Report on Chemical Admixtures for Concrete

Reported by ACI Committee 212

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Report on Chemical Admixtures for Concrete

Reported by ACI Committee 212

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The committee would like to thank Ketan R. Sompura[*] and Caroline M. Talbot[*] for their contributions to this report.

Chemical admixtures, which are primarily water-soluble substances, are discussed in detail and, in this report, are classified into 13 groups: air-entraining; accelerating; water-reducing and set-retarding; admixtures for flowing concrete; admixtures for self-consolidating concrete; cold weather admixture systems; admixtures for very high-early-strength concrete; extended set control; shrinkage-reducing; corrosion-inhibiting; lithium; permeability-reducing; and miscellaneous. Chemical admixtures are used on a daily basis in the cast-in-place and precast concrete industries. Twelve categories of admixtures are described in detail as to type, current usage, and their effect on concrete in the plastic and hardened state. Their benefits and common usage are outlined.

Each category of admixture addresses the benefits obtainable with their use in a properly proportioned concrete mixture, types of batching systems, control measures, and test placements for mixture design verification. Mixture designs using multiple chemical admixtures have become more common. Their successful usage requires proper compatibility and, often, setting times and early strengths that are proper for the placing environment. The potential benefits are highlighted to all members of the concrete team, concrete contractor, concrete producer, admixture supplier, and testing personnel.

Finely divided mineral admixtures are addressed by ACI 232.2R "Use of Fly Ash in Concrete," ACI 232.1R "Use of Raw or Processed Natural Pozzolans in Concrete" and ACI 234R "Guide for the Use of Silica Fume in Concrete."

Keywords: accelerating; admixture; admixture system; air-entraining; alkali-aggregate reaction; flowing concrete; high-range water-reducing admixture; permeability-reducing admixtures; self-consolidating concrete; shrinkage-reducing; water-reducing and set-retarding.

ADMIXTURES, THEIR CHARACTERISTICS, AND USAGE

Admixture type	Effects and benefits	Materials
Air-entraining (ASTM C260 and AASHTO M154)	Improve durability in freezing and thawing, deicer, sulfate, and alkali-reactive environments. Improve workability.	Salts of wood resins, some synthetic detergents, salts of sulfonated lignin, salts of petroleum acids, salts of proteinaceous material, fatty and resinous acids and their salts, tall oils and gum rosin salts, alkylbenzene sulfonates, salts of sulfonated hydrocarbons.
Accelerating (ASTM C494/C494M and AASHTO M194, Type C or E)	Accelerate setting and early-strength development.	Calcium chloride (ASTM D98 and AASHTO M144), triethanolamine, sodium thiocyanate, sodium/calcium formate, sodium/calcium nitrite, calcium nitrate, aluminates, silicates.
Water-reducing (ASTM C494/C494M and AASHTO M194, Type A)	Reduce water content at least 5%.	Lignosulfonic acids and their salts. Hydroxylated carboxylic acids and their salts. Polysaccharides, melamine polycondensation products, naphthalene polycondensation products, and polycarboxylates.
Water-reducing and set-retarding (ASTM C494/C494M and AASHTO M194, Type D)	Reduce water content at least 5%. Delay set time.	See water reducer, Type A (retarding component is added).
High-range water-reducing (ASTM C494/C494M and AASHTO M194, Type F or G)	Reduce water content by at least 12 to 40%, increase slump, decrease placing time, increase flowability of concrete, used in self-consolidating concrete (SCC).	Melamine sulfonate polycondensation products, naphthalene sulfonate polycondensation products, and polycarboxylates.
Mid-range water-reducing (ASTM C494/C494M, Type A)	Reduce water content by between 5% and 10% without retardation of initial set.	Lignosulfonic acids and their salts. Polycarboxylates.
Extended set control (hydration control) (ASTM C494/C494M, Type B or D)	Used to stop or severely retard the cement hydration process. Often used in wash water and in returned concrete for reuse, and can provide medium- to long-term set retardation for long hauls. Retain slump life in a more consistent manner than normal retarding admixtures.	Carboxylic acids. Phosphorus-containing organic acid salts.
Shrinkage-reducing	Reduce drying shrinkage. Reductions of 30 to 50% can be achieved.	Polyoxyalkylene alkyl ether. Propylene glycol.
Corrosion-inhibiting (ASTM C1582/C1582M)	Significantly reduce the rate of steel corrosion and extend the time for onset of corrosion.	Amine carboxylates aminoester organic emulsion, calcium nitrite, organic alkyidicarboxylic. Chromates, phosphates, hypophosphites, alkalis, and fluorides.
Lithium admixtures to reduce deleterious expansions from alkali-silica reaction	Minimize deleterious expansions from alkali-silica reaction.	Lithium nitrate, lithium carbonate, lithium hydroxide, and lithium nitrite.
Permeability-reducing admixture: non-hydrostatic conditions (PRAN)	Water-repellent surface, reduced water absorption.	Long-chain fatty acid derivatives (stearic, oleic, caprylic capric), soaps and oils (tallows, soya-based), petroleum derivatives (mineral oil, paraffin, bitumen emulsions), and fine particle fillers (silicates, bentonite, talc).
Permeability-reducing admixture: hydrostatic conditions (PRAH)	Reduced permeability, increased resistance to water penetration under pressure.	Crystalline hydrophilic polymers (latex, water-soluble, or liquid polymer).
Bonding	Increase bond strength.	Polyvinyl chloride, polyvinyl acetate, acrylics, and butadiene-styrene copolymers.
Coloring	Colored concrete.	Carbon black, iron oxide, phthalocyanine, raw burnt umber, chromium oxide, and titanium dioxide.
Flocculating	Increase interparticle attraction to allow paste to behave as one large flock.	Vinyl acetate-maleic anhydride copolymer.
Fungicidal, cermicidal, insecticidal	Inhibit or control bacterial, fungal, and insecticidal growth.	Polyhalogenated phenols, emulsion, and copper compounds.
Rheology/viscosity-modifying	Modify the rheological properties of plastic concrete.	Polyethylene oxides, cellulose ethers (HEC, HPMC), alginates (from seaweed), natural and synthetic gums, and polyacrylamides or polyvinyl alcohol.
Air-detraining	Reduce air in concrete mixtures, cement slurries, and other cementing applications.	Tributyl phosphate, dibutyl phosphate, dibutylphthalate, polydimethylsiloxane, dodecyl (lauryl) alcohol, octyl alcohol, poly-propylene glycols, water-soluble esters of carbonic and boric acids, and lower sulfonate oils.

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CHAPTER 1—INTRODUCTION
1.1—Introduction
An admixture is defined as "a material other than water, aggregates, hydraulic cement, and fiber reinforcement used as an ingredient of concrete or mortar, and added to the batch immediately before or during its mixing" (American Concrete Institute 2010; ASTM C125). Chemical admixtures are primarily water-soluble substances used to enhance the properties of concrete or mortar in the plastic and hardened state. These benefits include increased compressive and flexural strength at all ages, decreased permeability and improved durability, corrosion reduction, shrinkage reduction, initial set adjustments, increased slump and workability, improved pumpability, finish and finishability, rheology modification, improved cement efficiency, alkali-silica reaction (ASR) reduction, and concrete mixture economy.

An admixture or combination of admixtures may be required to achieve the specific desired results; however, proper mixture designs are required for optimum benefits. In certain instances, a desired objective may be best achieved by mixture changes in addition to proper admixture usage. Chemical admixtures are not a substitute for suitable concrete mixture proportions and acceptable construction practices.

This report deals with commonly used admixtures other than those assigned to other ACI committees. Materials, such as mineral admixtures, used to produce concrete are not discussed in this report.

The chemical admixtures are classified generically or with respect to their characteristics. Information to characterize each class is presented with brief statements of the general purposes and expected effects of each group of materials. The wide scope of the admixture field, the continued entrance of new or modified materials into this field, and the variations of effects with different concreting materials and conditions preclude a complete listing of all admixtures and their effects on concrete. Summaries of the state of the art of chemical admixtures include Ramachandran and Malhotra (1984), Ramachandran and Mailvaganam (1992), Mather (1994), Nkinamubanzi and Aïtcin (2004), Collepardi and Valente (2006), and "Chemical Admixtures for Concrete," *ACI Education Bulletin* E4-03 (ACI Committee E703 2003).

CHAPTER 2—DEFINITIONS
2.1—Definitions
ACI provides a comprehensive list of definitions through an online resource, "ACI Concrete Terminology," http://terminology.concrete.org. Definitions provided herein complement that resource.

admixture—a material other than water, aggregates, cementitious materials, and fiber reinforcement, used as an ingredient of a cementitious mixture to modify its freshly mixed, setting, or hardened properties and that is added to the batch before or during its mixing.

admixture, accelerating—an admixture that causes an increase in the rate of hydration of the hydraulic cement and thus shortens the time of setting, increases the rate of strength development, or both.

admixture, air-entraining—an admixture that causes the development of a system of microscopic air bubbles in concrete, mortar, or cement paste during mixing, usually to increase its workability and resistance to freezing and thawing.

admixture, retarding—an admixture that causes a decrease in the rate of hydration of the hydraulic cement and lengthens the time of setting.

admixture, water-reducing—an admixture that either increases slump of a fresh cementitious mixture without increasing water content or maintains slump with a reduced amount of water, the effect being due to factors other than air entrainment.

admixture, water-reducing (high-range)—a water-reducing admixture capable of producing great water reduction, great flowability, or both, without causing undue set retardation or air entrainment in cementitious paste.

adsorption—development (at the surface of either a liquid or solid) of a higher concentration of a substance than exists in the bulk of the medium; especially formation of one or more layers of molecules of gases, of dissolved substances, or of liquids at the surface of a solid (such as cement, cement paste, or aggregates), or of air-entraining agents at the air-water interfaces; also the process by which a substance is adsorbed.

air, entrained—microscopic air bubbles intentionally incorporated in a cementitious paste during mixing, usually by use of a surface-active agent; typically between 0.0004 and 0.04 in. (10 and 1000 μm) in diameter and spherical or nearly so.

air content—the volume of air voids in cement paste, mortar or concrete, exclusive of pore space in aggregate particles, usually expressed as a percentage of total volume of the paste, mortar, or concrete.

concrete, flowing—a cohesive concrete mixture with a slump greater than 7-1/2 in. (190 mm).

concrete, high-performance—concrete meeting special combinations of performance and uniformity requirements that cannot always be achieved routinely using conventional constituents and normal mixing, placing, and curing practices.

concrete, mass—volume of concrete with dimensions large enough to require that measures be taken to cope with the generation of heat and temperature gradients from hydration of the cementitious materials and attendant volume change due to internal or external restraint.

concrete, ready mixed—concrete manufactured for delivery to a purchaser in a fresh state.

corrosion inhibitor—a chemical compound, either liquid or powder, usually intermixed in concrete and sometimes applied to concrete, and that effectively decreases corrosion of steel reinforcement.

durability—the ability of a material to resist weathering action, chemical attack, abrasion, and other conditions of service.

reaction, alkali-silica—a generally deleterious dissolution and swelling of siliceous aggregates in the presence of pore solutions comprised of alkali hydroxides; the reaction products may cause abnormal expansion and cracking of concrete.

rheology—the science dealing with deformation and flow of materials.

self-consolidating concrete (SCC)—highly flowable, nonsegregating concrete that can spread into place, fill the formwork, and encapsulate the reinforcement without any mechanical consolidation. SCC has also been described as self-compacting concrete, self-placing concrete, and self-leveling concrete, which are subsets of SCC.

slump—a measure of consistency of freshly mixed concrete, mortar, or stucco equal to the subsidence measured to the nearest 1/4 in. (5 mm) of the molded specimen immediately after removal of the slump cone.

slump flow—a measure of the unconfined flow potential of a freshly mixed self-consolidating concrete or grout. The value is equal to the average of two perpendicular diameters of the material measured to the nearest 1/2 in. (12.5 mm) after it is released from the slump cone and stops flowing.

strength, concrete compressive—the measured maximum resistance of a concrete specimen to axial compressive loading; expressed as force per unit cross-sectional areas.

strength, early—strength of concrete or mortar usually as developed at various times during the first 72 hours after placement.

stress, shear—intensity of internal force (that is, force per unit area) exerted by either of two adjacent parts of a body on the other across an imagined plane of separation; when the forces are parallel to the plane, the stress is called shear stress.

viscosity—the property of a material that resists change in the shape or arrangement of its elements during flow, and the measure thereof.

water, adsorbed—water held on the surface of a material by intermolecular forces and having physical properties substantially different from those of absorbed or chemically combined water at the same temperature and pressure.

water-cement ratio—the ratio of the mass of water, exclusive only of that absorbed by the aggregate, to the mass of cement in a mixture, stated as a decimal and abbreviated as *w/c*.

water-cementitious material ratio—the ratio of the mass of water, excluding that absorbed by the aggregate, to the mass of cementitious material in a mixture, stated as a decimal and abbreviated as *w/cm*.

water repellent—resistant but not impervious to penetration by water.

yield stress—the critical shear stress value below which a viscoplastic material will not flow and once exceeded, flows like a viscous liquid.

CHAPTER 3—GENERAL INFORMATION
3.1—Sustainability

Chemical admixtures can improve sustainability by producing mixture designs that use lower water contents, incorporate higher quantities of supplementary cementitious materials, and lower cement contents by improving cement efficiency. Proper use of chemical admixtures improves concrete performance in the hardened state and, therefore, increases the duration of the concrete life cycle.

3.2—Admixture benefits

Chemical admixtures are used singularly or in combination to improve the desired properties of concrete or mortar in the plastic and hardened states. Types and dosages are selected in accordance with climatic conditions for maintaining workability and pumpability, strength, *w/cm*, air content, setting time, and early and final strengths. Proposed mixtures and admixture choices are often confirmed with successful test placements on site.

3.2.1 *Modification of fresh concrete, mortar, and grout*—Admixtures are used to modify and improve properties of fresh concrete, mortar, and grout. Examples are:
- Increase the workability without increasing the water content, or decrease the water content without changing the workability;
- Increase the slump or slump-flow without increasing the water content;
- Retard or accelerate the time of initial setting;
- Reduce or prevent settlement, or create a slight expansion;
- Modify bleeding characteristics;
- Reduce segregation;
- Improve finishability;
- Improve pumpability;
- Modify rheological properties;
- Reduce the rate of slump loss; and
- Increase placement rate.

3.2.2 *Modification of hardened concrete, mortar, and grout*—Admixtures are used to modify properties of hardened concrete, mortar, and grout. Examples are:
- Reduce the rate of heat evolution during early cement hydration;

- Accelerate the rate of strength development at early ages;
- Increase strength (compressive, tensile, or flexural);
- Increase resistance to freezing and thawing;
- Reduce scaling caused by deicing salts;
- Decrease permeability;
- Reduce expansion caused by alkali-aggregate reaction;
- Increase bond to steel reinforcement and between existing and new concrete;
- Improve impact resistance and abrasion resistance;
- Inhibit corrosion of embedded metal;
- Produce colored concrete or mortar; and
- Reduce drying shrinkage and curling.

3.3—Specifications for admixtures

The following standard specifications cover the admixture types that make up the bulk of products covered in this report:
- Air-entraining admixtures: ASTM C260 and AASHTO M154;
- Water-reducing and set-controlling admixtures: ASTM C494/C494M and AASHTO M194;
- Calcium chloride: ASTM D98 and AASHTO M144;
- Admixtures for use in producing flowing concrete: ASTM C1017/C1017M; and
- Pigments for integrally colored concrete: ASTM C979.

ASTM recently approved a Type S (specialty admixture) designation that includes admixtures not covered by other ASTM standards. The results obtained from tests done in accordance with ASTM C494/C494M will ensure that these products give values that closely matched those of the untreated reference concrete and therefore meet all the requirements of the standard.

3.4—Sampling and testing

Admixture samples for testing and evaluation should be obtained by the procedures prescribed for each admixture's specifications using random sampling from plant production, previously unopened packages or containers, or fresh bulk shipments.

Admixtures are tested to determine compliance with specifications; evaluate effects on the properties of concrete made with materials under the anticipated ambient conditions and construction procedures; determine uniformity of the product within or between batches, lots, or containers; or reveal any undesirable effects. The quality-control procedures used by producers of admixtures should ensure product compliance with provisions of ASTM or other applicable specifications, including uniformity. Because a producer's quality-control test methods can be developed around a particular proprietary product, they may not be applicable for general use or use by consumers.

ASTM provides procedures for testing concrete containing admixtures. Producing concrete should be preceded by testing that allows observation and measurement of the performance of the admixture under concrete plant operating conditions in combination with the constituent materials that will be used. Uniformity of results is as important as the average result, with respect to each significant property of the admixture or the concrete.

3.5—Cost effectiveness

Economic evaluation of an admixture should be based on the test results obtained when used with the specified concrete under conditions simulating those expected on the job. The characteristics of the cementitious materials and aggregate; their relative proportions; and the temperature, humidity, and curing conditions influence the test results. When evaluating an admixture, its effect on the volume of a given batch should be taken into account. If the admixture increases the volume of the batch (the yield), the admixture should be considered as a basic ingredient together with the cementitious materials, aggregate, and water. All changes in the composition of a unit volume of concrete should be taken into account when testing the direct effect of the admixture and in estimating its benefits.

The cost effectiveness of an admixture should be based on the cost of the concrete in place, rather than the cost of the concrete alone. The cost in place, which includes transporting, placing, and finishing costs, is of greatest interest to the owner. The admixture benefits can allow the use of less-expensive construction methods or allow structural designs that offset the added cost due to its use. For example, novel and economical structural designs have resulted from the use of high-range water-reducing admixtures (HRWRAs). They are essential ingredients of cost-effective, high-performance concrete.

Water-reducing and set-retarding admixtures permit placement of large volumes of concrete over extended periods, minimizing the need for forming, placing, and joining separate units. Accelerating admixtures reduce finishing and forming costs. Required physical properties of lightweight concrete may be achieved at a lower density by using air-entraining and water-reducing admixtures.

3.6—Selection and evaluation

Careful attention should be given to the instructions and recommendations provided by the manufacturer of the admixture. An admixture's effects should be evaluated whenever possible using the specified materials under site conditions.

This is particularly important when:
- The admixture has not been used previously with the particular combination of materials;
- Special types of cementitious materials are specified;
- More than one admixture is to be used; or
- Mixing and placing is done at temperatures outside recommended temperature ranges for concrete.

The use of admixtures also requires a review of the concrete mixture design constituents. Prime concerns are:
- Type and amount of cement;
- Type and amount of supplementary cementitious materials;
- Combined aggregate gradation, water and air content; and
- Climatic conditions.

On-site testing of the proposed mixture to verify proper workability, finishability, pumpability, and setting time is recommended.

Many admixtures affect more than one property of concrete. Rapid stiffening and significant retardation are not desirable. The cause of abnormal setting behavior should be determined through studies on how such admixtures affect the cementitious material to be used. Early stiffening is often caused by changes in the reaction rate between the tricalcium aluminate and sulfate ions in solution in the pore fluid. Excessive retardation can be caused by an overdose of admixture or by a lowering of ambient temperature, both of which delay the hydration of the calcium silicates (Hansen 1960).

Another important consideration when using admixtures arises when there is a limit on the measurable amounts of chloride ions permitted in the concrete (ACI 318; ACI 222R). These admixtures should not contain more chloride ions than are present in the drinking water at the city of manufacture. These limits are usually expressed as maximum percent of chloride ion by mass of cement, although the amount of water-soluble chloride ion per mass of cement or concrete is sometime specified. The procedures of ASTM C1152 and C1218/C1218M can be used to measure acid-soluble and water-soluble chloride, respectively, in mortar or concrete. It is necessary to know the chloride-ion content of an admixture to ensure that it will not jeopardize the concrete conforming to a specified chloride limit. In spite of the use of such terms as "chloride-free," all admixtures sold as solutions will contain small but measurable amounts of chloride ions coming from municipal drinking water.

Although specifications deal primarily with the influence of admixtures on specific properties of fresh and hardened concrete, the concrete supplier, contractor, and owner of the construction project may be interested in other features of concrete construction. Of primary concern may be workability, pumping qualities, placing and finishing qualities, early strength development, reuse of forms or molds, or the appearance of formed surfaces. These additional features are important when an admixture is selected and its dosage rate is determined.

Guidance for using different classes of admixtures is given in the relevant chapters of this report. Those responsible for construction of concrete structures should bear in mind that increasing material costs and continuing development of new and improved admixtures warrant the continuous reevaluation of the benefits of using admixtures.

3.7—Proportioning and batching

The concrete mixture should be proportioned in accordance with ACI 211.1 or ACI 211.2 and provide the specified qualities and characteristics as outlined by the purchaser and/or project specification. The admixtures selected should be compatible in the mixture and added separately to the batch. The choice of admixtures will be based on the required water content; w/cm; compressive and flexural strengths; air content; target slump or slump/flow; setting times; early strength development, if required; and ultimate compressive and flexural strength. Strength, air content, slump or slump/flow, and setting time can be based on previous experience or trial batches. It is recommended that workability, finishability, pumpability, setting time, and other characteristics required in the plastic state be verified with a successful test placement on site.

3.7.1 *Liquid batching systems*—Ordinarily, liquid admixtures are not batched by mass because mass-batching devices are more expensive than volumetric dispensers, although a few concrete plants do use mass-batching systems. In some cases, it is necessary to dilute admixture solutions to obtain a sufficient quantity for accurate measurement by mass. Most methods of batching liquid admixtures require a visual volumetric container, called a calibration tube, to enable the plant operator to verify the accuracy of the admixture dosage. The simplest batching method consists of a visual volumetric container, whereas others include positive volumetric displacement. Positive displacement (PD) flow meters make accurate volumetric flow measurements taking finite increments or volumes of the fluid. There are several types. The nutating disk type is commonly used for liquid admixtures. Some of these methods can be used readily with manual, semiautomatic, and automatic systems and can be operated easily by a remote control with appropriate interlocking in the batch sequence. Simple manual dispensing systems, which are designed for low-volume concrete plants, depend on the concrete plant operator batching the proper amount of admixture into a calibration tube and discharging it into the batch. More sophisticated systems intended for automated high-volume plants provide automatic fill and discharge of a sight or calibration tube. Adding an admixture at the job site can also be accomplished with a tank and a pressurized dispensing system. A calibrated holding tank and a mechanical or electromechanical dispensing device should be part of the system so the plant operator can verify the proper amount of admixture has been batched into the concrete mixer or into the truck-mounted tank.

Flow meters and calibration tubes equipped with floats or probes are often combined with pulse-emitting transmitters that give readouts on electromechanical or electronic counters. These are often set by inputting the dosage per unit of cementitious material. The amount of cementitious material input into the batching panel, combined with the dosage rate, sets the dispensing system to batch the proper amount of admixture. Timer-controlled systems involve the timing of flow through an orifice. Considerable error can be introduced by changes in power supply, partial restrictions of the measuring orifice, and changes in viscosity of the solution. Viscosity is affected by temperature and admixture concentration. Timer-controlled systems should be recalibrated in accordance with project documents or manufacturer recommendations. The plant operator should verify the proper admixture dose by observing the calibration tube. Although timer-controlled systems have been used successfully, their use is not recommended, except for dispensing calcium chloride solution. Because of the marked effect of admixtures on concrete performance, care and attention to the timing and accuracy of admixture batching are necessary to avoid serious problems. Job-site introduction of HRWRAs is addressed in Chapter 6.

3.7.2 *Maintenance*—Batching systems require routine periodic maintenance to prevent inaccuracies developing

from such causes as sticky valves, buildup of foreign matter in meters or in storage and mixing tanks, or worn pumps.

Components should be protected from dust and temperature extremes, and be kept readily accessible for visual observation and maintenance. Although admixture-batching systems are usually installed and maintained by the admixture producer, plant operators should thoroughly understand the system and be able to adjust it and perform simple maintenance. Plant operators should recalibrate the system on a regular basis, preferably at intervals of not more than 90 days, noting any trends that indicate worn parts needing replacement.

Tanks, conveying lines, and ancillary equipment should be drained and flushed on a regular basis, and calibration tubes should have a water fitting installed to allow the plant operator to flush the tube so that divisions or markings may be clearly seen at all times.

3.7.3 *Storage*—Admixtures should be stored in strict accordance with the manufacturer's recommendations. Most admixtures are not damaged by freezing. The manufacturer's instructions should be followed regarding the effects of freezing the product. An admixture stored beyond its recommended shelf life should be retested before use.

CHAPTER 4—AIR-ENTRAINING ADMIXTURES
4.1—Introduction
An air-entraining admixture is "an admixture that causes the development of a system of microscopic air bubbles in concrete, mortar, or cement paste during mixing," usually to increase workability and resistance to freezing and thawing. The entrained air-void system is distinct from air voids physically entrapped in concrete during placement and consolidation. Air-entraining admixtures function by stabilizing the air voids folded into the concrete during the mixing process. Air entrainment should always be required when concrete will be subjected to freezing and thawing and where the use of deicing chemicals is anticipated. Highway pavements, parking structure slabs, bridge decks, garage floors, driveways, curbs, and sidewalks located in cold climates will probably be exposed to such conditions. Specified air content shall be achieved by batching an air-entraining admixture and measuring the air content of fresh concrete with air meters and/or unit weight tests. The resistance of concrete to freezing and thawing is affected by placing, consolidating, finishing, and curing procedures; therefore, acceptable construction practice in these respects should be followed (ACI 201.2R, ACI 302.1R, ACI 304R, ACI 308R).

Extensive laboratory testing and long-term field experience have demonstrated conclusively that portland-cement concrete should contain at least a minimum amount of properly entrained air to resist the action of freezing and thawing (Cordon 1946; Blanks and Cordon 1949; Mather 1990). The process by which air is entrained in concrete and the mechanism by which such air entrainment prevents damage due to freezing and thawing is beyond the scope of this report, but is summarized in various textbooks (Powers 1968; Mindess and Young 1981; Mehta and Monteiro 1993) and in ACI 201.2R. More detailed discussions can be found in research papers (Cordon 1966; Litvan 1972; MacInnis and Beaudoin 1974; Powers 1975; Whiting and Nagi 1998).

4.2—Materials for air entrainment
Many materials can function as air-entraining admixtures, but those used to create cellular concrete, by creating gas bubbles inside the concrete (ACI 523.1R), such as hydrogen peroxide and powdered aluminum metal, are not acceptable air-entraining admixtures.

4.2.1 *Water-soluble compounds*—Water-soluble, air-entraining admixtures are formulated using salts of wood resins, synthetic detergents, salts of petroleum acids, salts of proteinaceous acids, fatty and resinous acids and their salts, and organic salts of sulfonated hydrocarbons. Not every material that fits the preceding description, however, will produce a desirable air-void system. All air-entraining admixtures should meet the requirements of ASTM C260. Most commercial air-entraining admixtures are in liquid form, although a few are powders, flakes, or semisolids. The proprietary name and the net quantity in kilograms (pounds) or liters (gallons) should be indicated on the containers in which the admixture is delivered.

4.2.2 *Solid materials*—Solid particles that have a high internal porosity and suitable pore size have been added to concrete and seem to act like air voids. These particles can be hollow plastic spheres, crushed brick, expanded clay or shale, or spheres of suitable diatomaceous earth. Research has indicated that when using inorganic particulate materials, the optimum particle size should be 300 μm to 1.18 mm (0.01 to 0.05 in.) (No. 16 to 50 sieves). The total porosity of the particles should be at least 30% by volume, and the pore-size distribution should be between 0.05 and 3 μm (0.000002 and 0.0001 in.) (Gibbons 1978; Sommer 1978). Inclusion of such particulates in the proper proportion has produced concrete with excellent resistance to freezing and thawing in laboratory tests using ASTM C666/C666M (Litvan and Sereda 1978; Litvan 1985). Particulate air-entraining admixtures have the advantage of stability of the air-void system. Once added to the fresh concrete, changes in mixing procedure or time; changes in temperature, workability, or finishing procedures; or the addition of other admixtures, such as fly ash, or other cementitious materials such as ground slag, will not change the air content, as may be the case with conventional air-entraining admixtures.

4.2.3 *Entrained air-void systems*—Improvements in resistance to freezing and thawing are due to the presence of minute air bubbles dispersed uniformly through the cement-paste portion of the concrete that provide relief from the pressure of freezing water. Because of the bubble's size, there are literally billions of bubbles in each cubic meter of air-entrained concrete. To provide adequate protection with a relatively low total volume of void space, the bubbles should be small (0.0004 to 0.004 in. [10 to 100 μm] in diameter).

The cement paste in concrete normally is protected against the effects of freezing and thawing if the spacing factor (Powers 1949) does not exceed 0.008 in. (0.20 mm), as determined in accordance with ASTM C457/C457M. This is generally achieved when the surface area of the air voids is greater than

600 in.^{2}/in.^{3} (24 mm^2/mm^3) of air-void volume, and the number of air voids per 1 in. (25 mm) of traverse are 1.5 times greater than the numerical value of the percentage of air in the concrete (Hover 1994). Many investigators (Tynes 1977; Mather 1979; Schutz 1978; Whiting 1979; Litvan 1983) report that the addition of some HRWRAs to air-entrained concrete increases the spacing factor and decreases the surface areas of the air-void systems beyond the accepted limits. Numerous studies (Kobayashi 1981; Malhotra and Malanka 1979; Philleo 1986), however, indicate that such admixtures do not reduce the freezing-and-thawing resistance of concrete.

The air content and the size distribution of air voids produced in air-entrained concrete are influenced by many factors (Backstrom et al. 1958; Mielenz et al. 1958a,b)—most importantly, by the nature and quantity of the air-entraining admixture, the nature and quantity of the constituents of the concrete, the type and duration of mixing employed, the consistency and slump of the concrete, and the kind and degree of consolidation applied in placing the concrete. Admixtures react differently with varying concrete constituents, temperatures, slumps, and cements. Field evaluations are often beneficial because uniformity of air content throughout a project is essential. Field tests should be used to verify the uniform performance of the proposed air-entraining admixture. Therefore, the air-entraining admixture choice on a given project should be based on current information and recent field test data. Air content in hardened concrete is determined either by the linear traverse or point-count technique and generally is slightly lower than values obtained from tests of the fresh concrete (Carlson 1967; Reidenour and Howe 1975). Differences may generally differ by less than two percentage points (Pinto and Hover 2001).

Newlon (1971), analyzing field data on cores taken from bridge decks, found that 22 of 26 samples were within 1.25 percentage points of the air content measured in the fresh concrete. When considerable amounts of entrapped air are present in core specimens; however, air contents, as determined by linear traverse, can be up to 3 percentage points less than those determined by the pressure meter (Amsler et al. 1973). Occasionally, measured air contents in hardened concrete can be as much as twice those measured in as-delivered concrete. Explanations of this phenomenon include the incompressibility of very small (0.0002 in. [<50 μm] diameter) air voids (Hover 1989) and the transfer of air between small and large air bubbles (Fagerlund 1990). Attempts to reproduce this phenomenon under controlled laboratory and field conditions have not been successful (Ozyildirim 1991).

Air content readings should be verified on site by unit weight (density) tests. The use of air meter buckets to determine density, regardless of nominal maximum size of coarse aggregate, is preferable to not performing density tests. Concrete suppliers should determine the relationship between density and air content for various concrete mixtures, as explained in the last sentence of Section 4.8.3. Also, concrete cylinders should be weighed after demolding and before capping, and the weight recorded on strength test reports. This provides useful information relative to cylinder manufacture, density, yield, air content, and strength.

4.3—Selection and evaluation

To improve resistance to freezing and thawing, intentionally entrained air should have certain characteristics as outlined in Section 4.2.3. An admixture that meets the requirements of ASTM C260 will produce a desirable air-void system when recommended air contents are achieved. Improvements in resistance to freezing and thawing are due to the presence of minute air bubbles uniformly dispersed throughout the concrete. ASTM C260 also sets limits on the effects of any given air-entraining admixture on bleeding, time of setting, compressive and flexural strength, resistance to freezing and thawing, and length change on drying of a hardened concrete mixture in comparison with a similar concrete mixture that contains a standard reference air-entraining admixture, such as neutralized thermoplastic resin. Acceptance testing should follow ASTM C231/C231M. ASTM C457/C457M can be used to determine the actual parameters of the air-void system in hardened concrete to provide greater assurance that satisfactory resistance to freezing and thawing will be obtained.

4.4—Applications

Air-entrained concrete should be used wherever concrete contains absorbed moisture and is exposed to freezing and thawing, especially when deicing chemicals are used. Because air entrainment also improves the workability of concrete, it is particularly effective in lean mixtures and in various kinds of lightweight-aggregate concrete. Air entrainment is used in insulating and fill concrete (ACI 523.1R), structural lightweight concrete, and normalweight concrete. Blisters and delaminations can occur when normal-weight concrete with an air content above 3% receives a hard-troweled finish (ACI 302.1R; Bimel 1998).

No general agreement exists on the benefits of using air-entraining admixtures in the manufacture of concrete block (Farmer 1945; Kennedy and Brickett 1986; Kuenning and Carlson 1956), and air entrainment is used in some areas and is specified in other areas. Air-entraining admixtures, however, are marketed specifically for zero- and low-slump concrete to produce a stable air-void system with proper bubble size and spacing.

Air entrainment is desirable in wet-process shotcrete for the same purposes as in conventional concrete. The process of pumping, spraying, and impinging on a surface limits the air content of in-place shotcrete to approximately 4%, in spite of higher air contents before pumping (Morgan 1991).

In dry-process shotcrete, using air-entraining admixtures is questionable because there is no mixing to develop an acceptable air-void system (Segebrecht et al. 1989). Nevertheless, air-entrained dry-process shotcrete exhibits excellent durability when exposed to freezing and thawing (Litvin and Shideler 1966; Gebler 1992). ACI 506R recommends the air-entraining admixture be introduced to the mixture at the nozzle in combination with the mixing water.

4.5—Proportioning concrete

4.5.1 Air entrainment changes the properties of fresh concrete. Mixture designs should be proportioned in accordance with ACI 211.1 or ACI 211.2. Air-entrained

concrete will require an adjustment in proportions to achieve the required yield as compared to non-air-entrained concrete. The increased volume of air will require an equal volume reduction of aggregate, typically sand. Air entrainment may reduce water, particularly at low cementitious contents and often improves workability compared to non-air-entrained concrete at the same slump. At high cementitious material contents, air-entrained concrete becomes sticky and difficult to finish. Workability, finish, and setting time of the proposed mixture design can be verified with a successful placement on site. Air entrainment also reduces the accumulation of laitance or weak material at the surface of a lift. Air entrainment usually reduces the compressive strength of hardened concrete, particularly in concretes with moderate to high cementitious material contents. The reduction is approximately 5% for each percent of entrained air, but the rate of reduction of strength increases with higher amounts of air. Adding entrained air, however, reduces the water content required to maintain a specified slump. The w/cm can partially offset the reduction in strength. This is particularly true of lean mass concretes or concretes that contain a large maximum size aggregate. In these cases, air entrainment can cause a small decrease in strength, or even an increase. Nevertheless, while a proper air-void system should be provided, excessive amounts of entrained air should be avoided. A maximum air content of 3% should be specified for concrete receiving a steel-troweled finish. Air contents above that have resulted in significant blisters and slab delaminations (ACI 302.1R).

4.5.2 *Effects of materials and proportions*—Many factors can influence the amount of air entrained in concrete (Whiting 1983; Whiting and Nagi 1998). The dosage of an admixture required to obtain a given air content varies depending on the particle shape and grading of the aggregate. Organic impurities in the aggregate usually decrease the air-entraining admixture requirements. Hardness of water generally does not significantly affect the air-entraining admixture requirements (Wuerpel 1946). As concrete temperature increases, higher dosages of air-entraining admixtures are required to maintain the desired air content.

Increasing the cement content or the fineness of a cement decreases the amount of air entrained by a given amount of an admixture. Thus, larger amounts of air-entraining admixture are required in concrete containing high-early-strength Type III cement or portland-pozzolan cement (Type IP). High-alkali cements require a smaller amount of air-entraining admixture to obtain a given air content than do low-alkali cements. Similarly, increasing the amount of finely divided materials in concrete (by using fly ash, slag, or other pozzolans, carbon black or other pigments, or bentonite) also decreases the amount of air entrained by a fixed dosage of an admixture. An air-entraining admixture generally produces more air when calcium chloride is used as an accelerator. This effect is more pronounced with certain water-reducing admixtures where the amount of air-entraining admixture required to produce a given air content can be reduced by 1/3 or more (Dodson 1990). A satisfactory air-void system is required. Therefore, if the mixture constituents have not previously

proven to develop a satisfactory air-void system, they should be verified before use on a project.

The proportioning of air-entrained concrete is similar to that of non-air-entrained concrete. Methods of proportioning air-entrained concrete should follow the procedures of ACI 211.1 or ACI 211.2. These procedures incorporate the reduction in water and fine aggregate permitted by the improved workability of air-entrained concrete. The highest amount of air per unit of air-entraining admixture is developed within the 4 to 7 in. (100 to 175 mm) slump range. Within this slump range, as the w/cm is increased, air contents can increase, but the required characteristics of the air-void system may not be maintained (Dolch 1971).

4.6—Effect on fresh and hardening concrete
4.6.1 *Effect on fresh concrete*—Air entrainment in properly proportioned concrete may increase workability in low or moderate contents of cementitious materials. Air entrainment reduces segregation and bleeding, which helps to prevent the formation of pockets of water beneath coarse aggregate particles and embedded items such as reinforcing steel. Reduced bleeding and segregation minimizes the accumulation of laitance at the lift surface.

A properly air-entrained concrete would reduce bleeding and segregation characteristics and can improve pumpability. Air entrainment will not affect the setting time of the mixture. Air-entrained concrete may exhibit increased surface crusting and plastic cracking when placed in conditions of high temperature, low humidity, and wind.

4.6.2 *Effect of mixing*—The amount of air entrained varies with the type and condition of the mixers. Mixers become less efficient as the blades become worn or when hardened material is allowed to accumulate in the drum and on the blades. The air content may also change if there is a significant variation in batch size for a given mixer, especially if the batch size is different from the rated capacity of the mixer. Adams and Kennedy (1950) found that for various laboratory mixers, air content increased from approximately 4% to as much as 8% as the batch size was increased from 40 to 100% of rated mixer capacity.

Laboratory studies (Bloem and Walker 1946) have shown that the amount of entrained air increases with mixing time up to a maximum value, beyond which it slowly decreases. The air-void system, as characterized by a specific surface and spacing factor, usually is not harmed by prolonged mixing. If more water is added to achieve the desired slump, the air content should be checked because some adjustment may be required. Adding water without complete mixing may result in nonuniform distribution of air and water within the batch. Air void clustering may occur (Kozikowski et al. 2005). See ACI 304R for further details.

4.6.3 *Effect of transporting and consolidation*—The methods used to transport concrete after mixing, such as pumping, can affect both the amount and quality of air in the concrete. It has been reported that pumping can reduce the air content in concrete (Hover 1989; ACI 304.2R). Some admixtures, however, result in an increase in the air content during pumping (Burg 1985). The increase is apparently

caused by the increased shearing action imposed by the screw that moves the concrete from the hopper into the pump cylinder.

The type and degree of consolidation used in placing concrete can reduce the air content. Vibration applied to air-entrained concrete removes air as long as the vibration is continued (Backstrom et al. 1958); however, laboratory tests have shown that concrete's resistance to freezing and thawing is not reduced by moderate amounts of vibration. Stark (1986), however, has shown that extended vibration, particularly at high frequencies, can significantly reduce this resistance and can disrupt the smaller bubbles.

4.7—Effects on hardened concrete

4.7.1 *Freezing-and-thawing cycles*—Properly proportioned air-entrained concrete is resistant to freezing-and-thawing cycles after achieving 4000 psi (27.6 MPa).

4.7.2 *Compressive strength*—Air entrainment reduces the compressive strength of hardened concrete, particularly with moderate to high cementitious material contents. Reduction is approximately 5% for each percent of entrained air, however, the rate of reduction of strength increases with higher amounts of air. Adding entrained air reduces the water content required to achieve the specified slump. The result in *w/cm* can partially offset the reduction of strength. This is particularly true of lean cementitious content concretes and/or concretes that contain a large maximum-size aggregate. In these cases, air entrainment may cause only a small decrease in strength or possibly a slight increase in strength.

4.7.3 *Flexural strength*—Air-entrained concrete with the same *w/cm* shows a slight decrease in flexural strength (Mailvaganam 1984; Departments of the Army and the Air Force 1987).

4.7.4 *Permeability*—Air-entrained concrete with a *w/cm* of 0.45 or less will reduce permeability by intersecting internal capillaries that can provide ingress for liquids (Lukas 1981).

4.8—Quality assurance

4.8.1 *Benefits of air entrainment*—The full benefits of air-entrained concrete can only be realized when the mixture design provides consistent air contents that should be checked and verified in accordance with the recommendations of ACI 311.1R and ACI 311.4R. Proper air content in the hardened concrete is the key requirement. Air losses due to pumping, handling, transportation, and consolidating are not detected by air content tests performed at the mixer (ACI 309R). For control purposes, samples for determining air content should be taken directly from concrete at the point of deposit (ACI 301). The pumping process should eliminate freefall by a loop or slight curve in the line. When air loss between delivery and point of deposit becomes consistent, air content tests may be made at the point of delivery. Proper air content in the hardened state is the goal.

4.8.2 *Air control tests*—Air content tests of concrete should be made at regular intervals or whenever there is a reason to suspect a change in air content. The properties of the concrete-making materials, the proportioning of the concrete mixture, and all aspects of mixing, handling, and placing should be maintained as constantly as possible to ensure that the air content will be uniform and within the range specified for the work. Too much air may reduce strength without a commensurate improvement in durability, whereas too little air will fail to provide desired durability and workability.

4.8.3 *Test methods*—In general, air content tests are taken each time compressive and/or flexural test specimens are taken and at any other time so designated by the purchaser. Unit weight tests are recommended in addition to air meter tests to ensure that all the entrained air is recorded. Sometimes air meters do not detect the smaller entrained air bubbles. A chart indicating air contents versus unit weights can be established by the testing agency and be kept on site to quickly detect deviations from the specified air content envelope.

4.8.4 *ASTM standards*—There are three standard ASTM methods for measuring the air content of fresh concrete:
- The gravimetric method, ASTM C138/C138M;
- The volumetric method, ASTM C173/C173M; and
- The pressure method, ASTM C231.

The pressure method, however, is not applicable to lightweight concrete. The Chace Air Indicator (Grieb 1958), which is an adaptation of the volumetric method, has not been standardized and should not be used to determine compliance with specification limits. The ASTM methods measure only air volume and not the air-void characteristics. While the spacing factor and other significant parameters of the air-void system in hardened concrete have traditionally been determined only by microscopic methods such as those described in ASTM C457/C457M, methods have been developed (Wojakowski 2003; Whiting l993) that determine air-void parameters of fresh concrete.

4.9—Batching

4.9.1 *Uniformity*—To achieve the greatest uniformity between batches of a concrete mixture, water-soluble, air-entraining admixtures should be added to the mixture in the form of solutions rather than solids. Generally, only small quantities of air-entraining admixtures—approximately 0.05% of active ingredients by mass of cementitious materials—are required to entrain the desired amount of air. If the admixture is in solid or semisolid forms, a solution should be prepared before use, following the recommendations of the manufacturer.

4.9.2 *Dosages*—The dosage required to achieve the desired air content should be determined by trial mixtures, starting from the manufacturer's recommendations or from experience. For any given set of conditions and materials, the amount of air entrained is roughly proportional to the amount of admixture used. Proper air content problems are particularly acute during hot weather.

4.10—Storage

Air-entraining admixtures should be stored in strict accordance with the manufacturer's recommendations. Although most admixtures usually are not damaged by freezing, the manufacturer's instructions should be followed regarding the effects of freezing the product. An admixture stored beyond its recommended shelf life should be retested before use.

CHAPTER 5—ACCELERATING ADMIXTURES
5.1—Introduction

An accelerating admixture is "an admixture that causes an increase in the rate of hydration of the hydraulic cement and thus shortens the time of setting, increases the rate of strength development, or both" (American Concrete Institute 2010). Accelerating admixtures purchased for the use in concrete should meet the requirements of ASTM C494/C494M for Type C, accelerating admixtures, or Type E, water-reducing and accelerating admixtures.

Accelerating admixtures are used to decrease setting time and increase early strength gain, particularly in cold weather, to expedite the start of finishing operations, reduce finishing time, and reduce the time required for proper curing and protection; and to increase the early-strength level to permit earlier form removal and decrease the overall construction time. Accelerators are normally used in conjunction with other recommended practices (ACI 306R) to counteract the effects of low temperatures. Quick-setting admixtures permit more efficient plugging of leaks against hydrostatic pressure and produce rapid setting of concrete placed by shotcreting.

Certain accelerating admixtures used in combination with high-range water-reducing admixtures significantly lower the freezing point of concrete and allow concrete placement to 20°F (–7°C). These admixtures and their effects are discussed in detail in Chapter 9, Cold Weather Admixture Systems.

5.2—Materials

Accelerating admixtures can be divided into four groups: those that contain soluble inorganic salts; those that contain soluble organic compounds; quick-setting admixtures; and miscellaneous solid admixtures. Water-reducing and accelerating admixtures are often formulated with one or more of the compounds listed in Section 6.2.2 to produce the required water reduction.

5.2.1 *Soluble inorganic salts*—Studies (Edwards and Angstadt 1966; Rosskopf et al. 1975) have shown that a variety of soluble inorganic salts, including chlorides, bromides, fluorides, carbonates, thiocyanates, nitrites, nitrates, thiosulfates, silicates, aluminates, and alkali hydroxides, decrease the setting time of portland cement. Of these salts, calcium chloride is the most widely used because it is the most cost-effective. Research by numerous investigators has shown that inorganic accelerating admixtures act primarily by accelerating the hydration of tricalcium silicate (Ramachandran and Malhotra 1984). Calcium chloride should meet the requirements of ASTM D98. Forms of calcium chloride and their equivalent masses are shown in Table 5.1.

5.2.2 *Soluble organic compounds*—The most common organic accelerating admixtures in this class are triethanolamine and calcium formate, which are commonly used to offset the retarding effects of water-reducing admixtures or to provide noncorrosive acceleration. The effectiveness of calcium formate depends on the tricalcium aluminate-to-sulfur trioxide ratio (C_3A/SO_3) of the cement (Gebler 1983). Cements that are under-sulfated ($C_3A/SO_3 > 4.0$) provide the best potential for calcium formate to accelerate the early-age

Table 5.1—Calcium chloride: amount introduced

Calcium chloride by mass of cement, %	Solid form, %		Liquid form, 29% solution[‡] L/100 kg (qt/100 lb)	Amount of chloride ion added, %
	Dihydrate[*]	Anhydrous[†]		
0.5	0.7	0.5	0.57 (0.6)	0.3
0.8	1.0	0.8	0.95 (1.0)	0.5
1.0	1.3	1.0	1.14 (1.2)	0.6
1.5	2.0	1.5	1.70 (1.8)	1.0
2.0	2.6	2.0	2.27 (2.4)	1.3

[*]Commercial flake products generally have an assay of 77 to 80% calcium chloride, which is often close to dihydrate.

[†]Commercial anhydrous calcium chloride generally has an assay of 94 to 97% calcium chloride. Remaining solids are usually chlorides of magnesium, sodium, or potassium, or combinations thereof. Thus, the chloride content, assuming the material is 100% calcium chloride, introduces very little error.

[‡]A 29% solution often is the concentration of commercially used liquid forms of calcium chloride and is made of dissolving 0.45 kg (1 lb) dihydrate to make 0.95 L (1 qt) of solution.

strength of concrete. The production of ettringite is greater in mixtures containing calcium formate (Bensted 1978).

Accelerating properties have been reported for calcium salts of carboxylic acid, including acetate (Washa and Withey 1953), propionate (Arber and Vivian 1961), and butyrate (RILEM 1968). Salts of the higher homologs, however, are retarders (RILEM 1968).

Studies (Ramachandran 1973, 1976a) indicate that triethanolamine accelerates the hydration of tricalcium aluminate but retards hydration of tricalcium silicate. Thus, triethanolamine can act as a retarder of cement at high dosages or low temperatures. A number of other organic compounds have been found to accelerate the setting of portland cement when a low *w/cm* is used. Organic compounds reported as accelerating admixtures include urea (RILEM 1968), oxalic acid (Bash and Rakimbaev 1969; Djabarov 1970), lactic acid (Bash and Rakimbaev 1969; Lieber and Richartz 1972), various cyclic compounds (Lieber and Richartz 1972; Wilson 1927), and condensation compounds of amines and formaldehyde (Rosskopf et al. 1975; Kossivas 1971). Retardation can occur if high dosages are used, because like triethanolamine, such compounds will retard the hydration of tricalcium silicate.

5.2.3 *Quick-setting admixtures*—Quick-setting admixtures are used to produce quick-setting mortar or concrete suitable for shotcreting and sealing leaks against hydrostatic pressure. These admixtures are believed to act by promoting the flash setting of tricalcium aluminate (Schutz 1977). Ferric salts, sodium fluoride, aluminum chloride, sodium aluminate, and potassium carbonate are reported to produce quick-setting (Mahar et al. 1975) mortars, but many proprietary formulations are mixtures of accelerating admixtures.

Quick-setting admixtures for shotcrete, employed extensively in both the dry and wet processes (ACI 506R), are a specific class of quick-setting admixtures, traditionally based on soluble aluminates, carbonates, and silicates. These materials are caustic, hazardous, and require special handling (refer to material safety data sheets from the manufacturer). Newer, neutral-pH, chloride-free proprietary admixtures, based on specific sugar-acid compounds, are available to overcome these deficiencies. Generally, the wet-process shotcrete mixture quickly stiffens and reaches a rapid initial

set, with final set occurring within 60 minutes. The early stiffening imparted by the accelerator, however, aids in vertical and overhead placement. Using dry-process shotcrete and a compatible cement and accelerator, an initial setting time of less than 1 minute and a final setting time of less than 45 minutes can be attained. The rate of strength gain can be greatly accelerated using quick-setting admixtures in dry-process shotcrete. Strength in excess of 3000 psi (1 MPa) in 8 hours is typical for a noncaustic accelerator and 2000 psi (14 MPa) is typical for a conventional caustic accelerator.

5.2.4 *Miscellaneous solid admixtures*—In certain instances, hydraulic cements have been used in place of accelerating admixtures. For example, calcium-aluminate cement can cause flash setting of portland-cement concrete (Robson 1952) depending on the dosage rate. Various silicates have been found to act as accelerating admixtures (Angstadt and Hurley 1967; Kroone 1968). Finely divided silica gels and soluble quaternary ammonium silicates have been found to accelerate strength development (Stein and Stevels 1964; Nelson and Young 1977; Wu and Young 1984) through the acceleration of tricalcium silicate hydration. Silica fume also accelerates tricalcium silicate hydration (Kurdowski and Nocum-Wezelik 1983; Lu et al. 1993). Adding finely divided magnesium carbonate (Ulfstedt et al. 1961) or calcium carbonate (RILEM 1968) decreases setting times.

5.3—Selection and evaluation
The selection of an accelerator should be based on its performance with local cements, blended cements, and mixtures containing supplementary cementitious materials. Optimum dosage will also vary with the job-site temperatures. Historical test data can be used to guide the accelerator selection. The effects on a specific mixture design should be determined by individual tests simulating the expected usage conditions. Accelerators will vary in relative performance based on different cement characteristics and concrete temperatures. Nonchloride accelerators are cement-sensitive and produce significantly different results with respect to setting time as well as early strength gain with different cements. The overall effect of their usage with mixtures containing pozzolans or slag is generally proportional to the amount of cement in the mixture.

Nonchloride accelerators are increasingly being used because of corrosion concerns of engineers and users. Caution is urged with the use of accelerating admixtures in concrete containing shrinkage-compensating cements or shrinkage-compensating components (ACI 223). Such concretes require evaluation on a case-by-case basis, as the accelerator can affect the timing and the amount of expansion.

Calcium chloride should not be used with calcium aluminate cement because it often retards the hydration of the aluminates. Similarly, both calcium chloride and potassium carbonate retard the setting time and decrease the early strength development of rapid-hardening cements based on calcium fluoroaluminate ($C_{11}A_7$-CaF_2). Strengths at 1 day, however, are improved by these admixtures.

Evaluation of the accelerator requires the comparison of decreased setting time, increased early strength, and the cost of the accelerator versus the nonaccelerated mixture design performance with respect to finishing time, stripping time, and hardened concrete properties. For example, extended retardation of floor and slab concrete allows excessive bleeding, segregation, and early cracking, thereby reducing surface quality. In addition, labor costs are increased because of the extended finishing time or because of form removal delays. Thus both quality and cost considerations can favor the use of accelerating admixtures. Alternate choices in cold weather include the use of high-early-strength cement instead of Type I cement.

5.4—Applications
5.4.1 *Reduce placing and finishing time*—Accelerating admixtures are commonly used in concrete slabs placed at air temperatures below 50°F (10°C). They will often be used in formed concrete placed at air temperatures below 40°F (4°C). Accelerating admixtures are often used to reduce or normalize the initial set of floors and slabs to reduce the overall placing and finishing time and prevent the ill effects of extended retardation on the quality of the final product.

5.4.2 *Increase early strength gain*—Accelerating admixtures are regularly used, in a properly proportioned mixture, to achieve early strength gain required by the project specification or the contractor's schedule.

5.4.3 *Rapid cycle elevated slab construction*—Accelerators are frequently chosen for this type of construction to reduce initial set and provide high early strength. Initial set reduction is required because the contractor will be walking on the slab in the late morning or early afternoon to lay out and form vertical members for the upper floor. High early strength levels must be achieved to allow early stripping and reuse of forms.

5.5—Proportioning concrete
5.5.1 *Fresh concrete properties*—Accelerating admixtures change the properties of fresh concrete. Mixture designs should be proportioned in accordance with ACI 211.1 or ACI 211.2. The accelerator dosage will be determined by the desired initial setting time and early strength gain. Water-reducing and accelerating admixtures reduce the water content more than 5%. This dosage will be influenced by the setting characteristics of the cement chosen, the member mass, and climatic conditions of temperature and wind. Accelerating admixtures Type C or Type E generally replace the Type A admixture used in a normal setting mixture. They are added to mixture designs containing high-range water-reducing admixtures. In this case, the benefits of the high-range water-reducing admixture, with respect to water content, slump level, and *w/cm*, must be maintained. The accelerating admixture dosage is selected to normalize setting time and early strength gain; to significantly increase early strength levels; or, as outlined in Chapter 9, Cold Weather Admixture Systems, allow concrete operations to take place during cold weather conditions that normally preclude concrete placement.

5.5.2 *Initial mixture design*—The initial mixture design testing is normally done in a laboratory. The final mixture design selection is based on successful on-site placement to

verify setting time; early strength gain; and the standard mixture design qualities such as satisfactory workability, pumpability, or, for slabs, finishing characteristics.

5.5.3 *Dosages*—Accelerating mixture designs are often prepared with varying dosages. This allows the contractors to base their daily mixture design selections on the actual temperatures and wind conditions, as well as the setting characteristics of the concrete being supplied that day. Often the mixture design on rapid cycle projects has a higher dosage of accelerator in the first half of the slab since that area must set so that the contractor can walk on it in the late morning or early afternoon without marring the surface. In other projects, the accelerator dosage is increased in the last portion of slab concrete to minimize finishing over time.

5.6—Effects on fresh and hardening concrete

5.6.1 *Time of setting*—Initial and final setting times are reduced by an amount dependent on the dosage of accelerator used, the temperature of the concrete, the ambient temperature, and the characteristics of other materials used in the concrete. Many accelerators have a greater accelerating effect at 32 to 41°F (0 to 5°C) than at 77°F (25°C). High dosages of accelerating admixtures can cause very rapid setting in hot weather. Excessive dosage rates of certain organic compounds may result in extended times of setting. Similarly, at high dosages (6% by mass of cement), calcium nitrate begins to show retarding properties (Murakami and Tanaka 1969), whereas ferric chloride retards at additions of 2 to 3% by mass, but accelerates at 5% (Rosskopf et al. 1975). With quick-setting admixtures, setting times as short as 15 to 30 seconds can be attained. Prepackaged mortar formulations are available that have an initial time of setting of 1 to 4 minutes and a final setting time of 3 to 10 minutes They are used to seal leaks in below-grade structures, for patching, and for emergency repair. The ultimate strength of such mortar is much lower than if no accelerating admixture had been added.

5.6.2 *Air entrainment*—When an accelerating admixture is used, different dosages of air-entraining admixture may be required to produce the required air content. In some cases, however, larger bubble sizes and higher spacing factors are obtained, possibly reducing the beneficial effects of entrained air. Concrete containing a specific admixture may be evaluated to ascertain air-void parameters using ASTM C457/C457M or resistance to freezing and thawing using ASTM C666/C666M.

5.6.3 *Freezing and thawing*—Concrete must achieve a compressive strength of 500 psi (3.4 MPa) before freezing. Concrete exposed to freezing and thawing in service must achieve a compressive strength of 4000 psi (27.6 MPa) prior to being exposed to freezing-and-thawing cycles. Properly proportioned mixture designs with accelerators can achieve this strength more quickly.

5.7—Effects on hardened concrete

5.7.1 *Discoloration of flatwork*—Discoloration of concrete flatwork has been associated with the use of calcium chloride (Greening and Landgren 1966). Two major types of mottling discoloration can result from the interaction

between cement alkalis and calcium chloride. The first type has light spots on a dark background and is characteristic of mixtures in which the ratio of cement alkalis to calcium chloride is relatively low. The second consists of dark spots on a light background, and is characteristic of mixtures in which the ratio of cement alkalis to chlorides is relatively high. The magnitude and permanence of discoloration increase as the calcium chloride concentration increases from 0 to 2% by mass of cement. Discoloration can be aggravated by high rates of evaporation during curing and by improper placement of vapor barriers (the use of a sheet membrane for curing that is not kept flat on the surface). Using a continuous fog spray during placement or a proper curing compound can help alleviate this problem.

5.7.2 *Strength development*—Many accelerators increase compressive strength substantially at early ages. In some cases, later strength may be reduced slightly. Strength gains up to 200%/day can be achieved with varying dosages of many accelerators. These early strength levels are very dependent on the strength potential of the selected cement. Flexural strength of 400 psi (2.76 MPa) has been achieved in 4 hours with certain accelerators, cements, and high-range water-reducing admixtures. Certain accelerators with high-range water-reducing admixtures have easily achieved 4000 psi (27.6 MPa) in 12 hours in the laboratory and in the field. The percentage increase in flexural strength is usually less than that of the compressive strength (Ramachandran 1976b). The effects of other accelerating admixtures on strength development are not completely known, although other calcium salts behave similarly. Because accelerated strength development depends on accelerated hydration, heat of hydration also develops faster, but there is no appreciable effect on total heat generation. Quick-setting admixtures, such as carbonates, silicates, and aluminates, may decrease concrete strengths and ultimate strengths as early as 1 day (Mailvaganam 1984). Quick-setting mixtures of portland cement and calcium-aluminate cement behave similarly. Organic compounds such as triethanolamine and calcium formate appear to be sensitive in their accelerating action to the particular concrete mixture to which they are added, and to the ambient temperature.

Preliminary laboratory tests should be followed by field tests to assure that the proposed mixture design easily achieves the target strength levels at early and late ages without presenting placing or finishing problems due to too quick setting characteristics.

5.7.3 *Volume change*—Accelerating admixtures can increase the volume changes that occur under moist curing and drying conditions. Calcium chloride can increase creep and drying shrinkage of concrete (Shideler 1942). Mather (1964) offered an alternative hypothesis to the presumed association of the use of calcium chloride with increased drying shrinkage. Bruere et al. (1971) observed that such volume changes depend on the length of curing before beginning measurements, the length of the drying or loading periods, and the composition of the cement used. They also noted that changes in the rate of deformation are greater than changes in the total deformation. Berger et al. (1967)

suggested that the influence of calcium chloride in drying shrinkage can result from changes in the size distribution of capillary pores due to calcium chloride's effect on hydration of the cement. Drying shrinkage and swelling in water are higher for mixtures containing both portland calcium-aluminate cements and calcium chloride, and their durability may be adversely affected by using an accelerating admixture (Feret and Venuat 1957).

Excessive shrinkage and subsequent cracking can significantly decrease durability characteristics. Therefore, shrinkage tests on the proposed mixtures should be required.

5.7.4 *Freezing and thawing*—Properly proportioned mixtures with the proper air content and *w/cm* and many accelerators provide very satisfactory long-term resistance to freezing and thawing.

5.7.5 *Chemical attack*—Resistance to sulfate attack is decreased when conventional portland-cement concrete mixtures contain calcium chloride (USBR 1975), but when used with Type V cement to mitigate the effects of cold weather, it is not harmful (Mather 1992). The expansion produced by alkali-silica reaction (ASR) is greater when calcium chloride is used (USBR 1975). Nonchloride admixtures may increase expansion.

5.8—Corrosion of metals

One of the major disadvantages of calcium chloride is that it induces corrosion of metals embedded in concrete when in the presence of sufficient moisture and oxygen. ACI 318 lists the chloride limits for concrete in new construction that should be used to determine the maximum permissible water-soluble chloride-ion content for concrete in various types of construction (shown in Table 5.2). Table 5.3 shows the acid-soluble and water-soluble chloride limits for new construction reported by ACI 222R. Gaynor (1985) discusses the calculation of chloride contents for comparison with these limits, as seen in Table 5.4. The user should evaluate the chloride levels from all ingredients. Other factors such as moisture and oxygen are always necessary for electrochemical corrosion. Many nonchloride-based accelerators are available. The use of calcium chloride will aggravate the effects of poor-quality concrete construction, particularly when the concrete is exposed to chlorides during service. When good construction practices are followed, the limits listed in Table 5.2 have shown to be highly effective in limiting corrosion. The user should determine whether a nonchloride accelerator would be a better choice in the particular type of construction. The chlorides contributed by all ingredients should then be determined. The potential for in-service corrosion should be evaluated accordingly.

Background chloride contents in concrete are naturally-occurring chlorides in the concrete materials. When background chloride or when the chloride content is found to be excessive, the Soxhlet Method should be conducted for final acceptance. The Soxhlet Method for aggregates is detailed in ASTM C1524 and the Soxhlet Method for concrete is detailed in ACI 222.1.

If the concrete or mortar fails the acid-soluble test according to ASTM C1152/C1152M, then the water-soluble test must be conducted according to ASTM C1218/C1218M.

Table 5.2—Maximum chloride-ion concentration for corrosion protection (ACI 318-08)

Type of member	Maximum water-soluble chloride ion in concrete, percent by mass of cement
Prestressed concrete	0.06
Reinforced concrete exposed to chloride in service	0.15
Reinforced concrete that will be dry or protected from moisture in service	1.00
Other reinforced concrete construction	0.30

Table 5.3—Chloride limits for new construction (ACI 222R)

	Chloride limit for new construction, percent by mass of cement		
	Test method		
	Acid-soluble	Water-soluble	
Category	ASTM C1152/C1152M	ASTM C1218/C1218M	Soxhlet[*]
Prestressed concrete	0.08	0.06	0.06
Reinforced concrete in wet conditions	0.10	0.08	0.08
Reinforced concrete in dry conditions	0.20	0.15	0.15

[*]The Soxhlet test method is described in ACI 222.1.

Table 5.4—Calculation of total chloride-ion content[*]

1	2	3	4	5
Ingredient	lb/yd^3 (or dosage)	Total Cl$^-$, percent by weight of each material	Calculation	Total Cl$^-$, lb
Cement	600	0.005	$(0.005)(600)$ (10^{-2})	0.03
Sand (SSD)	1150	0.01	$(0.01)(1150)$ (10^{-2})	0.115
Coarse aggregate (SSD)	1800	0.106	$(0.106)(1800)$ (10^{-2})	1.908
Water	280	250 ppm	$(205)(280)$ (10^{-6})	0.07
Admixture	(5 oz/100 lb)[†]	800 ppm	$(800)(5)(6)$ $(1/16)(10^{-6})$	0.0015

Total Cl$^-$ in yd^3 = 2.1245 lb
Total chloride, percent by weight of cement = (2.1245/600)100 = 0.354%

[*]From Gaynor (1985).
[†]Per 100 lb of cement.
Note: 1 lb/yd^3 = 0.5933 kg/m^3; 1 lb = 0.4536 kg; 1 yd^3 = 0.7646 m^3; and 1 oz = 29.574 mL.

If the results from the water soluble test fail, then the Soxhlet method for water-soluble (extractable) chloride may be conducted.

Admixtures based on calcium nitrate or thiocyanates have been proven effective in accelerating initial set and early strength gain. The fact that an accelerating admixture does not contain significant amounts of chloride, however, does not necessarily render it noncorrosive; for example, Manns and Eichler (1982) report that thiocyanates may promote corrosion. Nmai and Corbo (1989), however, found that the threshold level for initiation of corrosion by sodium thiocyanate lies between 0.75 and 1.0% by mass of cement, and

concluded that the use of sodium thiocyanate-based accelerating admixtures is safe for reinforced concrete applications up to these concentrations. Typical dosages of accelerating admixtures containing sodium thiocyanate contribute between 0.05 and 0.1% sodium thiocyanate by mass of cement, and extremely high dosages may contribute as much as 0.2% sodium thiocyanate. Users may request that suppliers of all nonchloride admixtures provide information regarding the corrosion of steel in concrete. The information should include corrosion results within the intended dosage range.

5.9—Quality assurance

Accelerator performance in properly designed mixtures should be monitored regularly by checking concrete temperatures, initial set, and the early strength levels expected. A correlation should be developed between laboratory-cured compressive strength cylinders versus in-place concrete strengths determined from cores, and monitored in accordance with the maturity method. Cylinders are often cured in the field to verify the predicted early strength levels are being achieved. Care should be given as to the curing of the test specimens because their mass is dissimilar to that of the concrete. The maturity method, based on thermocouple probes inserted into the slab, has proven accurate in predicting early strengths based on temperature developments of the pretested mixture design.

5.9.1 *Strength development*—The strength level of the actual concrete member is particularly important so that the project schedule can be met without risk to the concrete team. Cold weather concreting operations present a challenge to the concrete contractor and concrete producer. The number and type of tests used to assure strength level attainment should be thoroughly discussed at the preconcrete conference and implemented carefully in the field.

5.9.2 *Field testing*—Valuable field testing also involves monitoring the temperature of the concrete upon arrival and later in the slab. Because the concrete temperature directly affects the hydration process, it is an accurate predictor of concrete performance that day. Concrete that loses 5°F (3°C) or more in the first hour after placement indicates that the mixture design contains slow-setting cement, excessive supplementary cementitious materials, and/or a too-low dosage or the wrong choice of an accelerator. An increase in dosage may solve the problem. The measures advocated in ACI 306R should be implemented in all cases.

5.10—Batching

5.10.1 *Dosage rates*—Accelerating admixtures should be added to the mixture in solution form. The nonchloride accelerators are generally added at a dosage range of 10 to 30 oz/100 lb (652 to 1956 mL/100 kg) of cementitious material. Calcium chloride solutions, where permitted, are generally added at 1 to 2% lb of solids/100 lb of cement (kg/mass of cement). The typical calcium chloride-based accelerator solids content is 30% or approximately 10.6 lb/gal. (1.3 kg/L). The nonchloride accelerators range in solids content from 40 to 60%. The correct density should be obtained from the supplier.

5.10.2 *Specific gravity*—The specific gravity should be checked periodically and should be within ±0.05 of the manufacturer's designated specific gravity.

5.11—Storage

Accelerators should be stored in strict accordance with the manufacturer's recommendations. Most admixtures are not damaged by freezing. The manufacturer's instructions should be followed regarding the effects of freezing the product. An admixture stored beyond its recommended shelf life should be retested before use.

CHAPTER 6—WATER-REDUCING AND SET-RETARDING ADMIXTURES

6.1—Introduction

Water-reducing admixtures reduce the water requirements of a concrete mixture for a given slump and may modify the time of setting. Water-reducing admixtures are formulated for normal, retarding, and accelerating setting characteristics. Chapter 5, Accelerating Admixtures, addresses water-reducing and accelerating admixtures. Admixtures formulated for normal water reduction and normal setting characteristics always meet the requirements of ASTM C494/C494M Type A. Retarding admixtures and water-reducing and retarding admixtures must meet the requirements of ASTM C494/C494M Types B and D, respectively. At higher dosages, some water-reducing admixtures have a tendency to retard the setting time of the concrete, mortar, or grout, thus limiting the water reduction to less than 10%. Often, water-reducing admixtures that do not retard setting time are produced by combining water-reducing materials with an accelerating component. The change in time of setting (retarding, non-retarding normal setting, or accelerating) depends on the relative amounts of each ingredient used in the formulation.

Water-reducing admixtures formulated for normal setting characteristics at higher dosages, using the above approach, that also often include the addition of nonionic surfactants to aid water reduction and workability, are known as mid-range water-reducing admixtures (MRWRA) (Nmai et al. 1998a). Although there is no classification for MRWRA, these admixtures always meet the requirements of ASTM C494/C494M Type A water-reducing admixtures, and sometimes meet ASTM C494/C494M Type F HRWRAs. HRWRAs may achieve up to 40% water reduction at higher dosages, such as 0.8% per 100 lb (45.4 kg) of cementitious materials. A Type A water-reducing admixture may retard set at a dosage higher than 0.2% per 100 lb (45.4 kg). of cementitious materials. MRWRA may provide up to 12% water reduction without significantly delaying the setting time of the concrete. Conventional water-reducing admixtures cannot do this because they become too retarding at higher dosages. HRWRAs must meet the requirements of ASTM C494/C494M Type F HRWRAs, or Type G high-range water-reducing and retarding admixtures. HRWRAs are addressed in more detail in ACI 212.4R. Normal-setting HRWRAs differ from conventional water-reducing admixtures in that they do not significantly delay the hydration

process until much higher dosages are used (up to 0.75% by mass of cement). Therefore, HRWRAs can provide significantly greater water reduction without excessive air entrainment or retardation. At lower concentrations, they impart the same water reduction and strength benefits as other water-reducing admixtures.

6.2—Materials

6.2.1 *Classification*—Water-reducing and set-controlling admixtures should meet the applicable requirements of ASTM C494/C494M, which defines seven types:
- Type A—Water-reducing admixtures;
- Type B—Retarding admixtures;
- Type C—Accelerating admixtures (refer to Chapter 5);
- Type D—Water-reducing and retarding admixtures;
- Type E—Water-reducing and accelerating admixtures;
- Type F—Water-reducing, high-range admixtures; and
- Type G—Water-reducing, high-range, and retarding admixtures.

ASTM C494/C494M gives detailed requirements with respect to water requirement, setting time, flexural and compressive strength, drying shrinkage, and resistance to freezing and thawing. ASTM C494/C494M Types F and G are also covered by ASTM C1017/C1017M as Type I and Type II (refer to Chapter 7). ASTM recently approved a Type S (specialty admixture) designation that includes admixtures not covered by other ASTM standards.

The specific effects of water-reducing admixtures, however, vary with different cements, addition sequences, changes in *w/cm*, mixing temperature, ambient temperature, and other site conditions (ACI 212.4R). Most water-reducing admixtures perform considerably better than the minimum requirements of ASTM C494/C494M regarding water reduction and compressive strength. The dosage at which a water-reducing admixture meets the performance requirements in ASTM C494/C494M with a given cement may be higher or lower when tested with different concrete ingredients and proportions.

6.2.2 *Compositions*—Materials generally available for use as water-reducing admixtures fall into one of seven general categories of compounds. Formulations can include, but are not limited to, compounds from more than one category:
1. Lignosulfonic acids and their salts and modifications and derivatives of these;
2. Hydroxylated carboxylic acids and their salts and modifications and derivatives of these;
3. Carbohydrate-based compounds such as sugars, sugar acids, and polysaccharides;
4. Salts of sulfonated melamine polycondensation products;
5. Salts of sulfonated napthalene polycondensation products;
6. Polycarboxylates; and
7. Other materials such as nonionic surface-active agents; amines and their derivatives; organic phosphonates including zinc salts, borates, phosphates, and certain polymeric compounds, including cellulose-ethers, silicones, and sulfonated hydrocarbon acrylate derivatives may be used to modify the formulations.

6.3—Selection and evaluation

If adequate information is not available, tests should be done to evaluate the effect of the water-reducing admixture on the properties of concrete made with job materials under the anticipated ambient conditions and construction procedures. Tests of water-reducing admixtures should indicate their effect on the following properties of concrete, insofar as they are pertinent to the job:
- Water requirement;
- Air content;
- Slump;
- Bleeding and possible loss of air from the fresh concrete;
- Setting time;
- Compressive and flexural strength at 28 days, or the specified age of the concrete;
- Required strength development;
- Resistance to freezing and thawing; and
- Drying shrinkage.

When water-reducing admixtures are evaluated in laboratory trial batches before use, a series of mixtures should be planned to provide the necessary information. The mixtures need not follow ASTM C494/C494M procedures. The trial mixtures should be made with the same cementitious materials and other concrete-making materials that will be used on the project and as close to job conditions as possible. Temperature is particularly important to setting time and early strength development. Air content and setting time of field concrete can differ considerably from that of laboratory concrete with the same materials and mixture proportions. The action of a water-reducing admixture may differ in a truck mixer from that seen in a laboratory mixer. The admixture dosage will probably have to be adjusted to get the same performance in the truck. In most cases, HRWRAs will be more efficient when mixed in a truck and the dosage will come down. All parties should be alert to this possibility at the start of a job and should be ready to adjust the amounts of materials (particularly air-entraining admixtures) to achieve the specified properties of the concrete at the project site.

6.4—Applications

Water-reducing admixtures lower the *w/cm* and are used to produce higher strength and increased durability, to obtain a required strength at lower cement content, or to increase slump without an increase in water content, or combinations of these objectives. They also may improve the properties of concrete containing aggregates that are harsh, poorly graded, or both, or may be used in concrete that will be placed under difficult conditions. Water-reducing admixtures are useful when placing concrete by pump or tremie.

Water-reducing and retarding admixtures are used primarily to offset the accelerating effect of high ambient temperature (hot weather) and to keep concrete workable during the entire placing period. This method is particularly valuable to prevent cracking of concrete beams, bridge decks, or composite construction caused by form deflections. Water-reducing and retarding admixtures are also used to keep concrete workable long enough so that succeeding lifts can be placed without development of cold joints in the

structural unit. Their effects on rate of slump loss vary with the particular combinations of materials used. In hot weather conditions, concrete should be placed in accordance with ACI 305R.

MRWRAs are typically used to produce concrete within a slump range from 75 to 200 mm (3 to 8 in.). MRWRAs are beneficial in improving the finishing and pumping characteristics of concrete.

HRWRAs can produce large reductions in the water content of concrete—over 30% reduction has been achieved. HRWRAs are often used in the production of high-strength concrete, precast/prestressed concrete, architectural concrete, parking and bridge structures, rapid-recycle high-rise projects, industrial slabs, and massive concrete structures (ACI 212.4R). HRWRAs are often used to produce flowing concrete with slump in excess of 8 in. (200 mm) (refer to Chapter 7). Some HRWRAs can be used in conjunction with proper mixture proportioning and other materials to produce self-consolidating concrete (SCC) with slump flow values up to 30 in. (760 mm). HRWRAs also have been used to reduce cement content. Because the *w/cm* affects the strength of concrete, the cement content may be reduced with a proportional reduction of the water content for equivalent or higher-strength concrete due to increased cement efficiency, resulting in cost savings. In mass concrete, low cement content is particularly desirable because it lowers the temperature rise of the concrete, as detailed in Section 6.7.7 of this document.

6.5—Dosage

The expected performance of a given brand, class, or type of water-reducing admixture may be estimated from one or more of the following sources of information:

- Results from jobs where the admixture has been used under good field control, preferably using the same materials and under conditions similar to those anticipated;
- Laboratory tests made to evaluate the admixture; and
- Technical literature and information from the manufacturer.

The dosage of the admixture should be determined from information provided by one or more of these sources. Varying results can be expected with a given admixture due to differences in cements, aggregates, other materials, and weather conditions. In the production of high-strength concrete (above 6000 psi [41 MPa]), it is beneficial to increase the dosage of the admixture. This usually provides extra water reduction and typically a delay in setting time and slow early strength gain. Concrete with slow early strength gain generally exhibits higher later strengths (Rixom and Mailvaganam 1999; ACI 363R).

Concrete containing an HRWRA sometimes has rapid slump loss. To overcome this, a second addition of the HRWRA may be used to restore the slump, without any negative effects. Generally, more than two additions are less effective and concrete may lose its workability faster than with a single dose. Redosing may result in lower air content, on the order of 1 to 2 percentage points for each redose. When redosages are used, the concrete may have a greater potential for bleeding, segregation, and possible retardation of setting time. Therefore, trial mixtures should be conducted to determine the effects of redosing. If slump loss is a concern, the type of HRWRA should be reviewed. The period of required plasticity should be verified by placing the proposed mixture on the project. Products that increase efficiency, improving cohesiveness and maintaining workability for longer periods of time, are available. These HRWRAs can be added at the batch plant rather than at the job site, thereby reducing wear on truck mixers and lessening the need for ancillary equipment such as truck-mounted admixture tanks and dispensers (ACI 212.4R).

6.6—Proportioning concrete

When a concrete mixture that is considered satisfactory in workability and finishing qualities is modified to incorporate a water-reducing admixture, the ratio of mortar to coarse aggregate by volume should remain the same. Changes in water content, cementitious material content, and air content are compensated for by corresponding changes in the content of fine aggregate—all on a solid or absolute volume basis—so that the volume of mortar remains the same. Procedures for proportioning and adjusting concrete mixtures are covered by ACI 211.1. Most water-reducing admixtures are water solutions. The water they contain becomes a part of the mixing water in the concrete and should be considered in the calculation of *w/cm*, if the added amount of water is significant. The proportional volume of the solids included in the admixture is so small in relation to the size of the batch that it can be neglected.

Concrete proportioned for high-strength concrete (8000 psi [55 MPa] at 28 days or higher) using HRWRAs, usually has a sufficiently high cement content to supply the fines required for good workability. Such concrete can be reproportioned by making up the volume of water reduced by increasing the volume of coarse or fine aggregate equally. If trial mixtures are sticky, the volume of coarse aggregate should be increased, and that of the fine aggregate reduced. This usually results in a mixture that is easier to place and finish.

6.7—Effects on fresh and hardening concrete

6.7.1 *Water reduction*—ASTM C494/C494M Type A water-reducing admixtures and Type D water-reducing and retarding admixtures decrease the water required for the same slump concrete by at least 5%, and in some cases water-reducing admixtures decrease the water by up to 12%, as is the case with MRWRAs. Concrete containing lignosulfonate or hydroxylated carboxylic acid salts reduce the water content 5 to 10% for a given slump and cement content. HRWRAs should reduce the water requirement at least 12%, but there is no upper limit to water reduction. Reductions of over 30% have been reported (Portland Cement Association 2009) and HRWRAs can be used to significantly increase slump without increasing water content and may be used to achieve a combination of these two objectives—a slump increase with a reduction in water content.

As the cement content of a concrete mixture increases, the required dosage of an HRWRA, as a percentage by mass of cement, is reduced (Collepardi 1984). The effects of these admixtures also are dependent on the calculated C_3A, C_3S, and alkali contents of the cement. Concrete made with

cements meeting requirements for Type II and Type V cements require lower admixture dosages than concrete containing Type I or Type III cements. In some cases, a higher SO_3 content in the cement may be desirable when using HRWRAs.

6.7.2 *Air entrainment*—Some water-reducing admixtures may entrain air. Lignosulfonates entrain air to various degrees ranging from 2 to 6%, although higher amounts have been reported (Tuthill et al. 1960). The air-entraining properties may be controlled by modifying formulations. As explained in Section 6.2.2, materials in Categories 4, 5, and 6 usually do not entrain air, but materials in all seven categories may affect the air-entraining capability of both air-entraining cement and air-entraining admixtures. This is particularly true in the case of some HRWRAs. The entrained air can consist of large, unstable bubbles that contribute little resistance to freezing and thawing, therefore, the entrained air-void characteristics should be evaluated whenever questions about the performance of the concrete arise. Testing for resistance to freezing and thawing in the evaluation is prudent, as in some instances the concrete may still be durable even though the spacing factors may exceed accepted limits of 0.008 in. (0.20 mm) (Mather 1979).

6.7.3 *Workability*—When comparing a concrete mixture without a water-reducing admixture of the same slump and air content, differences in workability are difficult to detect because no standard test exists. Howard et al. (1960) reported the use of the Kelly Ball (ASTM C360) detected increases in workability that was missed by the slump test. Rheometers are useful in determining workability, flowability, and viscosity (Ferraris et al. 2000). Concrete containing a water-reducing admixture, however, is less likely to segregate and sometimes has better flowability.

Water-reducing admixtures affect bleeding capacity in varying degrees. For example, unmodified admixtures in Category 2 (Section 6.2.2) tend to increase bleeding whereas their modifications and derivatives do not. Admixtures in Category 1 reduce bleeding and segregation in freshly mixed concrete, partly due to the air entrainment. HRWRAs derived from Categories 4, 5, and 6 decrease bleeding, except at very high slump.

6.7.4 *Rate of slump loss*—The rate of slump loss may be decreased by adding water-reducing and set-retarding admixtures. Because of slump loss, some HRWRAs may be added at the job site. Working time can be extended with the careful use of an ASTM C494/C494M Type B retarding or Type D water-reducing and retarding admixture, or with the use of a Type G retarding HRWRA. The working time depends on many factors, including the HRWRA dosage, use of other chemical admixtures, cement characteristics, *w/cm*, concrete temperature, slump, and age of the concrete when the HRWRA is introduced. Some HRWRAs extend the time before slump loss, allowing batch plant addition and maintaining normal setting-time characteristics (Guennewig 1988; Collepardi and Corradi 1979).

6.7.5 *Finishing*—Some water-reducing admixtures, water-reducing and retarding admixtures, and MRWRAs improve the concrete's finishing characteristics compared to concrete containing other types of water-reducing admixtures or no admixture. This is beneficial where deficient aggregate properties or gradation result in finishing difficulties. At the high-water content reduction achieved with HRWRAs, finishing may become more difficult due to the decrease in bleeding, and surfaces may have a tendency to crust and promote plastic-shrinkage cracking. The surface can be kept from drying by fogging using an evaporation retarder or other procedures (ACI 308R). These treatments should be used with caution so that the durability of the surface is not adversely affected. It is common to use a combination of an HRWRA and an MRWRA to achieve both high levels of water reduction and enhanced finishing properties.

6.7.6 *Time of setting*—Water-reducing and set-retarding admixtures cause a delay in setting time that will increase with increasing dosages and lower temperatures. Normal-setting water-reducing admixtures are generally formulated with an accelerating component to produce a setting time within 1.5 hours of a reference mixture at normal dosage rates. These admixtures will also produce extended setting times when dosages increase beyond normal rates or when temperatures fall. The combination of conventional water-reducing admixtures and MRWRAs may cause retardation. The setting time of water-reducing and retarding admixtures generally increases as the dosage rate is increased. Normal-setting HRWRAs can be used at higher dosages without an appreciable increase in setting times; however, increasing dosages beyond normal rates may also result in setting time delays. Accelerators can decrease or eliminate retardation. Retarding admixtures are not recommended for controlling false set; some water-reducing and retarding admixtures have been reported to contribute to premature stiffening. Admixtures based on lignin can delay false set, and sugar-type admixtures can cause flash set if the cement has a low sulfate-to-aluminate ratio.

6.7.7 *Heat of hydration*—Within normal *w/cm* ranges, heat of hydration and adiabatic temperature rise are not reduced at equal cement contents with the use of water-reducing admixtures. Acceleration or retardation can alter the rate of heat generation, which can change the early rate of temperature rise under job conditions. If the use of water-reducing admixtures permits a reduction in cement content, the heat generated is proportionally reduced.

6.8—Effects on hardened concrete

6.8.1 *Strength*—In addition to the strength increase due to reduction of *w/cm*, strength is further increased due to modification of the paste microstructure by the water-reducing admixture. Used at unusually high dosages, retarding admixtures can decrease the strength at ages up to 24 hours, while the normal setting and accelerating types increase the very early strength. Later-age strength with a water-reducing admixture can increase 20% or more at the same cement content. Cement contents can thus be reduced without lowering 28-day strengths. When HRWRAs are used to decrease the *w/cm*, the 28-day compressive strength can increase by 25% or more. Because of their effectiveness in reducing *w/cm*, HRWRAs are helpful in producing concrete with compressive strengths greater than 6000 psi (41 MPa) at 28 days and are essential in achieving strengths that exceed 10,000 psi (69 MPa) (ACI

212.4R). Increases in flexural strength of concrete containing a water-reducing admixture are not proportionally as great as increases in compressive strength (Collepardi 1984).

6.8.2 *Shrinkage and creep*—Long-term shrinkage may be less than that of concrete not containing a water-reducing admixture. Creep is reduced in proportion to the increase in the strength of the concrete. How much a particular admixture in a given dosage affects shrinkage and creep depends on the composition of the cement (ACI 209R).

6.8.3 *Resistance to freezing and thawing*—Water-reducing admixtures typically have little effect on resistance to freezing and thawing, including deicer scaling, because the resistance is almost entirely a function of the air-void system in the hardened concrete. An improvement can result from a decrease in *w/cm* because of increased strength and density and reduced permeability, which allow the concrete to remain less than critically saturated in the presence of water while being tested.

6.9—Batching and quality control

Water-reducing admixtures should be batched and dispensed as liquids. When supplied as solids, they should be mixed to a suitable solution concentration following the manufacturer's recommendations. The density of admixtures mixed on site or applied as solutions should be determined and compared with the manufacturer's standards. Density can be determined easily and quickly with a hydrometer or volumetric flask. The determinations should be made at a standard temperature and recorded for future reference as part of the site quality-control program. Storage tanks for solutions should be clearly identified, and the solutions should be protected from contamination, dilution, evaporation, and freezing.

It is sometimes necessary or desirable to determine that an admixture is similar to a previously tested material, or that successive lots of shipments are similar. Tests used to identify admixtures include solids content, density, infrared spectrophotometry for organic materials, chloride content, and pH. Guidelines for determining the uniformity of chemical admixtures are given in ASTM C494/C494M. Project inspectors may be instructed to sample deliveries of the admixture as part of the project quality control or quality assurance. Admixture users should become familiar with appearances and odors of the admixtures; this knowledge can prevent errors.

6.10—Storage

Water-reducing admixtures should be stored in strict accordance with the manufacturer's recommendations. Most admixtures are not damaged by freezing. The manufacturer's instructions should be followed regarding the effects of freezing the product. An admixture stored beyond its recommended shelf life should be retested before use.

CHAPTER 7—ADMIXTURES FOR FLOWING CONCRETE
7.1—Introduction

ASTM C1017/C1017M defines flowing concrete as "concrete that is characterized as having a slump greater than 7-1/2 in. (190 mm) while maintaining a cohesive nature..." Flowing concrete should be obtained through the use of a plasticizing admixture, conforming to ASTM C1017/C1017M, and a uniform combined aggregate gradation. The uniform combined aggregate gradation will usually produce a cohesive, workable concrete mixture. Plasticizing admixtures are typically HRWRAs conforming to ASTM C494/C494M Types F and G (refer to Chapter 6). Depending on travel time, temperature, and mixture, the concrete may need to be redosed on the job site because adding water may result in lower-quality concrete. Concrete may be delivered to the job site at an initial slump of 2 to 3 in. (50 to 75 mm) and the plasticizing admixture then added to increase the slump up to 10 in. (250 mm) with an equivalent slump flow of 17 in. (425 mm). Alternatively, the plasticizing admixture could be added at the plant to achieve a high slump so that the concrete arrives at the job site with the slump required for placement. The dosage required to increase the slump to flowing consistency varies depending on the cementitious material, the initial slump, *w/cm*, temperature, time of addition, and concrete mixture proportions. The dosage required to increase slump from 2 to 8 in. (50 to 200 mm) may be 50% higher than that required if the starting slump is 3 in. (75 mm).

7.2—Materials

Admixtures used to achieve the flowing concrete should meet the requirements of ASTM C1017/C1017M, Type I or Type II (retarding). Commonly used materials:
- Sulfonated naphthalene condensates;
- Sulfonated melamine condensates;
- Modified lignosulfonates;
- Polycarboxylates; and
- A combination of the above compounds with either a Type A water-reducing admixture or a Type E water-reducing and accelerating admixture.

7.3—Selection and evaluation

When deciding to produce and use flowing concrete, consider the type of admixture to be selected. Factors include:
- Type of construction;
- Restrictions imposed on the chloride-ion content;
- Time interval from the introduction of cementitious materials and water into the mixer;
- Availability of accurate admixture dispensing equipment at the plant, job site, or both;
- Ambient temperature; and
- Form, geometry, and reinforcing bar spacing.

The proposed flowing concrete mixture should be used initially on noncritical work or in a test pour so that proportions and procedures can be verified before the mixture is used in the areas requiring flowing concrete. The proportions of the various concrete ingredients can be adjusted and the dosage or the type of admixture varied to achieve an acceptable final slump, rate of slump loss, and setting characteristics. If the plasticizing admixture is to be added at the job site, an accurate means of introducing the admixture into the concrete mixer should be ensured. Truck mixers should be equipped with tanks designed to introduce the admixture into the concrete mixer so that it can be distributed evenly throughout the

batch. Adequate mixing speed and revolutions should be maintained as defined in ASTM C94/C94M. The concrete plant should be equipped to accurately measure the admixture into the truck-mounted tanks. Accurate measurements of the admixture dosage are critical, and proper mixing is essential to realize the full benefit of the admixture. The required mixing time or revolutions to adequately disperse the admixture throughout the load should be known. In addition, a redosing chart that provides the quantity of admixture to be added per yard (per meter) to increase the slump in the required increments along with mixing time should be on site from the concrete producer.

The expected performance of a given brand, class, or type of admixture can be estimated from one or more of the following sources:

- Results from jobs where the admixture has been used under good technical control, preferably using the same materials and under conditions similar to those anticipated;
- Laboratory tests made to evaluate the admixture; and
- Technical literature and information from the manufacturer of the admixture.

ASTM C1017/C1017M provides for compliance with specifications under controlled conditions of temperature, fixed cementitious material content, slump, and air content, using aggregates graded within stipulated limits. This standard requires certain minimum differences in concrete strength, range of setting time, and requirements regarding other aspects of performance such as shrinkage and resistance to freezing and thawing.

7.4—Applications

Flowing concrete is commonly used in areas requiring maximum placement rates, such as slabs, mats, and columns, and in congested locations where the finished concrete surface is aesthetically sensitive and is unusually shaped or heavily reinforced (Nmai and Violetta 1996). It can be used in areas of limited access or where the maximum horizontal movement of the concrete is desirable. Flowing concrete is useful for pumping because it reduces pumping pressure and increases both the rate and distance that the concrete can be pumped. It is useful for projects that require rapid form cycling with a maximum volume of concrete placed per day. Coupled with a low w/cm, the early strengths required for stripping or post-tensioning can be achieved. An example is flowing concrete with a low w/cm obtaining a compressive strength of 3000 psi (20 MPa) or greater in 24 hours.

Flowing concrete is often desirable for use in mass placements. The cement content can be kept low, which minimizes heat development, and the lower water content reduces drying shrinkage. The plasticizing admixture does not lower the temperature rise in concrete except as a result of reducing cement concrete. The early temperature-rise characteristics can be modified with the use of the retarding version of the plasticizing admixture (Type II) or in combination with a conventional water-reducing retarding admixture (Type D).

High-performance concrete (HPC) has higher-than-normal compressive strength, reduced permeability, increased durability, or reduced shrinkage. The necessity to reduce the w/cm to 0.45 or lower to produce HPC while achieving a placeable concrete requires the use of an HRWRA (Aïtcin and Neville 1993). Concrete with a low w/cm and a compressive strength higher than 8000 psi (55 MPa) can be produced as flowing concrete. Flowing concrete, being easier to consolidate, also contributes to the proper bond between reinforcing steel and concrete in areas where reinforcement is congested.

Using plasticizing admixtures to increase slump from 2 to 3 in. (50 to 75 mm) to 7.5 to 10 in. (187.5 to 250 mm) or greater also reduces the amount of cement required to achieve a particular strength. Because concrete is seldom placed at a slump level of 2 to 3 in. (50 to 75 mm), the additional water required to raise the slump would need to be matched with an increase in the cement content if the strength and w/cm were kept constant. The higher paste content would result in a concrete with a higher shrinkage and permeability; therefore, reducing the concrete durability.

7.5—Proportioning concrete

When admixtures are evaluated in laboratory trial mixtures before job use, the series of mixtures should be planned to provide the necessary project information. Assuming that specification compliance has been established, the tests need not follow ASTM C1017/C1017M test conditions for slump, air content, and cementitious material content. The test conditions, however, should be consistent with the project requirements with respect to target slump, air content, setting time, and strengths at various ages. The trial mixtures should be made with the same materials, particularly cementitious material that will be used on the job site, and should simulate the site conditions as closely as possible. Temperature is particularly important to setting times and early-strength development. Trial mixtures can be made with a starting slump and air content in the specified range. The dosage of the plasticizing admixtures can be varied to achieve different slump increases. If allowed, the initial slump may also be varied. The specified w/cm should be maintained in each case, and a range of slumps can be reviewed. In this manner, the optimum mixture proportions can be selected and the desired results achieved.

A concrete mixture usually needs reproportioning when a plasticizing admixture is added to achieve flowing concrete. Procedures for proportioning and adjusting concrete mixtures are covered in ACI 211.1 and ACI 211.2. The appendix to ACI 211.1 provides procedures and guidelines for proportioning coarse and fine aggregates to produce a more workable concrete mixture, less susceptible to segregation, and requires a lower paste content to produce a required slump. Fine-to-coarse aggregate ratio may require adjustment to ensure that sufficient fines are present to allow a flowable consistency to be achieved without excessive bleeding or segregation. Increasing the cement content or adding other fine materials such as pozzolan or slag may also be necessary. Because 0.5 gal. (2 L) or more of plasticizing admixture is customarily used per cubic yard (cubic meter) of concrete to produce flowing concrete, the water in the admixture should be accounted for when calculating w/cm

and the effect on mixture volume. The air content and setting time of job concrete differ considerably from those of laboratory concrete with the same materials and mixture proportions. Therefore, adjusting the proposed admixture dosages on the job site before its use in the required locations may be necessary.

7.6—Effects on fresh and hardening concrete

7.6.1 *Setting time*—ASTM C1017/C1017M Type I admixtures are required to have a negligible effect on initial and final setting times. Therefore, flowing concrete will set as quickly as concrete without the admixture, but with the same water content. At increased concrete mixture temperatures, the setting time of concrete containing the Type I admixture is decreased. A Type II admixture can reduce slump loss significantly and retard the initial setting time of the concrete. Retarding the setting time of slabs and pavement and deck concrete can produce excessive plastic and shrinkage cracks if the concrete it not properly protected and cured. In formed concrete, a retarded netting time can produce more pressure on the forms.

7.6.2 *Workability and finishing*—When concrete mixtures are properly proportioned, flowing concrete is extremely workable without bleeding and segregation. The upper slump limit at which flowable concrete still remains cohesive can be determined by testing the mixture before use. Segregation and bleeding can be reduced by increasing the fine-to-coarse aggregate ratio, improving the aggregate grading, or adding other fine material. Producing a uniform combined aggregate gradation in accordance with ACI 211.1 will greatly reduce or eliminate segregation. Excessive bleeding can be reduced by air entraining the concrete mixture. Flowing concrete should be vibrated to achieve proper consolidation as per ACI 309R. The response of flowing concrete to machine finishing is similar to that of conventional concrete made with the same ingredients. Successful finishing requires proper timing. If a concrete contains too much fine aggregate, the air content is too high, or both, the surface of the concrete may tend to dry before it sets. This condition could cause the concrete to feel rubbery or jelly-like and can cause finishing problems because of its stickiness and rolling. The problem of excessive air content in concrete used in floor slabs is particularly apparent when the initial machine-finishing operations begin. The air content of trowel-finished floors should not exceed 3%.

7.6.3 *Rate of slump loss*—The rate of slump loss in flowing concrete containing an HRWRA will be affected by: the type of HRWRA used; the dosage used; the simultaneous use of an ASTM C494/C494M Type A, B, or D admixture; the type and brand of cement; and the concrete temperature. These factors are by no means the only ones affecting slump loss, but they can typically be controlled by the user (Ramachandran and Malhotra 1984). Ambient temperature is not as controllable, but can have a dramatic effect on the performance of an HRWRA. Ravina and Mor (1986) have shown that the higher the HRWRA dosage, the lower the rate of slump loss. Each product has an operating range beyond which other properties of the concrete may be affected; if

this range is exceeded to further reduce the slump loss, the results may include changes in initial setting times, segregation, or bleeding.

As a result in HRWRA technology and the numerous products available, it has become advantageous to describe these products not only by the requirements of ASTM standards, but also by the method of addition. Although both specifications for HRWRAs (ASTM C494/C494M and C1017/C1017M) mention slump loss, neither currently requires tests for slump-loss characteristics. When some HRWRAs are added at the job site, the concrete exhibits moderate to rapid slump loss and normal or retarded initial setting times. HRWRAs designed to be added at the batch plant can extend slump retention in concrete (Collepardi and Corradi 1979) along with either normal or retarded initial setting times. The difference in performance does not indicate that one admixture is better than another, but rather that certain admixtures are more appropriate in some construction situations than in others.

7.6.4 *Additional dosages*—An additional dosage of plasticizing admixture should be used when delays occur and the required slump has not been maintained. Two additional dosages have been used with success; more dosages generally are less effective. Redosing with an HRWRA after approximately two dosages with the same amount of HRWRA will not produce the same increase in workability and slump gain. Furthermore, retarded set times may be produced. Every plasticizer cannot be redosed; however, nonretarding plasticizers can be redosed several times. In general, the compressive strength level is maintained or increased and the air content is decreased. Therefore, if air entrainment is a concern, it should be checked after the concrete has been redosed and returned to its intended slump.

7.6.5 *Heat of hydration and temperature rise*—The total amount of heat produced by hydration is not changed if the cementitious material is not altered, but the rate of evolution can be altered. If the use of flowing concrete involves the use of lower cementitious content, less heat will be evolved.

7.7—Effects on hardened concrete

7.7.1 *Strength*—Because flowing concrete is often batched initially with a water content resulting in a slump of 2 to 4 in. (50 to 100 mm), the *w/cm* is lower than that of conventional concrete with a similar cementitious material content and a 5 in. (125 mm) slump, improving the strength. Flowing concrete often is stronger than conventional concrete at the same *w/cm*, due to increased dispersion, resulting in a more efficient cement hydration. The flexural strength of flowing concrete is not significantly changed from that of the initial concrete with the same *w/cm* at a lower slump.

7.7.2 *Shrinkage and creep*—The drying shrinkage of low-slump concrete is approximately the same as that of flowing concrete with the same *w/cm* and lower water content (Gebler 1982). If the cement content is kept constant to produce flowing concrete with a lowered water content, then drying shrinkage can be reduced. If both cement and water contents are reduced, then drying shrinkage can be reduced. When compared with concrete with the same *w/cm*, concrete

with an HRWRA shows little change in creep characteristics (Brooks et al. 1981; ACI 209R).

7.7.3 *Resistance to freezing and thawing*—Conventional and flowing concrete with the same *w/cm* and a comparable air-void system exhibit a similar resistance to freezing and thawing. Compared with conventional concrete, the higher dosages of air-entraining admixture usually are required to flowing concrete to maintain proper air content. For a given air content, the air-void system may have larger spacing factors and a decrease in the number of voids per unit length compared with the control concrete; however, satisfactory resistance to freezing and thawing has been achieved in most cases. As with any air-entrained concrete, the air content in the field should be checked so that the air-entraining admixture dosage can be modified to keep the air content in the specified range.

7.7.4 *Permeability*—Flowing concrete with a *w/cm* below 0.40 can be placed easily; therefore, the resultant concrete, if properly cured, can have extremely low permeability and good resistance to the penetration of aggressive solutions. Resistance to chloride penetration is similar to, or slightly better than, that of conventional concrete with the same *w/cm* (Lukas 1981). When the admixture is used to reduce the *w/cm*, the resistance to the chloride penetration is even greater. Flowing concrete shows better consolidation, reduced bleeding, and increased cement hydration—all of which contribute to lower permeability.

7.7.5 *Bond*—Flowing concrete can improve bond strength to reinforcing steel when compared to similar concrete with a 4 in. (100 mm) slump (Collepardi and Corradi 1979). Brettman et al. (1986) found that flowing concrete showed no change in bond strength compared with lower-slump concrete with an equal *w/cm,* providing the concrete was vibrated and set rapidly after consolidation. Bond strength in reinforced concrete beams having equal *w/cm*, however, was decreased if the flowing concrete's setting time was delayed. Proper consolidation around the reinforcement is more easily achieved with flowing concrete, but adequate vibration is required.

7.8—Quality assurance

7.8.1 *Testing admixtures*—Determining that an admixture is similar to that previously tested or that successive lots or shipments are similar is desirable and sometimes necessary. Tests that can be used to identify admixtures include solids content, density, infrared spectrophotometry for organic materials, chloride content, and pH. Admixture manufacturers can recommend which tests are most suitable for their admixtures and the results that should be expedited. Guidelines for determining uniformity of chemical admixtures are given in ASTM C1017/C1017M.

7.8.2 *Field control of concrete containing HRWRAs*—For both plant-added or job-site-added HRWRAs, ensure from batch records that the water content and the *w/cm* are within specification. HRWRAs can be added at the plant or job site and thoroughly mixed into the batch to produce the desired workability while also maintaining mixture stability. For air-entrained concrete, the air content also should be checked at the point of discharge from the transportation unit. There-

fore, if the flowing concrete is pumped into place, the air content should be measured at the point of discharge into the forms. It has been shown that placing concrete with a pump can significantly impact air content (Whiting and Nagy 1998). Therefore, it may be necessary to measure air content at the point placement to determine the difference from that delivered. Rate of slump loss, initial setting time, and early and final strength results may require mixture adjustments. Slump loss and setting characteristics may be adjusted by changes in the HRWRA dosage or by the concurrent use of accelerating or retarding admixtures. When the concrete placement is abnormally slow, the temperature is high, or both, the use of an high-range water-reducing Type G admixture can be desirable. However, care should be taken with mixture proportions and ambient conditions to ensure that excessively long setting times do not result. Because variations in cement composition, aggregate grading, or both can cause significant variations in the flowing-concrete characteristics, these changes should be minimized. When pumping, flowing concrete should be placed in accordance with ACI 304.2R and consolidated in accordance with ACI 309R.

7.9—Storage

HRWRAs should be stored in strict accordance with the manufacturer's recommendations. Most admixtures are not damaged by freezing. The manufacturer's instructions should be followed regarding the effects of freezing the product. An admixture stored beyond its recommended shelf life should be retested before use.

CHAPTER 8—ADMIXTURES FOR SELF-CONSOLIDATING CONCRETE
8.1—Introduction

Self-consolidating concrete has many potential benefits. It offers opportunity to strongly reduce construction time and labor, and achieve improved formed surface finish and acceptance of architectural treatment. As consolidation is not required, construction problems related to inadequate consolidation can be avoided. Given the extensive discussion in ACI 237R, this chapter will emphasize admixture types and selection, and treat other issues only as needed for clarity. The reader is referred to ACI 237R to refer to basic principles in detail and to understand many of the terms used in the following.

8.2—Materials for SCC admixtures

Both HRWRAs and viscosity-modifying admixtures (VMAs) used for SCC are discussed herein. Refer to Section 16.5 for additional information on VMAs. Other admixtures may be used as well; this chapter will deal with these other admixtures with respect to compatibility only. To discuss the materials, a brief review of concrete rheological principles is needed.

8.2.1 *SCC rheological principles*—Details of SCC rheology are available in ACI 237R and in the literature developed in the last 10 years (Wallevik 2003; ACI 238.1R). A simplified outline is given herein to enable a discussion of the impact of various admixture types.
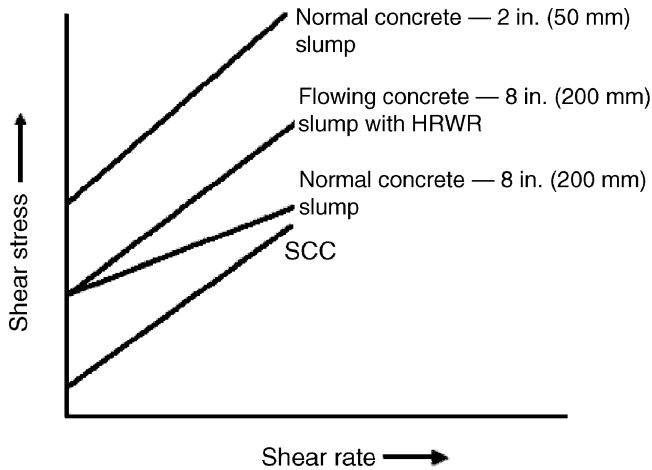
Fig. 8.1—Stress-strain diagram.
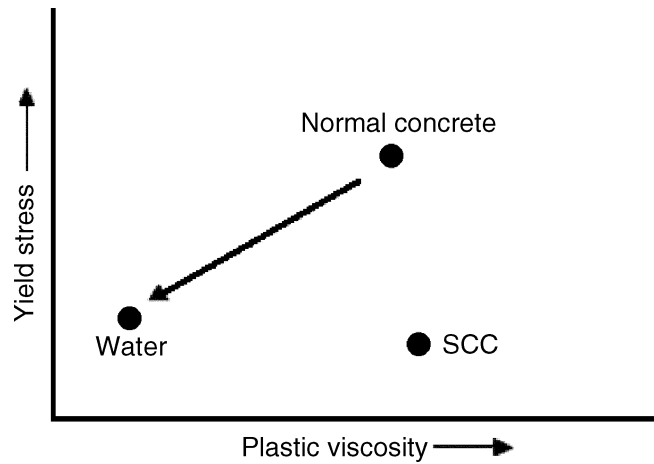
Fig. 8.2—Yield stress-plastic viscosity.
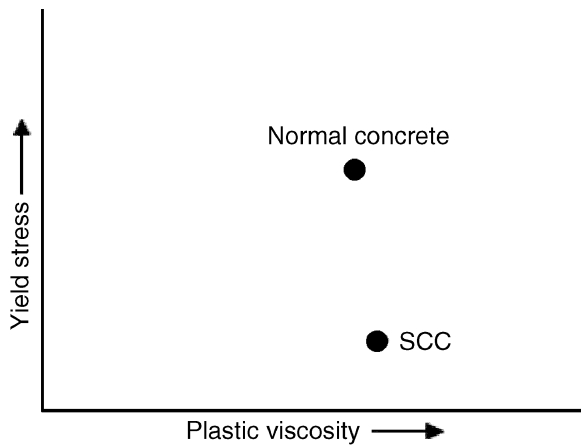
Fig. 8.3—Yield stress-plastic viscosity.
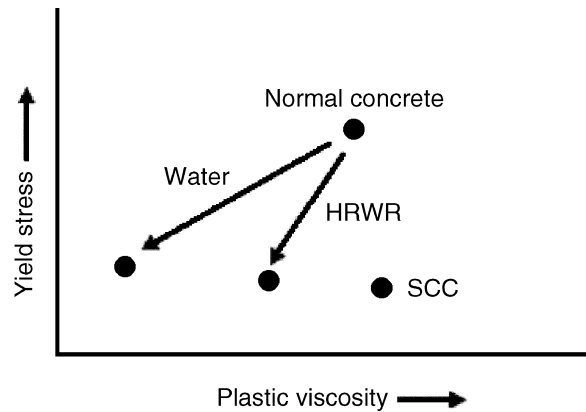
Fig. 8.4—Yield stress-plastic viscosity.

A conceptual stress-strain diagram of several types of concrete is given (Fig. 8.1). Concrete approximates a Bingham fluid, in that it shows a yield stress, below which it will not move. This is represented as the intercept on the *y*-axis. The slope of the stress-strain curve is the plastic viscosity, the resistance of the concrete to moving faster. Concrete workability, whether measured by slump (conventional concrete) or slump flow (SCC), is related to both yield stress and plastic viscosity. Low-slump concrete has a higher yield stress, whereas high-slump concrete has a lower yield stress. As seen in Fig. 8.1, adding water to concrete lowers both the yield stress and plastic viscosity, whereas adding HRWRAs tends to lower the yield stress while having little impact on the plastic viscosity. That is why flowing concrete made with HRWRAs can be stable at high slumps (low yield stresses) where concrete with the same slump achieved with water is not.

To achieve required flow and filling ability, SCC must have even higher fluidity, yet continue to have enough cohesion to resist segregation and to "pull" aggregate through close gaps between reinforcing bars (so-called passing ability). To achieve these properties, SCC must have a very low yield stress, but higher plastic viscosity than conventional concrete would at such low yield stress. These yield stress-plastic viscosity relationships can be

represented with the plastic viscosity on the *x*-axis and the yield stress on the *y*-axis, as shown in Fig. 8.2. (Tattersall and Banfill 1984; Wallevik 2003).

To better understand what is involved in moving the concrete rheology to the required region in this diagram, consider the impact of simply adding water to decrease yield stress to the level needed for SCC, as shown in Fig. 8.3. Yield stress is reduced, but plastic viscosity is reduced severely as well, and the concrete becomes highly segregating.

If, instead of water, a normal HRWRA is added without restructuring the mixture proportions, the result will be a decrease in yield stress with relatively small changes in plastic viscosity, as show in in Fig. 8.4.

One of the typical means of making SCC is to proportion a high-fines mixture. The net effect of adding higher fines is to increase interparticle attraction, thus increasing the plastic viscosity and concrete cohesion, as shown in Fig. 8.5. Increased cohesion also improves the passing ability of the mixture—the ability of the paste to pull coarse and fine aggregate through narrow spaces in the formwork.

Increased cohesion and plastic viscosity can also be achieved through use of VMAs, which is described in Section 8.2.4. Either high-molecular-weight water-soluble polymers or dispersions of very fine particles will function

much like adding extra fines. They permit design of SCC with lower total fines content, which may be technically or economically beneficial.

Another key rheological parameter is thixotropy, which is the reversible buildup of interparticle attraction while a concrete is at rest. In practical terms, this implies that when a concrete is placed in motion at a fixed shear rate, the viscosity decreases with time. Or conversely, the viscosity increases with time when the concrete is at rest. Thus, a thixotropic material will behave with lower viscosity while under movement than after a period of rest. Therefore, if two SCC mixtures display the same yield stress and the same plastic viscosity while under movement, the one displaying higher thixotropy will be more resistant to static segregation. Mixtures with higher thixotropy tend to reduce form pressure more quickly, leading to potential increases in possible placement rate within a given limit of form pressure. The effect of SCC on form pressure is a critical and complicated area of ongoing work, and will not be addressed further herein.

In recent years, developments in the design of high-range water-reducing polymers and formulation of these with other materials has permitted the development of admixtures that allow the reduction in yield stress while increasing plastic viscosity, as shown in Fig. 8.6. These permit formulation of SCC with lower powder contents; reduction in the use of additional VMAs; and, in some cases, increased thixotropy.

In field applications, slump flow (ASTM C1611/C1611M) approximates the yield stress (higher slump flow = lower yield stress) whereas the plastic viscosity is approximated by the T_{50} time (longer time = higher plastic viscosity). Concrete is generally considered to be SCC when the slump flow lies between 22 and 30 in. (550 and 750 mm). T_{50} times from 2 to 10 seconds are generally used, depending on applications (ACI 237R).

Passing ability is measured by an adaptation of the slump flow test called the J-ring test, in which a circle of bars surrounds the slump cone when it is raised. The spread with the ring in place is compared to that without; a concrete with high passing ability will have similar slump-flow diameters. Many other tests have also been developed to measure passing ability, but they are beyond the scope of this discussion. There is currently no accepted field test method for measuring thixotropy.

The stability of an SCC mixture is estimated by the Visual Stability Index, a comparative appraisal of the degree of segregation observed in the slump flow patty. A rating of 0 is highly stable, 1 is stable, 2 is unstable, and 3 is highly unstable. This measures the tendency for paste to separate from the aggregate during and after the slump flow measurement. When the paste is seen to readily separate, steps must be taken to increase the paste viscosity itself, either by adding powder, reducing water, changing to a more cohesive HRWRA, or adding a VMA. Another static stability test, the Column Segregation Test, is now under development. In this test, a three-part plastic pipe is filled with SCC, allowed to rest a fixed length of time, and the top third and bottom third of concrete separated and washed out, to enable comparison of the coarse aggregate content. This measures the tendency
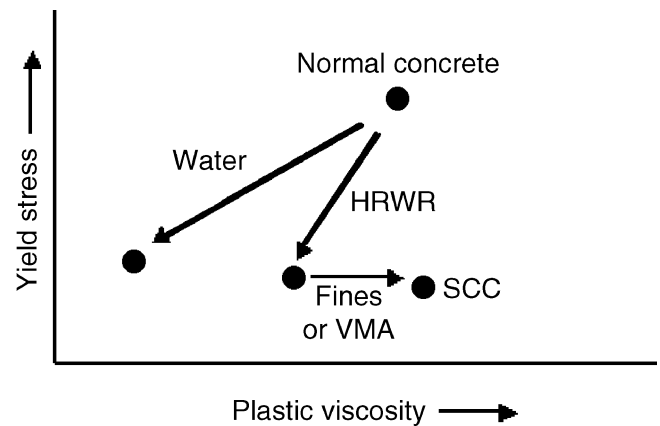
Fig. 8.5—Yield stress-plastic viscosity.
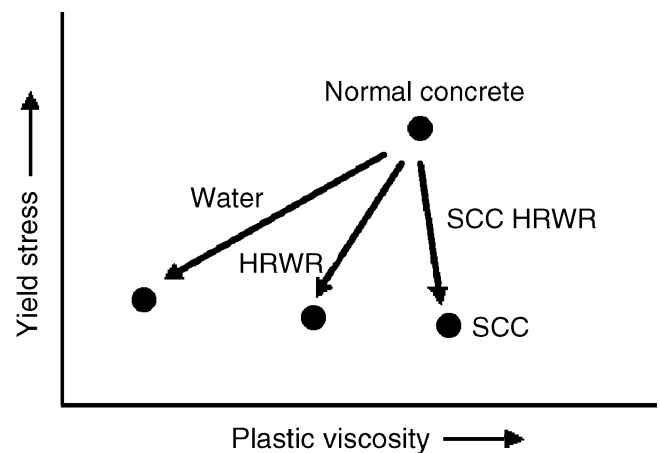
Fig. 8.6—Yield stress-plastic viscosity.

for the aggregate to settle in the concrete, which may not be directly comparable to the paste stability.

8.2.2 *Critical attributes of SCC admixtures*—Admixtures for SCC have to be able to impart very strong high-range water reduction characteristics, ±30%, giving large slump flows while increasing plastic viscosity to impart stability and passing ability, and in some applications, thixotropy. In materials proportioning and admixture selection for SCC, the selection of the appropriate SCC admixtures depends on the degree of SCC characteristics required, and the starting constituents of the concrete mixture. The more well-graded and shaped the aggregates are (that is, lower water demand), and the more powder content there is in the mixture, the less critical the admixture selection. ACI 237R cites three methods of SCC formulation: high powder content with HRWRAs, low powder content with VMAs, and moderate powder content with HRWRAs and low VMA doses. In fact, there are a wide range of approaches (trading off the various attributes and costs of base materials selection and control) and admixtures chosen.

Other properties required for reliable production of SCC include resistance to loss of slump flow so that adequate filling ability will be found after delivery and possible delays on the job site. Newer SCC admixtures can ensure long

Evolution of water tolerance, SCC HRWR
704 lb/yd^3 (418 kg/m^3) powder content
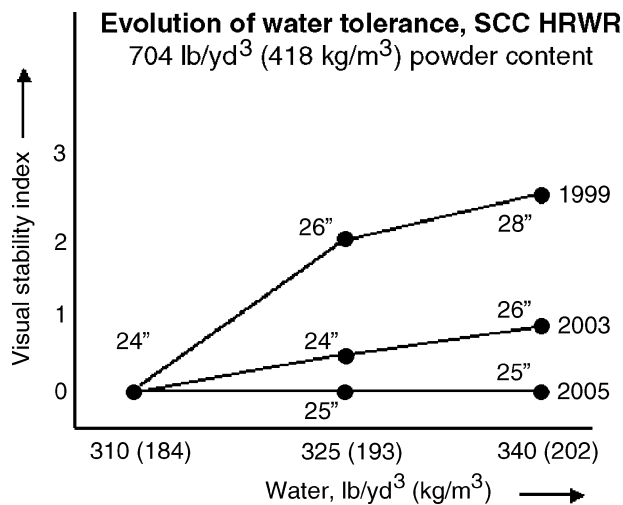
Fig. 8.7—Visual stability index-water content.

retention of needed slump flow. Use of retarders is frequently effective in prolonging slump life, but with the attendant increase in setting time, which may influence pour rates in situations where form pressure restrictions exist.

Significant progress has been made in water tolerance, which is needed so that variances due to changing water demand of the materials, or moisture content of the aggregates, do not cause the SCC to segregate. Recent work (Cornman 2005) has shown that virtually any level of water tolerance is now technically possible (Fig. 8.7).

8.2.3 *SCC HRWRAs*—As outlined in ACI 237R, the principles of mixture proportioning for SCC involve reducing the amount and size of coarse aggregate to improve blocking resistance, increasing the paste content to improve cohesion, and use of HRWRAs to reduce the yield stress to give the needed slump flow to achieve desired filling ability. In high-paste, high-fines situations, normal HRWRAs have been found to work successfully. Thus, it is possible to use materials in Categories 1 through 6 when following Section 6.2.2 of this document to make SCC. SCC based on conventional naphthalene sulfonate HRWRAs was used in high volumes in major projects in the 1980s, made possible due to very high cementitious contents and use of silica fume (Kuennen 1996).

In the last 20 years, the development of polycarboxylate-based HRWRAs has improved the ease of SCC production, as polycarboxylate-based HRWRAs tend to improve cohesion relative to naphthalene or melamine-based HRWRAs. These polymers are sometimes termed "comb polymers" in that they are shaped like a comb, with a polycarboxylic acid backbone (typically acrylic, methacrylic, or maleate in nature, with polyoxyalkelene side chains attached as esters, amides, or imides. Inclusion of other chemical groups at low levels is frequently encountered. The carboxylic acid groups are typically neutralized with sodium.

These carboxylate groups act to attach the polymer to the powder surfaces, while the side chains fill space and thereby function to disperse the system through a steric repulsion effect. A number of variables, including backbone length, ratio of carboxylate to side chains, and length and composition

of side chains, allow the molecules to be fine-tuned for various attributes such as speed of slump flow development, slump flow loss, and cohesion.

This flexibility has allowed special SCC admixtures to be developed comprising blends of different polycarboxylate polymers that have different rates of adsorption on the powder substrates. By adjusting the ratio of different polymers, slump flow in many cases can be maintained as long as is practicably needed—up to several hours with little or no retardation. These may actually allow for an increase in slump flow with time. Other materials may be included to adjust performance. Different products will impart a decreased tolerance to moisture variation (Koyata and Cornman 2005).

8.2.4 *SCC viscosity-modifying admixtures*—Viscosity-modifying admixtures are the other major admixture class used for SCC. They are generally water-soluble polymers, frequently natural polysaccharides such as gums or starches, oxygenated polymers, or dispersions of fine particles such as colloidal silica. While many of the natural polymers are practically available only as powders, there are some products in liquid form at concentrations practical for addition to production concrete. Whether polymer- or fine-particle-based, they work to mimic the effect of higher fines—substituting polymer interaction or ultra-fine particle inter-action to achieve the cohesive effect achieved by much higher levels of conventional fine particles. This allows achievement of stability and passing ability at lower levels of cement or cementitious materials. Refer to Section 16.5 for more information on VMAs.

8.3—Selection and evaluation

Self-consolidating concrete is much more sensitive to changes in materials, including HRWRAs and VMAs, than conventional concrete. The ultimate mixture proportion of an SCC depends on the admixture in a fundamental way. Once a set of materials is qualified, great caution should be used, including requalification, before changing any constituents. In developing mixtures, a basic understanding of the available aggregates will help choose the types of admixtures that should be evaluated. If the aggregates are very well graded and shaped and if relatively high powder contents are acceptable, a conventional polycarboxylate HRWRA without a VMA may be acceptable. As the aggregates depart from ideality, becoming either gap graded or harsh and angular, the water demand will rise and admixtures imparting more cohesion will be necessary. Generally either a conventional polycarboxylate HRWRA with a VMA or a special SCC HRWRA will be needed. When the aggregates are far from ideal, or when powder content is limited—for instance, due to considerations for shrinkage—both a special SCC HRWRA and VMA may be necessary. Finally, when production considerations indicate control of water may be a limiting factor for SCC production, those SCC admixtures imparting reduced sensitivity to water may be needed.

8.4—Proportioning concrete

As reviewed extensively in ACI 237R, SCC proportioning starts with understanding the anticipated application to which the concrete will be placed. Greater element intricacy, closer reinforcement, and higher demand on surface finish all require higher slump flow. Once the target application is known, the coarse aggregate size is chosen, frequently smaller than in standard concrete to minimize segregation potential, and using a lesser amount than in normal concrete. Highly angular coarse aggregates are generally avoided, as their water demand makes stability difficult. One widely used starting point is to have 50% of the volume occupied by the coarse aggregate (13.5 ft^3 [0.38 m^3]). Next, the powder content is chosen with higher levels usually selected for higher slump flows, as this both increases cohesion and paste density. Use of supplementary cementitious materials or fillers can reduce the cement content needed to reach required powder levels. Higher paste density helps because the difference in density between the paste and the aggregate is the driving force for aggregate settlement, and stability is improved at higher paste density. Finally, the admixture or combination of admixtures is chosen. Then the trial mixture is made, tested, and adjusted. Frequently, it is also useful to obtain slump results prior to SCC admixture addition to provide a baseline reference for tracking of material changes.

At this point, the principles outlined previously become critical to understand. As higher slump flow is needed, stability becomes more difficult to achieve. Well-graded and shaped aggregates will result in lower water volumes, resulting in a decreased need for very high powder contents. It then becomes a trade-off between the cost and difficulty of controlling aggregate grading and shape and the increased admixture cost of a special SCC HRWRA and/or added VMA. Test placements on site are required to verify optimum slump/flow, stability, setting time, and finish, if required.

8.5—Effects on fresh and hardening concrete

The major effect of SCC admixtures on fresh concrete is on the rheology, as reviewed in Section 8.2.1. Some SCC admixture combinations may retard slightly, so combinations with other admixtures, which can cause retardation, should be carefully checked. Air entrainment can be difficult if the mixture becomes so fluid that insufficient paste viscosity remains to retain the air. Switching to a more cohesive HRWRA, adding a VMA, or increasing fines may be necessary. In some combinations of materials, air void systems may be found to be too coarse, in which case changing the air-entraining admixture or the HRWRA may be needed.

Due to its high fluidity, SCC is expected initially to provide full hydraulic pressure to the forms. Thixotropy will reduce this pressure prior to actual setting, but the actual effect in the forms can also be altered by the placement method, as fresh SCC being placed on top of SCC already undergoing thixotropic set can reestablish full pressure head (Brameshuber and Uebachs 2003; Fedroff and Frosch 2004; Billberg et al. 2005) For now, prudent practice is to establish pour rates that do not exceed the pressure rating of the forms.

8.6—Effects on hardened concrete

As reviewed in ACI 237R, SCC has largely been found to behave as normal concrete would be expected to, given the substantial differences in proportions. That is, the admixtures have not altered the performance outside the expected envelope. SCC generally has very high powder and paste contents, which lead to high strength, but may also lead to higher shrinkage, creep, and a greater potential for cracking. Paying close attention to aggregate selection to reduce water demand and using admixture systems that permit the needed rheological properties, without excessive powder contents, can reduce this tendency. Due to the low w/cm, permeability is generally low and durability is high. Frequently, strengths are much higher than required for the structural design, which can lead to issues of crack width if cracking occurs and the reinforcement level is not adequate to keep crack widths narrow.

8.7—Quality assurance

Production of SCC requires significantly higher levels of plant and site quality assurance than conventional superplasticized concrete, especially during development and initial production. In the initial proportioning process, proper selection of aggregate size, shape, and amounts; selection of paste volume and supplementary cementitious materials; and selection of admixtures is required. Quality assurance methods must be in place to assure that the materials used in initial trials are reproduced during production. Critical areas are consistency of cement and cementitious material supply, consistency of aggregate grading and shape, and control of moisture content. Adequate personnel are necessary to make adjustments in the mixture as the inevitable material changes do occur. The mixture design must be robust enough to perform well on a daily basis with the normal variations, cementitious materials, and aggregate gradation. The mixture should always be within ±2 in. (50 mm) slump flow of the target slump flow. Active communication between site quality control personnel and plant production personnel is critical to make adjustments in a timely manner.

8.8—Batching

Due to SCC's requirement for consistency, adhering to strictly controlled batching procedures is very important. Batching less than full mixer or truck loads can be problematic, as batching precision suffers, mixing energy changes, and the impact of extraneous material increases. Each producer will have to determine his/her ability to produce smaller loads and restrict production to the levels found to be reproducible.

Water control is essential. Make absolutely sure the mixer or each truck is empty prior to batching. As little as 1 gal. of water/yd^3 (5 L of water/m^3) may be the difference between stable and segregating SCC. All possible measures to control and adjust for aggregate moisture need to be implemented. In central mixers, using the mixer ammeter to set a baseline amperage that produces good SCC after admixture dosage, then controlling to that amperage prior to admixture addition can be helpful. Changes in that number can reflect loss of moisture control. With truck mixers, occasionally confirm

moisture control by measuring the slump before SCC admixture addition.

Recognize that some SCC admixtures take time to develop slump flow. This may be more important with materials that impart higher mixture stability. Determine the time for the materials being used, and make sure that adequate mixing time is given. Reduce mixing speed to prevent excessive splashing. A folding action is desirable. This may be critical in controlling air generation and stability. Due to the very fluid nature of SCC, reduction in batch size may be required to limit spillage.

8.9—Storage
Admixtures for self-consolidating concrete should be stored in strict accordance with the manufacturer's recommendations. Most admixtures are not damaged by freezing. The manufacturer's instructions should be followed regarding the effects of freezing the product. An admixture stored beyond its recommended shelf life should be retested before use.

CHAPTER 9—COLD WEATHER ADMIXTURE SYSTEMS
9.1—Introduction
There has been increased need to place concrete under conditions where it may freeze before gaining significant strength. Freeze-resistant admixtures have been used in the former Soviet Union since the 1950s to suppress the freezing point of concrete and permit placement and curing of concrete below the freezing point of water (Brook and Ryan 1989). Typically, nonchloride set accelerators are basic ingredients of freeze-resistant admixtures. When used for this purpose, dosage rates are much higher than those used at temperatures above freezing.

For concrete cured at low temperatures, early strengths are low, even though strengths can be similar to normally cured concrete at later ages. Admixtures made from nonchloride accelerators have shown no tendency to cause corrosion of embedded reinforcing steel (U.S. Army Corps of Engineers 1994). Nitrite salts actually reduce corrosion potential when used in amounts suitable for anti-freeze performance. Proprietary accelerating admixtures that provide water-reduction and accelerate hydration down to 20°F (–7°C) without harmful side effects are available (Brook and Ryan 1989). Sodium and potassium salts, however, should not be used with potentially reactive aggregates due to an increased risk of alkali-silica reaction, nor should they be used in concrete subject to wetting and drying in an aggressive, marine, or sulfate environment.

The U.S. Army Corps of Engineers identified combinations of commercially available admixtures to allow fresh concrete to fully cure while its internal temperature is below 32°F (0°C) without harming its performance compared with that of normal concrete cured at normal temperatures (Korhonen et al. 2004).

ASTM accepted a new standard for cold-weather admixture systems in 2005—ASTM C1622/C1622M, "Standard Specification for Cold-Weather Admixture Systems."

9.2—Materials
Currently, cold-weather admixture systems are made by using admixtures that meet ASTM C494/C494M requirements or that are commercial products otherwise accepted by industry practice. The admixtures are mainly selected for their individual abilities to depress the freezing point of water or to accelerate the hydration rate of cement at low temperatures. When dispensed separately into concrete, they must be compatible with one another so as to not promote corrosion. The admixture system should conform to ASTM C1622/C1622M. In recent studies, eight admixture systems were identified that, during laboratory tests and field trials, yielded fresh concrete with a depressed freezing point of 23°F (–5°C) or lower and had reasonable transit life and good job-site workability (Korhonen et al. 2004).

9.3—Selection and evaluation
Each cold-weather admixture system consisted of up to five commercial products: water reducers (ASTM Type A and F) to lower the water content in concrete while maintaining workability; accelerators (ASTM Type C and E) to decrease the time of setting and aid in early strength gain as well as providing some freezing point depression; retarders (ASTM Type B) to sometimes assist if early setting is a problem; and corrosion inhibitors and shrinkage reducers, not so much for their implied properties, but for their added freezing point depression.

9.4—Proportioning concrete
To proportion a concrete mixture that can gain appreciable strength at temperatures below 23°F (–5°C), begin with a standard winter concrete mixture design that is workable, durable, and strong. Typically, mixture designs that contain at least 610 lb/yd^3 (359 kg/m^3) of cement, 0.45 or lower w/cm, and adequate entrained air are acceptable. Converting standard winter concrete into cold-weather concrete simply requires adjusting the amount of mixing water to account for the water in the admixtures and defining when each admixture should be dispensed into the concrete.

9.5—Batching
Before cold-weather concrete is placed on the job, it must be confirmed through a series of trial batches that prove a given cold-weather admixture system can produce concrete of acceptable workability and air content. Trial batches help determine the best timing for the addition of each admixture into the concrete. Several 3 to 5 yd^3 (2.3 to 3.8 m^3) trial batches should be made to confirm mixture proportions and to reveal how the concrete behaves during each stage of the process. Use cold water for all batching operations to create an initial mixture temperature of 50 ± 3°F (10 ± 5°C). Higher temperatures tend to cause cold-weather concrete mixtures to stiffen too rapidly. Obtain periodic slump measurements, air contents, and concrete temperature readings to establish that the mixture behaves as desired until it is placed and finished. The trial batches will provide the opportunity to experiment with various admixture dosing procedures and to train the batch plant operators, truck drivers, and job supervisor

in working with this concrete. Three admixture dosing procedures have been field-tested thus far.

The first procedure dispenses the entire cold-weather admixture system into the concrete at the concrete plant. This has the advantage that once the truck leaves the plant, no further effort is required. The disadvantage, however, is that the high concentration of hydration-accelerating admixtures in these systems will cause the concrete to lose slump rapidly. Travel times should be limited to 20 minutes, but experience has shown that large slump loss could be recovered with additional plasticizer dosed into the mixture after travel times of up to 45 minutes. The mixture may have to be dosed with additional air-entraining admixture at the job site. Workers typically have approximately 20 to 30 minutes to work with this concrete.

The second procedure delays dispensing the fastest-setting admixture into the concrete until it arrives at the job site while all others are dispensed at the concrete plant. This reduces slump loss during transit and air content may be more stable than in the first procedure. The mixture, however, may need higher doses of HRWRA to keep it mobile during transit. The concrete team needs to know the mixture in transit will have a low water content and slump. Water must not be added to the mixture. Transit times of 45 minutes or more are possible. Working times of 30 minutes can be expected.

The third procedure dispenses all admixtures at the job site. The advantage is that the admixtures do not begin reacting with the cement until the construction crew needs the concrete. Because the admixtures contain water, however, the concrete must begin with a very low *w/cm*. The concrete team needs to know that the mixture in transit will be low water content and low slump. Transit times of up to 1 hour have not been a problem and working times at the job site have exceeded 45 minutes.

9.6—Trial placement
The proposed cold weather concrete mixture should be used initially in a test placement so that proportions and dosing procedures can be verified before the mixture is used in job applications. The proportions of the various concrete ingredients can be adjusted and the dosage of admixtures varied to achieve an acceptable final slump, rate of slump loss, freezing point, and setting characteristics.

9.7—Placing and finishing
The substrate against which fresh concrete is to be placed must be free of ice and snow. It is permissible for its temperature to be below freezing, but all sources of excess water must be removed.

The behavior of cold weather concrete in its plastic state is very similar to that of high-cement-content, low-*w/cm* concrete. This concrete can be sticky to finish but tends to lose its stickiness as setting proceeds.

Continuously place the concrete within 20 to 30 minutes or according to the working time determined during the trial batching and trial placement tests. As the concrete is placed, immediately strike off excess concrete to bring the surface to proper elevation. Following screeding, bull float the surface to embed aggregate and smooth the surface. Be careful not to seal the surface. The magnesium float must be used with care so as not to prematurely seal the surface, which can cause delaminations. Wait until the concrete can be walked on without leaving footprints more than 1/4 in. (6.4 mm) deep before floating. A float finish followed by texturing the surface with a broom is recommended for flatwork exposed to outdoor conditions.

No experience is available with hard-troweling this concrete, partly because delamination could occur at air contents higher than 3%.

Once finishing is complete, exposed surfaces must be protected against drying. The surface should be covered with a sheet of plastic, or a spray-on curing compound, or both, as soon as the surface is tack-free. This happens very quickly. Cover protruding metal with insulation because it acts as a conduit to freeze surrounding concrete. Be sure to insulate the ends of metal form ties.

9.8—Effects on fresh and hardening concrete
Cold weather concrete mixtures are sensitive to water content when it comes to freezing point depression. They tend to lose slump very rapidly and have set, under field conditions, within 1 hour of placement. They are sticky to finish and require detailed attention when admixtures are added into the mixing process. Air contents are less stable in cold weather concrete compared to normal concrete. In some cases, air contents have increased within cold weather concretes as mixing time increased, while in other cases it decreased. One admixture has been reported that seemed to remove air from concrete. Cold weather concrete generally does not bleed when it is properly batched, which, when coupled with its fast setting nature, allows finishing operations to begin soon after the concrete is consolidated and leveled, even in very cold weather. At very low slumps, the concretes have responded well to vibration.

9.9—Effects on hardened concrete
As with normal concrete, strength gain of cold weather concrete depends on its internal temperature. In the laboratory, when cooled to 23°F (–5°C) soon after mixing and then held constant at that temperature, cold weather concrete is expected to develop compressive strength at least as rapidly as control concrete cured at 40°F (5°C). It has been known to often surpass this requirement. In the field, where cooling may take several days, concrete structures such as bridge curbs and pavements have been returned to service in less than 1 week. This is comparable to what occurs in the summer.

Cold weather admixture systems have not been found to reduce the freezing-and-thawing resistance of concrete. When non-air-entrained concrete was tested in accordance with ASTM C666/C666M, Procedure B, both cold weather and control concrete failed in a like manner well before attaining 300 cycles of freezing and thawing. When both concretes were properly entrained with air, neither concrete noticeably deteriorated after experiencing 300 cycles. In test data, cold weather concrete generally has been more durable than control concrete.

9.10—Quality assurance

Because very high doses of admixtures are used in this concrete, adequate mixing is essential. A critical question to be answered for any concrete structure is "when will it be ready for use?" There are a number of tests, both destructive and nondestructive, that can be used to determine this, but the maturity method, as reported by ACI 306R, is favored.

The freezing point of fresh concrete is critical to know. It is affected by the type and dosage of admixture used and the total amount of mixing water in the concrete batch. Mixing water consists of water added to the batch, water occurring as surface moisture on aggregates, and water in the admixtures. Although the dosage of admixture and water added to the batch can be accurately controlled, the total amount of mixing water in a batch can vary by several percentage points, owing to changes in aggregate moisture and the tendency of contractors to add water at the job site. Moisture variations are especially true if heavy snow covers the aggregate piles. Thus, the final freezing point of the concrete could be considerably different than the desired freezing point.

Until a better method is developed, a rudimentary way to measure the freezing point of fresh concrete in the field is proposed by Korhonen et al. (2004). It consists of making several 2 x 4 in. (50.8 x 101.6 mm) cylindrical samples, installing thermocouples at their centers, and placing them into a picnic cooler containing dry ice. The freezing point is identified as the location on the temperature versus the time plot from the cylinders being cooled where the initial slope of the cooling curve (the mostly linear portion above 0°C [32°F]) suddenly changes. As soon as there is a noticeable increase in temperature (a matter of tenths of a degree Celsius) caused by the latent release of heat of fusion, that part of the curve is identified as the freezing point (Fig. 9.1). If the freezing point was not met, the concrete can be rejected, or an appropriate amount of extra admixture could be added into the concrete, or the structure could be thermally protected to prevent freezing.

9.11—Cost benefit

Freeze protection is a major cost multiplier on winter concreting projects. The primary difference between protecting normal winter concrete against freezing compared to cold weather concrete is the heat, temporary shelter, and labor needed to protect normal concrete versus the admixtures needed to protect cold weather concrete. Though cold weather admixture systems can sometimes double the cost of ready mixed concrete, the in-place cost of cold weather concrete is typically 2/3 the in-place cost of the normal winter concrete. In some cases, where elaborate temporary heated shelters had to be constructed, normal concrete construction was estimated to cost 10 times more than using cold weather concrete without the shelter.

With the relaxation of concrete placing and curing temperature limits brought by this new cold-weather concrete technology, a significant extension of the construction season is feasible. It has been estimated that with the new 23°F (–5°C) limit, the concrete construction and repair season can be extended by 3 to 4 months across the continental U.S.
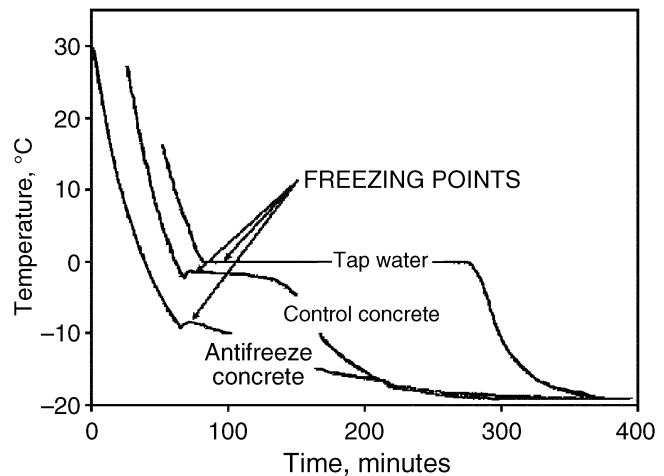
Fig. 9.1—Cooling curves for water, control concrete, and antifreeze concrete. (Note: 1°F = 5/9 × °C.)

9.12—Storage

Admixtures used to produce freeze-resistant concrete should be stored in strict accordance with the manufacturer's recommendations. An admixture stored beyond its recommended shelf life should be retested before use.

CHAPTER 10—ADMIXTURES FOR VERY HIGH-EARLY-STRENGTH CONCRETE

10.1—Introduction

Very high-early strength concrete (VHESC) is concrete designed to achieve extremely high early strengths within the first few hours after placement. VHESC has been produced for the rapid repair of concrete structures for several years now, yet there has been no standard definition for it. The requirement of early strength with respect to time has slightly varied for different projects wherever VHESC has been used.

One application for its use is for the rapid repair of concrete pavements. For this purpose, state agencies generally specify a minimum compressive strength of 2000 psi (13.8 MPa) or flexural strength of 400 psi (2.8 MPa) within 4 to 8 hours of concrete placement so that the road may be re-opened quickly (Kurtz and Constantiner 2004; Smith et al. 2001).

In a research study conducted in 1993 under the Strategic Highway Research Program (SHRP-C-363), very early-strength (VES) concrete was defined as a concrete that will produce a minimum compressive strength of 2000 psi (13.8 MPa) in 6 hours after mixing when Type III cement is used. When alkali-activated proprietary cement was used, a strength of 2500 psi (17.5 MPa) in 4 hours was required. Further, it is also necessary that the VES concrete achieve a minimum durability factor of 80% after 300 cycles of freezing and thawing when tested in accordance with ASTM C666/C666M, Procedure A.

Based on the two sets of requirements in the aforementioned cases, it may be said that if concrete achieves a minimum compressive strength of 2000 psi (13.8 MPa) or a minimum flexural strength of 400 psi (2.8 MPa) within 4 to 8 hours of its placement and meets the outlined durability criteria, it may be classified as VHESC.

During the repair and rehabilitation of pavements that carry heavy traffic volumes, time is the most critical factor. In such situations, the cost of materials is less important than the costs associated with traffic diversions and the closing of pavement sections. The use of VHESC is ideal in such situations. VHESC can be used to do full-depth pavement repairs, short stretches of new pavement, bridge decks, overlays, loading docks, or any slab where an owner requires minimal down time (Anderson et al. 2003).

VHESC is also commonly used by precast producers to manufacture precast concrete elements when faster turnaround of forms is required. Placing of high-temperature concrete (approximately 90°F [32°C]) along with accelerated curing enables the in-place concrete to achieve very high early strengths within a short time. Although the material cost of VHESC is higher than regular concrete, its added value to the precast producer makes it a popular choice in the precast industry.

10.2—Materials for very high-early-strength concrete

VHESC can be produced by either using an ordinary portland cement in combination with a system of chemical admixtures or by using specialty cements. Materials used to produce VHESC, in both ways, are described in the following.

10.2.1 *VHESC using portland cement and admixture systems*—In this method to produce VHESC, a portland cement Type I, II, or Type III may be used. The use of Type III cement, however, is more beneficial than a Type I or II cement due to its inherent ability to produce high early strengths. Mixture proportioning of the concrete is similar to that of a conventional high-strength concrete, but generally a slightly higher cement factor and a high dosage of the set accelerator are used.

The admixture system used in VHESC requires a high-range water reducer, a set accelerator, and an air-entraining admixture if freezing-and-thawing resistance is required. Fine and coarse aggregates that are locally available can be used.

VHESC is generally produced at a concrete plant and transported to the job site. If the transit time from the plant to the job site is long, the accelerator is added when the truck arrives at the job site. Job-site addition will help to avoid stiffening of concrete during transit and allows sufficient time for placing and finishing the concrete. If job-site addition is not possible and the transit time is anticipated to be lengthy, a retarding or hydration control admixture might be required. Its use, however, should be evaluated prior to mixing as it may delay the development of the specified high early strength.

In the aforementioned admixture system, a strength accelerator can be used instead of a set accelerator. A strength accelerator is an admixture that, unlike a set accelerator, does not cause an earlier set of the concrete, but dramatically increases strength gain after the concrete's initial set occurs (Ansari et al. 1997). Use of a strength accelerator may allow the convenience of adding admixture at the plant rather than the job site.

10.2.2 *VHESC using special cements*—VHESC can also be produced using special cements such as high-alumina cement, calcium sulfoaluminate cements, calcium fluoroaluminate cement (regulated set cement), and magnesium phosphate-based cements. Locally available fine and coarse aggregates can be used to produce VHESC using these cements.

Blended high-alumina cement is obtained by blending high-alumina cement with appropriate proportions of portland cement. These cements have a faster strength gain compared with Type III cement and produce concrete that is more resistant to sulfate attack. One of the main limitations of this cement, however, is a conversion reaction it undergoes, resulting in considerable loss of strength and decrease in solid volume.

Calcium sulfoaluminate cement is produced by adding calcium sulfate to the clinkers of a Type I cement. Strengths as high as 5800 psi (40 MPa) can be produced within 6 hours of placement (Ambroise and Pera 2003).

Calcium fluoroaluminate cement is produced by replacing C_3A in cement with a different compound, calcium fluoro-aluminate. This cement is extremely fast setting. The setting characteristics are controlled by the addition of calcium sulfate hemihydrate or sodium sulfate and are extended with an organic retarder such as citric acid; hence, it is also known as regulated set cement. The high early strengths for both of these cements can be attributed to formation of ettringite; however, the long-term sulfate resistance of these cements may not be high (Mindess et al. 2003).

Magnesium phosphate-based cements are formed by the reaction between magnesium oxide and a soluble phosphate, such as ammonium phosphate monobasic. Strengths in excess of 2200 psi (15.2 MPa) can be produced within 1 hour (Yang 1999).

Some of the aforementioned specialty cements are used to make prebagged, quick-setting mortars. These prebagged mortars are ready to use and only require the addition of water during mixing at the job site. Among other admixtures, latex polymers (styrene butadiene) have been used in many cases along with special cements to produce very high-early-strength latex-modified concrete. The early strength is due to higher fineness and the chemical composition of the cement. Latex is added at a rate of 15 to 20% by solid weight and replaces a large amount of mixing water. The addition of latex improves the compressive and flexural strength and provides greater resistance to freezing-and-thawing damage as well as chloride intrusion. Strengths as high as 3720 psi (25.6 MPa) within 3 hours have been produced using very early-strength latex-modified concretes made with special cements having high aluminum oxide and sulfate content (Sprinkel 1998).

VHESC produced using special cements have a very short workable life, hence they are generally produced at the job site using a mobile mixer.

10.2.3 *Early strengths of concrete*—In an ordinary portland-cement concrete mixture, hydration reaction begins as soon as water comes into contact with the cement. Among the cement compounds, the rate of hydration is highest for tricalcium aluminate (C_3A) and tricalcium silicate (C_3S) followed by tetracalcium aluminoferrite (C_4AF) and dicalcium silicate (C_2S). The presence of gypsum slows the early rate of hydration of C_3A and C_4AF. The rate of hydration

of the individual cement compounds does not have a direct relation with the ultimate strength of the concrete. The early-age strength of concrete is primarily due to hydration of C_3A and in some part to C_3S, which also plays a role along with C_2S in the later-age strength development.

The early-age strength development of VHESC produced using portland cement is due to the reaction between the accelerating admixture and the hydration products of cement, mainly C_3A and C_3S. For VHESC produced using special cements, early strengths are mainly due to rapid reaction between the cement and mixing water.

10.3—Selection and evaluation

For the production of VHESC, materials such as aggregates and cement should be selected based on their local availability. If early strength requirements are not met using a Type I or Type II cement, Type III cement should be used. HRWRAs can achieve up to 40% water reduction. These admixtures allow the use of workable, low-*w/c* concrete that sets and develops strength faster and thus should be considered for use in VHESC. Some HRWRAs based on polycarboxylate technology have been found to produce higher early strengths in comparison to conventional HRWRAs based on sulphonated naphthalene and melamines.

Selection of the right accelerating admixture is very important to produce VHESC. Accelerating admixtures of different base materials react with different hydration products of the cement. The performance of accelerating admixtures has also been found to be sensitive to different cements in terms of set time and early-age strength. Some accelerators at lower dosages retard the set time of concrete when used at lower dosages but accelerate the set time when used at higher dosages (sodium and potassium carbonate, for example) whereas some accelerators containing triethalomine delay the set time used at higher dosages (Ramachandran 1995). Hence, proper evaluation of an accelerator at different dosages is necessary during the trial mixture design process.

Accelerators based on calcium chloride produce very high early strengths, but are generally not used, as they can promote corrosion, alkali-aggregate reaction, and lower resistance to sulfate attack. In the field, nonchloride inorganic accelerators such as nitrites and nitrates have shown good performance in terms of high early strengths for air-entrained VHESC. The influence of different accelerators on different cements is discussed in Chapter 5, Accelerating Admixtures.

Air-entraining admixtures that produce satisfactory results and are compatible with the other materials should be used in environments where exposure to cycles of freezing and thawing must be considered.

In case of VHESC, the dosage of set accelerator is generally higher as compared to its use in conventional concrete. This can reduce the workable life of the concrete significantly. For this reason, realistic transport, placement, and finishing time of the concrete should be calculated and considered when deciding if the set accelerator should be added at the plant or when the truck reaches the job site. The timing of addition of the accelerator in trial mixtures should be based on this, and trial batches should be conducted to simulate the entire concrete operation on the given day of concreting. The early strength of concrete is highly influenced by the temperature of the concrete and ambient temperature. Laboratory trial batches should be run to simulate the time required for mixing, transport, placing, and finishing operations at the job site and early strength should be measured. Trial mixtures should also be carried out at different admixtures dosages at different temperatures. The rate of development of early strength should be monitored using the concrete maturity concept. Maturity correlation relationships should be developed in the laboratory for all the mixtures prior to field application.

If the VHESC is to be produced using special rapid-hardening cement, as discussed in Section 10.2.1, cement should be selected based on the availability, early strength required, and previous historic data. Trial mixtures should be carried out to simulate concrete operations at the job site. When prebagged rapid-repair mortars are selected for use, recommendations provided by the manufacturer should be followed for using them.

10.4—Proportioning concrete

The proportioning of constituents of VHESC depends on the rate of early strength gain needed, workability, and the time required from mixing to finishing operation. Mixture designs can be proportioned in accordance with ACI 211.1. The cement contents for VHESC are typically higher than that of conventional concrete to meet the high early strength criteria. The early strength may also be governed by the dosage of the accelerator and the final strength by the *w/cm* of the concrete.

Alternately, an experience and evaluation approach can be adopted to proportion VHESC mixtures. A given cement content and *w/cm* should be selected based on prior experience. Aggregates should be proportioned based on their gradations and the mixture should be designed using the absolute volume method. Air entrainment and an HRWRA should be added to achieve the desired air content and workability. The accelerator should be added to the concrete at the same time it is added to the concrete on the day of production of VHESC. The amount of water in the accelerator should be accounted for and the *w/cm* should be adjusted accordingly. If retarding or hydration control admixtures are needed, their influence on workability retention and strength development should be evaluated. Depending on the results obtained, suitable adjustments should be made in the mixture proportions, *w/cm*, and the admixture dosages. Mixtures using special cements should be designed based on historical field data, research data, and a trial-and-error approach.

10.5—Effects on fresh and hardening concrete

10.5.1 *Workability*—The use of an HRWRA enables high water reduction and produces workable mixtures, even at a low *w/cm*. The loss of workability of VHESC is faster than for conventional concrete. This is due to the use of high dosages of the accelerator and the use of Type III cement. When using special cements, the loss in workability is extremely fast due to rapid reaction of these cements with water.

10.5.2 *Setting time*—The initial and final set time of the VHESC is less with respect to control concrete depending on the dosage of the accelerator, base material of the accelerator, the ambient temperature, concrete temperature, and the *w/cm*. As discussed in Chapter 5, different accelerators react with components of the cement differently, increasing the rate of hydration and accelerating its set.

10.6—Effects on hardened concrete
10.6.1 *Early and later age strength*—Compressive strengths above 2000 psi (13.8 MPa) have been achieved within 4 hours of placement in the field. The early strength development primarily depends on the dosage of the accelerator, cement type, and the *w/cm*. The strength development of VHESC increases with the increase in the dosage of the accelerator and reduction in the *w/cm*. Some accelerators cause a delay in set time and strength development and should not be used for this application.

The ultimate strength of the VHESC depends on the *w/cm* of the concrete mixture. Although accelerators increase the development of early-age strength, the ultimate strength with some accelerators have been observed to slightly decrease when compared with conventional concrete used without accelerator at the same *w/cm*.

10.6.2 *Freezing-and-thawing and scaling resistance*—VHESC likely to be exposed to freezing-and-thawing environments should be air-entrained. Properly designed air-entrained VHESC having an adequate spacing factor can achieve very high-early strength and is resistant to damage due to freezing and thawing and scaling.

10.7—Quality assurance
As construction time is critical, production of VHESC requires good quality control and proper coordination of construction activities. Trial batches should be run in the laboratory to simulate mixing, transport, and sequence of addition of materials on the day of production. The rate of strength development of cast-in-place concrete is generally higher when compared with that of lab specimens. This is because the larger volume of the cast-in-place concrete results in a greater temperature rise during hydration, which further accelerates strength gain.

Further recommended guidelines include:
1. The surface of the placed concrete should be covered with insulated blankets or burlap to avoid the escape of heat that builds up within the concrete;
2. Thermocouples should be inserted approximately 1 in. (25 mm) from side corners and at approximately 2 in. (50 mm) from the top and bottom of the slab. The maturity of the slab from the thermocouple showing the lowest temperature should be used to govern the maturity of the pavement;
3. Cylinders that are cast at the site should be conditioned to represent the cast-in-place condition; for example, placed in an insulated box or similarly shielded from heat loss; and
4. The dosage of the accelerator should be altered according to the concrete and ambient temperature.

Although VHESC is released to service within 4 to 8 hours after its placement, proper curing procedures should be adopted to allow complete hydration of the cement. Proper curing will generally consist of measures to retain the mixing water.

10.8—Batching
Because the early-age characteristics of the VHESC are important, proper batching procedures should be followed during production. Moisture corrections should be applied properly for each batch and the appropriate dosages of high-range water reducer and air entrainer should be used to achieve the desired workability and air content. The dosage of accelerator should be decided based on the ambient temperatures.

10.9—Storage
Admixtures for very high-early-strength concrete should be stored in strict accordance with the manufacturer's recommendations. Most admixtures are not damaged by freezing. The manufacturer's instructions should be followed regarding the effects of freezing the product. An admixture stored beyond its recommended shelf life should be retested before use.

CHAPTER 11—EXTENDED SET-CONTROL ADMIXTURES
11.1—Introduction
Extended set-control admixtures (ESCA) (also commonly referred to as hydration-controlling admixtures) are used to stop or severely retard the cement hydration process in unhardened concrete. The ESCA should be added and thoroughly mixed with the unhardened concrete (either freshly batched or returned) before the concrete approaches its initial setting time. ESCAs differ from conventional set-controlling admixtures in that they stop the hydration process of both the silicate and aluminate phases in portland cement. Regular set-controlling admixtures act only on the silicate phases.

11.2—Materials
The most effective materials are carboxylic acids and phosphorus-containing organic acids and salts (Kinney 1989; Senbetta and Dolch 1991; Senbetta and Scanlon 1991). Such admixtures have gained increased acceptance since their introduction in 1986.

11.3—Selection and evaluation
These admixtures must be evaluated for their effects on set time under the existing environmental conditions and with actual materials to be used. As they are typically used at high dosages, slight differences in the response seen with normal doses of ordinary retarders as cements or other material change can be amplified. Testing at expected concrete temperatures with actual materials is therefore essential. Proper mixture proportioning is essential for maintaining specified concrete quality in both the plastic and hardened state.

11.4—Applications
The technology of ESCAs has shown value in two basic application areas for the concrete producer:

1. They are used to shut down ongoing hydration of cementitious products in returned/waste concrete or in wash water (treated in the truck or in a concrete reclaimer system), allowing these products to be recycled back into concrete production so that they need not be disposed of; and

2. They are used to stabilize freshly batched concrete to provide medium- to very long-term set retardation. This allows concrete to remain plastic during very long hauls, or in long-distance pumping situations requiring long slump life, in a more predictable fashion than normal retarders.

11.4.1 *Treating concrete wash water in mixer drum*—This process eliminates the disposal of water used to wash out the inside of truck mixers while still keeping the blades and inner surface of the drum clean. This process is designed for overnight or weekend stabilization of 40 to 70 gal. (270 L) of wash water using a low dosage of an extended set-control admixture. Following the stabilization period, the water content of the freshly batched concrete is reduced to compensate for the stabilized residue held in the truck mixer. Concrete containing stabilized residue shows setting times equal to concrete without stabilized residue, with performance characteristics equal to or better than conventional concrete.

11.4.2 *Stabilization of returned unhardened concrete*—In this application, returned concrete can receive same-day stabilization for 1 to 4 hours or longer with a low dosage of an ESCA. This application reuses returned unhardened concrete during the same production day instead of disposal, typically without any added accelerator because the ESCA doses are low. Another option is to treat returned unhardened concrete overnight. Depending on the blend ratio of stabilized to fresh concrete, an accelerating admixture (chloride-bearing or nonchloride) may need to be added the next morning to reinitiate hydration. Fresh concrete is batched on top of the stabilized or stabilized and activated concrete to complete the normal load. The combination of fresh concrete and stabilized concrete should harden similarly to conventionally batched concrete without an extended set-controlled admixture, provided the manufacturer's guidelines and testing described in the following are carefully followed. Guidelines on the type of mixtures and time/temperature constraints on mixtures eligible for stabilization must be established by testing, and adhered to. Of special importance is determining the acceptable ratio of stabilized to fresh concrete. This is especially important in overnight stabilization, as the typical busy nature of the early morning batching tends to make following these guidelines difficult. If too much stabilized concrete is combined with too little fresh concrete, excessive retardation can result. Extensive testing and ongoing monitoring is required for the successful practice of this method to maintain correct doses of ESCA (and accelerator where required) as the result of changing materials and temperature conditions.

The purchaser's consent should always be obtained for delivery of loads containing a blend of fresh and stabilized concrete.

11.4.3 *Stabilization of cement fines in gray water (concrete slurry water) in reclaimer systems*—In this application, ESCAs are used to enhance traditional concrete reclaimer systems by stabilizing the hydration of cement fines in the slurry (or gray) water. This can reduce maintenance issues with the reclaimer by preventing hydration, which may adversely affect the equipment, and improve the resulting concrete by stopping the hydration of the cement in the gray water. Several different combinations of this technology and reclaimer systems have been used, but the most successful are modeled after the prevailing practice in Japan as described by Nakamura and Roberts (1998).

In this type of arrangement, a set dose of ESCA is added to a tank of water. This treated water is then used to rinse out returning trucks and recirculated until the suspended solids (composed primarily of partially hydrated cement grains) reach a predetermined limit. This gray water of known solids content is transferred into another tank that is then used to make up as much as 100% of the batch water used in regular concrete production. ASTM C94/C94M has optional limits on suspended solids in batch water of 5% by weight, although recycling systems containing ESCAs have been shown to operate successfully with gray water containing 10% or more suspended solids. ASTM C94/C94M allowance of wash water use in ready mixed concrete mandates that set time not vary from reference by more than 1 hour earlier, nor more than 1.5 hours later; and compressive strength at 7 days shall not be less than 90% of reference. By using the proper amount of ESCA in this type of system, the incorporation of the gray water is essentially neutral regarding set and slump life while providing modest strength enhancement (due to the extra unreacted cement content) relative to identical concrete batched with potable water.

11.4.4 *Stabilization of freshly batched concrete for long hauls*—The technology of ESCA admixtures can be used to stop the hydration process for extended hauls and to reduce or eliminate slump loss and concrete temperature increase during transit. For this application, the ESCA is added during or immediately after the initial batching process. Once the admixture is thoroughly mixed into the fresh concrete, the mixer drum should turn as slowly as possible. The stabilizer dosage should be adjusted so the setting time of the concrete is extended for the duration of the haul. Ideally, on arrival at the job site, the effects of the admixture should be completed. This will allow the stabilized concrete to set similarly to normal concrete at the site. This application is especially helpful in summer months when hydration is accelerated due to elevated ambient and material temperatures.

11.4.5 It is reported that ESCAs are commonly used in pervious concrete to extend the window of placeability and compaction by extending the period of fluidity of the cement paste (Huffman 2005; Bury et al. 2006).

11.5—Proportioning concrete

Dosage rates vary widely depending on the type of ESCA, application type, duration of set stabilization, materials treated, and environmental conditions. For use in freshly batched concrete to extend set times, the doses will vary from

as little as 2 oz/cwt (1.304 mL/kg) to as much as 48 oz/cwt (26.08 mL/kg). To stabilize returned concrete, the dose may vary from 4 oz/cwt (2.608 mL/kg) to as much as 128 oz/cwt (83.456 mL/kg). To stabilize wash water in a concrete truck, the dose may vary from 4 oz (118 mL) to as much as 64 oz (1.89 L) per truck (with 10 to 70 gal. [38 to 266 L] of water). For use in reclaimer systems, the dose to treat 1000 gal. (3800 L) of gray water is typically in the range of 0.75 to 2 gal. (2.85 to 10 L) of ESCA, depending on temperature conditions and maximum expected residence time of the gray water. Refer to Nakamura and Roberts (1998) for an explanation of dosing per unit water. For all situations, it is essential to test with actual materials to be used at the prevailing temperature conditions.

11.6—Effects on fresh and hardening concrete

When used to extend set in freshly batched concrete, the dominant effect is merely to increase set time. Once the retarding effect wears off and hydration commences, the concrete will typically exceed the strength of a reference concrete exposed to the same curing conditions. It is important that concrete with extended set characteristics be protected against excessive water loss due to evaporation prior to set. Although the ECSA materials have little direct impact on air entrainment, concrete with extended set may have the tendency to lose air in the extended plastic state.

When used properly to stabilize wash water in a truck mixer or in reclaimer systems, the concrete batched using the treated gray water should have plastic properties very similar to a reference concrete, although the paper by Nakamura and Roberts (1998) does caution the reader on potential issues with air entrainment. If the ESCA is overdosed, it will result in retardation of the concrete. If it is underdosed, the set may be accelerated and the concrete will experience more rapid slump loss than a reference mixture. Typically, the concrete containing ECSA-treated gray water will have higher compressive strengths than a reference mixture of similar water content, even if the ECSA is somewhat under- or over-dosed. Proper use in stabilization of returned concrete that is then blended with fresh concrete will result in essentially similar properties to reference concrete.

11.7—Effects on hardened concrete

11.7.1 *Effect on concrete*—Senbetta and Scanlon (1991) discuss test results of concrete in which an ESCA was used and reactivation was carried out after 18 hours of storage. When tested for resistance to freezing and thawing, it gave results comparable to untreated concrete while complying with ASTM C494/C494M. The same ESCA reported by Senbetta and Scanlon (1991) were studied by Senbetta and Dolch (1991). The effects on the cement paste were evaluated using X-ray diffraction, thermogravimetric analysis, differential thermal analysis, and scanning electron microscopy. The nonevaporable water content, surface area, and pore size distribution were determined. No significant differences were noted between treated and untreated pastes. The effect of using these admixtures on compressive strength, tensile strength, flexural strength, air void system parameters,

durability, and shrinkage are discussed by Ragan and Gay (1995). No detrimental effects were reported.

11.8—Quality assurance

Trial batches should be run in the laboratory to simulate mixing, transport, and sequence of addition of materials on the day of production.

Further recommended guidelines include:
1. Cylinders that are cast at the site should be conditioned to represent the cast-in-place condition;
2. The dosage of the ESCA should be determined for a range of desired set times under varying temperatures;
3. Extensive pretesting and ongoing monitoring is required for stabilization of returned unhardened concrete; and
4. The accelerator dosage to reactivate the stabilized concrete must be related to concrete temperatures and additional fresh concrete.

11.9—Batching

Both liquid and dry powder versions of ESCAs exist commercially. A liquid solution dispensed through an approved dispensing system is the most controllable and verifiable means to introduce the product. The dry powder versions have the advantage of being easily transportable in a concrete truck where they can be used as needed for emergency situations.

11.10—Storage

Extended set-control admixtures should be stored in strict accordance with the manufacturer's recommendations. Most admixtures are not damaged by freezing. The manufacturer's instructions should be followed regarding the effects of freezing the product. An admixture stored beyond its recommended shelf life should be retested before use.

CHAPTER 12—SHRINKAGE-REDUCING ADMIXTURES

12.1—Introduction

Shrinkage in concrete and mortar occurs in three basic modes: plastic, autogenous, and drying. Plastic shrinkage occurs before final set due to the rapid evaporation of bleed water from the exposed surface of the concrete. Autogenous shrinkage is the change in volume under constant temperature and without loss of moisture from the concrete to the environment (Tomita 1992), and originates from the reduction of the relative humidity in the pores as the hydration of the cement takes place (Berke et al. 1997; Shoya et al. 1990). Most autogenous shrinkage deformation occurs in the course of the first 7 days after casting. Drying shrinkage occurs after final set due to a reduction in volume caused by the evaporation of water from the pores of the concrete. For high-strength, low-water-content concretes, drying shrinkage and particularly autogenous shrinkage are the most detrimental because they increase the potential for severe cracking. Autogenous shrinkage is less significant than drying shrinkage for normal-strength concrete (<5000 psi [<34 MPa] in 28 days). The susceptibility of concrete to cracking due to drying shrinkage depends on whether the concrete is restrained or unrestrained. Because most concrete is restrained by subgrades,

foundations, reinforcement members, or connecting members, it often develops tensile stresses high enough to cause cracking.

One of the measures taken to reduce shrinkage cracking has been the use of high-range water reducers to attain a very low *w/cm* and reduced cement contents. Another method used to alleviate the effect of shrinkage was the use of shrinkage-compensated concrete. These systems are based on expansion of the concrete rather than reduction of shrinkage. Expansion can be obtained mainly through ettringite formation (Type K, calcium sulfoaluminate, or calcium aluminate-based system) or calcium hydroxide formation (lime-based system). Care has to be taken to prevent rapid set, loss of workability, and most importantly, the amount and when the expansion occurs in these systems. Shrinkage-reducing admixtures (SRAs) were introduced in Japan in 1985 and to the North American market in 1995. SRAs are reported to chemically alter the shrinkage mechanism without expansion.

12.2—Materials

SRAs are typically comprised of polyoxyalkylene alkyl ether or similar composition. According to published patents, the general composition of the SRA is indicated as $R_1O(AO)nR_2$; where A is an alkyl group having a carbon chain number of 2 to 4 or two different types of alkyl groups. R_1 and R_2 are selected from the hydrogen, hydroxyl, alkyl, phenyl, and cycloalkyl groups. The variable n is an integer between 2 and 10, indicating the degree of polymerization (Tomita 1992). Most commercially-available SRAs are a glycol ether blend (Berke et al. 1997; Rixom and Mailvaganam 1999; Bentz et al. 2001).

12.3—Mode of action

The driving force for drying shrinkage is evaporation of water from capillary pores in hydrated cement paste at the surface, which are exposed to air with a relative humidity lower than that within the capillary pores. The water in the capillary pores, called free water, is held by forces that are stronger the smaller the diameter of the capillary pore. It is not the presence of drying shrinkage that matters, but the occurrence of cracking caused by drying shrinkage. It is only when the tensile stress induced in the hydrated cement paste by the capillary forces exceeds the local tensile strength of the concrete that cracks occur (Aïtcin et al. 1997).

Capillary Tension Theory, the leading theory explaining the mechanism of drying shrinkage, states that one of the main causes of drying shrinkage is the surface tension developed in the small pores of the cement paste of concrete. When these pores lose moisture through evaporation, a meniscus forms at the air-water interface. Surface tension in the meniscus pulls the pore walls inward, and the concrete responds to these internal forces by shrinkage. This shrinkage mechanism occurs only in pores within a fixed range of sizes. The amount of cement-paste shrinkage caused by surface tension depends primarily on the *w/cm*, but is also affected by cement type and fineness and by other ingredients (such as admixtures and supplementary cementitious materials), which affect pore size distribution in the hardened paste.

The SRA reduces shrinkage by reducing the surface tension of water in the pores. The SRA is dispersed in the concrete during mixing. After the concrete hardens, the admixture remains in the pore system where it continues to reduce the surface tension effects that contribute to drying shrinkage. In both laboratory and field tests of various concrete containing the admixture, the product seemed to be most effective when added at a rate of 1.5 to 2.0% by weight of cement (Tomita 1992; Berke et al. 1994). However, dosages of 1 to 2.5% can be used to obtain desired level of shrinkage without adverse side effects (Rixom and Mailvaganam 1999; Bentz et al. 2001).

12.4—Applications

Shrinkage reduction is highly advantageous in many applications such as architectural precast, pneumatically-applied concrete; water-retaining structures; and for most horizontal slab applications such as floors, roofs, and parking decks. The capacity for minimizing cracking, thereby potentially allowing a reduction in contraction joints, and the reduction in curling makes the SRA ideally suited for slab applications. In structures where water leakage is a problem, the use of these admixtures can result in the reduction of the number of cracks. SRAs are reported to reduce the loss of prestress in prestressing applications (Nmai et al. 1998b). SRAs are also used to offset the effects of certain high-shrinkage aggregates (Holland 1999). For this application, a comparison of the cost of the SRA with the cost of obtaining a better aggregate must be determined.

12.5—Proportioning concrete

It is recommended to add the SRA after all other admixtures have been introduced into the mixture. As the dosage of an SRA is increased within the recommended dosage range, the drying shrinkage decreases. Trial mixtures adjusting the amount of cement, aggregate, and SRA must be conducted to determine the optimal mixture proportions required to meet the desired shrinkage. SRAs can interact with air-entraining agents destabilizing the concrete air content. Trial mixtures should also be run to verify fresh concrete characteristics.

12.6—Effects on fresh and hardening concrete

Although the primary impact of the SRA is to reduce autogenous and drying shrinkage, the admixture may also affect other fresh properties of the concrete. When added at a dosage of 2% by mass of cement to the concrete mixture without an adjustment for the volume of the water introduced by the admixture, the concrete's slump is increased. When substituted for an equal volume of water, however, the SRA has little to no effect on slump. Some SRAs may have a slight retarding effect on the rate of hydration and may extend the setting time up to approximately 1 hour (Nmai et al. 1998b). The SRA may affect the air content and the air void distribution or parameters of fresh concrete and, therefore, when used in air-entrained concrete, the dosage of the air-entraining admixture often needs to be increased to achieve a proper spacing factor. Successful placements on site of the proposed mixture containing SRA are essential to assure

proper workability, finishability, and setting time for the slab or formed member placement.

12.7—Effects on hardened concrete

12.7.1 *Drying shrinkage*—The amount of shrinkage reduction depends very much on the ambient conditions (temperature and relative humidity), mixture design, and the materials used. Generally, a reduction of 30 to 50% shrinkage can be achieved. Higher percentages of reduction have been achieved with specific materials and mixture designs, but it is important to evaluate a given set of materials to make recommendations on dosage and performance.

12.7.2 *Compressive strength*—Previous work has shown that adding some SRAs to concrete at a 2% dosage by mass of cement can reduce the strength as much as 15% at 28 days (Balogh 1996; Shoya et al. 1990). In general, the strength reduction is less in concretes with lower *w/cm*. Strength reduction can be counteracted by lowering the *w/cm* using an HRWRA and/or slightly reducing the SRA dosage (Nmai et al. 1998b). Some manufacturers recommend the addition of enough HRWRA to reduce the mixing water by 10% minimum while keeping the cement content constant (Berke et al. 1994).

12.7.3 *Thermal cracking*—A large percentage of cracks in concrete can be attributed to thermal effects. Two basic causes of thermal cracking are temperature differences within massive sections of concrete and overall volume change of thinner sections of concrete caused by cooling. Due to their retardation effect on hydration and attendant reduction of peak temperatures, SRAs can reduce thermal cracking because of the decreased thermal contraction on cooling.

12.7.4 *Curling*—The curling of concrete slabs is caused by the top surface drying and shrinking faster than the core concrete. In laboratory testing with 8 x 4 ft (2.44 x 1.22 m) slab specimens, SRAs showed a significant tendency to reduce curling of the slab. This property of the admixture was confirmed in a field trial conducted by the Virginia Department of Transportation, where 1.5 gal./yd^3 (7.35 L/m^3) was used in a test overlay for the Lesner Bridge (Berke et al. 1994).

12.7.5 *Air-void parameters, freezing-and-thawing resistance, and salt scaling resistance*—Generally, concrete mixtures containing 6% air or more will have adequate spacing factors (0.003 to 0.01 in. [100 to 300 μm]) and will therefore be resistant to cyclic freezing, especially in the presence of deicing salts. However, surfactants used in some SRAs, even though yielding proper spacing factors, cause the concrete to readily attain saturation, rendering it more susceptible to freezing-and-thawing attack. It is possible that these surfactants are acting as wetting agents and promoting the inhibition of water into the concrete. There are two potential problems. One is freezing-and-thawing damage because of a saturated top surface, even though the air void spacing is correct. The other is if the SRA adversely affects the air void system, the concrete is susceptible to freezing-and-thawing damage. Trial mixtures are recommended to ensure proper air void spacing to resist this type of exposure.

12.8—Quality assurance

SRA dosage and post-placing curing conditions affect the shrinkage properties of concrete and hence, selection, of an appropriate dosage would depend on the level of shrinkage desired, the degree of set retardation that is acceptable, and curing conditions. Proper placing and curing procedures are critical for SRA applications.

12.9—Storage

SRAa should be stored in strict accordance with the manufacturer's recommendations. Most admixtures are not damaged by freezing. The manufacturer's instructions should be followed regarding the effects of freezing the product. An admixture stored beyond its recommended shelf life should be retested before use.

CHAPTER 13—CORROSION-INHIBITING ADMIXTURES

13.1—Introduction

Steel in concrete is normally protected from corrosion by the high pH of the concrete environment, which creates a stable passivation layer of iron hydroxides on the steel surface. Chlorides, however, can penetrate this layer and soluble iron chloride complexes form that weaken this layer due to the increased solubility of the iron. These allow iron to migrate from the bar surface outward in the cement paste, which leads to active ongoing corrosion of the steel. This corrosion reduces the cross-sectional area of the reinforcing steel and often leads to spalling of the concrete over it because of the increased volume of the corrosion products. For these reasons, admixtures that mitigate the corrosion process are useful in extending the life of concrete structures, sometimes by themselves, sometimes in conjunction with other techniques to limit the intrusion of chlorides.

Corrosion inhibitors are described in ACI 222R as admixtures that will either extend the time to corrosion initiation or significantly reduce the corrosion rate of embedded metal, or both, in concrete containing chlorides in excess of the accepted corrosion threshold value for the metal in untreated concrete. In ASTM C1582/C1582M, a material to be considered a corrosion inhibitor must show reduction in corrosion rate and corroded area of bars in concrete containing chloride at the level that induced corrosion in the reference test specimens. Techniques or materials that reduce the actual intrusion of chloride, while being useful, are not corrosion inhibitors. Most corrosion protection systems employing corrosion inhibitors today also use various methods to reduce chloride intrusion to be efficient in the use of the corrosion inhibitor, and combine this with a conservative depth of concrete over the reinforcement. These methods may include, but are not limited to, reducing the *w/cm*, inclusion of various supplementary cementitious materials that reduce permeability, and the use of a variety of organic materials that restrict wetting. An advantage of corrosion inhibitors lies in their ability to extend time to corrosion without requiring an extreme reduction in permeability, because systems that attempt to protect against corrosion entirely by restricting chloride ingress may have problems with placement because of rheological properties, early-age

cracking (high silica fume contents and very low *w/c*), requirement for extended curing (high pozzolan levels), or restricted strength development at early ages (high pozzolan and slag). Some of these effects may reduce the actual corrosion protection afforded, especially if cracking results. Therefore, the use of moderate levels of corrosion inhibitor with moderate levels of permeability reduction from supplementary cementitious materials may result in the needed protection while resulting in concrete that is easier to place (Berke et al. 2005). Corrosion inhibitors that intrinsically reduce the permeability of the concrete also may provide this protection without the need of supplementary materials.

13.2—Materials

Many chemicals have been evaluated in the past as potential corrosion-inhibiting admixtures for concrete (Verbeck 1975; Clear and Hay 1973; Griffin 1975; Berke 1989). These include chromates, phosphates, hypophosphites, alkalis, nitrites, and fluorides. Four corrosion-inhibiting admixtures are supported commercially at the present time: an amine carboxylate, an amine-ester organic emulsion, calcium nitrite, and an organic alkenyl dicarboxylic acid salt. These four will be dealt with in depth in the rest of this chapter.

Amine derivatives have been used commercially as corrosion inhibitors in the U.S. since the mid-1980s and have an extensive track record both in laboratory and field studies. They are generally available as concentrated liquids or powders. The latest versions of amine derivative corrosion inhibitors are based on a synergistic blend of amine carboxylates with the addition of metal salts of carboxylic acids and nonorganics (hereafter referred to as amine carboxylates).

Amine carboxylates — $\left[R-C{\overset{\nearrow O}{\underset{\searrow O^{\ominus}}{}}} \right] {\overset{\oplus}{\underset{R}{\overset{R'}{\underset{R''}{N}}}}}$ — are classified as mixed inhibitors, meaning they affect both anodic and cathodic portions of the corrosion cell. Each amine carboxylate molecule is a dipole and has positive and negative charges that are attracted to the anodic and cathodic portions of a corrosion cell. These inhibitors adsorb onto metal, forming a protective molecular layer on steel surfaces (Fig. 13.1). This film prevents corrosive elements from further reacting with embedded reinforcement, and also reduces existing corrosion rates. Adsorption of the inhibitor onto the metal through its polar functional group takes place with the nonpolar or hydrophobic chain of the inhibitor molecule oriented perpendicular to the metal surface. The hydrophobic chains not only repel aqueous corrosive fluids, but interact with each other to form aggregates, thereby forming a tight film on the metal surface (Sastri 1998).

Amine carboxylates reach embedded reinforcement in several ways. First, the inhibitor is dispersed through the concrete with adequate mixing. Second, the amine carboxylate inhibitors have a vapor pressure that allows them to migrate through the pore structure of the concrete in a gaseous state. The molecules move randomly from areas of high concentration to areas of low concentration until equilibrium is reached (Fick's Second Law). Finally, when the molecules come into contact with embedded metals, they have a specific ionic
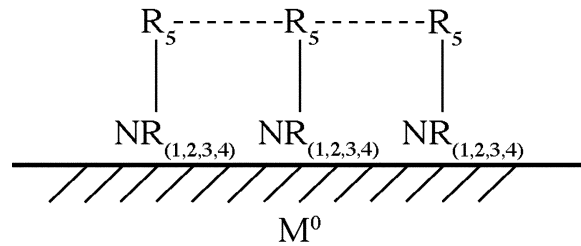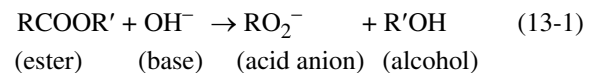

Where: $R_{1,2,3,4}$ is H or ALKYL
R_5 is COOH

Fig. 13.1—Illustration of protective layer formed by amine carboxylate organic inhibitor.

attraction to it. The positive and negative charges within amine carboxylate molecules are attracted to anodic and cathodic microcells on the metal surface, forming a protective, monomolecular layer that also reduces the corrosion rate (Bavarian and Reiner 2004). As amine carboxylates migrate through the concrete, some of them will react with calcium hydroxide in the concrete to form calcium oxalate $[Ca(COO)_2]$, an insoluble salt, which effectively blocks some of the pores, making future ingress of chlorides and other contaminants more tortuous (Sastri 1998).

The amine-ester organic corrosion inhibitor has been used commercially since 1990 and it is available as a milky-white emulsion. It consists of fatty-acid esters and amines (Nmai et al. 1992) and surfactants that provide stability to the emulsion and also enhance corrosion-protection performance. This organic corrosion inhibitor provides protection against chloride-induced corrosion of steel in concrete via a twofold mechanism that involves the formation of a protective film on the steel surface and a reduction in chloride permeability of the concrete (Nmai et al. 1992).

When the amine-ester organic inhibitor is first added to concrete, the esters become hydrolyzed by the alkaline mixture water to form carboxylic acid and its corresponding alcohol. This reaction, under alkaline conditions, is favorable and is not easily reversed (Carey and Sundberg 1984). The reaction proceeds (as shown in Eq. (13-1)), where R and R′ represent different hydrocarbon molecules

$$RCOOR' + OH^- \rightarrow RO_2^- + R'OH \qquad (13\text{-}1)$$
$$\text{(ester)} \quad \text{(base)} \quad \text{(acid anion)} \quad \text{(alcohol)}$$

The carboxylic anion is quickly converted in concrete to the insoluble calcium salt of the fatty acid (Carey and Sundberg 1984). The fatty acids that are formed and their calcium salts provide a hydrophobic coating within the pores that causes a reversed angle of contact in which the surface tension forces now push water out of the pore instead of into the pore (Ramachandran 1995). The hydrophobic calcium salt lining also reduces the diameter of the pores, thus reducing the migration of water and attendant contaminants through the capillary pore matrix. After the concrete mixture is placed, the key components of the amine-ester organic inhibitor are adsorbed onto the surface of the reinforcing

steel to form a protective film. Simplistically, the film-forming amine component, FFA, which can be described most effectively as a surface-acting chelants (Bobrowski and Youn 1993; Buffenbarger et al. 2000), bonds with the steel and the fatty-acid esters chain over the nonpolar tails to form a tight mesh (Fig. 13.2) that restricts moisture, chloride, and oxygen availability at the steel surface. Hence, the organic corrosion inhibitor functions as a mixed inhibitor, affecting the anodic reaction by raising the chloride threshold for corrosion initiation and the cathodic corrosion reaction by restricting moisture and oxygen availability.

The film-forming mechanism by which the amine-ester organic inhibitor inhibits corrosion is the same mechanism by which other organic corrosion inhibitors function, that is, by adsorption on the metal surface. In addition, this barrier may be enhanced by the ability of the hydrophobic tails of the chelated FFA to attract other hydrocarbon molecules, such as additional FFA molecules or the waterproofing ester, to create an additional water-repellent oil film (Nathan 1973). The hydrophobic lining of the pores and the protective film at the steel surface created by the amine-ester organic inhibitor are formed immediately after concrete placement and are very stable (Bobrowski and Youn 1993; Buffenbarger et al. 2000). The organic corrosion inhibitor will not migrate through the concrete matrix and will allow only miniscule leaching.

Calcium nitrite ($Ca(NO_2)_2$) is classified as an anodic inhibitor that interferes with the chloride complexing process by oxidizing the more easily attacked Fe^{2+} form of iron to the more stable Fe^{3+} form. The nitrite species is responsible for this effect and, therefore, sodium nitrite has a similar corrosion inhibiting ability, but at levels needed for corrosion inhibition, it adds excessive alkali to the concrete, so it cannot typically be used. The more stable barrier increases the concentration of chlorides needed to start corrosion, and reduces the rate of corrosion once initiated (Berke and Rosenberg 1989). Although this process strengthens the passivating barrier, due to inevitable imperfections in this barrier, it does not make the steel immune to high concentrations of chloride, so different levels of calcium nitrite will be required, depending on the chloride level expected during the design life of the structure. The threshold limit for corrosion initiation in the absence of a corrosion inhibitor is generally in the range of 0.6 to 1.0 kg Cl/m^3 (1.3 to 2.2 lb Cl/ft^3) of concrete, but this is variable depending on the *w/c* of the concrete, with higher *w/c* concretes sometimes having appreciably lower corrosion thresholds. In some accelerated tests, the chloride intrusion rate can be so quick that samples just going into corrosion are found to have higher Cl concentrations because the concentration rises so quickly, the actual initiation concentration is exceeded. For this reason, highly accelerated testing is inappropriate for determining corrosion thresholds both with and without corrosion inhibitors. Calcium nitrite has been used commercially in the U.S. since 1978 and has an extensive track record, both in the field and in laboratory studies (Berke et al. 1994). It is generally available as a 30% solution, and some versions contain a retarder to reduce the accelerating
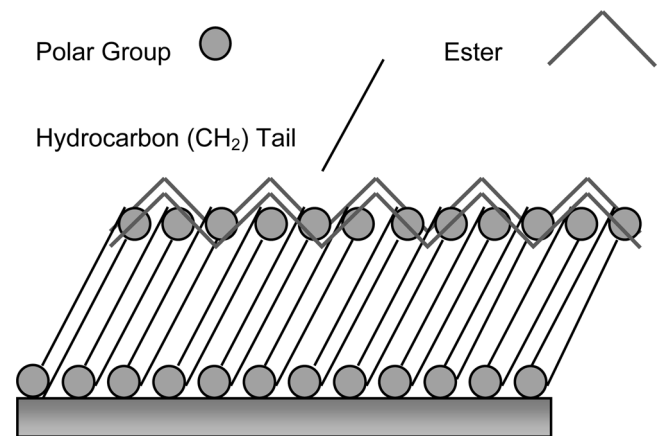

Fig. 13.2—Illustration of protective layer formed by amine-ester organic inhibitors on surface of metal.
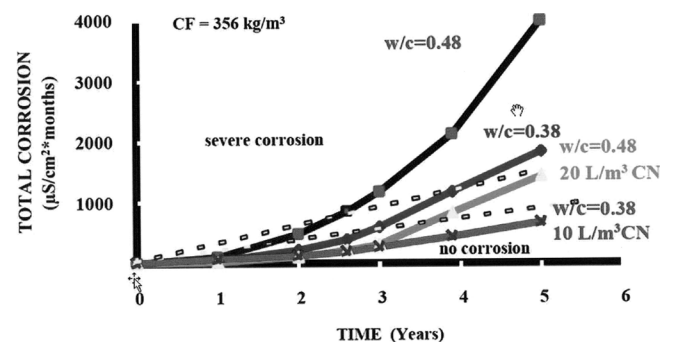
Fig. 13.3—Effect of various dosage of calcium nitrite on corrosion over time.

effect of the material while maintaining the same concentration of nitrite. An example of the positive impact of the material is shown in Fig. 13.3.

The organic alkenyl dicarboxylic acid salt is available as a water-based solution. It has been referred to as DSS in several reports because a key component of the chemically-active part of the molecule is a disodium succinate. The organic alkenyl dicarboxylic acid salt will be referred to as DSS in this chapter. It can be classified as a dual-action corrosion inhibitor, affecting the anodic reaction at the steel and restricting moisture used in the cathodic reaction. It is an adaptation of the corrosion-inhibitor technology used in automotive engine oil. The technology had to be made compatible with a water-based system for use in concrete instead of the petroleum-based system of oils. The molecule has a long-chain hydrocarbon on one end that is hydrophobic and a highly electronegative end (with a charge of –2) on the other end. When introduced into concrete, some of the DSS reacts with the available divalent ions such as iron and calcium in the cement to form a low-solubility divalent salt/polymeric material, which then can form even larger molecules of even less solubility. Because much calcium is available in solution in the capillary pores as they are being formed, the DSS is drawn to this portion of the paste reacting with free metallic ions. The hydrophobic end of this molecule is then present within the walls of the capillary pores and very effectively serves to repel moisture (and attendant

Fig. 13.4—Corrosion rate for various corrosion inhibitors at approximately 35 weeks (Goodwin et al. 2000).

Fig. 13.5—Effect of admixtures and combination mixture on iron loss in precracked specimens (Civjan et al. 2003).
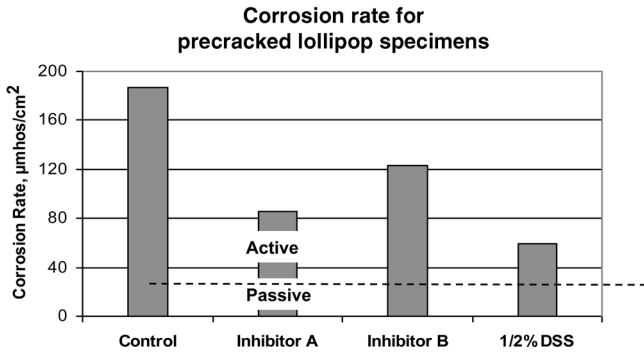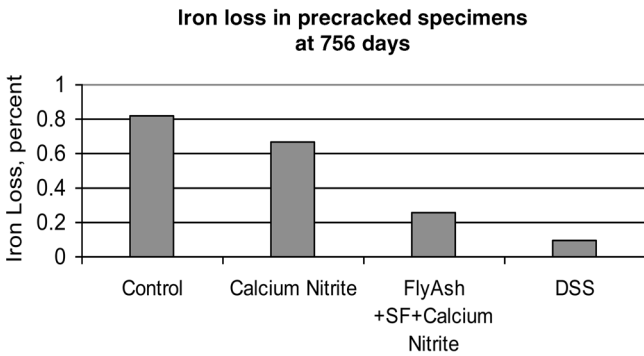

Fig. 13.6—Chloride content versus depth after 7 years of exposure at Treat Island. (Note: 1 in. = 25.4 mm).

contaminants) that may try to enter through the pores. This is evidenced by resistance to chloride ion penetration from testing by the University of Connecticut (Goodwin et al. 2000). The rest of the DSS is available to react with iron that has lost electrons and would normally corrode. When the DSS reacts with the Fe^{2+}, it forms a stable salt, inhibiting corrosion (unlike a normal corrosion process reaction, which is an ongoing, unstable process). Because the end product of this reaction is electrically neutral and therefore stable, the chloride level is not a significant factor in the corrosion process of reinforcing steel. The availability of an adequate amount of DSS is the most important factor in corrosion mitigation. Availability is affected by the dosage rate of the DSS, the amount of the metallic ions in the fresh concrete, and the capillary pore system among other factors. As indicated previously, DSS acts as a corrosion protection system provided by a single admixture; decreasing the permeability of the concrete as well as providing corrosion protection. In testing conducted by the University of Connecticut (Goodwin et al. 2000) and the University of Massachusetts (Civjan et al. 2003; Civjan and Crellin 2008), DSS inhibited corrosion more than the other materials and systems tested (Fig. 13.4 and 13.5).

13.3—Selection and evaluation

The dosage rate of amine carboxylates is independent of the expected chloride levels. The recommended dosage rate is a sufficient concentration of inhibitor to form a monomo-

lecular film on embedded metals and that dosage rate is not dependent on chloride concentrations.

The recommended dosage of the amine-ester organic corrosion inhibitor for protection of steel in concrete is 5 L/m^3 (1 gal./yd^3). This dosage is optimized to provide effective corrosion inhibition while minimizing the impact of the inhibitor on the fresh and hardened properties of concrete, in particular, air entrainment and compressive strength. Synergistic reduction in chloride ingress is obtained when the amine-ester organic inhibitor is used in combination with silica fume, and by extension other permeability-reducing supplementary cementitious materials, as shown by the data in Fig. 13.6. The data were obtained from chloride profile tests performed on specimens exposed to the marine environment at the U.S. Army Corps of Engineers Treat Island Weathering Station for a period of 7 years. Therefore, for severe corrosion environments, the use of the amine-ester organic inhibitor, or other corrosion inhibitors, is recommended to be used in combination with supplementary cementitious materials, a low *w/cm* (≤0.40), and adequate clear cover over steel.

Calcium nitrite is not a product with one set dosage. The dose can be adjusted to match the durability and life cycle cost requirements of the structure being considered. Increasing the dosage of calcium nitrite will protect steel from corroding for longer periods of time by protecting against higher concentrations of chloride that permeate into the concrete, as detailed in Table 13.1. The prediction of the chloride concentrations in concrete at the reinforcing bar level as a function of time is a process that has been well researched and published over the last 10 to 15 years (Berke et al. 1998, 2005; Berke and Hicks 2004; Samson and Marchand 2006). These chloride ingress prediction models vary from relatively simple ones based on Fick's Law of Diffusion (Berke et al. 1998; Ehlen et al. 2009) to more complex ones, including capillary suction and chemical reaction terms (Samson and Marchand 2006). Using the methods

discussed in these references or using publicly available software such as Life-365 (Violetta 2002; Ehlen 2009) allows an engineer to compare the impact of different doses of calcium nitrite on expected time to corrosion and on life cycle cost impact.

Figure 13.7 displays predicted chloride levels from a diffusion calculation for a marine pile after 50 years of exposure in warm water/weather conditions as a function of concrete cover. This figure clearly identifies the advantage of lower-*w/c* concrete, low-coulomb concrete, and increased concrete cover to reduce the chloride concentration in concrete. Figure 13.8 plots chloride levels from a similar diffusion calculation for a parking deck slab as a function of time at one given cover depth. Based on the chloride level expected at design life at the level of the steel for a structure, a dosage is selected from Table 13.1, which gives levels of calcium nitrite levels conservatively found to afford protection.

Due to the economic trade-offs necessary between calcium nitrite dose, cost of reducing the *w/c*, costs of increasing reinforcing steel cover, the widely differing costs of pozzolans, and cost of future repair, several of the models allow cost inputs and trade-off analyses of alternative design approaches in terms of net present value of each approach.

Selecting an appropriate dosage of DSS is dependent on the chloride exposure of the concrete. For a moderate exposure such as chlorides in the groundwater, the dosage typically recommended is 1 gal./yd^3 (5 L/m^3). For more severe exposures such as bridge decks that are salted or marine

applications, 2 gal./yd^3 (10 L/m^3) of DSS is appropriate, with a maximum *w/c* of 0.40 and 2 in. (50.8 mm) of cover over the reinforcing steel. Salt ponding tests showed that chloride ingress into DSS concrete was significantly less than ingress than that into the control concrete (Civjan and Crellin 2008). DSS apparent diffusion coefficients calculated from the data were approximately 2.5% of the control concrete coefficient. The corrosion inhibiting properties of DSS are projected to add significantly to this service life based on results of cracked specimen testing.

13.4—Applications

Amine carboxylate-based admixtures are appropriate to use for reducing chloride-induced corrosion of any good-quality concrete, from seawater, salt-laden air, and deicing salt exposure. They are also effective in reducing corrosion due to carbonation (or combinations of the two) (Xu et al. 2004).

The amine-ester organic corrosion inhibitor is recommended for use in extending the service life of steel-reinforced concrete structures exposed to chlorides in service. In accordance with code requirements, it has to be used in good-quality concrete with a maximum *w/cm* of 0.40 and an appropriate level of clear cover over the reinforcing steel. It has, however, also been shown to provide effective corrosion protection for steel in concrete at a *w/cm* of up to 0.50 because of its effectiveness in reducing chloride ingress under cyclic wetting and drying exposure conditions (Nmai and McDonald 2000).

Calcium nitrite is appropriate to use for reducing chloride-induced corrosion of any good-quality concrete, from seawater, salt-laden air, and deicing salt exposure. It is not
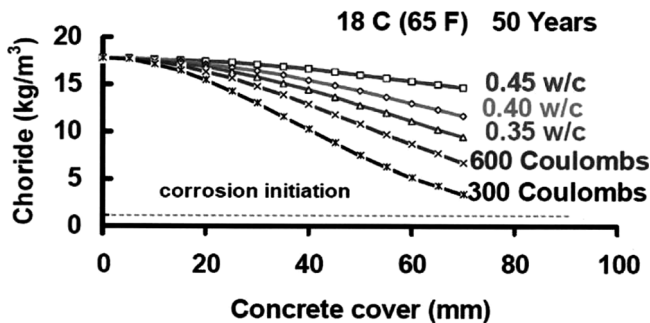
Fig. 13.7—Graph of chloride versus depth for marine piles. (Note: 1 mm = 0.0394 in.; 1 kg/m^3 = 1.686 lb/yd^3.)

Table 13.1—Calcium nitrite dosages for expected chloride levels

Chloride ion, lb/yd^3 (kg/m^3)	Calcium nitrite 30% solution, gal./yd^3 (L/m^3)
6 (3.6)	2 (10)
9.9 (5.9)	3 (15)
13 (7.7)	4 (20) 13 lb/yd^3
15 (8.9)	5 (25) 15 lb/yd^3
16 (9.5)	6 (30) 16 lb/yd^3
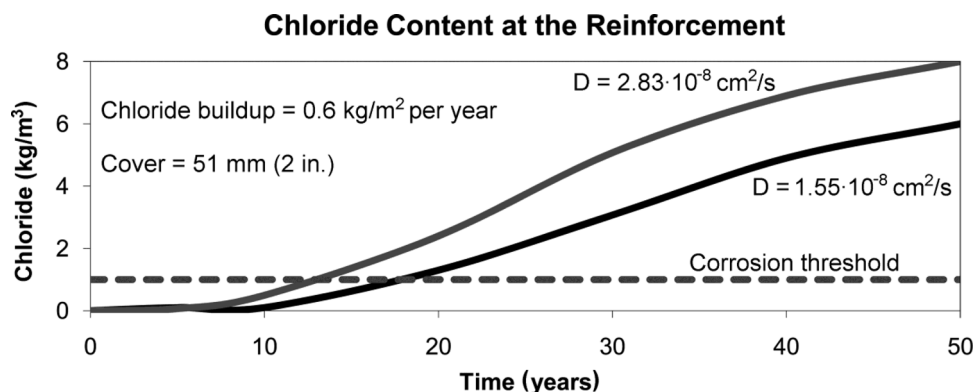
Fig. 13.8—Graph of chloride buildup over time at fixed depth. (Note: 1 kg/m^3 = 1.686 lb/yd^3; 1 kg/m^2 = 0.2 lb/ft^2; 1 cm^2 = 0.155 in.^{2})

applicable for poor-quality concrete or concrete with very low clear cover over the reinforcing steel, as in those situations the chloride levels build so rapidly that the protection from calcium nitrite lasts an uneconomically short time.

DSS is also appropriate for use in reducing chloride-induced corrosion of properly proportioned concrete from seawater, salt-laden air, and deicing exposure. Properly proportioned concrete should have a maximum *w/cm* of 0.40 and the appropriate clear cover over the reinforcing steel.

13.5—Proportioning concrete

General guidelines for proportioning good concrete mixtures are applicable to mixtures containing corrosion-inhibiting admixtures. Because durability in a corrosive environment is the reason for the use of these admixtures, a low *w/c* is advisable. The type of admixture, the environment, and the design life of the structure (along with other factors), however, will dictate the proportioning of the mixture. Guidance is presented in the following.

The standard dosage rate for amine carboxylates is 1.0 to 1.5 pt/yd^3 (0.6 to 1 L/m^3) for liquids and 1 lb/yd^3 (0.6 kg/m^3) for powder versions. Amine carboxylates can be added with the mixture water to concrete at a concrete plant, or added on the job site as a powder. They are generally compatible with the use of pozzolans or slag, and do not affect the finishing properties of the concrete when used in combination with them. Because the dosage rate is so low, there is no need for adjustments to the mixture design.

For the amine-ester organic inhibitor, proportioning in accordance with ACI 318 for concrete that would be exposed to chlorides in service is appropriate. The ACI 318 requires a maximum *w/cm* of 0.40 and a minimum compressive strength of 34.5 MPa (5000 psi). In most applications, the compressive strength achieved with the use of such a low *w/cm* would exceed the specified strength. Consequently, a modification in mixture proportions may not be required to compensate for the marginal decrease in compressive strength that can occur with the use of the amine-ester organic inhibitor. If desired or if the decrease in compressive strength is unacceptable, however, the *w/cm* of a mixture treated with the amine-ester organic corrosion inhibitor should be reduced slightly to offset the strength decrease.

For calcium nitrite, generally permeation and economic modeling shows that concrete should be proportioned at a *w/c* of 0.40 or less, although moderate design life concretes can be achieved with a *w/c* of 0.45 with a pozzolan or slag.

HRWRAs are used to achieve the required *w/cm* without requiring an increase in cementitious content. Due to the permeability-reducing benefits of slag and pozzolans, dosage rates of calcium nitrite above 4 gal./yd^3 (20 L/m^3) are unusual (Berke and Rosenberg 1989), as long as pozzolans or slag are available, cover is adequate, and design service lives are not extreme. Calcium nitrite requires high volumes of product to attain results, as high as 6 gal./yd^3 (30 L/m^3).

This volume must be accounted for in mixture proportions; for the typical 30% calcium nitrite solution, approximately 85% of the volume is water. Care must be taken to ensure that the calcium nitrite is added separately from other admixtures, preferably near the completion of the batching sequence. Some problems were encountered in the early use of calcium nitrite when the strength requirements of the concrete design and the *w/c* required for permeability control were incompatible. That is, a design strength of, for example, 30 MPa (4350 psi) was required, but a *w/c* of 0.37 cited. While proper following of mixture proportioning principles of ACI 211.1 would identify that the *w/c* was controlling, in some cases producers tried to take standard mixtures and drive down the *w/c* with artificially high levels of high-range water reducer. This led to high slump loss and control issues not directly related to the calcium nitrite.

Testing has indicated that using DSS, or the other cited corrosion inhibitors, in concrete with a maximum *w/cm* of 0.40 will result in a long service life. A water-reducing admixture will likely be needed. As the *w/c* increases, some decrease in service life can be expected. Only moderate amounts of cement (approximately 600 lb/yd^3 [356 kg/m^3]) are needed to achieve normal strength and durability, though higher cement contents may be used. DSS also usually entrains air and, as such, additional air-entraining admixtures may not be needed. If adjustments are needed to increase the desired air content, standard air-entraining admixtures can be used. If a low or lower air content is desired, it can be obtained through the use of a defoaming agent. DSS is commercially available as a 20% solution with customized doses of defoaming agent to control air entrainment in concrete. Users may request that suppliers of DSS provide information regarding the acceptability of the air-void system produced. Because 80% of the DSS is water, this must be taken into account in the mixture design. DSS is generally not reactive with other admixtures, but it is recommended that they be introduced separately into the mixture, with the DSS being introduced last. Trial batches are recommended. Pozzolans, Class C fly ash, or slag may be used in the mixture but are not necessary for corrosion inhibition.

13.6—Effects on fresh and hardening concrete

Amine carboxylates can retard setting times 3 to 4 hours at 70°F (20°C); however, normal set (NS) versions containing an accelerator so that they set similarly to a control (mixture with no amine carboxylate) are available. These generally have little effect on the early fresh properties of concrete, as long as proper mixture proportioning has been followed. Testing should be done when amine carboxylate-based admixtures are used together with lignin or naphthalene sulphonate HRWRAs to establish that the setting time is acceptable. To avoid this problem, it is recommended to use melamine or polycarboxylate-based HRWRAs when using amine carboxylate-based corrosion inhibitors.

The amine-ester organic corrosion inhibitor generally has little effect on the fresh and plastic properties of concrete, including time of setting. Depending on mixing efficiency and the characteristics of a mixture, however, an increase in the dosage of air-entraining admixture and additional mixing or a change in batching sequence, or both, may be required to achieve the desired air content.

Calcium nitrite generally has little effect on the early fresh properties of concrete, as long as proper mixture proportioning has been followed. In a few cases, the acceleratory effect of the material has been found to be associated with slump loss. In this case, the retarded version may be more helpful than adjusting set time with separate retarders, as the retarding component is intimately mixed with the calcium nitrite, giving no opportunity for cement to encounter the calcium nitrite in the absence of retarder. Calcium nitrite is an accelerator of both set and strength development of concrete and meets the requirements for accelerators (Type C) in ASTM C494/C494M.

DSS generally has little effect on the fresh properties of properly proportioned concrete. The nature of the molecule will, however, make the paste more cohesive and perhaps reduce the slump slightly. Bleeding characteristics of the concrete are not significantly affected. The more cohesive paste will make the concrete less susceptible to segregation during handling and placing.

In some instances, when using a particular cement, a retardation of the initial and final set of up to 1 hour is possible. Conversely, other mixtures have seen a small acceleration of the set times. In either case, adjustments can be made as needed by using conventional set accelerators or retarders.

13.7—Effects on hardened concrete

The corrosion-inhibiting effect has been discussed previously. Amine carboxylates would have strengths similar to a control and would experience similar amounts of shrinkage as a control. They also will not have any effect on rapid chloride permeability testing (RCPT) of concrete (AASHTO T277 or ASTM C1202).

Depending on the type and proportions of the mixture ingredients, the amine-ester organic inhibitor may also result in a reduction in compressive strength, typically in the range of 5 to 10% at the low *w/cm* used in proportioning concretes exposed to chlorides in service. As a result of its permeability-reducing characteristic, the amine-ester organic inhibitor will reduce the chloride diffusion coefficient and sorption rate of concrete as indicated by the chloride flux, chloride migration, and sorptivity data summarized in Table 13.2 and the long-term cyclic chloride ponding data shown in Fig. 13.9.

The data in Fig. 13.9 and additional chloride content data obtained after 2240 days of cyclic ponding in the same evaluation showed that chloride ingress into a 0.50 *w/c* concrete treated with the amine-ester organic inhibitor was less than the chloride ingress into the companion 0.40 *w/c* concretes. Therefore, the amine-ester organic inhibitor may be more forgiving in situations where a specified *w/cm* is inadvertently exceeded through the use of additional water in a concrete mixture, or when for one reason or other the *w/cm* of a mixture is greater than code requirements for corrosion protection of steel in concrete. For example, concretes used in balconies of high-rise residential buildings with close proximity to the marine environment would be typical of the latter case. As shown by the corrosion data in Fig. 13.10, effective corrosion protection of steel in concrete is provided by the amine-ester organic inhibitor through the
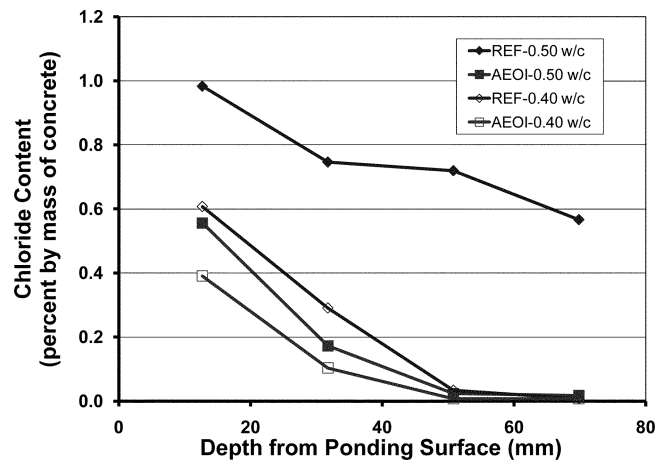

Fig. 13.9—Chloride content versus depth after 1000 days of cyclic ponding (from Nmai and McDonald [2000]). (Note: 1 mm = 0.0394 in.)

Table 13.2—Chloride flux, chloride migration, and capillary absorption data for amine-ester organic inhibitor (Buffenbarger et al. 2000)

Mixture	Chloride flux,[*] mm^2/year	Chloride migration,[†] mm^2/year	Capillary absorption,[*] $g/m^2 s^{1/2}$
Reference average	39	64	7.6
Amine-ester organic inhibitor	34	42	3.3

[*]Average of two specimens.
[†]Average of three specimens.
Note: nominal cement contents of 356 kg/m^3; *w/cm* of 0.45; air entrained. 1 mm^2 = 0.002 in.^{2}; 1 g/m^2 = 0.03 oz/yd^2; 1 kg/m^3 = 0.06 lb/ft^3.

combined effects of the protective film that it forms and the significant reductions in chloride ingress that it provides.

Calcium nitrite's corrosion-inhibiting effect has been discussed previously. Aside from this, calcium nitrite also has the effect of increasing the strength of concrete, significantly at early ages, but measurably at 28 days. In some cases, especially with the use of polycarboxylate high-range water reducer, this strength increase can be significant. As in all such interactions, the strengths achieved depend on the specific materials used and must be determined by testing. When the rapid chloride permeability test (RCPT) (AASHTO T277 or ASTM C1202) is used to estimate the permeability of concrete, adjustment in the number expected must be made if calcium nitrite is used. The test estimates a concrete's permeability by essentially measuring its conductivity—the amount of charge passed in coulombs over a certain time. This is a good approximation of how easily chloride will move through the concrete because the charge passed depends on the amount of conducting liquid phase and its interconnectivity in the concrete. The assumption is made in comparing different concretes that the actual conductivities of the liquid phases themselves are similar. However, because calcium nitrite is a salt, and as such increases the conductivity of the liquid phase itself, the rapid chloride number will generally be higher by as much as 30%, at equivalent true chloride permeability levels as measured
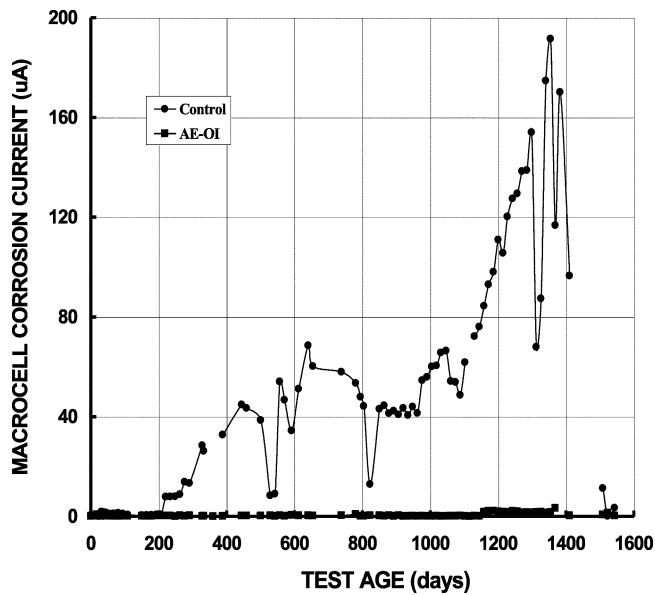
Fig. 13.10—Macrocell corrosion currents from long-term corrosion evaluation of 0.40 w/c concretes with and without amine-ester organic inhibitor (from Nmai and McDonald [2000]).

by long-term ponding tests. Accordingly, if design comparisons are being made on an RCPT basis, the best estimate for design purposes of the RCPT of a calcium nitrite concrete is to measure the RCPT for a companion concrete made without the calcium nitrite, but which is otherwise identical.

In addition to the corrosion-inhibiting effect discussed previously, DSS will affect a few of the other properties of hardened concrete. For an identical mixture, the addition of DSS may typically give 28-day strengths that are approximately 15% lower, but this will vary with the particular ingredients used in the mixture. If a higher strength is required to meet design specifications, adjustments to the mixture can be made and trial batches tested to verify the strength. A polycarboxylate high-range water reducer is very compatible with DSS and is useful in this regard.

Because it is a salt, DSS increases the conductivity of the pore water solution of concrete. This is more evident if the concrete is vacuum-saturated and ionic solutions are placed against the surface of the concrete. These are the conditions used in the rapid chloride test that was originally designed to be used with ordinary concrete mixtures. The rapid chloride test values are dependent on the conductivity of the concrete, but they have been correlated to levels of chloride intrusion obtained from the salt ponding test. When any admixture, including DSS, changes the conductivity of the pore water solution of the concrete, the correlated values of permeability are not applicable. Therefore, the salt ponding test or another test method insensitive to the conductivity of the pore water solution of the concrete or measuring the actual ingress of chloride into the concrete should be used.

13.8—Quality assurance
Normal, good-quality control is necessary for concrete containing corrosion-inhibiting admixtures, as it is for all

quality concrete. Because the corrosion-inhibiting admixture will provide vital protection necessary for long life of the structure, the need for proper proportioning, batching, and dosing the admixture cannot be overemphasized. All of the items mentioned Section 13.6 for the particular corrosion-inhibiting admixture selected should be addressed.

13.9—Storage
Corrosion-inhibiting admixtures should be stored in strict accordance with the manufacturer's recommendations. Most admixtures are not damaged by freezing. The manufacturer's instructions should be followed regarding the effects of freezing the product. An admixture stored beyond its recommended shelf life should be retested before use.

CHAPTER 14—LITHIUM ADMIXTURES TO REDUCE DELETERIOUS EXPANSION FROM ALKALI-SILICA REACTION
14.1—Introduction
Deleterious expansions from ASR can occur in concrete when susceptible siliceous minerals are present in the aggregate. These minerals can begin to dissolve in the highly alkaline pore solution within the concrete, and then react with sodium, potassium, and other ions in solution. These reaction products then combine with water and may produce pressures sufficient to produce deleterious effects in the concrete, such as cracking, popouts, and overall expansion.

The materials-related approach to preventing these deleterious expansions involves four basic approaches, used either alone or in combination. These are the use of nonreactive aggregates, limiting the alkali content of the concrete mixture, the use of suitable pozzolans in the proper amount, and the use of lithium-bearing admixtures.

14.2—Materials
Currently, there are two solid (powder) forms of lithium admixture and one liquid form of lithium admixture available commercially. The solid forms are lithium hydroxide monohydrate and lithium carbonate, and the liquid form is 30% by weight lithium nitrate solution in water. The lithium hydroxide monohydrate is caustic and needs more careful handling than lithium carbonate or the lithium nitrate solution. In addition, an admixture containing lithium nitrite to suppress both ASR and corrosion has been patented, and is available from Japan (Takakura et al. 1990; Stokes and Manissero 2001).

14.3—Mechanism
In the pore solution of the concrete, dissolved silica can combine with sodium (or potassium) ions to form the basis for an alkali-silica gel that can absorb water and expand with deleterious effects on the concrete. If lithium ions are present in a sufficient ratio to the sodium or potassium ions, then lithium will preferentially combine with the available silica present and form relatively stable, insoluble lithium silicates. Evidence for this has been provided indirectly in analysis of extracted pore solutions (Stark et al. 1993) and directly from X-ray diffraction analysis of reaction products (Tremblay et al. 2004). As long as sufficient lithium ions are present in the

pore solution, this protection is assumed to last indefinitely (Diamond 1999). The ratio of lithium ions to the sum of the sodium and potassium ions necessary for control depends mainly on the aggregate, but is nominally 0.74 on a molar basis (Boudreau et al. 2006).

The anion of the lithium compound used can impact the effectiveness of the lithium ion in suppressing deleterious expansions. In particular, lithium hydroxide monohydrate and lithium carbonate will both boost the hydroxide concentration of the pore solution in the concrete in amounts approximately equal to their dosage, whereas lithium nitrate does this to a far lower degree (Stokes et al. 1997). Thus lithium nitrate will in general be effective at lower dosages than lithium hydroxide monohydrate and lithium carbonate, in terms of the lithium ion supplied (Fig. 14.1). The anion will also have different effects on concrete properties, with the nitrate form having the least effect on concrete properties in general (Thomas et al. 2003).

14.4—Dosage

Lithium admixtures are dosed relative to the sodium equivalent of the portland cement loading of the concrete mixture. In general, an admixture dose that supplies a 0.74 molar ratio of Li ion to the sodium plus potassium ions supplied by the portland cement is termed the standard, normal, or 100% dose (Stokes and Manissero 2001). The amount needed in a given mixture will vary with the alkali loading of the mixture, the aggregate used, and the presence, amounts, and composition of any supplementary cementitious components present in the mixture, but can be referenced as the percent of standard dose. For lithium nitrate admixture (which is supplied as a 30% aqueous solution by weight) this is 1.2 gal./oz (4.6 L/kg) of sodium equivalent supplied by the portland cement in the unit volume of concrete. The sodium equivalent of portland cement is calculated as follows:

$$\text{sodium equivalent} = \text{wt\% sodium oxide} + 0.658 \times \text{wt\% potassium oxide}$$

The sodium equivalent for a unit volume of concrete is calculated as follows:

$$\frac{\text{sodium equivalent}}{\text{unit volume of concrete}} = \frac{\text{kg portland cement}}{\text{unit volume of concrete}} \times \frac{\text{sodium equivalent}}{100}$$

For lithium hydroxide monohydrate, the standard dose is 1 lb/lb (1 kg/kg) of sodium equivalent supplied by the portland cement in the unit volume of concrete. For lithium carbonate, the standard dose is 0.88 lb/lb (0.88 kg/kg) of sodium equivalent supplied by the portland cement in the unit volume of concrete.

Because of the relatively small volumes of the solid lithium admixtures that may be used in a given concrete mixture, either special equipment is needed to add the material to the mixture, or the material is added manually. The aqueous lithium nitrate admixture is added with conventional admixture dosing equipment.
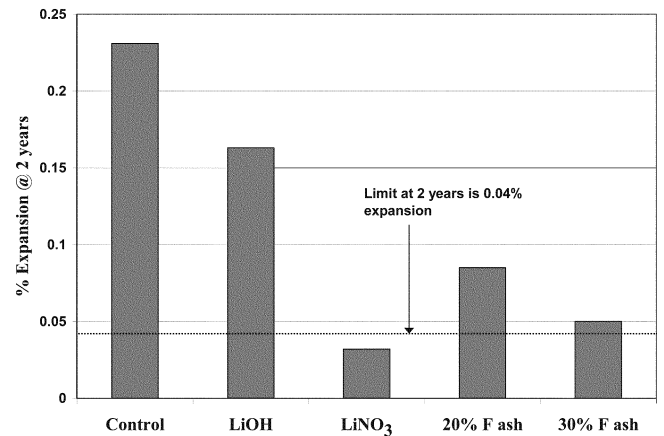

Fig. 14.1—Example of testing for effectiveness against deleterious ASR by use of concrete prism expansion at 2 years of age (Fournier et al. 2003).

14.5—Effects on concrete properties

The effects on both hardened and plastic properties of concrete from the use of these admixtures depends greatly on the particular lithium compound used, with lithium hydroxide and lithium carbonate having more pronounced effects in general. These effects are mainly differences in set times. Set times are generally increased with hydroxide. While the carbonate is a very strong accelerator for calcium aluminate cement chemistries, it works as a retarder in portland cement systems. Lithium nitrate in general has the least effect on concrete properties (Thomas et al. 2003), and because it has very little potential for adding hydroxide to the pore solution and is more effective at lower dosages, it is generally the preferred form for use in concrete (Folliard et al. 2003). There is generally no particular significant effect with nitrate on any concrete property, hardened or plastic, with the use of lithium nitrate admixture, except a tendency toward acceleration. This effect is not universal enough, nor strong enough, to consider the admixture an accelerator (Thomas et al. 2003). As with all admixtures, however, specific interactions with the vast possibilities of combinations of materials and other admixtures dictates that proper mixture designs be evaluated in a laboratory prior to use in the field.

14.6—Performance tests for effectiveness

There are currently no standard test methods for evaluating the effectiveness of lithium admixtures in concrete. Most ASR mitigation specifications allowing lithium admixtures are based either on a prescriptive specification, such as the standard dose, or describe modifications to either ASTM C1293 or ASTM C1260 (Folliard et al. 2003). In the case of ASTM C1293, the normal modification employed is to add the lithium admixture to the mixture and note the percent expansion at 2 years (Folliard et al. 2003). Modifications involving ASTM C1260 generally involve adding the admixture to both the mortar and to the soak solution (Folliard et al. 2003). The actual expansion limits used to evaluate these results varies with the specifying agency. These may range from as high as 0.1% at 16 days to as low as 0.08% at 28 days in modifications to the accelerated

mortar bar tests (ASTM C1260 or ASTM C1567). For testing in ASTM C1293, the limit is generally less than 0.04% at 2 years.

In Fig. 14.1, the LiOH and $LiNO_3$ were both added at the 100% dose; note the greater effectiveness of the $LiNO_3$. As a demonstration of the high reactivity level of this aggregate, note that levels of Class F fly ash up to 30% were not sufficient to control the expansion of this aggregate. Often, 30% of Class F fly ash will suppress expansion of most aggregates used for concrete manufacture in North America. The 100% dose of $LiNO_3$ will not always be sufficient for every aggregate. Performance testing is recommended when using Li-based admixtures.

14.7—Storage

Lithium admixtures should be stored in strict accordance with the manufacturer's recommendations. Most admixtures are not damaged by freezing. The manufacturer's instructions should be followed regarding the effects of freezing the product. An admixture stored beyond its recommended shelf life should be retested before use.

CHAPTER 15—PERMEABILITY-REDUCING ADMIXTURES

15.1—Introduction

While it is generally accepted that well-proportioned and properly cured concrete produced using a low *w/cm* will result in a finished product with good durability and low permeability, no concrete structure is absolutely waterproof or "bottle tight" (Perkins 1986). Concrete is a porous material, and water can penetrate concrete through pores and microcracks due to capillary absorption (often referred to as wicking) or due to hydrostatic pressure. Capillary absorption is the movement of water through the small pores in concrete in the absence of an externally applied hydraulic head, and is the result of surface interactions between the water and the pore wall. The permeability of concrete is the movement of water due to a pressure gradient, such as water in contact with a concrete structure installed underground. In some cases, porosity may be exacerbated by external factors such as incomplete consolidation and curing, which may ultimately lead to reduced durability. The addition of supplementary cementing materials (SCMs) into concrete mixtures has been gaining acceptance with respect to improving durability and reducing permeability (Munn et al. 2005). In addition, a class of materials referred to as permeability-reducing admixtures (PRAs) have been developed to improve concrete durability through controlling water and moisture movement (Roy and Northwood 1999) as well as by reducing chloride ion ingress (Munn et al. 2003) and permeability (Munn et al. 2005). PRAs encompass a range of materials with variances in performance.

Although PRAs are traditionally subcategorized as damproofing and waterproofing admixtures (Ramachandran 1995; ACI 212.3R; Aldred 1989), perhaps it is too absolute to state that concrete can be made waterproof. Further complicating matters, many concrete professionals use the term "permeability" to mean the resistance of concrete to water ingress under actual service conditions. This definition is not technically correct as it could refer to either permeability or capillary absorption as defined previously; however, permeability is commonly understood to refer to any passage of water through concrete. For the purpose of this chapter, admixtures intended to reduce water ingress will be split into two subcategories: PRAs for concrete exposed to nonhydrostatic conditions (PRAN) and PRAs for concrete exposed to hydrostatic conditions (PRAH). In addition to permeability reduction, some PRAs may exhibit other beneficial characteristics such as reduced drying shrinkage (Munn et al. 2003), lowered chloride ion penetration (Munn et al. 2003), enhanced freezing-and-thawing resistance (Ramachandran 1995; Rixom and Mailvaganam 1999), and enhanced autogenous sealing (Skoglund and Johansson 2003; Kubal 2000).

15.2—Materials

Depending on the manufacturer, PRAs include, but are not limited to, materials from one or more chemical families. They are as follows:

- Hydrophobic or water-repellent chemicals are the largest group and include materials based on soaps and long-chain fatty acid derivatives, vegetable oils (tallows, soya-based materials, and greases), and petroleum (mineral oil, paraffin waxes, and bitumen emulsions). These materials provide a water-repellent layer along pores in the concrete, but the pores remain physically open;
- Finely divided solids include materials such as inert and chemically active fillers (talc, bentonite, silicious powders, clay, hydrocarbon resins, and coal tar pitches) and chemically active fillers (lime, silicates, and colloidal silica). Fine solids act as densifiers and physically restrict the passage of water through the pores. Some authors include SCMs in this category as well; and
- Crystalline materials consist of proprietary active chemicals provided in a carrier of cement and sand. The hydrophilic nature of these materials causes them to increase the density of calcium silicate hydrate (CHS) and/or generate pore-blocking deposits that resist water penetration.

These families of materials are used alone or in combination to give varying ranges of performance.

Perhaps the most widely used PRANs for damproofing protection under nonhydrostatic conditions are hydrophobic materials based on salts of fatty acids. Calcium, ammonium, and butyl stearates are perhaps the most common, as well as oleic, caprylic, and capric derivatives (Ramachandran 1995; Rixom and Mailvaganam 1999). According to Ramachadran (1995), these materials react according to the following reaction

$$Ca(OH)_2 + RCOOH \rightarrow Ca^+COOR^- + H_2O$$

calcium hydroxide + stearate admixture → insoluble calcium + water.
(lime)   stearate
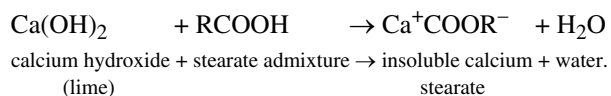
The insoluble stearate created by the reaction between the admixture and the lime forms a hydrophobic layer on the walls of the concrete pores. Waxes and bituminous emulsions

are other materials that can deposit hydrophobic particles in the concrete pores, although there is no chemical reaction involved in that process. Hydrophobic admixtures are effective at reducing the capillary absorption and chloride ingress of concrete under nonhydrostatic conditions as shown in Fig. 15.1 and 15.2, respectively (Aldred et al. 2001; Civjan and Crellin 2008).

In theory, the hydrophobically-modified concrete should be able to resist water up to 13.12 ft (4 m) head pressure (Ramachandran 1995) and even up to 45.92 ft (14 m) (Aldred et al. 2001), but after accounting for the fact that the material is unlikely to completely and uniformly coat all pores, plus the presence of larger voids, concrete treated in this way can usually only withstand a few centimeters of head pressure (Ramachandran 1995). For this reason, stearates and other hydrophobic materials are generally used only in conditions in which there is little or no hydrostatic pressure.

Polymer materials coalesce within the concrete mass to form water-repellent films. Others have been reported to form globules that plug capillaries once hydrostatic pressure has been applied. Some of these materials have been found to resist hydrostatic pressure (Ramachandran 1995) and can be categorized as PRAHs. Nevertheless, concrete structures containing these materials cannot be considered completely watertight because polymers lack the ability to bridge cracks formed by thermal or mechanical movement of the concrete (Kubal 2000). Leaking cracks are often addressed separately using suitable repair methods. The admixture supplier should be consulted regarding the recommended method of crack repair, particularly for hydrophobic admixtures, which may repel water-based repair materials. One major use of polymer-latex admixtures has been to reduce permeability of concrete overlays for bridge decks and parking decks.

Finely-divided solids may reduce permeability under nonhydrostatic conditions by increasing density or by simply filling up voids, leading to repellency. The denser concrete has reduced porosity, which restricts the movement of water; however, the pores are usually not completely blocked. These products are typically used for nonhydrostatic conditions (PRAN) and in some cases are used in combination with hydrophobic chemicals for a synergistic effect.

SCMs such as fly ash, raw or calcined natural pozzolans, silica fume (ACI 232.1R; 232.2R; 234R), or slag cement (ACI 233R), although not chemical admixtures, can contribute to reducing concrete permeability and can be a complementary component in a well-proportioned mixture incorporating permeability-reducing admixtures. Figures 15.3 and 15.4 demonstrate the permeability under pressure of concrete mixtures containing fly ash and similar mixtures containing a crystalline PRA at the age of 10 months. The crystalline admixture resulted in a significant reduction in permeability when added to the fly ash mixture.

Unlike hydrophobic materials, crystalline admixtures are hydrophilic, and the active ingredients react with water and cement particles in the concrete to form calcium silicate hydrates and/or pore-blocking precipitates in the existing microcracks and capillaries. The mechanism is analogous to the formation of calcium silicate hydrates and the resulting
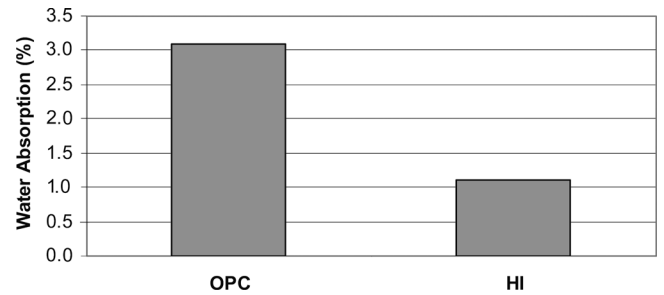
Fig. 15.1—Water absorption for ordinary portland cement (OPC) concrete with hydrophobic ingredient (BS EN 1881-122) with an age of 28 days and a w/cm of 0.40.
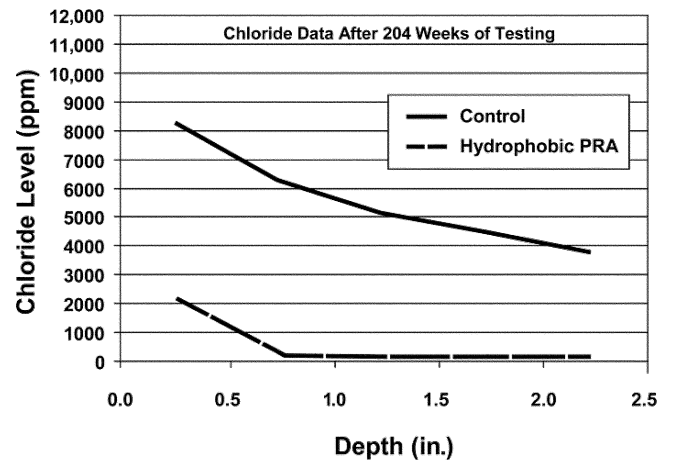
Fig. 15.2—Chloride penetration of a hydrophobic PRA subjected to ponding. Tested using modified chloride ponding protocol (not the AASHTO T259 procedure discussed in Section 15.3). Cementitious content is 690 lb/yd³ and w/cm is 0.40. (Note: 1 in. = 25.4 mm; 1 lb/yd³ = 0.5933 kg/m³.)

crystalline deposits become integrally bound with the hydrated cement paste. The resulting concrete has significantly increased resistance to water penetration under pressure. An overview of the general process may be represented by the following:

$$3CaO\text{-}SiO_2 + M_xR_x + H_2O \rightarrow Ca_xSi_xO_xR\text{-}(H_2O)_x + M_xCaR_x\text{-}(H_2O)_x$$

(calcium silicate + crystalline promoter + water →
modified calcium silicate hydrate + pore-blocking precipitate)
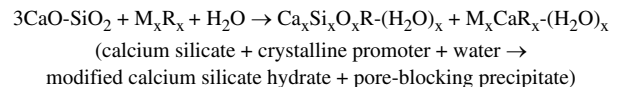
Similar reactions may exist involving the calcium aluminates, but the aforementioned process is expected to predominate due to the abundance of calcium silicates.

These crystalline deposits develop throughout the depth of the concrete and become a permanent part of the concrete mass. The crystalline deposits resist water penetration against hydrostatic pressure, and can be categorized as PRAHs. As hairline cracks form over the life of concrete, crystalline admixtures continue to activate in the presence of moisture and seal additional gaps (Kubal 2000; Skoglund and Johansson 2003). Cracks may still develop that exceed the self-sealing property, and admixture suppliers should be consulted regarding the recommended method of repair. It has been reported that once fully cured, crystalline systems
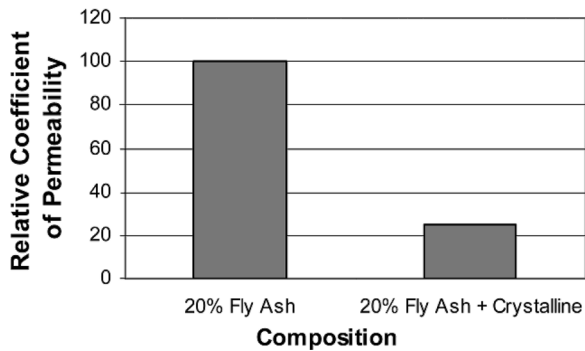
Fig. 15.3—Permeability of concrete containing 20% Type F fly ash and crystalline admixture.

Fig. 15.4—Permeability of concrete containing 30% Type F fly ash and crystalline admixture.

can withstand hydrostatic pressures of 400 ft (122 m) of head (Kubal 2000).

15.3—Selection and evaluation

The selection of a permeability-reducing admixture depends largely on the service conditions. Nonhydrostatic service conditions can be defined as those exposed to little or no water under hydrostatic head pressure, primarily when the main mechanism of water movement is capillary absorption. In these situations, hydrophobic and water-repellent PRANs are often sufficient. On the other hand, under hydrostatic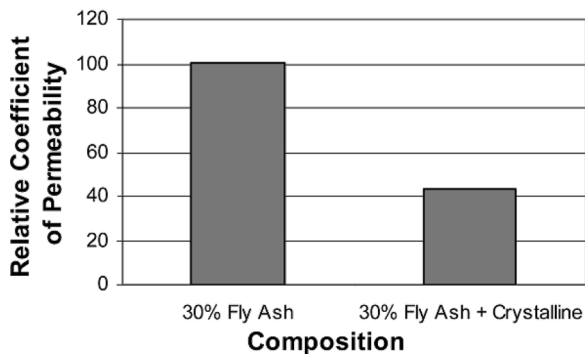 conditions, moisture is transported into concrete under pressure. Whereas PRANs are unable to effectively block the movement of water under hydrostatic head pressure (Ramachadran 1995) experienced in below-grade structures and water-retaining structures, PRAHs are well suited to these applications. PRAHs are also suited to withstand ponded water (Palmer 2004). To resist hydrostatic pressure, PRAHs employ a pore-blocking mechanism from crystalline growth, polymer coalescence, or other filler, although the ability to withstand hydrostatic pressure will depend on how completely the pores are blocked and the stability of the deposits under pressure. The distinction should be made based on the admixture's demonstrated ability to reduce water penetration under the expected service conditions. It should be emphasized that a PRAN should not be used in the presence of hydrostatic pressure if the penetration of water is expected to damage the structure or compromise interior spaces.

In addition to service conditions and level of performance, other factors will also contribute to the selection of a PRA. Some materials may affect the plastic properties of concrete such as air entrainment, setting time, and water reduction. Also, depending on the manufacturer, PRAs are available in either liquid or solid form, and this will affect the method of addition. The basis for achieving low-permeability concrete and optimizing the performance of PRAs and other admixtures is to address factors affecting the quality of the mixture, including proper proportioning and *w/cm*, quality of raw materials, and inclusion of supplementary cementing materials and other admixtures. Recommendations from manufacturers of each PRA can guide the user with respect to the correct dosage rate and directions for use.

The effects of the admixtures can be evaluated by testing the permeability of concrete through both direct and indirect methods. The U.S. Army Corps of Engineers CRC C48-92 (1992) test method is a direct measurement of concrete permeability resistance during exposure to water under 200 psi (1.28 MPa) of hydrostatic pressure. After a steady state of flow has been established, Darcy's equation can be used to calculate the coefficient of permeability, *K*. European versions of this methodology, such as DIN 1048-5 and BS EN 12390-8, measure the penetration of water under hydrostatic pressure into a concrete specimen. The European standards instruct the user to expose the concrete to 72.5 psi (0.5 MPa) of water for 72 hours. The specimens are then split in half and the depth of water penetration is measured. A widely used modification of the European standard is to expose the concrete to 150 psi (1.0 MPa) for 96 hours, and then use Valenta's equation to calculate the coefficient of permeability based on penetration depth (Taywood/Valenta method). The use of Valenta's equation requires the increase in mass for each specimen to be accurately measured to determine the volume fraction of discreet pores in the concrete (Neville 1995), which is not part of BS EN 12390-8. Figure 15.5 shows the reduction in permeability for several PRAs compared to reference concretes from testing conducted for the British Board of Agrément using the modified European standard (British Board of Agrément 2000, 2005, 2006). Each series, summarized in Table 15.1 should be considered only as a comparison of the PRA-treated concrete to its respective concrete. A direct comparison of different technologies cannot be made from the data provided because each series used a unique reference concrete.

PRAs are often supplied as multi-component systems that incorporate HRWRAs in addition to hydrophobic or pore-blocking ingredients. Therefore, the reported reduction in permeability may be partly due to reduced water contents and partly due to the other components. When tested at equal cement and water contents with a *w/cm* of 0.45, PRAHs can result in a significant reduction in water penetration under pressure compared to a reference concrete. Reductions in the depth of water penetration of 50 to 90% have been reported using penetration methods such as BS EN 12390-8 or DIN 1048-5 (Morelly 2003).

One widely-used indirect method for inferring permeability information is ASTM C1202. This method measures the
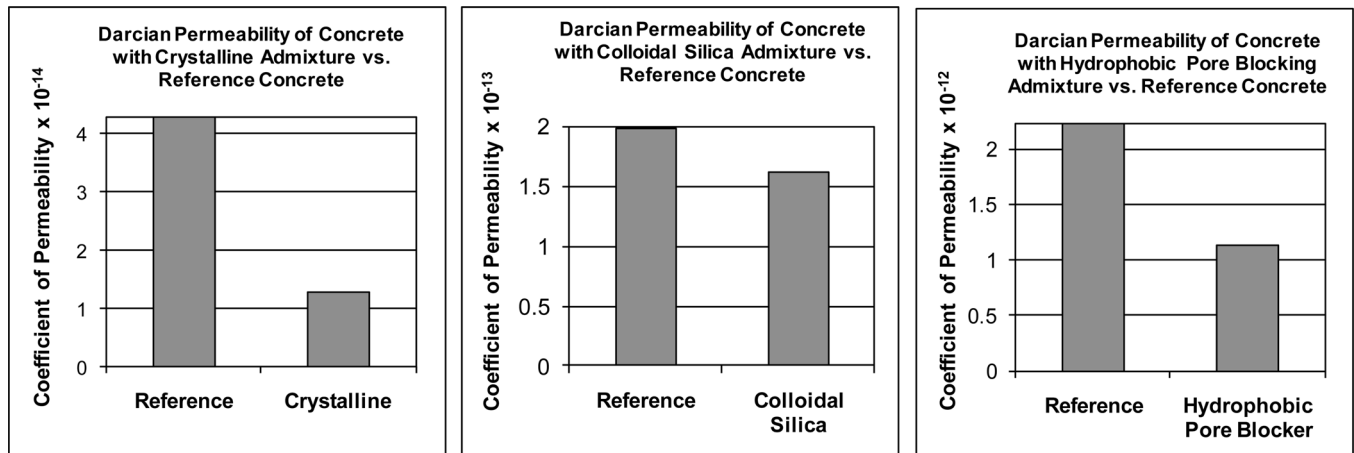
Fig 15.5—Reduction in permeability of concrete using PRAs. Tested using modified BS EN 12390-8. Pressure = 150 psi (1.0 MPa). Time = 96 hours.

current that passes through a concrete specimen exposed to electrolyte solutions and an electric potential. This test method is commonly referred to as the rapid chloride permeability test (RCPT); however, this description is technically inaccurate because the test procedure measures the charge passed through a concrete sample and not the concrete permeability. While widely recognized, this test method cannot distinguish between the charge passed due to the presence of chlorides compared with other ions in the pore solution. Results can vary when different chemistries are introduced into the mixture, causing misleading results (Obla and Lobo 2007). Alternate electrical migration techniques have been proposed, including the rapid migration test that measures chloride penetration by splitting the specimens open and applying a silver nitrate indicator (Stanish et al. 1997); however, standardized procedures have not been published. The use of electric potential to facilitate chloride penetration does not necessarily replicate the transport of chloride ions in real-life situations (Neville 1995); however, it allows results to be obtained quickly. Resistance to chloride-ion penetration can also be determined by ponding a chloride solution on a concrete surface and, after 90 days, determining the chloride content of the concrete at particular depths (AASHTO T259; AASHTO T260). The results from this test can be used to compute an apparent diffusion coefficient using ASTM C1556. Various absorption methods are used as well, including ASTM C1585 and British Standard BS EN 1881:Part 122. The choice of test depends on whether the concrete must withstand exposure to water under hydrostatic pressure, and whether a direct measurement is required.

15.4—Applications

PRAs can be incorporated into virtually any concrete mixture. Usage of these admixtures, however, is usually limited to structures that will be exposed to moisture, salt, salt water, wicking, or water under hydrostatic pressure. Prevention of water-related problems such as water migration, leaking, freezing-and-thawing damage, corrosion, carbonation, and efflorescence are reasons to choose a PRA. PRAHs are

Table 15.1—Reduction in permeability of concrete using PRAs

Admixture type	Coefficient of permeability of reference concrete	Coefficient of permeability of test concrete	Percent reduction in permeability
Crystalline	4.29×10^{-14}	1.28×10^{-14}	70
Colloidal silica	1.98×10^{-13}	1.61×10^{-13}	19
Hydrophobic pore blocker	2.23×10^{-12}	1.14×10^{-12}	49

appropriate for water-containment structures, below-grade structures, tunnels and subways, bridges and dams, and recreational facilities such as aquatic centers. These materials in a properly proportioned mixture with a *w/cm* of 0.45 or less can generally withstand aggressive environments with exposure to salt spray and some chemicals.

PRANs are used normally for repelling rain and minimizing dampness. These admixtures can improve the quality of concrete pavers, tiles, bricks, blocks, and cladding panels where the additional benefits of reduced efflorescence, the maintenance of clean surfaces and the more even drying of adjacent bricks and panels are desired. PRANs may reduce the penetration of water into concrete, thus delaying the effects of damage caused by freezing and thawing by reducing the amount or rate of moisture entering the concrete.

15.5—Proportioning concrete

PRAs are intended to be used in, and complement, well-proportioned concrete mixtures, and are not intended as a substitute for poorly proportioned concrete mixtures. Although recommendations differ from manufacturer to manufacturer, a *w/cm* of 0.45 or less is typical for concrete designed to be a barrier to water movement. Proportioning recommendations for various PRAs will differ based on parameters such as chemical reactivity and whether the admixture is in solid or liquid form. The PRAs are generally added at a prescribed percentage by weight of cement or cementitious content. Admixture manufacturers can provide more detailed guidelines for their type of PRA.

15.6—Effects on fresh and hardened properties

PRAs are usually added into concrete for the sole purpose of reducing or blocking the passage of water. These admixtures, however, can have a range of secondary effects in the plastic and hardened concrete. Some PRAs will act as low-range water reducers, entrain air, or affect the setting time of concrete. In the plastic state, these materials can affect finishing properties, consistency, and scheduling. In the hardened state, changes to compressive strength, freezing-and-thawing resistance, and shrinkage often result. Trial batches are recommended to ensure that the plastic and hardened properties of the concrete meet expectations.

15.7—Quality assurance

Determining that an admixture is similar to that previously tested or that successive lots or shipments are similar is desirable and sometimes necessary. Tests that can be used to identify admixtures include solids content, density, infrared spectrophotometry for organic materials, chloride content, and pH. The uniformity requirements in ASTM C494/C494M are a useful guide; however, ASTM C494/C494M does not specifically cover PRAs. Admixture manufacturers can recommend which tests are most suitable for their admixtures and the results that should be expected.

15.7.1 *Field control at job site*—Field control testing can vary depending on the type of admixture used and the manufacturer's recommendations. Trial batches are necessary to help optimize the mixture design and ensure the mixture meets the specifications. In addition, an on-site placement to verify proper workability, finishability, and setting time is beneficial. On-site quality control testing should include water content, slump, air content, and concrete temperatures. Cylinders are usually cast for compressive strength testing, and additional samples may be cast for permeability testing. If permeability samples are prepared, it is useful to obtain a reference concrete either by taking a sample before the PRA is added or by performing trial batches. Water-resisting performance should be measured on the approved trial mixture using suitable procedures depending on the application and as advised by the PRA supplier (for example, absorption, permeability, and coulomb). In the event that future troubleshooting is necessary, or for the purpose of analyzing historical trends, accurate record-keeping becomes important. In addition to the plastic properties, information such as lot numbers, dosage rates, dates, and environmental conditions should be recorded.

15.8—Batching

Batching recommendations for various PRAs will differ based on parameters such as chemical reactivity and whether the admixture is a solid or a liquid. Admixture manufacturers can provide guidelines for their type of PRA, stipulating the addition rate, order of addition, mixing time, and compatibility with other materials.

15.9— Storage

PRAs should be stored in strict accordance with the manufacturer's recommendations. In general, storage conditions for liquid PRAs include keeping the product in its original container, preferably unopened, at temperatures above freezing but below 100°F (38°C). The manufacturer's instructions should be followed regarding the effects of freezing the product. Powder PRAs should be kept dry, preferably in an unopened container. An admixture stored beyond its recommended shelf life should be retested before use.

CHAPTER 16—MISCELLANEOUS ADMIXTURES
16.1—Bonding admixtures

16.1.1 *Materials*—Admixtures formulated to enhance bonding properties of hydraulic-cement-based mixtures generally consist of an organic polymer dispersed in water (latex) (Goeke 1958; Ohama 1984). In general, the latex forms a film throughout the mixture. Polymer latex for use as a concrete admixture is formulated to be compatible with the alkaline nature of the portland cement paste and the various ions present. Unstable latex will coagulate in the mixture, rendering it unsuitable for use. When used in the quantities normally recommended by manufacturers (5 to 20% of polymer solids by mass of cement), different polymers can affect the unhardened mixture differently. For example, a film-forming latex can cause skinning upon contact with air. Concrete and mortar modified with polymers are more fully addressed in ACI 548.3R.

16.1.2 *Curing*—Water is still necessary to hydrate the portland cement of the cement-polymer system. The polymer latex carries a portion of the mixing water into the mixture; the water is released to the cement during the hydration process. Removing water causes the latex to coalesce, forming a polymer film. Therefore, after an initial 24 hours of moist curing to reduce plastic-shrinkage cracking, additional moist curing is not necessary and is actually undesirable because the latex film needs an opportunity to dry and develop the desired properties. The polymer improves the bond between the various phases and also fills microvoids and bridges microcracks that develop during the shrinkage associated with curing (ASTM C881/C881M; Isenburg 1971; Whiting 1981; Shen et al. 2007; Wu and Huang 2008). This secondary bonding action preserves some of the potential strength normally lost due to microcracking.

16.1.3 *Effect on concrete properties*—Greater tensile strength and durability are associated with latex mixtures. The surfactants used in producing latex act as water-reducing admixtures, resulting in more fluidity than in mixtures without latex, but with a similar *w/cm*. The compressive strength of moist-cured grouts, mortars, and concrete made with these materials is often less than that of mixtures with the same cementitious material content without the admixture, depending on the admixture used. The increases in bond, tensile, and flexural strengths, however, can outweigh the disadvantage of a compressive-strength reduction. Polymer-modified concrete has better abrasion resistance, better resistance to freezing and thawing, and reduced permeability compared with similar concrete not containing the polymer.

16.1.4 *Limitations*—Surfactants present in latex can entrain air and require that a foam-suppressing agent (defoamer) be used. Air-entraining agents are not recommended for use

with polymer-modified concrete. Some polymers, such as vinyl acetate homopolymer, decompose (hydrolyze) and soften in the presence of water and should not be used in concrete that will become moist during service. The result obtained with a bonding admixture is only as good as the surface to which the mixture is applied. The surface should be clean, sound, and free from such foreign matter as paint, grease, and dust.

16.2—Coloring admixtures

16.2.1 *Materials*—Coloring admixtures specifically prepared for use in concrete and mortar are available both as natural or synthetic materials, and in liquid or dry forms (Ball and DeCandia 2002). They produce adequate color without affecting the desirable physical properties of the mixture. Coloring admixtures are often multi-component materials that contain pigments that are in compliance with ASTM C979. The pigments listed in Table 16.1 may be used to obtain a variety of colors.

The addition rate of any pigment to concrete normally should not exceed 10% by mass of the cementitious material (Wilson 1927; ASTM C979); however, some fine pigments, such as carbon black, should be used at much lower addition rates. Natural pigments are usually not as finely ground nor as pure as synthetic materials and, consequently, do not produce as intense a color. Brilliant concrete colors are not possible with either natural or synthetic pigments due to their low allowable addition rates and the masking effects of the cement and aggregates. Cleaner colors can be obtained if white rather than gray cement is used. Liquid coloring admixtures are generally dispensed using automated equipment, providing increased accuracy in dosing and cleaner operations.

16.2.2 *Effects on concrete properties*—Except for carbon black, adding less than 6% of pigment has little or no effect on the physical properties of the fresh or hardened concrete. Larger quantities can increase the water requirement of the mixture to such an extent that the strength and other properties, such as abrasion resistance, are adversely affected. Adding unmodified carbon black considerably increases the amount of air-entraining admixture needed to provide resistance of the concrete to freezing and thawing (Taylor 1948; Ball and DeCandia 2002). Some carbon blacks available for coloring concrete may contain surfactants in sufficient quantity to offset the air-entraining, inhibiting effect of the carbon black.

16.3—Flocculating admixtures

Synthetic polyelectrolytes, such as vinyl acetate-maleic anhydride copolymer, have been used as flocculating admixtures. Published reports (Bruere and McGowan 1958; Vivian 1962) indicate that these materials increase the bleeding rate, decrease the bleeding capacity, reduce flow, increase cohesiveness, and increase early strength. Although the mechanism of this action is not fully understood, it is believed that these compounds, containing highly charged groups in their chains, are absorbed on cement particles, linking them together. The net result is equivalent to an increase in interparticle attraction, which increases the tendency of the paste to behave as one large flock. Bruere

Table 16.1—Pigments used to produce various colors

Color	Pigment
Gray to black	Black iron oxide Carbon black (indoors)
Blue	Phthalocyanine blue (indoors) Cobalt blue
Red	Red iron oxide Brown iron oxide
Brown	Raw burnt umber Chromium oxide
Green	Phtalocanine green
Yellow	Yellow iron oxide
Ivory, cream, or buff	Yellow iron oxide (with white cement)
White	Titanium dioxide (with white cement)

and McGowan (1958) discuss uses for these admixtures, including use as an alternative to importing fine sand to correct deficiencies in sand gradings, reducing bleeding and segregation, and improving green strength of molded products.

16.4—Fungicidal, germicidal, and insecticidal admixtures

Certain materials have been suggested as admixtures for concrete or mortar to impart fungicidal, germicidal, and insecticidal properties. The primary purpose of these admixtures is to inhibit and control the growth of bacteria and fungi on concrete floors and walls or joints. The materials that have been found to be most effective are polyhalogenated phenols (Levowitz 1952), dieldrin emulsion (Gay and Wetherly 1959), and copper compounds (Robinson and Austin 1951; Young and Talbot 1945). Addition rates vary from 0.1 to 10% by mass of the cement, depending on the concentration and composition of the chemical. Rates above 3% may reduce the strength of the concrete. The effectiveness of these materials (particularly the copper compounds) is reportedly temporary and probably varies with the type of exposure and cleaning methods used.

16.5—Rheology- and viscosity-modifying admixtures

16.5.1 *Introduction*—Rheology-modifying admixtures (RMAs) and viscosity-modifying admixtures (VMAs) are typically water-soluble polymers added to concrete to modify its rheological properties. Refer to Section 8.2.4 for information on the use of VMAs in SCC.

16.5.2 *Materials*—The materials commonly used as VMAs are polyethylene oxides, cellulose ethers (HEC, HPMC), alginates (from seaweed), natural and synthetic gums, and polyacrylamides or polyvinyl alcohol. Other materials used are finely divided solids such as starches, clays, lime, and polymer emulsions. The solid materials tend to reduce the strength of the concrete and are primarily used in grouts when strength is not of major importance.

16.5.3 *Effect*—Although some products have an increasing effect on the yield stress value, most high-molecular-weight, water-soluble polymers described previously and used in these products increase the viscosity or thicken the interstitial water. Such compounds increase the cohesiveness of fresh

concrete, reducing its tendency to segregate and bleed. These admixtures are helpful in improving the properties of lean concretes with low cement contents or gap-graded aggregates, for example. They also provide body to the mixture, giving better finishing characteristics and better pumpability. In the latter case, they reduce pumping pressure through improved lubricating properties, as well as reducing segregation tendencies. For this reason, they are also often used as pumping aids. Common applications for these products are grouting, post-tensioning and injection, oil field cement, and self-consolidating concrete (SCC). Reports indicate that RMAs increase the productivity and surface quality of low-slump concrete extruded through a slipform paving machine (Huffman 2005; Bury et al. 2008). Increased thixotropy from the use of VMAs is potentially helpful in reducing form pressure. Refer to Section 8.2.1 for additional information on rheological principles and viscosity-modifying admixtures.

16.5.4 *Anti-washout admixtures*—Anti-washout admixtures (AWAs) increase the cohesiveness of concrete to be placed under water by pumping. The most common AWAs are based on natural or synthetic gums and cellulose-based thickeners. Silica fume can also be beneficial in enhancing cohesion. Loss of cementitious material due to washout can be reduced by as much as 50% by the inclusion of an AWA (U.S. Army Corps of Engineers 1994). Compatibility between other admixtures and AWA has to be tested, as excessive amounts of air have been observed. Most natural gum-based AWAs retard setting time (up to 24 hours at high dose rates) and most AWAs eliminate bleeding (Neeley 1988).

16.6—Air-detraining admixtures

16.6.1 *Introduction*—Air-detraining admixtures, sometimes referred to as defoamers or deaerators, are used to reduce the air content in a variety of applications including, but not limited to, well cementing, cement slurries, and concrete mixtures.

16.6.2 *Materials*—The most widely used air-detraining chemicals are tributyl phosphate, dibutyl phosphate, dibutylphthalate, polydimethylsiloxane, dodecyl (lauryl) alcohol, octyl alcohol, polypropylene glycols, water-soluble esters of carbonic and boric acids, and lower sulfonate oils. Air-detraining admixtures lower surface tension and need to be insoluble in water to be effective.

16.6.3 *Effect*—High air contents can be caused by inadvertently overdosing the air-entraining agent or by using other admixtures that have a tendency to entrain air. Some aggregates or contaminants can increase the total air content of concrete. Air-detraining admixtures are added in small amounts—approximately 0.2% by weight of cement is a starting point. Air-detraining admixtures do not normally remove all entrained air so they must be used judiciously for the concrete to end up with the correct amount of air. While these admixtures are appropriate for interior floors, they should only be used in air-entrained exterior work if prior testing has shown resulting air to be of required quality.

16.7—Storage

Miscellaneous admixtures should be stored in strict accordance with the manufacturer's recommendations.

Most admixtures are not damaged by freezing. The manufacturer's instructions should be followed regarding the effects of freezing the product. An admixture stored beyond its recommended shelf life should be retested before use.

CHAPTER 17—REFERENCES
17.1—Referenced standards and reports

The standards and reports listed in the following were the latest editions at the time this document was prepared. Because these documents are revised frequently, the reader is advised to contact the proper sponsoring group if it is desired to refer to the latest version.

American Association of State Highway and Transportation Officials (AASHTO)

M144	Standard Specification for Calcium Chloride
M154	Standard Specification for Air-Entraining Admixtures for Concrete
M194	Standard Specification for Chemical Admixtures for Concrete
T259	Standard Method of Test for Resistance of Concrete to Chloride Ion Penetration
T260	Standard Method of Test for Sampling and Testing for Chloride Ion in Concrete and Concrete Raw Materials
T277	Standard Method of Test for Electrical Indication of Concrete's Ability to Resist Chloride Ion Penetration

American Concrete Institute

201.2R	Guide to Durable Concrete
209R	Prediction of Creep, Shrinkage, and Temperature Effects in Concrete Structures
211.1	Standard Practice for Selecting Proportions for Normal, Heavyweight, and Mass Concrete
211.2	Standard Practice for Selecting Proportions for Structural Lightweight Concrete
212.4R	Guide for the Use of High-Range Water-Reducing Admixtures (Superplasticizers) in Concrete
222R	Protection of Metals in Concrete Against Corrosion
222.1	Provisional Standard Test Method for Water-Soluble Chloride Available for Corrosion of Embedded Steel in Mortar and Concrete Using the Soxhlet Extractor (withdrawn)
223	Standard Practice for Use of Shrinkage-Compensating Concrete
232.1R	Use of Raw or Processed Natural Pozzolans in Concrete
232.2R	Use of Fly Ash in Concrete
233R	Slag Cement in Concrete and Mortar
234R	Guide for the Use of Silica Fume in Concrete
237R	Self-Consolidating Concrete
238.1R	Report on Measurements of Workability and Rheology of Fresh Concrete
301	Specifications for Structural Concrete
302.1R	Guide to Concrete Floor and Slab Construction
304R	Guide to Measuring, Mixing, Transporting, and Placing Concrete

304.2R	Placing Concrete by Pumping Methods
305R	Guide to Hot Weather Concreting
306R	Guide to Cold Weather Concreting
308R	Guide to Curing Concrete
309R	Guide for Consolidation of Concrete
311.1R	ACI Manual of Concrete Inspection (SP-2)
311.4R	Guide for Concrete Inspection
363R	Report on High-Strength Concrete
318	Building Code Requirements for Structural Concrete
506R	Guide to Shotcrete
523.1R	Guide for Cast-in-Place Low-Density Cellular Concrete
548.3R	Report on Polymer-Modified Concrete

ASTM International

C94/C94M	Standard Specification for Ready-Mixed Concrete
C125	Standard Terminology Relating to Concrete and Concrete Aggregates
C138/C138M	Standard Test Method for Density (Unit Weight), Yield, and Air Content (Gravimetric) of Concrete
C173/C173M	Standard Test Method for Air Content of Freshly Mixed Concrete by the Volumetric Method
C231/C231M	Standard Test Method for Air Content of Freshly Mixed Concrete by Pressure Method
C260	Standard Specifications for Air-Entraining Admixtures for Concrete
C360	Test Method for Ball Penetration in Freshly Mixed Hydraulic Cement Concrete (withdrawn)
C457/C457M	Standard Practice for Microscopical Determination of Parameters of the Air-Void System in Hardened Concrete
C494/C494M	Standard Specifications for Chemical Admixtures for Concrete
C666/C666M	Standard Test Method for Resistance of Concrete to Rapid Freezing and Thawing
C881/C881M	Standard Specification for Epoxy-Resin-Base Bonding Systems for Concrete
C979	Standard Specification for Pigments for Integrally Colored Concrete
C1017/C1017M	Standard Specification for Chemical Admixtures for Use in Producing Flowing Concrete
C1152/C1152M	Standard Test Method for Acid-Soluble Chloride in Mortar and Concrete
C1202	Standard Test Method for Electrical Indication of Concrete's Ability to Resist Chloride Ion Penetration
C1218/C1218M	Standard Test Method for Water-Soluble Chloride in Mortar and Concrete
C1260	Standard Test Method for Potential Alkali Reactivity of Aggregates (Mortar-Bar Method)

C1293	Standard Test Method of Determination of Length Change of Concrete Due to Alkali-Silica Reaction
C1524	Standard Test Method for Water-Extractable Chloride in Aggregate (Soxhlet Method)
C1556	Standard Test Method for Determining the Apparent Chloride Diffusion Coefficient of Cementitious Mixtures by Bulk Diffusion
C1567	Standard Test Method for Determining the Potential Alkali-Silica Reactivity of Combinations of Cementitious Materials and Aggregate (Accelerated Mortar-Bar Method)
C1582/C1582M	Standard Specification for Admixtures to Inhibit Chloride-Induced Corrosion of Reinforcing Steel in Concrete
C1585	Standard Test Method for Measurement of Rate of Absorption of Water by Hydraulic-Cement Concretes
C1611/C1611M	Standard Test Method for Slump Flow of Self-Consolidating Concrete
C1622/C1622M	Standard Specification for Cold-Weather Admixture Systems
D98	Standard Specification for Calcium Chloride

European standards

BS 1881-122	Testing Concrete. Method for Determination of Water Absorption
BS EN 12390-8	Testing Hardened Concrete. Depth of Penetration of Water under Pressure
DIN 1048-5	Testing Concrete. Testing of Hardened Concrete (Specimens Prepared in Mould)

These publications may be obtained from the following organizations:

American Association of State Highway and Transportation Officials
444 N. Capitol Street NW, Suite 225
Washington, DC 2001
www.aashto.org

American Concrete Institute
P.O. Box 9094
Farmington Hills, MI 48333-9094
www.concrete.org

ASTM International
100 Barr Harbor Drive
West Conshohocken, PA 19428-2959
www.astm.org

BSI British Standards
389 Chiswick High Road
London, W4 4AL
United Kingdom

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Advancing concrete knowledge

As ACI begins its second century of advancing concrete knowledge, its original chartered purpose remains "to provide a comradeship in finding the best ways to do concrete work of all kinds and in spreading knowledge." In keeping with this purpose, ACI supports the following activities:

· Technical committees that produce consensus reports, guides, specifications, and codes.

· Spring and fall conventions to facilitate the work of its committees.

· Educational seminars that disseminate reliable information on concrete.

· Certification programs for personnel employed within the concrete industry.

· Student programs such as scholarships, internships, and competitions.

· Sponsoring and co-sponsoring international conferences and symposia.

· Formal coordination with several international concrete related societies.

· Periodicals: the *ACI Structural Journal* and the *ACI Materials Journal*, and *Concrete International*.

Benefits of membership include a subscription to *Concrete International* and to an ACI Journal. ACI members receive discounts of up to 40% on all ACI products and services, including documents, seminars and convention registration fees.

As a member of ACI, you join thousands of practitioners and professionals worldwide who share a commitment to maintain the highest industry standards for concrete technology, construction, and practices. In addition, ACI chapters provide opportunities for interaction of professionals and practitioners at a local level.

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Report on Chemical Admixtures for Concrete

The AMERICAN CONCRETE INSTITUTE

was founded in 1904 as a nonprofit membership organization dedicated to public service and representing the user interest in the field of concrete. ACI gathers and distributes information on the improvement of design, construction and maintenance of concrete products and structures. The work of ACI is conducted by individual ACI members and through volunteer committees composed of both members and non-members.

The committees, as well as ACI as a whole, operate under a consensus format, which assures all participants the right to have their views considered. Committee activities include the development of building codes and specifications; analysis of research and development results; presentation of construction and repair techniques; and education.

Individuals interested in the activities of ACI are encouraged to become a member. There are no educational or employment requirements. ACI's membership is composed of engineers, architects, scientists, contractors, educators, and representatives from a variety of companies and organizations.

Members are encouraged to participate in committee activities that relate to their specific areas of interest. For more information, contact ACI.

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