature on the temperature of freshly mixed concrete. When the temperature of each of the individual components is known, it is estimated (in ACI 305R,) that a 1.2 C (2 F) change in aggregate temperature has the same 0.6 C (1 F) change in a usually proportioned concrete mixture as does a 5 C (9 F) cement temperature change. While cement temperature does affect the concrete temperature, the other components should not be overlooked for their influence on the concrete temperature.

It is important to distinguish between normal slump loss of concrete with time and the effects of a false-setting cement. Normal slump loss is gradual and more or less proportional to time until there is no slump. Ordinary slump loss cannot be restored by remixing. With a severe false set, all slump may be lost in 5 or 10 min, but remixing will restore nearly all of the original slump. This phenomenon is the result of the use of some of the mixing water to rehydrate the dehydrated calcium sulfate phases present. A mild or moderate case of false set may result in only a high rate of slump loss shortly after mixing. False set is less affected by the temperature of the concrete than slump loss, which is more rapid in warmer weather. In some cases, false set and excessive slump loss occur together and the problems tend to merge. In stationary plant mixers operating with mixing times less than 1 min, increasing the mixing time will frequently alleviate false set and the associated early slump loss. Flash set is another phenomena associated with slump loss, but is typically more severe and less recoverable. Flash set is a result of the mixing water being chemically combined by the C₃A or free lime component of cement or fly ash in the cementitious system. This water, however, is not released and therefore slump is not recovered. The rate of the calcium sulfate solubility in the system is the key to reducing flash set when it is associated with the C₃A phase. Increasing of the calcium sulfate content, or increasing of the solubility rate of the existing calcium sulfate present during

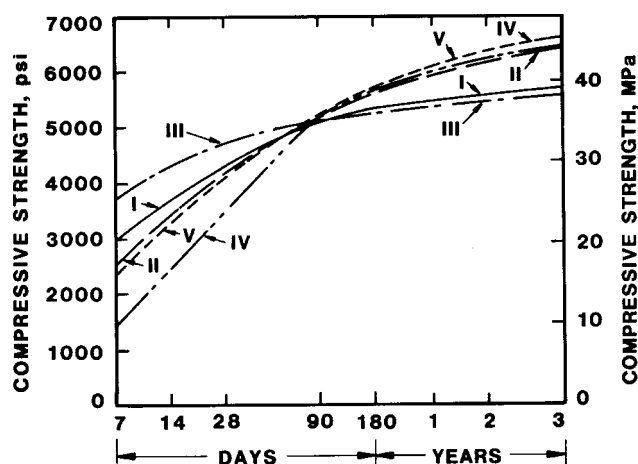


Fig. 6.1—Rates of strength development for concretes made with various types of ASTM C 150 portland cement and subjected to continuous moist curing. (U.S. Bureau of Reclamation Concrete Manual 1981.)

the manufacture of the cement, helps to eliminate this phenomenon.

Concrete containing water-reducing or retarding admixtures may exhibit faster slump loss than similar concretes without the admixtures. This effect is especially pronounced and common with high-range water-reducing admixtures. Certain admixtures can cause significant changes in setting time (Hersey 1975).

As discussed in ACI 223, shrinkage-compensating expansive cements may show somewhat greater slump loss than portland cements in hot weather.

6.3—Strength

A number of researchers have studied the possibility of predicting the compressive strength potential of portland cements from the chemical composition expressed either as potential phases or oxides and physical characteristics such as fineness (Alexander 1972; Blaine et al. 1968; Gonnerman 1934; Gonnerman and Lerch 1951; Popovics 1976).

Cement composition— C_3S , C_2S , and C_3A are the principal strength-producing phases in portland cement (Lea 1970; Taylor 1964). The proportions of these can be varied in the manufacturing process and can change both the early-strength characteristics and the long-term strength. The following paragraphs describe these effects for curing temperatures between 2 and 90 C (35 and 190 F).

Increasing the proportion of C_3S increases strength at ages from 10 to 20 h through 28 days. The percentage of C_3S in portland cements typically ranges from 35 to 70%. In the case of Type IV cements, however, C_3S can be as low as 20% and C_2S can be as high as 55%. (Type IV cements are now very rarely made.)

C_2S contributes slightly to strength at ages as early as 1 or 2 days and significantly to 28-day strength. Its major effect is to increase later age strengths. Increasing proportions of C_2S with proportional decreases in C_3S content, however, generally reduces 28-day strength and increases strength at ages of 45 to 60 days through 5 yr and more. The long-term

strength contributions of C_2S are dependent on extended availability of moisture. In relatively thin sections of concrete that are permitted to dry at early ages, hydration stops when the internal relative humidity falls below 80% and the later age strength benefits of C_2S may not be obtained. Floors above grade are often examples of such concrete. Thick sections of concrete tend to retain moisture and benefit from the long-term strength contributions of C_2S . Some of these benefits occur in sections of 200 mm (8 in.) thickness, but the major effects will be in sections with thicknesses of 600 mm (2 ft) or more, depending on the drying conditions. Most portland cements contain from 10 to 35% C_2S .

C_3A contributes principally to strength at 24 h or less. The C_3A itself hydrates quickly. At the same time, its hydration generates heat, which has a modest effect in accelerating the hydration of the C_3S and C_2S . The C_3A content of portland cements ranges from 0 to 17%.

C_4AF makes a smaller contribution to the strength of portland cement. It is present because it facilitates burning of the cement clinker and formation of the strength-producing silicates. Typical C_4AF contents for different portland cements range from approximately 5 to 20%. Strength development curves for concrete made with various cement types are shown in Fig. 6.1.

Some of the minor components of portland cement also affect the strength. In particular, the quantity of calcium sulfate is normally chosen to optimize strength and other properties under the most common conditions of curing and use.

The loss on ignition of a cement is generally an indicator of the amount of water or carbon dioxide, or both, chemically combined with the cement. Strengths tend to decrease with increasing ignition loss. Combined water in a cement may have come from clinker that has been stored outside. The presence of combined water produces a spurious increase (Blanks and Kennedy 1955) in the indicated air permeability fineness (Blaine method ASTM C 204), and to maintain the same actual fineness, the cement must be ground to a significantly higher fineness.

Small amounts of sodium and potassium from the fuel or raw materials, or both, are normally present in portland cements. The effects of these on strength are not well understood. Some tests have indicated that potassium causes small increases in strength in the first few days but has little effect on later-age strength. Conversely, sodium seems to have little effect on strength in the first few days but causes a moderate decrease in strength at ages greater than a month.

Magnesium oxide is usually present in portland cements because of its unavoidable occurrence in the raw materials. In the proportions usually present, it has little effect on strength. ASTM C 150 limits magnesium oxide to a maximum of 6.0% to avoid the possibility of unsoundness.

The strength gain characteristics of shrinkage-compensating expansive-cement concrete are comparable with those of Type I portland-cement concretes.

Fineness—Higher finenesses, such as are typical for high-early-strength cements, increase the strengths of portland cement at early ages and up to approximately 28 days. The ef-

fect is most pronounced at ages of 10 to 20 h and diminishes as the age increases. At 2 to 3 months age, under moist-curing conditions, high-fineness cement (approximately 500 m²/kg, [2445 ft²/lb], Blaine) provides strengths approximately equal to those of normal fineness (350 m²/kg, [1711.5 ft²/lb], Blaine). At ages greater than 2 to 3 months, the strengths of normal-fineness cements become greater than the strengths of high-fineness cements if moist curing is continued so that hydration may proceed. If the cement content is held constant, very high fineness may increase the water requirement to such an extent that the early strength benefits are partially offset by the higher *w/c* required for workability and placement.

The strength characteristics of portland cements are also affected by the heating and cooling rate conditions in the kiln, the incorporation of trace elements into the crystal structure, and the particle size distribution. For these reasons, there are moderate differences in cements of apparently similar composition and fineness.

When compared at constant *w/c* by mass and comparable fineness, the strengths of portland cements are usually higher than the strengths of blended cements at ages of 7 days or less, and lower at ages of 28 days or more. Blended cements are frequently ground finer than portland cements to make their early strengths more comparable with those of portland cements.

6.4—Volume stability

Concrete is subject to changes in volume both during the setting and initial hardening process and after it has gained significant strength (L'Hermite 1962). Freshly mixed concrete is subject to volume changes from bleeding, temperature changes, cement hydration reactions, and drying. Bleeding is the segregation of water at the surface of concrete or under aggregate particles and horizontal reinforcing bars due to the settlement of solid ingredients. The amount of bleeding is greatly influenced by the slump, *w/cm*, grading and amount of fines in aggregates, and other variables relating to the proportioning of the concrete. Cement properties that tend to decrease bleeding include increased fineness, particularly increased amounts of the smallest sizes present at the cement, increased alkali content, and increased C₃A content (Neville 1963; Kosmatka 1994).

The normal cement hydration reactions occurring during setting and hardening tend to produce small changes in the volume of the hydrating paste. Except in the case of expansive cements, these volume changes have not been shown to be of significance to concrete performance. Cements that contain significantly larger-than-normal quantities of free lime (CaO) or periclase (MgO) may have a potential for detrimental expansion due to the hydration of these phases. Cements that exhibit such detrimental expansion are said to be unsound. Unsoundness is very rare in present-day commercial cements because a tendency to unsoundness can be detected readily by the autoclave expansion test, ASTM C 151, which is carried out routinely in the testing of cements.

Rapid evaporation of water from concrete surfaces during and after the finishing process, but before final setting, is a

major cause of plastic-shrinkage cracking. The rate of evaporation depends upon wind velocity, relative humidity, and temperatures of the air and concrete surface (see nomograph in ACI 308). Concrete constituents—cement, aggregates, and admixtures—and their proportions are known to affect the bleeding, settlement, setting time, and rheological properties of the freshly mixed concrete. Attempts to relate these properties to the occurrence or extent of plastic cracking, however, have been largely unsuccessful (Shalon 1978).

Concrete changes in volume with changes in temperature. The coefficient of linear thermal expansion is generally between 6 and 12 millionths per degree C (3 to 7 millionths per degree F). The value of a particular concrete is the average of that of the cement paste and the aggregate, taking into account their proportions (Walker et al. 1952). The coefficients for cement paste vary with the moisture content of the paste, but appear to be substantially unaffected by the type, brand, or other characteristics of the cement.

The amount and rate of drying shrinkage of concrete is dependent on a large number of factors, including amount and type of aggregate, mixing-water content, presence and type of admixtures, proportions of ingredients, and the particular materials used. These factors are discussed in ACI 209R. The aggregate restrains the relatively high shrinkage potential of the cement paste; however, in some instances, high shrinkage is encountered when the aggregate has a low modulus of elasticity, or the aggregate contains materials that also change volume with changes in moisture content. The combined effects of unfavorable materials and practices can produce concretes with drying shrinkage perhaps seven times as large as those that could be obtained with a favorable selection of materials and practices (Powers 1959).

Cements can have important effects on the drying shrinkage of concrete. The effects are minimized if the cement is maintained at an optimum SO₃ content (Alexander 1972; Hobbs 1977; Lerch 1946; Mardulier et al. 1967). In tests of a large number of cements, there was no clear separation in shrinkage potential of different types of cement. Shrinkages for different cements ranged from approximately 25% less than the median value to 40 or 50% above the median. Cements with SO₃ contents 0.5% less than optimum could have drying shrinkages increased by 10 to 24% (Alexander 1972). Optimum SO₃ increases with concrete temperature and may increase when certain water-reducing admixtures are used (Verbeck 1966); expansions, however, may increase with curing temperatures above 70 C (Taylor 1997). An increase of 1.0% SO₃ results in an increase of approximately 15 m²/kg (73 ft²/lb) in air-permeability fineness (Blaine, ASTM C 204). This air-permeability fineness increase occurs due to the easier grindability of the calcium sulfate source (compared to clinker) during the cement manufacturing process. Calcium sulfate generates more surface area. The sulfate phase or phases in a cement may also affect the optimum SO₃. Sulfate present in the clinker as alkali sulfate (for example, Na₂SO₄ or K₂SO₄ or [Na, K]₂SO₄, apththolite) behaves somewhat differently from sulfate present as interground gypsum or other form of calcium sulfate.

6.5—Elastic properties

The modulus of elasticity of concrete is a function of the modulus of elasticity of the cement paste (that forms the continuous matrix of concrete), the modulus of elasticity of the aggregate (the particles of which exist as inclusions within the matrix), and the volume concentrations of each. Several equations have been proposed to express the relationship. The relationship has been detailed by Hansen (1960), Counto (1964), and Popovics (1980).

Hydrated portland cement has a nearly constant modulus of elasticity regardless of cement composition. Thus, the modulus of elasticity of cement paste just as compressive strength is a function of the degree of filling of the space available to the hydration product. The greater the degree of filling, the higher the modulus. The degree of filling increases as the w/c decreases and the degree of hydration increases. For the practical range of w/c and for the ages for which the information normally is desired, the modulus of elasticity of cement paste is between 7 and 14 GPa (1 and 2×10^6 psi). Because these values are below those of most normalweight aggregates and because the volume concentration of aggregate is usually three to four times that of cement paste, the aggregate is usually the principal determinant of modulus of elasticity of concrete. The minor effect of cement is to increase the modulus of elasticity of concrete as w/cm decreases and degree of hydration increases, and to reduce the modulus as the volume concentration of cement paste increases.

6.6—Creep

The ingredient of concrete that creeps (that is, undergoes time-dependent volume changes under sustained load) is the hydrated cement paste. For practical purposes, the aggregate consists of perfectly elastic inclusions that do not creep. The volume and stiffness of the aggregate, therefore, are important parameters in determining the creep of concrete. The stiffer the aggregate, the less the creep. The property of cement paste that most affects creep is its porosity. Cement pastes of lower porosity and lower w/cm impart lower creep to the concrete. There is virtually no direct effect of cement composition except that cements with gypsum contents significantly below optimum may demonstrate increased creep (Neville 1959). The effect of w/c on creep was investigated by Wagner (cited in Neville and Meyers 1964), and his work has been accepted by ACI Committee 209 as the definitive relationship between w/c and creep. For more information on creep, see ACI 209R.

6.7—Permeability

The phase composition of cement of a given fineness affects permeability of a paste of a given w/c at a given age only insofar as it influences the rate of hydration. The ultimate porosity and permeability are unaffected (Powers et al. 1954). For a given w/c , however, Powers et al. found that coarse cements tended to produce pastes with higher porosities than finer cements. There is also some evidence that the permeability of portland-cement pastes increases with the curing temperature (Bakker 1983; Roy and Goto 1981).

Clearly the permeability of concrete depends on the permeability of the paste as well as that of the aggregate and the relative proportions of each. It also depends greatly on placing, finishing, and curing procedures, particularly consolidation (Grube 1985). Permeability of concrete to liquid water or water vapor is not a simple function of its porosity, but depends also on the size, distribution, and continuity of the pores in both the cement paste and the aggregates. The pores in cement paste are of two kinds. Gel pores, constituting approximately 28% of the paste volume, are interstitial spaces between the gel particles. They are very small (between 1.5 and 3.0 nm [5.9×10^{-8} and 1.2×10^{-7} in.] in diameter). Capillary pores are larger (of the order of 1 μm) and are irregularly distributed throughout the cement paste. Because capillary pores represent the remains of spaces that were originally filled with mixing-water, their volume can vary between 0 and 40%, depending on the original w/c and the degree of hydration.

As hydration progresses, permeability decreases. The flow of water through concrete is fundamentally similar to flow through any porous medium. Powers (1958) presented a relationship between permeability and capillary porosity of cement paste, as shown in Fig. 6.2. For pastes hydrated to the same degree, the permeability becomes lower, the lower the w/c . This is shown in Fig. 6.3, which presents data obtained by Powers et al. (1954) for pastes with 93% of the cement hydrated.

Air entrainment might be expected to increase the permeability of concrete. Because air entrainment reduces mixing-water requirement and bleeding and improves workability, however, the overall effect of air entrainment will usually be reduced permeability.

There is evidence from laboratory experiments that pastes and concretes made with blended hydraulic cements containing silica fume, raw or calcined natural pozzolans, fly ash, or slag have lower permeabilities than comparable pastes and concretes made with portland cements (Hooton 1986; McGrath and Hooton 1997). The concepts of permeability and diffusion are seldom differentiated (transport of liquid or gas through a medium, and transport of ions through an existing liquid or gas medium, respectively). A few references on these subjects are: Garboczi and Bentz (1992); Martys and Ferraris (1996); Halamickova et al. (1995). There are also electronic publications available (<http://ciks.CBT.Nist.Gov/Garboczi/>).

6.8—Corrosion of embedded steel

Concrete that is properly proportioned, compacted, and cured, provides excellent protection against corrosion of embedded steel when the cover over the steel is adequate. These requirements are now well-defined (Lea 1970; Biczok 1964).

For corrosion to occur, water and oxygen must be available at the surface of the embedded steel, and the normal passivating alkalinity of the concrete must have been reduced to below approximately pH 9 (or a higher pH in the presence of chlorides). A drop in the pH to approximately 9 is sometimes caused by carbonation of the concrete or leaching out of the protective alkaline constituents. When the con-

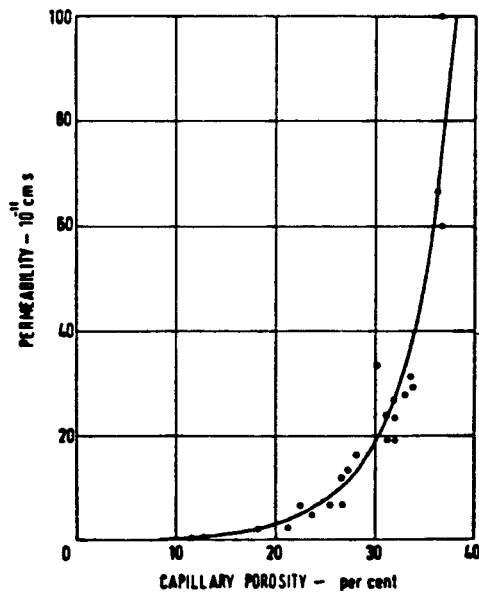


Fig. 6.2—Relationship between coefficient of permeability and capillary porosity for portland cement pastes (Powers 1958).

crete quality and cover are adequate, however, the most likely cause of any corrosion by far is the presence of chlorides. The presence of dissimilar metals embedded in concrete containing chloride is particularly conducive to rapid corrosion.

For portland cements, the cement type has only a minor effect on the level of protection of the steel. There are reports in the literature suggesting that cements with high alkali contents have shown superior performance in chloride environments. According to Verbeck (1968), the higher the C_3A content, the greater the amount of chloride ion that can be precipitated as calcium chloroaluminate, and thus be rendered innocuous, relative to steel corrosion. For this reason, Type V cements with their low C_3A contents make concretes that are less resistant to chloride-induced steel corrosion (Rasheeduz-zafar et al. 1992). There is some evidence that, when compared with portland cements, blended cements with substantial contents of mineral admixtures or blast-furnace slag have reduced permeabilities to chlorides (Bakker 1983; Short and Page 1982; Smolczyk 1984). Dense concrete of low permeability with adequate cover and low chloride levels should be used to provide protection against corrosion. Under severe exposure conditions, additional protection such as use of epoxy-coated reinforcement or corrosion-inhibiting admixtures may be needed to enhance corrosion protection. State-of-the-art information regarding corrosion of embedded steel in concrete is in ACI 222R.

6.9—Resistance to freezing and thawing

As discussed in ACI 201.2R, the vulnerability of concrete to damage by freezing and thawing depends on whether it becomes critically saturated with water. This, in turn, is a function of the pore structure of the paste and exposure to conditions that provide sufficient access to moisture. Critical

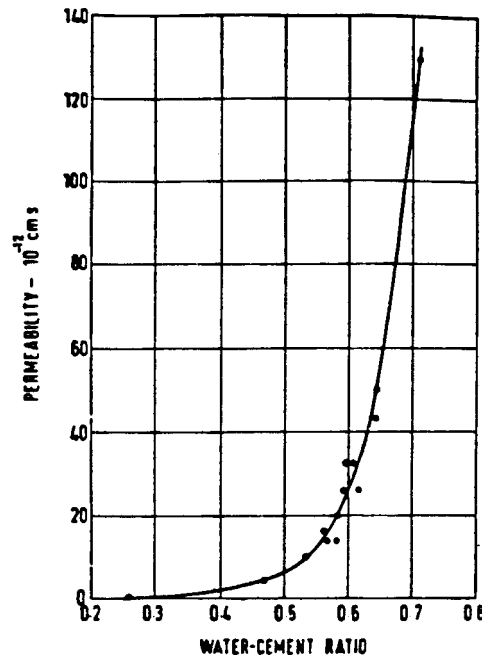


Fig. 6.3—Relationship between coefficient of permeability and w/c for mature portland cement pastes (Powers 1954).

saturation is the water content below which damage from freezing will not take place. It is usually approximately 90% of the volume required to fill the capillary-sized pores in the concrete completely. The beneficial effects of entrainment of a proper air-void system far outweigh influences of cement in providing resistance to freezing and thawing. Although, as shown in Table 2.1, air-entraining cement is available as an option, when resistance to freezing and thawing is required, it is usually preferable to make air-entrained concrete using an air-entraining admixture. Air-entraining cement may be useful where concrete is made under conditions where no quality control, particularly no means of measuring air content of freshly mixed concrete, is available.

The likelihood of a concrete becoming critically saturated with water depends, in part, on its permeability and on its air-void system. Thus, the effects of a cement on the resistance of a concrete to freezing and thawing depend on the degree to which its characteristics affect the permeability and the air-void system of the concrete.

As discussed earlier, permeability is reduced as hydration proceeds and therefore, as strength develops. Thus, the permeabilities of concretes of the same age and w/c will not be the same if the rate of strength gain, which is a function of cement characteristics, differs among the cements. Therefore, the properties of cement are important as they influence the strength and permeability of the concrete at the time of exposure to freezing and thawing. ACI 201.2R recommends that, before severe exposure to freezing and thawing, properly air-entrained concretes should have compressive strength of at least 28 MPa (4000 psi); the recommended minimum strength for moderate exposures is 21 MPa (3000 psi). This means that a thin section of concrete containing a cement with a lower rate of strength gain (such as some Type IP and Type

Table 6.4—Cement type and w/c recommendations for normalweight concrete exposed to sulfates

Exposure	Water soluble sulfate (SO ₄) in soil, %	Sulfate (SO ₄) in water, ppm	ASTM cement type of blend	w/c, maximum*
Mild	0.00 to 0.10	0 to 150	†	†
Moderate	0.10 to 0.20	150 to 1500	Type II, IP (MS), IS (MS), Type I + pozzolan‡	0.50
Severe	0.20 to 2.00	1500 to 10,000	Type V Type II + slag (> 60%) Type II + pozzolan‡	0.45
Very severe	Over 2.00	Over 10,000	Type V + pozzolan Type V + slag (>60%)	0.45

*A lower w/c may be necessary to prevent corrosion of embedded items (see Section 4.5.1.1 of ACI 201.2R).

†No special precautions needed.

‡A pozzolan that has been determined by test or service record to improve sulfate resistance when used with the type of cement to be employed in the work (see ACI 318).

IV cements) would generally require a longer curing period to have the same resistance to freezing and thawing as one with a cement with a higher rate of strength development.

Although the importance of a proper air-void system is paramount, the reduction of permeability by use of a low w/c and assurance of adequate hydration by proper curing are affected by the cement. All of the influences are covered in ACI 201.2R.

The influence of cement composition on resistance to freezing and thawing is important in only two respects:

1. The cement may affect the strength and permeability at the time freezing and thawing occur.
2. The cement may affect the air-entraining admixture requirements for production of a satisfactory air-void system.

6.10—Resistance to chemical attack

A primary requisite for chemical resistance of concrete is that it be made with the proper cement, cement-pozzolan combination, or cement-slag combination. Another important requirement is the use of a low w/c (0.40 or less; Stark 1989) with thorough compaction and proper curing to produce a dense concrete or mortar. Air entrainment is frequently helpful in that it reduces w/c for a given slump (Stark 1989).

Portland-cement based concretes are generally resistant to chemicals whose pH is higher than approximately 6. There are, however, notable exceptions and qualifying conditions. Tables 2.1, 2.2.3, and 2.2 of ACI 201.2R summarize factors leading to increasing or decreasing rate of deterioration. Sulfate attack (Table 6.4) is of special importance because of the widespread occurrence of sulfate in soils, seawater, groundwater, and chemical process effluents. Because of the tendency of high-C₃A portland cements to be susceptible to sulfate attack, the lower-C₃A cements (Types II and V) are often required for concretes to be used in sulfate environments (Tuthill 1936). Reducing the water to total cementi-

tious material, as it relates to decreased permeability of hardened concrete, is the single-most effective means of increasing resistance to sulfate attack (Stark 1989; Stark 1984). More detailed information about the response and protection of concretes to the various types of chemical attack is available in references listed (Czernin 1962; Eustache and Magan 1972; Fulton 1961; Hansen 1966; Kleinlogel 1960; Kuenning 1966; Langelier 1936; B. Mather 1966, 1979; K. Mather 1977; Miller and Manson 1951; Neville 1963a; PCA 1990; Robson 1962; Taylor 1964; USBR 1981; Woods 1968; ACI 201.2R; ACI 515.1R; and ACI 548.1R).

Calcium-aluminate cement may be required where concrete is to be used in a particularly aggressive environment in the pH range from 3.5 to 6, as calcium-aluminate cement concretes (see Appendix) resist a number of agents that attack portland-cement concretes.

If a mortar is intended to be chemically resistant to a particular solution, then the coarse aggregate used with it to make concrete should normally be similarly resistant. If an ordinary (non-acid-resistant) mortar is to be used in concrete exposed to acid, however, it may be advantageous to use acid-soluble coarse aggregate, such as limestone. In this case, the quantity of acid available to attack the mortar would be reduced by its attack on the sacrificial coarse aggregate.

Deicing chemicals such as sodium chloride and calcium chloride accelerate freezing and thawing damage to non-frost-resistant portland-cement concrete. These materials, by melting the ice and snow and suppressing the freezing point of the water due to the increased ion concentration, tend to increase the degree of saturation and hence increase the likelihood of damage by freezing and thawing. Entrained air is a necessary requirement for concrete to be frost resistant. Sodium chloride, used as a deicing agent, may aggravate alkali-silica reactions in concrete with reactive aggregates. Consequently, in climatic environments that cause deicing to be used in winter seasons and where summers are warm, precautions to prevent both kinds of deleterious reactions are appropriate.

6.11—Resistance to high temperatures

If properly cured and dried, normal portland-cement concretes can withstand temperatures up to 100 C (212 F) with little loss of strength. They can also withstand temperatures up to approximately 300 C (570 F) for several hours with only a slow loss of strength due to partial dehydration and alteration of the calcium silicate hydrate. If resistance to higher temperatures is needed, the properties of both the cement and the aggregate must be considered. Portland cements are being used in applications to temperatures as high as 1100 C (2000 F) with high temperature stable aggregates in noncyclic (repeated heating and cooling) operations. For the most demanding applications, high-purity, calcium-aluminate cements (Appendix) are combined with selected refractory aggregates to produce refractory concretes suitable for use at temperatures up to 1870 C (3400 F). ACI SP-57, ACI SP-74, ACI 547R, and 547.1R provide more information on refractory concretes using hydraulic-cement binders. Caution is re-

quired regarding the residual strength of concrete in structures that have suffered severe damage due to accidental fires. A decrease in strength and toughness of ordinary concrete may occur not only during the fire, but also during and after cooling of the structure.

6.12—Cement-aggregate reactions

In dense concrete, the hydration of cement develops strong adhesion bonding to the surfaces of aggregate particles. Where the pore fluid touches siliceous aggregate particles, calcium alkali-silica hydrates may form as the bonding material. Limestone may develop strong bonding by epitaxial interactions (crystal growth on other crystals resulting in similar structural orientation) between the calcium hydroxide and the limestone. These bond reactions constitute the reasons why concrete can be made to be a monolithic material.

The term “alkali-aggregate reactions” (AAR) is used for alkali-silica reactions (ASR) and alkali-carbonate rock reactions (ACR). These reactions with aggregate particles can cause fracturing and, sometimes, expansions or warping of field concrete as well as of test specimens of concrete or mortar.

Aggregate constituents readily decomposed by oxidation in the presence of water include a number of unstable sulfides of iron often associated with coal, lignite, and black shale. Their presence in aggregates may cause severe acid attack on concrete, and also expansive reactions due to formation of excessive amounts of calcium sulfoaluminate (ettringite). Aggregate constituents or contaminants that hydrate include anhydrite, periclase, quicklime, and portland-cement clinker. In sand and coarse-aggregate size ranges, some of these reactions may cause expansions to occur.

Alkali-silica reactions—The most important cement-aggregate reactions from the standpoint of potential for damage to mortar or concrete in service are those with alkalis. Of these, the best-known and longest-studied is the alkali-silica reaction. This reaction results from the presence of pore fluids with pH values of 13 or higher in the pores of the concrete. These are generated by the interaction of minor amounts of potassium or sodium, or both, in the cement, usually in the form of sulfates, during the early phase of the cement hydration, with the liquid phase in hydrating cement. As a result of the removal of calcium and sulfate ions as ettringite forms, sodium and potassium cations and hydroxyl ions (OH^-) accumulate in the liquid phase. During further hydration, the pH increases, and this renders the siliceous aggregate particles more soluble by the alkali-hydroxide. Elevated temperatures, as in summer seasons and hot climates, will further suppress the calcium hydroxide solubility.

Siliceous particles of cement-particle size, (that is, pozzolans and ground granulated blast-furnace slag) or finer (silica fume), in concrete may cause a favorable modification of an ASR, which densifies the concrete and concurrently exhausts the alkali-hydroxides so as to prevent deleterious reactions with aggregate particles.

Depending on the hydroxyl-ion concentration, the presence and proportion of reactive aggregate particles and their physical characteristics, the w/c , and the cement in the concrete, the product of the alkali-silica reaction may be a hydrous calcium-alkali-silica gel that is expansive only to a limited degree, or a hydrous alkali-silica gel that may imbibe water and expand much more and disrupt concrete.

Although opal is not a common constituent of aggregates, it has been used extensively in research on ASR. The first extensively studied case of ASR involved an aggregate called siliceous magnesium limestone that contained opal as its alkali-reactive ingredient. Small opaline shale grains, common in some aggregates in the middle western U.S., create small popouts on finished flatwork in 24 h. When all of the reactive aggregates that have affected structures are considered, more behave quite differently from opal than behave like it. The original period of investigation of alkali-silica reaction, from 1940 to about 1960, focused on many examples of rapidly reacting aggregates, mostly from the western U.S., and led to the tentative conclusion that rapid reaction will usually take place if the aggregate is reactive and the alkali content of the cement is high enough. For more information see “Guide Specifications to Concrete Subject to Alkali-Silica Reaction” (PCA 1995). Since that time, more and more structures containing aggregates with fairly low rates of expansive reactivity have been found that were not recognized as having problems involving alkali-silica reactions until the structures were 20 to 30, or more, years old. When evaluated in mortar bars in accordance with ASTM C 227, many of these aggregates produce expansions less than the criteria suggested in the Appendix to ASTM C 33 of 0.10% at 6 months. These reactive rock types include certain granite gneisses, schists, phyllites, quartzites, argillites, and greywackes, all of which contain microcrystalline and strained quartz (Dolar-Mantuani 1983; Buck 1983).

The use of low-alkali cements has been shown to control many known reactive aggregates. The use of low-alkali cement alone (not more than 0.60% alkali as equivalent Na_2O [ASTM C 150]), however, has been found to not always effectively control expansion due to alkali-silica reactivity. This situation has developed primarily with glassy or poorly crystalline volcanic rocks of rhyolitic to andesitic composition. Also, alkali from sources other than the cement, such as deicer salts, fly ashes, and alkalis initially present in aggregates, may exacerbate the problem. The extent of damage to the structures varies widely, probably as a result of differences in concrete proportions, w/c , mean annual relative humidity, annual precipitation, and mean annual temperature.

Table 6.5 provides information on reactive substances found in aggregates. It indicates that rocks containing opal, chalcedony, quartz, or may be reactive. It does not say whether the reaction will occur as a harmless modification or cause damage in days, months, or 1 to 50 yr after a structure is built. Low-silica rocks, like most basalts and diabbases, limestones without siliceous inclusions, and quartz sand are usually not reactive.

Table 6.5—Some reactive substances found in aggregates

Reactive substance	Chemical composition	Physical character
Opal	SiO ₂ nH ₂ O	Amorphous by light microscopy; includes a wide range of discolored cristobalite-tridymite stacking; micromorphology usually spherical when known (precious opal is made up of spherical bodies with ordered domains)
Chalcedony	SiO ₂ H ₂ O and air	Microcrystalline to cryptocrystalline, often fibrous
Quartz	SiO ₂	a) Microcrystalline to cryptocrystalline b) Crystalline but intensely strained or fractured and inclusion-filled, or both
Cristobalite	SiO ₂	Crystalline
Tridymite	SiO ₂	Crystalline
Glass from acid to intermediate rocks, and their cryptocrystalline devitrification products	Siliceous, with smaller proportions of Al ₂ O ₃ , Fe ₂ O ₃ , alkaline earths, and alkalis	Glass or cryptocrystalline materials as the matrix of volcanic rocks or fragments in the tuffs
Synthetic* siliceous glasses	Siliceous, with smaller proportions of alkalis, alumina, with or without other substances	Glass
Reactive rocks		
Opaline chert, chalcedonic chert, quartzose chert, opaline limestones and dolomites, cherty carbonate rocks; rhyolites, dacites, andesites, and their tuffs; opaline shales; phyllites and metamorphic subgraywackes containing strained quartz, argillites, quartzites, schists, granite gneiss, sandstones, and shales.		

*Synthetic glass is found in aggregates downstream from cities and towns.

To determine potential for expansive reactivity, aggregates should be evaluated from their service records, taking into account the alkali contents of the cementitious materials used, whether the aggregate was used alone or in combination with other aggregate, and the exposure conditions and of the concrete. In addition to a petrographic examination in accordance with procedures in ASTM C 295, the aggregate should be evaluated for potential for expansive alkali-silica reactivity using ASTM C 1260 or ASTM C 1293, or both. ASTM C 1260 requires 16 days to complete, and is overly severe with respect to anticipated performance in field structures (ASTM C 1260 Section 3.1). That is, if the aggregate is found to be innocuous in this test, one can be virtually certain that it will not react deleteriously in concrete structures. If the aggregate produces excessive expansion in ASTM C 1260, then further information is desirable, or certain mixture proportion precautions (such as the incorporation of pozzolans or slag) need to be taken in field concrete to avoid potential for expansive reactivity. For more information see “Guide Specification to Concrete Subject to Alkali-Silica Reaction” (PCA 1995).

If potentially reactive aggregates are to be used, the preferred remedies in random order are:

1. Specify use of a pozzolan, slag, or silica fume meeting the requirements of ASTM C 618, C 989, or C 1240, respectively. This can be accomplished either as a replacement for, or addition to, the portland cement, depending on other requirements such as strength development and economics. It should be pointed out that there is a possibility of increased alkali-silica reaction when small (pessimum) amounts, less than 15% by mass, of certain pozzolans are used (COE-EM 1110-2-2000).
2. Use a blended hydraulic cement meeting ASTM C 595 or ASTM C 1157 and invoking the optional requirement relating to alkali-silica mortar-bar expansion.

3. If pozzolans and blended hydraulic cements are unavailable, a low-alkali portland cement should be considered. Effectiveness of the cement alkali level should be tested by the appropriate test methods or evaluation should be based on the historical field performance of those materials.

4. The use of ASR-limiting chemical compounds (such as lithium) as an integral part of the cementitious materials or as an additive to the concrete has been found to provide ASR reduction (Stark 1993).

5. Limiting total alkali content of the concrete. See CAN/CSA-A23.1-M90.

Alkali-carbonate rock reactions—The second category of potentially damaging alkali-aggregate reactions is the alkali-carbonate rock reaction. Instances of internal expansion and cracking sometimes followed by disintegration of concrete made with crushed carbonate rock aggregates were described in the 1950s and 1960s from Ontario, Virginia, and a few other places. The phenomenon is generally associated with rocks that are neither approaching pure calcium carbonate, nor pure dolomite, CaMg (CO₃)₂; rather, such rocks consist of crystals of the mineral dolomite in a fine-grained matrix of clay and calcite. These rocks may react by decomposition of dolomite to form magnesium hydroxide or by reactions that also involve swelling of the clay constituent. ASTM C 586 can be used to identify carbonate rocks capable of expansive reaction with alkalis. Such tests should be used to supplement data from field service, petrographic examination, and tests of aggregate in concrete. An ASTM method for testing the aggregate in concrete has been developed (ASTM C 1105); and one has been adopted in Canada as CSA CAN3-A23.2-14A-M77. Appendix B to CAN-3-A23.2-M77, Section B3.5, referring to Test Method A23.2-14A, suggests limits on allowable expansion and notes that such expansive aggregates can generally be used safely with a low-alkali cement. ACI

201.2R suggests “low-alkali cement (probably 0.4% combined alkali or lower).” Combined alkali is normally calculated as $\text{Na}_2\text{O} + (0.658 \times \% \text{K}_2\text{O})$.

6.13—Color

The most important aspect of concrete color is usually its uniformity. The exact color of a concrete, however, is sometimes important to an architect or owner for its contribution to the esthetic value of a structure (Gage 1970). Variations in the color of concrete due to the cement may be minimized by purchasing the cement from a single plant and by strictly adhering to uniform quality-control procedures for proportioning, mixing, placing, forming, and curing the concrete.

The color of a concrete is dependent on, among other factors, the cement and other materials used. Cement color reflects chemical composition and processing conditions. Usually, cement colors vary from white to shades of gray and brown. Color differences are often discernible between cements manufactured from different plants. The influence on concrete color from the variation in the color of cement from a single plant is typically outweighed by concrete finishing and curing practices, w/cm , and use of mineral admixtures. White cements contain very little iron or other transition metal (for example, chromium, manganese, vanadium). Each transition metal makes its own contribution to cement color. For example, experimental cements made with unusually large quantities of chromium (but with no other transition metal present) are quite green. The common grey and brownish colors of commercial cements are primarily due to the iron compounds in them; small quantities of other transition metals also affect the color. Concretes made using ground granulated iron blast-furnace slag are typically dark green initially, but this fades on oxidation and the concrete typically becomes whiter than a portland-cement concrete. This is discussed in ACI 233R. Pigments are sometimes added to produce colored cements; they are covered by ASTM C 979.

The contribution of cement color to the color of the concrete depends on the pigments, fly ash, sand, or other fine particles present. Variations in color and grading of all fine particles may affect concrete color uniformity. Other factors relating to cement that may cause variations in concrete color are mixture proportions, moisture movement, curing conditions, efflorescence, and surface carbonation.

Mixture proportions—If, as is usual, the cement is the main contributor to the color of concrete, the color will become more intense and darker with increased cement content or decreased w/c .

Moisture movement—Moisture movement in concrete may affect the color of concrete as a result of changes in w/c at the surface through bleeding, absorption into form faces, and loss of water or mortar through formwork joints. Absorption of water into the form face while the concrete is hardening may cause darkening of the concrete.

Nonuniform curing—Concrete that has been allowed to dry quickly will initially be lighter in color than concrete that has been kept moist. As a result, differences in color from

one area of the concrete to another may occur when formwork is removed at significantly different ages after placement. The differences, however, will become less marked with time. Other factors being the same, concrete surfaces cured by different methods or processes, such as steam-cured versus not steam-cured, are likely to exhibit color differences. These differences may or may not diminish over time dependent upon natural weathering, chemical exposures or incorporation of exposure contaminants.

Efflorescence—Efflorescence is a deposit sometimes seen on surfaces of concrete or masonry. On concrete, the deposits are generally calcium carbonate, which is not readily soluble in water, although occasionally they contain sodium or potassium sulfate or bicarbonate, which are easily dissolved in water. Some of the abundant calcium hydroxide produced by normal cement hydration reactions is brought to the surface, deposited, and converted to calcium carbonate by the carbon dioxide in the air (Ritchie 1960; Taylor 1964). Incidence of efflorescence is regulated largely by the chemical composition of the concrete, the permeability and texture of the concrete surface and the rate of surface drying.

CHAPTER 7—CEMENT STORAGE AND DELIVERY

The performance of a cement in concrete can be affected by the conditions under which the cement has been stored and its handling during delivery. These effects will be reviewed to complete the discussions of factors affecting the performance of cements. This chapter relates to the handling of cement during delivery. The requirements for the protection of workers will also be mentioned.

Storage—Cement can be stored for an indefinite period of time as long as it is protected from moisture (including the moisture in the air). Storage life may be more limited in small bins under conditions where moisture might condense on the inside of the bins, but satisfactory storage for several months is not unusual.

The storage life of cement in paper bags is much more limited. In damp climates or damp weather conditions, cement can become lumpy in as little as 4 to 6 weeks. Special moisture-resistant bags are frequently used with white portland cements and some gray cements, particularly if over-water shipment is anticipated. Storage life in these bags is longer, but still limited.

Hard lumps are evidence of reaction with moisture. This condition is often referred to as warehouse set. One of the definitions given in ACI 116R is: “The partial hydration of cement stored for a time and exposed to atmospheric moisture, or mechanical compaction occurring during storage.” If the lumps are screened out, the remaining cement is normally satisfactory for use. Measures for minimizing the likelihood of warehouse set of packaged cement include the following:

- Use stock on a first-in, first-out basis.
- Keep storage areas dry.
- Store bags on pallets above ground.
- Store bags under a cover that will protect them from moisture.

Soft lumps may occur in the lower bags in a high stack simply from the pressure of the bags above. Rolling the bags a few times normally breaks up these lumps.

Measures for minimizing the formation of hard lumps during bulk storage and during transit include the following:

- Periodically inspect the loading hatches of bulk carriers for watertightness.
- Keep loading hatches closed when not in use.
- Compressed-air transit systems should have water traps and, in areas of extremely high humidity, the air lines should be equipped with air driers.
- Storage bins should be inspected periodically for possible water leaks (that is, roof, hatch covers, and welded seams).

Warehouse set of a different type can occur with fresh cement in storage at the manufacturing plant. This type of warehouse set, more appropriately called partial hydration, is characterized by soft lumps (lumps that break under light finger pressure) and reduced flowability. This condition can develop within a few days after production and is caused by chemical reaction of cement components during storage. Once the flow has been started and the rigidity of the bulk material broken, however, the potential for reoccurrence of the flow problems is practically nil. The tendency of cements to undergo prehydration depends on several factors, including chemical composition, storage temperature, grinding temperature, and the moisture available during grinding. The effect of storage on the quality of cement is generally negligible, but it can cause false setting and a slight loss in strength development (Richartz 1973; Thiesen and Johansen 1975).

Pack set (sticky cement)—Pack set of a cement material is evidenced by a higher than normal resistance to the initiation of flow. Pack set may be caused by interlocking particles, mechanical compaction, or electrostatic attraction between particles. The use of an appropriate amount of processing additions (complying with ASTM C 465) during the finish grinding process can typically eliminate the occurrence of the phenomena. Most often, a relatively small amount of mechanical effort will overcome the resistance to flow (Grace 1977).

The generally accepted explanation of pack set is that the surfaces created during grinding of portland cement clinker have areas with unsatisfied electrical forces. The active surfaces cause interparticle attraction resulting in agglomeration and pack set (Hansen and Offutt 1969; Mardulier 1961). The mechanism of pack set is different from that of warehouse set, which, as mentioned previously, is a loss of flowability caused by partial hydration of cement.

Cement manufacturers have long been familiar with the annoying problem of pack set. In the 1940s and early 1950s, it was the source of frequent customer complaints. Since the 1960s, wide acceptance of grinding aids by cement manufacturers has almost eliminated pack set problems. The grinding aids are added either with the mill feed or injected directly into the mill (Duda 1976).

Most grinding aids are substances that are adsorbed on the surfaces of the cement particles and reduce the surface energy so that no bonds remain to attract other particles and cause

agglomeration and pack set. In addition to inhibiting pack set, grinding aids prevent ball coating and increase mill efficiency. The resulting reduction in energy cost usually offsets the cost of the grinding aid.

ASTM C 150 permits the use of grinding aids in the manufacture of portland cement, provided that such materials in the amounts used have been shown not to be harmful to the quality of the finished cement. This is demonstrated by tests in accordance with ASTM C 465.

Delivery—Cement is available as a bulk powder or in paper bags. Bulk powder is shipped using closed tanker trucks, covered rail hopper cars, air-unloading tank cars, covered barges, or ships with closed compartments. Occasionally, bulk cement is delivered to very remote sites in large rubber containers (approximately 1 m³ or yd³ in size).

Contamination—Most contamination of cements occurs during shipping and handling. It is generally caused by failure to clean trucks and railcars in which it is to be shipped. Examples of effects that can result from contamination by common materials follow (Kleinogel 1960).

Very small amounts of sugar and starch can cause significant retardation, as can small amounts of lead, zinc, and copper compounds.

Ammonium fertilizers in cement will generate ammonia gas when the cement comes into contact with water. The smell of ammonia is unpleasant, even though the amount of fertilizer may be small and not harmful. With ammonium sulfate contamination, the sulfate content of the concrete may be increased to a level at which unsound concrete might result. Among other ammonium compounds, phosphates can cause retardation, and the nitrates could promote corrosion of reinforcing steel.

Contamination with dead-burned (slow reaction rate with water) dolomite, such as is used in the manufacture of refractories, can cause popouts or even unsound concrete. Contamination as low as 0.1% by volume of concrete can cause popouts, and an increase to 0.3% can result in self-destruction when the concrete is exposed to water (Scanlon, Connolly 1994).

Trace amounts of some contaminants may cause no problems. They may be tolerable in noncritical concrete if the concrete sets and gains strength in a normal manner. If there is any doubt, the contaminant should be identified to make sure that it will not cause problems with durability or strength, and the concentration of it should be shown to be minimal. Despite the fact that small amounts of some contaminants may be tolerable in noncritical concrete, strong efforts should be exerted to prevent contamination of cement and concrete.

Pneumatic (air) transport of portland cement can cause cement particle agglomeration, which is not normally a problem unless the concrete mixing time is very short (3 min or less). This particle agglomeration may be the result of electrostatic attraction, or particle hydration from water condensed out of the compressed air or is used in the transfer of cements, both within cement plants and terminals and in delivery to mixers in concrete plants. The amount of aeration in

these processes is normally so small that cement properties are not impaired.

Air handling frequently increases the apparent air permeability (Blaine fineness) though other properties are not affected. A fineness test on a field sample may be 10 or 20 m²/kg higher than that determined by the manufacturer during grinding. Aeration for long periods can induce slump loss, increase water requirement, and false set. It should therefore be avoided.

Cement in paper bags is subject to aeration. As a consequence, false set is not uncommon in bagged cement, and can occur long before there is evidence of hard lumps.

The top 25 to 50 mm (1 to 2 in.) layer of cement in a bulk truck or railroad car is aerated by the air above it. To minimize this effect, cements should be transported and stored in full, closed containers. A sample skimmed from the top may show false set that is not typical of the shipment as a whole. When the car or truck is unloaded and the top layer is mixed with the underlying cement, the cement usually performs normally. For this reason, cement should be sampled by digging below the surface layer.

Protection of workers—Workers should protect their skin and eyes from cement and mixtures containing cement, as cement can cause serious dermatitis and eye injuries. Skin contact with freshly mixed cement paste, mortar, concrete, or grout should be avoided. When contact occurs, skin areas should be washed promptly with water.

If any cement or cement mixture gets into the eyes, they should be flushed immediately and repeatedly with water. The person should get prompt medical attention.

CHAPTER 8—SAMPLING AND TESTING OF HYDRAULIC CEMENTS FOR CONFORMANCE TO SPECIFICATIONS

Preceding chapters have discussed factors affecting the performance of cements in concretes. To apply this knowledge, the user must know if the cements being purchased meet the appropriate specifications limits and whether, within the specification limits, a satisfactory degree of uniformity is being maintained. This chapter discusses the sampling and testing of cements to show their conformance to specifications and to indicate the magnitude of batch-to-batch variations. It also indicates the types of information the user may be able to obtain from the manufacturer in the user does not conduct a sampling and testing program.

Most building codes and job specifications require cement that meets the requirements of an applicable material specification such as ASTM C 150, ASTM C 595, ASTM C 1157, AASHTO M 85, or AASHTO M 240 in the U.S., or the CSA CAN 3-A5 and CSA A 362 in Canada. The ASTM cement specifications cite ASTM C 183 as the standard procedure for acceptance sampling and testing.

Although compliance with specification requirements can be assured by sampling and testing by the producer, the purchaser, or the purchaser's representative, only a few purchasers sample or test cement. Most often, the purchaser accepts the results supplied by the producer after proper cer-

tification or laboratory accreditation. There are several reasons for this. First, complete tests are considered unduly expensive by all but a few large specifiers or purchasers. Second, few commercial testing laboratories have a sufficient volume of cement testing to maintain an adequately skilled staff to be able to offer competent, timely, cement-testing services, whereas cement companies must maintain competence in cement testing at all times. Third, it is usually impractical to provide sufficient cement storage capacity to permit completion of tests requiring many days, such as 28-day strength or heat of hydration, before the cement is used in concrete. As a result, almost all cement testing is done by cement manufacturers. Among purchasers, only a few large users, such as the Corps of Engineers and state transportation departments, regularly test cement.

Tests carried out in the cement-plant laboratory are likely to include chemical analysis (ASTM C 114), autoclave expansion (ASTM C 151), surface area (Blaine method ASTM C 204), mortar cube strengths (ASTM C 109), and setting time (ASTM C 191 or C 266). Some purchasers use surface area measurements as an indication of uniformity.

Four main approaches (with variations) are customarily used for acceptance testing of cements.

8.1—The cement mill test report

The cement producer tests the cement, generally as it is being placed in a silo for shipment, and furnishes a Mill Test Report. The significance of the test data given in a mill test report varies from plant to plant. In some cases, the data are typical values that can be expected to be representative of cement shipped from a given bin or silo. In other cases, a composite sample or series of grab samples is collected from the mill stream during the time the silo or bin is being filled, and the data given in the mill test report are those obtained by testing the composite sample. The sample may also be obtained during transfer, or from storage by means of a tube sampler. Because of such differences, there is usually no assurance that the cement being shipped will have exactly the same physical and chemical characteristics as given in the mill test report. In rare instances, the mill test report may represent as much as a week's production; more often, it represents production in a period of between a few hours and 2 days.

The principal purpose of the mill test report is to certify that the cement in question complies with ASTM specifications (or other specifications as required by contract) and to provide typical test data for the cement. The purchaser relies primarily on the mill test results, although the purchaser may occasionally take random (or systematic) samples that are held for possible testing if there is a change in the performance, color, or some other characteristic of the concrete in which the cement was used. The purchaser may require the producer's testing laboratory to have established its credibility by participation in the reference sample and laboratory inspection programs of the ASTM-sponsored Cement and Concrete Reference Laboratory that is managed by the National Institute of Standards and Technology (NIST). Another tool that can be used by the purchaser to evaluate cement strength uniformity from a sin-

Table 8.1—Example of a sampling and testing schedule

Sample location*	Sample	Test	Frequency
1	Limestone being fed to raw mill	CO ₂ content	1/shift
2	Clay being fed to raw mill	H ₂ O content (if wet process) % finer than 75 μ m (No. 200) sieve	1/shift
3	Raw mill discharge and blending tank	CO ₂ content	2/shift
		H ₂ O content	2/shift
4	Kiln feed (from blending silo or tank)	CO ₂ content	2/shift
		H ₂ O content (if wet process)	2/shift
		% finer than 300 μ m (No. 50) sieve	2/shift
		% finer than 75 μ m (No. 200) sieve	2/shift
5	Clinker	Free CaO	2/shift
		Complete chemical analysis	1/shift
6	Cement	Free CaO	1/shift
		SO ₃	4/shift
		Fineness (air permeability)	4/shift
		Complete chemical analysis	1/day
		Complete physical tests	1/day
7	Cement	Retain sample for 120 days	—

*See Fig. 8.1.

gle source, is ASTM C 917. The ASTM C 917 report is a statistical summary of ASTM C 109 compressive strength tests on randomly sampled shipments.

8.2—Sealed silos

In the past, cement for special jobs was often placed in silos reserved for a single user. After sampling and testing by the user, the silo was sealed and reserved for the user's exclusive use. In recent times, this practice has become rare as it requires special silos at the cement plant and reserved bins at a concrete plant. Because it is unrealistic to expect 28-day results prior to shipment and it is often difficult for a cement manufacturer to provide silo storage sufficient to obtain 7-day results prior to shipment, the quality management approach described in the quality management section is being used increasingly.

8.3—Cement certification

The current trend with state transportation departments is to accept certification by the cement producer that the cement complies with specifications. As will be discussed later, the cement producer has a variety of types of information available (production and quality-control records) that may permit him to certify conformance without much, if any, additional testing of the product as it is shipped.

8.4—Quality management

Some Federal and other government agencies operate using a cement quality management approach based on statistical analysis of cement company test results coupled with periodic sampling and testing.

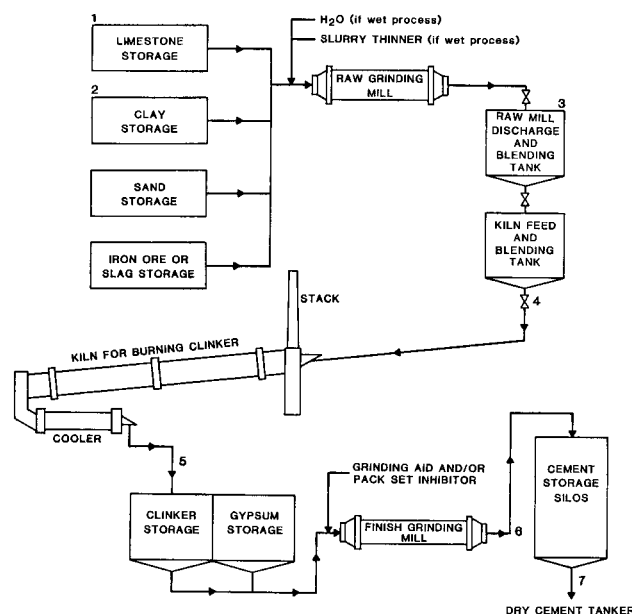


Fig. 8.1—Flowchart of a portland cement manufacturing operation showing points from which quality control samples might be taken by the producer.

8.4.1 Testing by the producer—The testing performed by the cement producer during various phases of the production varies greatly in frequency, depending upon the uniformity of the raw material, the uniformity of the fuel, particularly coal, and the physical plant facilities. Generally, composite samples of each cement type are analyzed for chemical and physical properties. Upon request, the mill test report can be furnished to the purchaser.

Figure 8.1 shows a cement manufacturing flowchart. The points at which quality-control samples are often taken are indicated by numbers. Table 8.1 shows an example of a sampling and testing schedule.

Sampling point

Each sampling point listed in Table 8.1 is described in the numbered items below. The item numbers refer to the sampling locations of Table 8.1.

1, 2. Sampling of the various individual raw materials that are to be blended.

3. Checking of the ground and homogenized blend of material for bulk chemical composition and fineness prior to burning. This blend may be contained in one or more storage containers and may be used directly or blended with the contents of other storage containers until the desired composition (kiln feed) is obtained prior to burning.

4. Sampling as the kiln feed is pumped to the kiln system as a final check before burning.

5. Samples of the kiln-fired clinker can be taken by the manufacturer. At this point, parameters such as bulk chemical composition and free lime content can be determined. Powder mount or polished section microscopic examination of the clinker is routinely used for additional process quality control. From this information, the kiln firing system is optimized and controlled as well as adjustments to the kiln feed chemical composition to accommodate the effects of kiln

dust loss and coal combustion ash. After leaving the kiln system, clinker can be stored in one or more storage containers prior to finish mill grinding. Clinker and calcium sulfate (usually gypsum) are ground in a mill to the desired fineness and at the necessary ratio to achieve the desired total sulfate content. The finish mill product is sampled frequently during grinding to determine its fineness and total sulfate content. Meanwhile, the clinker and gypsum feeders are usually monitored by computer control to confirm that the proper ratio of materials is being delivered to the grinding mill.

6. The finished product is stored in one or more storage silos (typically metal or concrete) until loaded into railcars, trucks, or until bagging operations occur.

7. Sampling of the finished cement can occur at the point where the cement is discharged from the storage container or along transfer lines or at the point of discharge into the final transport vehicle. Sampling can occur during or after the transport vehicle is loaded.

8.4.2 Sampling by the purchaser—When the purchaser desires to sample and test the cement to verify compliance with the applicable specification, sampling should be performed in accordance with ASTM C 183. The procedures described in that standard are not intended for use by the producer for quality control in manufacturing.

Several standard methods of sampling hydraulic cement are described in ASTM C 183. Cement samples may be obtained as grab samples in one operation, or as composite samples obtained by an automatic sampling device that continuously samples a cement stream at predetermined intervals. Grab samples, obtained at prescribed intervals, may be combined to provide a composite or test sample. The cement may be sampled at any of several places: 1) from the conveyor delivering to bulk storage; 2) during transfer of cement; 3) from bulk storage at points of discharge; 4) from bulk storage and bulk shipment by means of a slotted tube sampler or sampling pipe; 5) from packaged cement by means of a tube sampler; and 6) from bulk shipment by car or truck. Depending on where the sample is taken, the sample can represent cement in production, cement in storage, or cement being shipped.

Samples of cement should be protected by placing them directly in moisture-proof, airtight containers to avoid moisture absorption and aeration. Before testing the samples should be passed through a 850 μm (No. 20) sieve. Caution should be used to minimize aeration of the cement.

8.4.3 Testing by purchaser—The rate of testing should depend upon the quality history of the source. Samples for testing, from each lot of cement, should be collected in accordance with the ASTM C 183 method.

Test methods for hydraulic cements are normally the appropriate ASTM test methods listed in the *Annual Book of ASTM Standards*. Testing by the purchaser to confirm product compliance may include methods for either standard or optional requirements. ASTM C 150, ASTM C 1157, ASTM C 595, and ASTM C 845 list both the standard and optional requirements for each type of cement. Additional

information on special requirements should be available on request from the producer.

All tests are subject to testing variations. Larger variations are usually experienced between laboratories than is observed within a single laboratory. Expected variations are normally indicated under the precision and bias section of the test method. Testing cement properly requires a qualified laboratory with demonstrated experience in the test methods being used. This demonstration of performance can be determined from data derived from participation in the Cement and Concrete Reference Laboratory (CCRL) sample proficiency testing, internal cooperative testing, or other defined and comparable quality-control programs.

However achieved, adequate tests of cement, as well as concrete, are important. The cost of good testing and quality control is small compared with the cost of removal and replacement of concrete in a structure.

CHAPTER 9—REFERENCES

9.1—Recommended references

The documents of the various standards-producing organizations referred to in this document are listed below with their serial designation.

American Association of State Highway and Transportation Officials

- M-85 Specification for Portland Cements
- M-240 Specification for Blended Hydraulic Cements

American Concrete Institute

- 116R Cement and Concrete Terminology
- 201.2R Guide to Durable Concrete
- 207.1R Mass Concrete Structures
- 207.2R Effect of Restraint, Volume Change, and Reinforcement on Cracking of Massive Concrete
- 209R Prediction of Creep, Shrinkage, and Temperature Effects in Concrete Structures
- 212.3R Chemical Admixtures for Concrete
- 212.4R Guide for the Use of High-Range Water-Reducing Admixtures (Superplasticizers) in Concrete
- 222R Corrosion of Metals in Concrete
- 223 Standard Practice for the Use of Shrinkage-Compensating Concrete
- 224R Control of Cracking in Concrete Structures
- 232.1R Use of Natural Pozzolans in Concrete
- 232.2R Use of Fly Ash in Concrete
- 233R Ground Granulated Blast-Furnace Slag as a Cementitious Constituent in Concrete and Mortar
- 234R Guide to the Use of Silica Fume in Concrete
- 305R Hot Weather Concreting
- 308 Standard Practice for Curing Concrete
- 318 Building Code Requirements for Structural Concrete
- 515.1R Guide to Use of Waterproofing, Dampproofing, Protective, and Decorative Barrier Systems for Concrete
- 517.2R Accelerated Curing of Concrete at Atmospheric Pressure—State-of-the-Art

- 547R Refractory Concrete: State-of-the-Art Report
 547.1R State-of-the-Art Report: Refractory Plastics and Ramming Mixes
 548.1R Polymers in Concrete
 SP-57 Refractory Concrete
 SP-62 Superplasticizers in Concrete
 SP-68 Developments in the Use of Superplasticizers in Concrete
 SP-74 Monolithic Refractories
 SP-119 Superplasticizers and Other Chemical Admixtures in Concrete
- ACI-ASCE/TMS*
 ACI 530/ASCE 5/TMS 402 Building Code Requirements for Masonry Structures
 ACI 530R/ASCE 5/TMS 402 Commentary on Building Code Requirements for Masonry Structures
 ACI 530.1/ASCE 6/TMS 602 Specifications for Masonry Structures
 ACI 530.1R/ASCE 6/TMS 602 Commentary on Specifications for Masonry Structures
- American Petroleum Institute*
 API-10 Specifications for Materials and Testing for Well Cements
- ASTM*
 C 33 Standard Specification for Concrete Aggregates
 C 91 Standard Specification for Masonry Cement
 C 150 Standard Specification for Portland Cement
 C 151 Standard Test Method for Autoclave Expansion of Portland Cement
 C 183 Standard Methods of Sampling and Acceptance of Hydraulic Cement
 C 186 Standard Test Method for Heat of Hydration of Hydraulic Cement
 C 191 Time of Setting of Hydraulic Cement by Vicat Needle
 C 204 Test Method for Fineness of Hydraulic Cement by Air Permeability Apparatus
 C 227 Standard Test Method for Potential Alkali Reactivity of Cement-Aggregate Combinations (Mortar-Bar Method)
 C 265 Standard Test Method for Calcium Sulfate in Hydrated Portland Cement Mortar
 C 266 Time of Setting of Hydraulic Cement Paste by Gillmore Needles
 C 270 Standard Specification for Mortar for Unit Masonry
 C 295 Standard Practice for Petrographic Examination of Aggregates for Concrete
 C 441 Effectiveness of Mineral Admixtures or Ground Blast-Furnace Slag in Preventing Excessive Expansion of Concrete due to the Alkali-Silica Reaction
 C 465 Standard Specification for Processing Additions for Use in Manufacture of Hydraulic Cements
- C 494 Standard Specifications for Chemical Admixtures for Concrete
 C 586 Standard Test Method for Potential Alkali Reactivity of Carbonate Rocks for Concrete Aggregate (Rock Cylinder Method)
 C 595 Standard Specification for Blended Hydraulic Cements
 C 618 Standard Specification for Fly Ash and Raw or Calcined Natural Pozzolan for Use as a Mineral Admixture in Portland Cement Concrete
 C 845 Standard Specification for Expansive Hydraulic Cement
 C 979 Standard Specification for Pigments for Integrally Colored Concrete
 C 989 Standard Specification for Ground Blast-Furnace Slag for Use in Concrete and Mortars
 C 1012 Standard Test Method for Length Change of Hydraulic-Cement Mortars Exposed to a Sulfate Solution
 C 1017 Standard Specifications for Chemical Admixtures for Use in Producing Flowing Concrete
 C 1038 Standard Test Method for Expansion of Portland Cement Mortar Bars Stored in Water
 C 1105 Standard Test Method for Length Change of Concrete Due to Alkali-Carbonate Rock Reaction
 C1157 Standard Performance Specification for Blended Hydraulic Cement
 C 1240 Standard Specification for Silica Fume for Use in Hydraulic-Cement Concrete and Mortar
 C 1260 Standard Test Method for Potential Alkali Reactivity of Aggregates (Mortar-Bar Method)
 C 1293 Standard Test Method for concrete Aggregates by Determination of Length Change of Concrete due to Alkali-Silica Reactions
 C 1328 Standard Specification for Plastic (Stucco) Cement
 C 1329 Standard Specification for Mortar Cement
 STP 169C Significance of Tests and Properties of Concrete and Concrete-Making Materials
- Canadian Standards Association*
 CAN/CSA3-A 5-M88 Portland Cements
 CAN/CSA-A 362-M88 Blended Hydraulic Cement
 CAN/CSA-A 23.5-M88 Cementitious Hydraulic Slag
 CAN/CSA-A 23.1-M90 Concrete Material and Methods of Concrete Construction
 CAN/CSA-A 23.2-M90 Methods of Test for Concrete
- European Standards*
 ENV 197 Cement
- These publications may be obtained from the following organizations:
 American Association of State Highway and Transportation Officials
 444 N Capitol St NW, Suite 225
 Washington, DC 20001

American Concrete Institute
P.O. Box 9094
Farmington Hills, Mich. 48333-9094

American Petroleum Institute
1220 L Street NW
Washington, D.C. 20005

ASTM
100 Barr Harbor Dr.
West Conshohocken, Pa. 19428-2959

Canadian Standards Association
178 Rexdale Blvd
Rexdale, Ontario M9W 1R3

CEN
European Committee for Standardization
Central Secretariat:
Rue de Strassart, 36 B-1050
Brussels

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APPENDIX—CALCIUM-ALUMINATE CEMENTS

Manufacture and properties

Calcium-aluminate cements are hydraulic cements obtained by pulverizing a solidified melt or clinker that consists predominantly of hydraulic calcium aluminates formed from proportioned mixtures of aluminous and calcareous materials (Lea 1970; Robson 1962). They are generally divided into three groups based on the alumina and iron oxide contents (see Table A.1). The cements of higher alumina content are suitable for higher temperature applications. No standard specification for calcium-aluminate cements exists in the U.S.

The density of calcium-aluminate cements generally ranges from 2.90 to 3.25 Mg/m³ (g/cc) or 180 to 203 lb/ft³. The higher values reflect larger amounts of iron oxide in melted low-purity cements and free alumina in high-purity cements. The loosely compacted bulk density of the powdered product for shipping is approximately 65 to 100 lb/ft³.

Calcium-aluminate cements range in color from dark gray to white, depending mostly on the amount and oxidation state of iron oxide and the manufacturing process. The more iron oxide present either as ferrous or ferric oxide, or both, in the cement, the darker the color.

All three groups of high-alumina cement are manufactured throughout the world and are commercially available in North and South America. They are considerably more expensive than portland cements, ranging from approximately three to four times more for low-purity products to nine to 10 times more for high-purity products. Because of their high cost, intermediate- and high-purity calcium-aluminate cements are rarely, if ever, used for other than refractory applications.

Potential users of calcium-aluminate cements should contact the manufacturer of the product under consideration for information on mixture proportioning, aggregate selection, handling, placing, and curing requirements. They should be aware of the possible conversion of the hydration products from larger volume, metastable hexagonal products like (CAH₁₀) to smaller volume stable cubic products (C₃AH₆) resulting in strength retrogression (Robson 1962).

Table A1—Chemical composition and property ranges for calcium-aluminate cements

	Low purity	Intermediate purity	High purity
Al ₂ O ₃ , %	39 to 50	54 to 66	70 to 90
Fe ₂ O ₃ , %	7 to 16	1 to 3	0.0 to 0.4
CaO, %	35 to 42	26 to 36	9 to 28
SiO ₂ , %	3 to 9	3 to 9	0 to 0.5
Wagner surface, m ² /kg	140 to 180	160 to 200	>220
Blaine surface, m ² /kg	260 to 440	320 to 1000	360 to 1150
Time of setting			
Vicat initial (h:min)	3:00 to 9:00	3:00 to 9:00	0:30 to 6:00
Minimum compressive strength (ASTM C 109, 50 mm [2 in.] cubes), MPa (psi)			
1 day	24.1 (3500)	41.1 (6000)	17.2 (2500)
7 days	41.4 (6000)	58.6 (8500)	34.5 (5000)
28 days	48.3 (7000)	68.9 (10,000)	—

Influences of admixtures

Chemical and mineral admixtures used with portland and blended cements may not be satisfactory for use with calcium-aluminate cements. Whereas some will behave in a similar manner, the dosages required may differ greatly. Other admixtures may be of little value, be harmful, or act in an opposite fashion when used with calcium-aluminate cements. In addition, various types of calcium-aluminate cements may produce different results. Whenever possible, trial batches should be made with the intended cement, and technical advice should be sought from the manufacturer of the admixture or the cement. ACI 547 contains a list of various generic additions and admixtures and their effects on calcium-aluminate cements.

Influence of the environment

Curing temperatures during the first 24 h influence the strength development of calcium-aluminate cements concretes. Temperatures below 24 C (75 F) produce a high initial strength that will generally increase within 6 months and then decrease, because of volume change resulting from phase conversion, to strength values approaching the 1-day strength. Initial curing temperatures above 32 C (90 F) may provide lower 24 h strengths in calcium-aluminate cements, but retrogression of strength with time is minimized.

Curing compounds are effective in sealing the concrete surface temporarily to prevent water evaporation. Curing compounds should be applied as soon as possible after finishing is complete. Fog-spray curing should begin only after initial set of the concrete surface.

Potential users of calcium-aluminate cements should obtain further information on curing methods from the manufacturer of the product under consideration.

Heat of hydration

The hydration of calcium-aluminate cements can produce large amounts of heat during the first 24 h. Provisions for dissipating this heat should be considered, especially in thick

sections of concrete, for example, those greater than 150 mm (6 in.) in thickness.

Setting characteristics

Calcium-aluminate cements frequently have quite different setting characteristics from portland and blended hydraulic cements. When tested according to standard needle penetration tests (Vicat ASTM C 191, or Gillmore ASTM C 266), different calcium-aluminate cements provide a wide range of times of setting as shown in [Table A1](#). In addition, the period between time of initial and final setting is generally much shorter than with portland cements.

The slump cone should not be used for determining the workability characteristics of calcium-aluminate cements. Because some calcium-aluminate cements lose slump rather quickly, special care may be required in mixing, handling, placing, and finishing. Other calcium-aluminate cements remain workable longer than many portland cements. The manufacturer of the particular product under consideration should be consulted in this regard.

Strength

Calcium-aluminate cements gain much faster strength than portland cements (see [Table A1](#)). Although calcium-aluminate cements can produce mortars and concretes with very high early strengths, the strength may fall significantly at later ages if the w/c and curing temperature are not controlled as specified. This strength loss is associated with the conversion to the stable hydrate of the metastable calcium aluminate hydrates that form first, at temperatures below approximately 24 C (75 F). The rate at which the conversion occurs and its effect upon the strength (and permeability due to shrinkage microcracking) increases with the amount of water available above the critical w/c , the curing temperature (above approximately 30 C [86 F]), the relative humidity, and the time of exposure. The residual strength after complete conversion depends on the original w/c of the concrete. Because of the probability of conversion, the use of calcium-aluminate cements in load-bearing concrete structures should either be avoided or anticipated strength retrogression calculated when designing the structure.

Resistance to chemical attack

Calcium-aluminate cement concretes are resistant to a number of aggressive acidic agents that attack portland cement concretes. Calcium-aluminate cement was originally developed to resist attack by sulfates in soil, seawater, and indus-

trial waste waters. Experience has shown that concretes made with calcium-aluminate cement are more resistant to sulfate attack than concretes made with ASTM Type V portland cement. Mortars and concretes made with calcium-aluminate cements and suitable aggregates are more resistant to mild acids and acid industrial waste liquors than those made with portland cement. Calcium-aluminate cement has been used successfully for lining fossil fuel power plant stacks to resist mild sulfurous and sulfuric acid solutions. They have also been used in the following types of manufacturing plants to resist specific aggressive agents shown (see ACI 350R):

<u>Types of plants</u>	<u>Aggressive agents</u>
Ammunition	Nitric, sulfuric and other acids
Breweries	Dilute organic acids
Corn products plants	Dilute sulfurous acids, starch
Dairies, ice cream plants	Dilute lactic acid, brine
Milk product plants	Dilute lactic acid
Sugar mills and refineries	Can juice, molasses
Tanneries	Dilute tannic acid, dilute chromic and organic acids
Distilleries	Dilute organic acids
Chocolate plants	Cocoa butter
Fertilizer plants	Dilute ammonium sulfate
Meat packing plants	Dilute organic acids, blood, brine
Wastewater plants and sewers	Hydrogen sulfide and sulfuric acid
Water and wastewater	Chemicals used in processes

As a general guideline, the use of calcium-aluminate cements for resistance to acidic solutions is limited to applications where the pH is not less than 3.5 to 4.0. Whenever possible, however, and particularly when a new application is encountered, it is recommended that a trial section be installed.

Resistance to high temperatures

If resistance to temperatures higher than approximately 300 C (570 F) is needed, the properties of both the cement and the aggregate must be considered. For the most demanding applications, calcium-aluminate cement is combined with selected refractory aggregates to produce refractory concretes suitable for use at temperatures up to 1870 C (3400 F). ACI SP-57 and ACI 547R provide more information on refractory concretes using hydraulic-cement binders.