

Chemical Admixtures for Concrete

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This sixth report of ACI Committee 212, now named "Chemical Admixtures for Concrete," updates the previous reports of 1944, 1954, 1963, 1971, and 1981. Admixtures discussed herein are those known as chemical admixtures; finely divided mineral admixtures have been transferred to ACI Committee 226. Admixtures are classified into five groups: (1) air-entraining; (2) accelerating; (3) water-reducing and set-controlling; (4) admixtures for flowing concrete; and (5) miscellaneous.

Preparation and batching, which had a separate chapter in the 1981 report, are included here in Chapter 1. Chapter 5, "Admixtures for No wing Concrete," is new, representing technology that has matured since 1981. Any of those admixtures possessing properties identifiable with more than one group are discussed with the group that describes its most important effect on concrete.

Keywords: accelerating agents; adhesives; admixtures: air-entraining agents; alkali-aggregate reactions; bactericides; batching; calcium chlorides; colors (materials); concretes; corrosion inhibitors; expanding agents; flocculating; foaming agents; fungicides; gas-forming agents; insecticides; permeability-reducing admixtures; pigments; plasticizers; pumped concrete; retardants; waterproofing admixtures; water-reducing agents.

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ACI Committee Reports, Guides, Standard Practices, and Commentaries are intended for guidance in designing, planning, executing, or inspecting construction and in preparing specifications. Reference to these documents shall not be made in the Project Documents. If items found in these documents are desired to be part of the Project Documents they should be phrased in mandatory language and incorporated into the Project Documents.

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The 1991 revisions became effective July 1, 1991. A number of minor editorial revisions were made to the report, including Section 5.8.7. The year designations of the recommended references of standards-producing organizations have been removed so that the current editions become the referenced version.

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CHAPTER 1-GENERAL INFORMATION

1.1-Introduction

An admixture is defined in ACI 116R and in ASTM C 125 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." This report deals with commonly used admixtures other than pozzolans. Admixtures whose use results in special types of concrete are assigned to other ACI committees, such as: expansive-cement concrete (ACI Committee 223), insulating and cellular concretes (ACI Committee 523), and polymers in concrete (ACI Committee 548). Pozzolans used as admixtures are assigned to ACI Committee 226, which also deals with ground granulated iron blast-furnace slag (a latent hydraulic cement) added at the mixer.

Admixtures are used to modify the properties of concrete or mortar to make them more suitable for the work at hand, or for economy, or for such other purposes as saving energy. In many instances, (e.g., very high strength, resistance to freezing and thawing, retarding, and accelerating), an admixture may be the only feasible means of achieving the desired result. In other instances, certain desired objectives may be best achieved by changes in composition or proportions of the concrete mixture if so doing results in greater economy than by using an admixture.

1.2-Reasons for using admixtures

Some of the more important purposes for which admixtures are used are:

To modify properties of fresh concrete, mortar, and grout so as to:

- Increase workability without increasing water content or decrease the water content at the same workability
 - Retard or accelerate time of initial setting
 - Reduce or prevent settlement or create slight expansion
 - Modify the rate and/or capacity for bleeding
 - Reduce segregation
 - Improve pumpability
 - Reduce the rate of slump loss
- To modify properties of hardened concrete, mortar, and grout so as to:
- Retard or reduce heat evolution during early hardening
 - Accelerate the rate of strength development at early ages
 - Increase strength (compressive, tensile, or flexural)
 - Increase durability or resistance to severe conditions of exposure, including application of deicing salts
 - Decrease permeability of concrete
 - Control expansion caused by the reaction of alkalis with certain aggregate constituents
 - Increase bond of concrete-to-steel reinforcement
 - Increase bond between existing and new concrete
 - Improve impact resistance and abrasion resistance
 - Inhibit corrosion of embedded metal
 - Produce colored concrete or mortar

1.3-Specifications for admixtures

The following specifications cover the types or classes that make up the bulk of current products:

Air-entraining admixtures	ASTM:	C 260
	AASHTO:	M 154
Water-reducing and set-controlling admixtures	ASTM:	C 494
	AASHTO:	M 194
Calcium chloride.. . . .	ASTM:	D 98
	AASHTO:	M 144
Admixtures for use in producing flowing concrete	ASTM:	C 1017

1.4-Sampling

Samples for testing and inspection should be obtained by procedures prescribed for the respective types of materials in the applicable specifications. Such samples should be obtained by random sampling from plant production, from previously unopened packages or containers, or from fresh bulk shipments.

1.5-Testing

Admixtures are tested for one or more of three reasons: (a) to determine compliance with specifications; (b) to evaluate the effect of the admixture on the properties of the concrete to be made with job materials under the anticipated ambient conditions and construction procedures; and (c) to determine uniformity of product.

The manufacturer of the admixture should be required to certify that individual lots meet the requirements of applicable standards or specifications.

It is important that quality control procedures be used by producers of admixtures to insure product compliance with uniformity and other provisions of ASTM specifications and with the producer's own finished-product specifications. Since such test methods may be developed around a particular proprietary product, they may not be applicable to general use or use by consumers.

Although ASTM tests afford a valuable screening procedure for selection of admixtures, continuing use of admixtures in production of concrete should be preceded by testing that allows observation and measurement of the performance of the chemical admixture under concrete plant operating conditions in combination with concrete-making materials then in use. Uniformity of results is as important as the average result with respect to each significant property of the admixture or the concrete.

1.6-Cost effectiveness

Economic evaluation of any given admixture should be based on the results obtained with the particular concrete in question under conditions simulating those expected on the job. This is highly desirable since the results obtained are influenced to an important degree by the characteristics of the cement and aggregate and their relative proportions, as well as by temperature, humidity, and curing conditions.

In evaluating an admixture, its effect on the volume of a given batch should be taken into account. If adding the admixture changes the yield, as often is the case, the change in the properties of the concrete will be due not only to direct effects of the admixture, but also to changes in the yield of the original ingredients. If the use of the admixture increases the volume of the batch, the admixture must be regarded as effecting a displacement either of part of the original mixture or of one or another of the basic ingredients—cement, aggregate, or water. All such changes in the composition of a unit volume of concrete must be taken into account when testing the direct effect of the admixture and in estimating the benefits resulting from its use.

The increase in cost due to handling an additional ingredient should be taken into account, as well as the economic effect the use of the admixture may have on the cost of transporting, placing, and finishing the concrete. Any effect on rate of strength gain and speed of construction should be considered. An admixture may permit use of less expensive construction methods or structural designs to more than offset any added cost due to its use. For example, novel and economical designs of structural units have resulted from the use of water-reducing and set-retarding admixtures (Schutz 1959).

In addition, placing economies, ability to pump at greater heads, and economies of concrete cost versus competitive building materials have been realized. Wa-

ter-reducing and set-retarding admixtures permit placement of large volumes of concrete over extended periods, thereby minimizing the need for forming, placing, and joining separate units. Accelerating admixtures reduce finishing and forming costs. Required physical properties of lightweight concrete can be achieved at lower densities (unit weight) by using air-entraining and water-reducing admixtures.

1.7-Considerations in the use of admixtures

Admixtures should conform to ASTM or other applicable specifications. Careful attention should be given to the instructions provided by the manufacturer of the admixture. The effects of an admixture should be evaluated whenever possible by use with the particular materials and conditions of use intended. Such an evaluation is particularly important when (1) the admixture has not been used previously with the particular combination of materials; (2) special types of cement are specified; (3) more than one admixture is to be used; and (4) mixing and placing is done at temperatures well outside generally recommended concreting temperature ranges.

Furthermore, it should be noted that: (1) a change in type or source of cement or amount of cement, or a modification of aggregate grading or mixture proportions, may be desirable; (2) many admixtures affect more than one property of concrete, sometimes adversely affecting desirable properties; (3) the effects of some admixtures are significantly modified by such factors as water content and cement content of the mixture, by aggregate type and grading, and by type and length of mixing.

Admixtures that modify the properties of fresh concrete may cause problems through early stiffening or undesirable retardation, i.e., prolonging the time of setting. The cause of abnormal setting behavior should be determined through studies of how such admixtures affect the cement to be used: Early stiffening often is caused by changes in the rate of reaction between tricalcium aluminate and sulfate. 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.

Another important consideration in the use of admixtures relates to those cases where there is a limit on the amount of chloride ion that is permitted in concrete as manufactured. Such limits exist in the ACI 318 Building Code, the recommendations of ACI Committees 201, 222, 226, and others. Usually these limits are expressed as maximum percent of chloride ion by weight (mass)* of cement. Sometimes, however, it is chloride ion per unit weight (mass) of concrete, and sometimes it is "water-soluble" chloride ion per unit weight (mass) of cement or concrete.

Regardless of how the limit is given, it is obvious that to evaluate the likelihood that using a given admixture

*In this report, when reference is made to mass it is called "weight" because the committee believed this would be better understood; however, the correct term "mass" is given in parentheses.

will jeopardize conformance of concrete with a specification containing such a limit, one needs to know the chloride-ion content of the admixture that is being considered for use expressed in terms relevant to those in which the specification limit is given. If in using the available information on the admixture and the proposed dosage rate it is calculated that the specification requirement will be exceeded, alternate admixtures or procedures should be considered for achieving the results that were sought through the use of the admixture that cannot be used in the originally intended amount.

The user should be aware that in spite of such terms as "chloride-free," no truly chloride-free admixture exists since admixtures often are made with water that contains small but measurable amounts of chloride ion.

1.8-Decision to use

Although specifications deal primarily with the influence of admixtures on standard properties of fresh and hardened concrete, the concrete supplier, contractor, and owner of the construction project are 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, appearance of formed surfaces, etc. These additional features often are of great importance when the selection and dosage rate of an admixture are determined.

Specific guidance for use of accelerating admixtures, air-entraining admixtures, water-reducing and set-controlling admixtures, admixtures for flowing concrete, and admixtures for other purposes 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 reevaluation concerning the benefits of admixture use.

1.9-Classification of admixtures

In this report, admixtures are classified generically or with respect to the characteristic effects of their use. Information to characterize each class is presented along with brief statements of the general purposes and expected effects of the use of materials of each group. The wide scope of the admixture field, the continual 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.

Commercial admixtures may contain materials that separately would belong in two or more groups, or would be covered by two or more ASTM standards or ACI committees. For example, a water-reducing admixture may be combined with an air-entraining admixture, or a pozzolan may be combined with a water-reducing admixture. Those admixtures possessing properties identifiable with more than one group or one committee are considered to be in the group or committee that is concerned with their most important effect.

1.10-Preparation and batching

1.10.1 Introduction-The successful use of admixtures depends upon the use of appropriate methods of preparation and batching. Neglect in these areas may affect properties, performance, and uniformity of the concrete significantly.

Certain admixtures such as pigments, expansive agents, pumping aids, and the like are used in extremely small dosages and most often are batched by hand from premeasured containers. Other hand-added admixtures may include accelerators, permeability reducers, and bonding aids, which often are packaged in amounts sufficient for proper dosage per unit volume of concrete.

Most admixtures usually are furnished in ready-to-use liquid form. These admixtures are introduced into the concrete mixture at the concrete plant or into a truck-mounted admixture tank for introduction into the concrete mixture at the jobsite. Although measurement and addition of the admixture to the concrete batch or into the truck-mounted tank often is by means of a sophisticated mechanical or electromechanical dispensing system, a calibrated holding tank should be part of the system so that the plant operator can verify that the proper amount of admixture has been batched into the concrete mixer or into the truck-mounted tank.

1.10.2 Conversion of admixture solids to liquids-Most admixtures are furnished in liquid form and do not require dilution or continuous agitation to maintain their solution stability.

The preparation of admixtures may involve making dilutions of the various concentrations to facilitate accurate batching or dispensing. As a result, the recommendations of the manufacturer should be followed if there is any doubt about procedures being used.

Some chemical admixtures are supplied as water-soluble solids requiring job mixing at the point of use. Such job mixing may require that low-concentration solutions be made due to difficulty in mixing. In some cases, it is convenient to prepare standard solutions of uniform strength for easier use. Since many low-concentration solutions contain significant amounts of finely divided insoluble materials or active ingredients, which may or may not be readily soluble, it is important that precautions be taken to insure that these be kept in uniform suspension before actual batching.

1.10.3 Storage and protection-Because admixtures furnished as dry powders sometimes are difficult to dissolve, admixtures supplied as ready-to-use liquids may be of much higher concentrations than job-mixed solutions. As a result, any finely divided insoluble matter, if present, will tend to stay in suspension, and continuous agitation usually is not required. Admixture manufacturers ordinarily can furnish either complete storage and dispensing systems or at least information regarding the degree of agitation or recirculation required with their admixtures. Timing devices commonly are used to control recirculation of the contents of storage tanks to avoid settlement or, with some products, polymerization.

In climates subject to freezing, the storage tank and its contents must be either heated or placed in a heated environment. The latter is preferred for the following reasons:

1. If the storage tank contains pipe coils for heating the contents by means of hot water or steam, care must be taken to avoid overheating the admixture since high temperatures can reduce the effectiveness of certain admixture formulations.

2. Some heating probes can overheat the admixture locally, pyrolyze certain constituents, and produce explosive gases.

3. Electrical connections to heating probes, bands, or tapes can be disconnected, allowing the admixture to freeze and damage equipment.

4. The cost of operating electric probes, bands, tapes, etc. is normally higher than the cost of maintaining above-freezing temperatures in a heated storage room.

5. A heated admixture storage room protects not only storage tanks, but pumps, meters, valves, and admixture hoses from freezing and from other problems such as dust, rain, ice, and vandalism. Further, since the storage temperature is subject to less widespread variation throughout the year, admixture viscosity is more constant and dispensers require less frequent calibration.

6. If plastic storage tanks or hoses are used, care must be taken to avoid heating these materials to the point of softening and rupture.

Storage tanks should be vented properly so that foreign materials cannot enter the tank through the opening. Likewise, fill nozzles and any other tank openings should be capped when not in use to avoid contamination.

1.10.4 Batching-Batching of liquid admixtures and discharging into the batch, mixer, or truck-mounted tank generally is accomplished by a system of pumps, meters, timers, calibration tubes, valves, etc., generally called the admixture-dispensing system or dispenser.

Dispensing of admixtures into a concrete batch involves not only accurately measuring the quantity of admixture and controlling the rate of discharge but also the timing in the batching sequence. In some instances, changing the time at which the admixture is added during mixing can vary the degree of effectiveness of the admixture. For example, Bruere (1963) and Dodson, Farkas, and Rosenberg (1964) reported that the retarding effect of water-reducing retarders depends on the time at which the retarder is added to the mixture. The water requirement of the admixture also may be affected significantly.

For any given condition or project, a procedure for controlling the time and rate of the admixture addition to the concrete batch should be established and adhered to closely. To insure uniform distribution of the admixture throughout the concrete mixture during the charging cycle, the rate of admixture discharge should be adjustable.

Foster (1966) noted that two or more admixtures often are not compatible in the same solution. For ex-

ample, a vinsol resin-based air-entraining admixture and a water-reducing admixture containing a lignosulfonate should never come in contact prior to actual mixing into the concrete because of their instant flocculation and loss of efficiency of both admixtures. It is important, therefore, to avoid intermixing of admixtures prior to introduction into the concrete unless tests indicate there will be no adverse effects or the manufacturer's advice permits it. It generally is better to introduce the various admixtures into the batch at different times or locations during charging or mixing.

It is important that batching and dispensing equipment meet and maintain tolerance standards to minimize variations in concrete properties and, consequently, better performance of the concrete. Tolerances of admixture batching equipment should be checked carefully. ASTM C 94 requires that volumetric measurement of admixtures shall be accurate, to ± 3 percent of the total volume required or plus or minus the volume of dose required for 94 lb (43 kg, or one bag) of cement, whichever is greater. ASTM C 94 requires that powdered admixtures be measured by weight (mass), but permits liquid admixtures to be measured by weight (mass) or volume. Accuracy of weighed admixtures is required to be within ± 3 percent of the required weight (mass).

1.10.5 Batching equipment

1.10.5.1 General-In terms of batching systems, admixtures may be grouped in two categories: (a) those materials introduced into the batch in liquid form, which may be batched by weight (mass) or volume; and (b) powdered admixtures that normally are batched by weight (mass). The latter case includes such specialty materials as pumping aids and others that are added in extremely small amounts and, thus, often are introduced by hand in premeasured packages. When high-volume usage of these admixtures is contemplated, the manufacturer of the admixture normally supplies a suitable bulk dispensing system.

1.10.5.2 Liquid batching systems-Liquid admixture dispensing systems are available for manual, semiautomatic, and automatic batching plants. Simple manual dispensing systems designed for low-volume concrete plants depend solely on the care of the concrete plant operator in 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 the sight or calibration tube. It is necessary to interlock the discharge valve so that it will not open during the filling operation or when the fill valve is not closed fully. Usually, the fill valve is interlocked with the discharge valve so that it will not open unless the discharge valve is closed fully. A low-level indicator in the calibration tube often is used to prevent the discharge valve from being closed before all the admixture is dispensed into the batch.

Several methods of batching liquid admixtures are in common use. All require a visual volumetric container,

called a calibration tube, to enable the plant operator to verify the accuracy of the admixture dosage. The simplest consist of a visual volumetric container, while others include positive volumetric displacement, and a very limited number use weigh-batching systems. Some of these can be used readily with manual, semiautomatic, and automatic systems.

Positive volumetric displacement devices are well suited for use with automatic and semiautomatic batchers because they may be operated easily by remote control with appropriate interlocking in the batching sequence. They include flow meters and measuring containers equipped with floats or probes. Most meters are calibrated for liquids of a given viscosity. Errors caused by viscosity changes due to variations in temperature can be avoided by recalibration and adjustment made by observation of the visual volumetric container or calibration tube.

Flow meters and calibration tubes equipped with floats or probes often are combined with pulse-emitting transmitters that give readouts on electromechanical or electronic counters. Often they are set by inputting the dosage per unit of cementitious material. The amount of cementitious material input to the 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. There are a number of variables associated with these systems that can introduce considerable error. These variables include changes in power supply, partial restrictions of the measuring orifice, and changes in viscosity of the solution due to temperature.

Timer-controlled systems must be recalibrated frequently, and the plant operator must be alert to verify the proper admixture dose by observation of the calibration tube. Although timer-controlled systems have been used successfully, because of these inherent disadvantages, their use, in general, is not recommended, except perhaps for dispensing calcium chloride.

A number of different methods are used by admixture manufacturers to fill and discharge calibration tubes. A major objective is to insure that the fill valve will not open until the discharge valve is completely closed and to provide that, in the event of electrical or mechanical malfunction, the admixture cannot be overbatched.

Power-operated valves are used frequently; a vacuum release also may be provided to prevent venturi action from the concrete plant's water line, causing an overbatching. Prior to installation of the dispenser, the system should be analyzed carefully to determine what possible batching errors could occur and, with the help of the admixture supplier, they should be eliminated.

Discharge of the admixture from the calibration tube to the concrete batch should be to the point where the admixture achieves the greatest dispersion throughout the concrete. Thus, for example, the discharge end of the water line leading to the mixer is a preferred location, as is the fine-aggregate weigh hopper or the belt conveyor carrying fine aggregate.

Often, the calibration tube is emptied either by gravity or by air pressure and the admixture may have a considerable distance to flow through a discharge hose or pipe before it reaches its ultimate destination. Therefore, the dispenser control panel should be equipped with a timer-relay device to insure that all admixture has been discharged from the conveying hoses or pipes. If the admixture dispenser system is operated manually, the plant operator should be furnished a valve with a detente discharge side to prolong the discharge cycle until it is ascertained that all admixture is in the concrete batch.

When more than one admixture is intended for the same concrete batch, the dispenser must be designed so that: (1) an appropriate delay is built into the system to prevent the admixtures from becoming intermingled; or (2) each is batched separately so as to be properly maintained apart before entering into the mixer. Likewise, in a manual system, the operator must be instructed in methods to prevent such comingling of admixtures.

Weigh batching (batching by mass) of liquid admixtures ordinarily is not used because the weigh batching devices are more expensive than volumetric dispensers. In some cases, it is necessary to dilute admixture solutions to obtain a sufficient quantity for accurate weighing (determination of mass).

Because of the high rate of slump loss associated with certain high-range water-reducing admixtures (superplasticizers), jobsite introduction of such admixtures has become common. Such addition may be from truck-mounted admixture tanks or jobsite tanks or drums. When using drums, the dispensing system often is similar to that used in concrete plants, e.g., pumps, meters, pulse transmitters, and counters to dispense the proper admixture volume to the truck mixer at the jobsite.

If truck-mounted tanks are used, the proper dosage of admixture for the concrete in the truck is measured at the batch plant and discharged to the truck-mounted tank at a special filling station. At such a station, a series of lights or other signals tells the driver when the admixture batching is complete and when his tank contains the proper amount. At the jobsite, the driver sets the mixer at mixing speed and discharges the entire amount of admixture from the truck-mounted tank into the concrete.

Care should be taken that the mixer remain in the mixing mode until the admixture has been thoroughly distributed throughout the concrete. The condition of the mixer and its blades influences the distribution. To insure that all the admixture is introduced, air pressure should be used to force the admixture into all parts of the mixer drum. To shorten the mixing time, the truck mixer should operate at maximum speed, preferably over 19 rpm.

1.10.5.3 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. It is important to protect components from dust and temperature extremes, and they should be readily accessible for visual observation and maintenance.

Although admixture batching systems usually are installed and maintained by the admixture producer, plant operators should thoroughly understand the system and be able to adjust it and perform simple maintenance. For example, plant operators should recalibrate the system on a regular basis, not to exceed 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 water flush the tube so that divisions or markings may be clearly seen at all times. Because of the marked effect of admixtures on concrete performance, care and attention to the timing and accuracy of batching admixtures is necessary to avoid serious problems.

CHAPTER 2-AIR-ENTRAINING ADMIXTURES

2.1-Introduction

ACI 116R defines an air-entraining agent as “an addition for hydraulic cement or an admixture for concrete or mortar which causes entrained air to be incorporated in the concrete or mortar during mixing, usually to increase its workability and frost resistance.” This chapter is concerned with those air-entraining agents that are added to the concrete batch immediately before or during its mixing, and are referred to as air-entraining admixtures.

Extensive laboratory testing and long-term field experience have demonstrated conclusively that concrete must be properly air entrained if it is to resist the action of freezing and thawing (Cordon et al. 1946; Blanks and Cordon 1949). Air entrainment should always be required when concrete must withstand many cycles of freezing and thawing, particularly where the use of such chemical deicing agents as sodium or calcium chlorides is anticipated. Highway pavements, garage floors, and sidewalks placed in cold climates probably will be exposed to such conditions.

The mechanism of air entrainment in concrete has been discussed in the literature (Powers 1968) but is beyond the scope of this report. The resistance of concrete to freezing and thawing also is affected by placing, finishing, and curing procedures; therefore, acceptable practice in these respects must be followed (ACI 304R-85, ACI 308-81).

2.2-Entrained-air-void system

Improvements in frost resistance are brought about by the presence of minute air bubbles dispersed uniformly through the cement-paste portion of the concrete. Because of their size and great number, there are literally billions of such bubbles in each cubic yard of air-entrained concrete. The void size must be small to provide adequate protection with a relatively low total volume of void space.

The cement paste in concrete normally is protected against the effects of freezing and thawing if the spacing factor (Powers 1949) is 0.008 in. (0.20 mm) or less as determined in accordance with ASTM C 457. Additional requirements are that the surface of the air voids be greater than $600 \text{ in.}^2/\text{in.}^3$ ($23.6 \text{ mm}^2/\text{mm}^3$) of air-void volume, and that the number of air voids per 1 in. (25 mm) of traverse be significantly greater than the numerical value of the percentage of air in the concrete.

The air content and the size distribution of air voids produced in air-entrained concrete are influenced by many factors (Mielenz et al. 1958), the more important of which are the (1) nature and quantity of the air-entraining admixture; (2) nature and quantity of the constituents of the concrete admixture; (3) type and duration of mixing employed; (4) slump; and (5) kind and degree of consolidation applied in placing the concrete. The factors are discussed in more detail in Section 2.9.1. Vibration applied to air-entrained concrete removes air as long as the vibration is continued (Mielenz et al. 1958); however, laboratory tests have shown that the resistance of concrete to freezing and thawing is not reduced by moderate amounts of vibration.

Most investigators (Tynes 1977; Mather 1979; Schutz 1978; Whiting 1979; Litvan 1983) have found in laboratory tests that the addition of high-range water reducers to air-entrained concrete may increase the spacing factor and decrease the specific surface area of the air-void systems. However, early reports of a reduction in frost resistance of such concretes (Tynes 1977; Mather 1979) have not been substantiated by later research. Nevertheless, it would be prudent to evaluate the effect a specific high-range water reducer on the frost resistance of a concrete mixture if this is a significant factor and if the manufacturer cannot supply such an evaluation.

For a discussion of the mechanism of protection by air entrainment, other sources should be consulted (Cordon 1966; Litvan 1972; MacInnis and Beaudoin 1974; Powers 1975).

2.3-Effect on concrete properties

2.3.1 Fresh concrete-Air entrainment alters the properties of fresh concrete. These changes should be considered in proportioning a mixture (ACI 211.1 and 211.2; Powers 1964). At equal slump, air-entrained concrete is considerably more workable and cohesive than similar non-air-entrained concrete except at higher cement contents. Segregation and bleeding are reduced. The reduction in bleeding, in turn, helps to prevent the formation of pockets of water beneath coarse-aggregate particles and embedded items such as reinforcing steel, and also to prevent the accumulation of laitance or weak material at the surface of a lift. At high cement contents, air-entrained concrete becomes sticky and difficult to finish.

2.3.2 Hardened concrete-Air-entrainment usually reduces strength, particularly in concretes with moderate to high cement contents, in spite of the decreased water requirements. The reduction is generally propor-

tional to the amount of air entrained, but the rate of reduction increases with higher amounts. Therefore, while a proper air-void system must be provided, excessive amounts of air must be avoided. A detailed discussion of air requirements is included in ACI 211.1.

When the cement content and slump are maintained constant, the reduction in strength is partially or entirely offset by the resulting reduction in water-cement ratio (w/c) and fine-aggregate content. This is particularly true of lean mass concretes or those containing a large maximum-size aggregate. Such concretes may not have their strength reduced; strengths even may be increased by the use of air entrainment.

2.4-Materials for air entrainment

Many materials are capable of functioning as air-entraining admixtures. Some materials, such as hydrogen peroxide and powdered aluminum metal, can be used to entrain gas bubbles in cementitious mixtures but are not considered to be acceptable air-entraining admixtures, since they do not necessarily produce an air-void system that will provide adequate resistance to freezing and thawing.

2.4.1 Liquid or water-soluble powdered air-entraining agents-These agents are composed of salts of wood resins, synthetic detergents, salts of sulfonated lignin, salts of petroleum acids, salts of proteinaceous materials, fatty and resinous acids and their salts, and organic salts of sulfonated hydrocarbons. Not every material that fits the preceding description will produce a desirable air-void system.

Any material proposed for use as an air-entraining admixture should be tested for conformance with ASTM C 260. This specification is written to assure that the admixture functions as an air-entraining admixture, that it causes a substantial improvement in the resistance of concrete to freezing and thawing, and that none of the essential properties of the concrete are seriously impaired. Air-entrained concrete also can be made by using an air-entraining portland cement meeting ASTM C 150, Type IA, IIA, or IIIA.

2.4.2 Particulate air-entraining admixtures-Solid particles having a large internal porosity and suitable pore size have been added to concrete and seem to act in a manner similar to that of air voids. These particulate materials may be composed of hollow plastic spheres or certain crushed bricks, expanded clay or shale, or spheres of certain diatomaceous earths. These materials currently are not being used extensively.

Research has indicated that when using inorganic particulate materials, the optimum particle size should range between 290 and 850 μm , total porosity of the particles should be at least 30 percent by volume, and a pore-size distribution should be in the range of 0.05 to 3 μm (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 C 666 (Litvan and Sereda 1978; Litvan 1985).

Particulate air-entraining admixtures have the advantage of complete 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 cements such as ground slag, will not change the air content, as may be the case with conventional air-entraining admixtures.

2.5-Applications

The use of entrained air in concrete is recommended for several reasons. Because of its greatly improved resistance to frost action, air-entrained concrete must be used wherever water-saturated concrete is exposed to freezing and thawing, especially when salts are used for deicing. Its use also is desirable wherever there is a need for watertightness.

Since air-entrainment improves the workability of concrete, it is particularly effective in lean mixtures that otherwise may be harsh and difficult to work. It is common practice to provide air-entrainment in various kinds of lightweight aggregate concrete, including not only insulating and fill concrete (ACI 523.1R-67) but also in structural lightweight concrete. However, admixtures for cellular concrete are not covered in this report since ACI Committee 523 covers that subject.

There is no general agreement on benefits resulting from the use of air-entraining admixture in the manufacture of concrete block (Farmer 1945; Kennedy and Brickett 1986; Keunning and Carlson 1956). However, satisfactory results using air-entraining admixtures have been reported in the manufacture of cast stone and concrete pipe.

2.6-Evaluation, selection, and control of purchase

To achieve the desired improvement in frost resistance, intentionally entrained air must have certain characteristics. Not only is the total volume of air significant but, more importantly, the size and distribution of the air voids must be such as to provide efficient protection to the cement paste.

To assure that an air-entraining admixture produces a desirable air-void system, it should meet the requirements of ASTM C 260. This specification sets limits on the effects that any given air-entraining admixture under test may exert 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 containing a standard-reference air-entraining admixture such as neutralized vinsol resin. The method by which these effects may be determined is given in ASTM C 233.

Extensive testing and experience have shown that concrete having total air contents in the range of those recommended in ACI 211.1 generally will have the proper size and distribution of air voids when the air-entraining admixture used meets the requirements of ASTM C 260. Use of ASTM C 457 to determine the

actual characteristics of the air-void system in hardened concrete in investigations of concrete proportioning provides greater assurance that concrete of satisfactory resistance to freezing and thawing will be obtained.

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 pounds (kilograms) or gallons (liters) should be indicated plainly on the containers in which the admixture is delivered. The admixture should meet requirements on allowable variability within each lot and between shipments (see ASTM C 260). Acceptance testing should be as stated in ASTM C 233.

2.7-Batching, use, and storage

To achieve the greatest uniformity in a concrete mixture and in successive batches, it is recommended that water-soluble air-entraining admixtures be added to the mixture in the form of solutions rather than solids. Generally, only small quantities of air-entraining admixtures (about 0.05 percent of active ingredients by weight [mass] of cement) are required to entrain the desired amount of air. If the admixture is in the form of powder, flakes, or semisolids, a solution must be prepared prior to use, following the recommendations of the manufacturer.

If the manufacturer's recommended amounts of air-entraining admixture do not result in the desired air content, it is necessary to adjust the amount of admixture added. For any given set of conditions and materials, the amount of air entrained is roughly proportional to the quantity of agent used. However, in some cases, a ceiling may be reached. The ceiling may occur in low-slump, high cement-content mixtures made in hot weather with finely ground cements and containing fine aggregate with large amounts of material passing the 75 μm (No. 200) sieve. A change in the fundamental type of material used to make the air-entraining admixture or a change in the cement or fine aggregate or an increase in slump may be necessary to obtain the required air content.

Attention should be given to proper storage of air-entraining admixtures. The manufacturer's storage recommendations should be obtained and followed. Air-entraining admixtures usually are not damaged by freezing, but the manufacturer's instructions should be followed regarding the effects of freezing on the product. An admixture that is stored at the point of manufacture for more than six months after completion of tests prior to shipment, or an admixture in local storage in the hands of a vendor or contractor for more than six months, should be retested before use and rejected if it fails to conform to any of the requirements of ASTM C 260.

2.8-Proportioning of concrete

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 Committee 211. These procedures incorporate the reduction in water and fine aggregate permitted by the improved workability of air-entrained concrete.

2.9-Factors influencing amount of entrained air

2.9.1 Effects of materials and proportions-There are numerous factors that can influence the amount of air entrained in concrete. The amount of air-entraining admixture required to obtain a given air content will vary widely depending on the particle shape and grading of the aggregate used. Organic impurities in the aggregate usually decrease the air-entraining admixture requirements, while an increase in the hardness of water generally will increase the air-entraining admixture requirements.

As the cement content or the fineness of a cement increases, the air-entraining potential of a given amount of an admixture will tend to diminish. Thus, larger amounts of air-entraining admixture generally are required in concrete containing high early strength (Type III, ASTM C 150) or Portland-pozzolan cement (Type IP, ASTM C 595). High-alkali cements generally require a smaller amount of air-entraining admixture to obtain a given air content than do low-alkali cements.

Increasing the amount of finely divided materials in concrete by the use of fly ash or other pozzolans, carbon black or other finely divided pigments, or bentonite usually decreases the amount of air entrained by an admixture. As concrete temperature increases, higher dosages of air-entraining admixtures will be required to maintain proper air content. A given amount of an air-entraining admixture generally produces slightly more air where calcium chloride is used as an accelerator.

Similarly, the amount of air-entraining admixture required to produce a given air content may be reduced one-third or more when used with certain water-reducing admixtures. Various types of admixtures can influence the air content and quality of the air-void system; therefore, special care should be taken when such admixtures are used in conjunction with air-entraining admixtures to assure that there is compatibility.

Increasing the air content of concrete generally increases the slump. However, relatively high-slump mixtures may have a larger spacing factor and are therefore less desirable than low-slump mixtures. An increase in w/c is likely to result in an increase in air content and in larger air voids. As the temperature of the concrete increases, less air is entrained.

2.9.2 Effect of mixing, transporting, and consolidating-The amount of air entrained varies with the type and condition of the mixer, the amount of concrete being mixed, and the mixing speed and time. The efficiency of a given mixer will decrease appreciably as the blades become worn or when mortar is allowed to accumulate in the drum and on blades.

There also may be changes in air content if there is a significant variation in batch size for a given mixer, especially if the batch size is markedly different from the rated capacity of the mixer. Adams and Kennedy (1950)

found in the laboratory that, for various mixers and mixtures, air content increased from a level of about 4 percent to as much as 8 percent, as the batch size was increased from slightly under 40 percent to slightly over 100 percent of rated mixer capacity.

The amount of entrained air increases with mixing time up to a point beyond which it slowly decreases. However, the air-void system, as characterized by specific surface and spacing factors, generally is not harmed by prolonged agitation. If more water is added to develop the desired slump, the air content should be checked since some adjustment may be required; addition of water without thorough or complete mixing may result in nonuniform distribution of air and water within the batch. See ACI 304R for further details.

The methods used to transport concrete after mixing can reduce the air content. Pumping the concrete generally will reduce the air content.

The type and degree of consolidation used in placing concrete can reduce the air content. Fortunately, air-void volume lost by these manipulations primarily consists of the larger bubbles of entrapped air that contribute little to the beneficial effects of entrained air.

2.10-Control of air content of concrete

To achieve the benefits of entrained air in a consistent manner requires close control of the air content. For control purposes, samples for determination of air content should be obtained at the point of placement. Tests for air content of freshly mixed concrete should be made at regular intervals for control purposes. Tests also should be made when there is reason to suspect a change in air content.

The air content of importance is that present in concrete after consolidation. Losses of air that occur due to handling, transportation, and consolidation will not be reflected by tests for air content of concrete taken at the mixer (see ACI 309). This is why air content in the sample should be checked at the point of discharge into the forms.

There are three standard ASTM methods for measuring the air content of fresh concrete: (1) the gravimetric method, ASTM C 138; (2) the volumetric method, ASTM C 173; and (3) the pressure method, ASTM C 231, which, however, may not be applicable to lightweight concretes. An adaptation of the volumetric method using the so-called Chace Air Indicator (Grieb 1958), in which a small sample of mortar from the concrete is used, has not been standardized and should not be used to determine compliance with specification limits.

These methods measure only air volume and not the air-void characteristics. The spacing factor and other significant parameters of the air-void system in hardened concrete can be determined only by microscopical methods such as those described in ASTM C 457. The use of these methods in coordination with investigations of proportioning of concrete for new projects provides greater assurance that concrete of satisfactory resistance to freezing and thawing will be obtained. It

has been shown, however, that the air content of a concrete mixture generally is indicative of the adequacy of the air-void system when the air-entraining admixture used meets the requirements of ASTM C 260.

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 constant as possible so that the air content will be uniform and within the range specified for the work. This is important because too much air may reduce strength without a commensurate improvement in durability, whereas too little air will fail to provide desired workability and durability.

Proper inspection should insure that air-entraining admixtures conform to the appropriate specifications, that they are stored without contamination or deterioration, and that they are accurately batched and introduced into the concrete mixture as specified. The air content of the concrete should be checked and controlled during the course of the work in accordance with the recommendations of ACI Committee 311 as reported in the ACI Manual of Concrete Inspection (ACI SP-2). Practices causing excessive air loss should be corrected or additional compensating air should be entrained initially.

CHAPTER 3-ACCELERATING ADMIXTURES

3.1-Introduction

An accelerating admixture is a material added to concrete for the purpose of reducing the time of setting and accelerating early strength development.

Accelerators should not be used as antifreeze agents for concrete; in the quantities normally used, accelerators lower the freezing point of concrete only a negligible amount, less than 2 C (3.6 F). No commonly used accelerators will substantially lower the freezing point of water in concrete without being harmful to the concrete in other respects.

The best-known accelerator is calcium chloride, but it is not recommended for use in prestressed concrete, in concrete containing embedded dissimilar metals, or in reinforced concrete in a moist environment because of its tendency to promote corrosion of steel. Proprietary nonchloride noncorrosive accelerating admixtures, certain nitrates, formates, and nitrites afford users alternatives, although they may be less effective and are more expensive than calcium chloride. Other chemicals that accelerate the rate of hardening of concrete include triethanolamine and a variety of soluble salts such as other chlorides, bromides, fluorides, carbonates, silicates, and thiocyanates.

3.2-Types of accelerating admixtures

For convenience, admixtures that accelerate the hardening of concrete mixtures can be divided into four groups: (1) soluble inorganic salts, (2) soluble organic compounds, (3) quick-setting admixtures, and (4) miscellaneous solid admixtures.

Accelerators purchased for use in concrete should meet the requirements for Type C or E in ASTM C 494. Calcium chloride also should meet the require-

ments of ASTM D 98. Forms of calcium chloride are shown in Table 3.2.

3.2.1 Soluble inorganic salts—Studies (Edwards and Angstadt 1966; Roskopf, Linton, and Peppler 1975) have shown that a variety of soluble inorganic salts, such as chlorides, bromides, fluorides, carbonates, thiocyanates, nitrites, nitrates, thiosulfates, silicates, aluminates, and alkali hydroxides, will accelerate the setting of portland cement.

Research by numerous investigators over recent years has shown that inorganic accelerators act primarily by accelerating the hydration of tricalcium silicate; comprehensive calorimetric data illustrating this point have been reported.

Calcium chloride is the most widely used accelerator since it is the most cost effective.

It has been postulated (Tenoutasse 1969; Ramachandran 1972) that in portland cement concrete mixtures containing calcium chloride (CaCl_2), gypsum combines with the calcium aluminate to form ettringite (calcium trisulfoaluminate [$3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 3\text{CaSO}_4 \cdot 32\text{H}_2\text{O}$]) and the calcium chloride combines with the calcium aluminate to form calcium chloroaluminate ($3\text{CaO} \cdot \text{CaCl}_2 \cdot 10\text{H}_2\text{O}$).

3.2.2 Soluble organic compounds—The most common accelerators in this class are triethanolamine and calcium formate, which are used commonly to offset the retarding effects of water-reducing admixtures or to provide noncorrosive accelerators. Accelerating properties have been reported for calcium acetate (Washa and Withey 1953), calcium propionate (Arber and Vivian 1961), and calcium butyrate (RILEM 1968), but salts of the higher carboxylic acid homologs are retarders (RILEM 1968).

A number of organic compounds are found (Bash and Rakimbaev 1969) to accelerate the setting of portland cement when low water-cement ratios are used. Organic compounds reported as accelerators include urea (RILEM 1968), oxalic acid (Bash and Rakimbaev 1969; Djabarov 1970), lactic acid (Bash and Rakimbaev 1969; Lieber and Richartz 1972), various ring compounds (Lieber and Richartz 1972; Wilson 1927), and condensation compounds of amines and formaldehyde (Roskopf, Linton, and Peppler 1975; Kossivas 1971). However, severe retardation can be experienced when the amounts of these compounds used in a mixture are excessive.

Recent reports (Ramachandran 1973, 1976) indicate that triethanolamine accelerates the hydration of tricalcium aluminate but retards tricalcium silicate. Thus, triethanolamine can act as a retarder of cement hydration as well as an accelerator. Other organic accelerators may behave in a similar fashion.

Studies have shown that production of ettringite is greater in mixtures containing calcium formate (Bensted 1978). Also, other data (Gebler 1983) have shown that the effectiveness of formates is dependent on the sulfate content of the cement and the tricalcium aluminate-to-sulfate ratio ($\text{C}_3\text{A}/\text{SO}_3$). Cements that are undersulfated provide the best potential for calcium

Table 3.2 — Calcium chloride — Amounts of chloride ion introduced per 100 lb cement

Percent calcium chloride by mass of cement	Solid form, lb		Liquid form, 29 percent solution*		Amount of chloride ion added to concrete, lb
	Dihydrate*	Anhydrous [†]	lb	qt	
0.5	0.7	0.5	1.7	0.6	0.3
0.8	1.0	0.8	2.8	1.0	0.5
1.0	1.3	1.0	3.4	1.2	0.6
1.5	2.0	1.5	5.2	1.8	1.0
2.0	2.6	2.0	6.9	2.4	1.3

*Commercial flake products generally have an assay of 77 to 80 percent calcium chloride, which is close to the dihydrate.

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

*A 29 percent solution often is the concentration of commercially used liquid forms of calcium chloride, and is made by dissolving 1lb dihydrate to make 1 qt of solution.

formate to accelerate the early-age strength of concrete. If the value for $\text{C}_3\text{A}/\text{SO}_3$ is greater than 4.0, calcium formate has a good potential for accelerating the strength of concrete.

3.2.3 Miscellaneous solid admixtures—In certain instances, hydraulic cements have been used in place of accelerating admixtures. For example, calcium-aluminate cement can shorten the time of setting of portland cement concrete (Robson 1952).

The “seeding” of portland cement concrete with 2 percent by weight (mass) of the cement with finely ground hydrated cement has been reported (Baslazz, Kelmen, and Kilian 1959; Duriex and Lezy 1956) to be equivalent to the use of 2 percent calcium chloride. The effects of seeding, in addition to calcium chloride, are said to be supplementary.

Various silicate minerals have been found (Angstadt and Hurley 1967; Kroone 1968) to act as accelerators.

Finely divided silica gels and soluble quaternary ammonium silicates have been found (Nelson and Young 1977) to accelerate strength development, presumably through the acceleration of tricalcium-silicate hydration (Stein and Stevels 1974). Very finely divided magnesium carbonate has been proposed (Ulfstedt and Watesson 1961) for accelerating time of setting of hydraulic binders. Finely ground calcium carbonate tends to accelerate time of setting (RILEM 1968).

3.3-Use with special cements

It has been reported (USBR 1975) that the effectiveness of calcium chloride in producing accelerated strength of concrete containing pozzolans is proportional to the amount of cement in the mixture. Various effects may be produced when calcium chloride is used as an admixture in concrete containing shrinkage-compensating cement (ACI 223). The limited and conflicting data available on the effect of acceleration on the expansion of concrete containing shrinkage-compensating or self-stressing cements suggest that the concrete proposed for use should be evaluated with the accelerating admixture to determine its effect.

Calcium chloride should not be used with calcium-aluminate cement since it retards the hydration of the aluminates. Similarly, calcium chloride and potassium carbonate increase the time of setting and decrease the early strength development of rapid-hardening cements based on calcium fluoroaluminate ($C_{11}A_7 \cdot CaF_2$). However, strengths after one day are improved by these additions. The effects of calcium chloride on blended cements are similar to those for portland cements, the effects being greater for cements using ground granulated blast-furnace slag than for those using pozzolanic additions (Collepari, Marcialis, and Solinas 1973).

The usual tests should be made for the control of concrete, such as slump, unit weight, and air content. If the concrete stiffens rapidly and difficulty is encountered in achieving proper consolidation or finishing of the concrete, the accelerator used should be investigated.

3.4-Consideration of use

Accelerating admixtures are useful for modifying the properties of concrete, particularly in cold weather, to: (a) expedite the start of finishing operations and, where necessary, the application of insulation for protection; (b) reduce the time required for proper curing and protection; (c) increase the rate of early strength development to permit earlier removal of forms and earlier opening of construction for service; (d) permit more efficient plugging of leaks against hydrostatic pressure; and (e) accelerate time of setting of concrete placed by shotcreting.

The use of accelerators in cold-weather concrete usually is not sufficient in itself to counteract effects of low temperature. Recommendations for cold-weather concreting usually include such practices as heating the ingredients, providing insulation, and applying external heat (see ACI 306R). Accelerators should not be used as antifreeze agents for concrete.

Accelerators should be used with care in hot weather. Some of the detrimental effects that may result are very rapid evolution of heat due to hydration, rapid setting, and increased shrinkage cracking.

3.5-Effect on freshly mixed and hardened concrete

The effects of accelerators on some properties of concrete include the following:

3.5.1 Time of setting-Initial and final times of setting are reduced. The amount of reduction varies with the amount of accelerator used, the temperature of the concrete, the ambient temperature, and characteristics of other materials used in the concrete. Excessive amounts of some accelerators may cause very rapid setting; also, excessive dosage rates of certain accelerators may cause retardation.

Times of setting as short as 15 to 30 sec can be attained. There also are ready-to-use mixtures of cement, sand, and accelerator that have an initial set of 1 to 4 min and a final set of 3 to 10 min. Mortars thus prepared are employed to seal leaks in below-grade struc-

tures, for patching, and for emergency repair. The ultimate strength of such mortars will be much lower than if no accelerator had been added.

The concentration of an admixture may determine its behavior. For example, at high rates of addition (6 percent by weight [mass] of cement), calcium nitrate begins to show retarding properties (Murakami and Tanaka 1969). Ferric chloride is a retarder at additions of 2 to 3 percent by weight (mass) but is an accelerator at 5 percent (Roskopf, Linton, and Pepler 1975). The use of calcium-aluminate cement as an admixture may cause flash set depending on dosage rate.

Temperature also may be an important parameter since calcium chloride is stated (RILEM 1968) to have a greater accelerating effect at 0 to 5 C (32 to 41 F) than at 25 C (77 F).

3.5.2 Air entrainment-Less air-entraining admixture may be required to produce the required air content when an accelerator is used. However, in some cases, large bubble sizes and higher spacing factors are obtained, possibly reducing the beneficial effects of purposely entrained air. Evaluation of concrete containing the specific admixture(s) may be performed to ascertain air-void parameters or actual resistance to freezing and thawing using tests such as ASTM C 457 and C 666, respectively.

3.5.3 Heat of hydration-Earlier heat release is obtained, but there is no appreciable effect on the total heat of hydration.

3.5.4 Strength -When calcium chloride is used, compressive strength may be increased substantially at early ages; later strength may be reduced slightly. The percentage increase in flexural strength usually is less than that of the compressive strength.

The effects of other accelerating admixtures on strength development are not completely known, although a number of salts that accelerate setting may decrease concrete strengths even as early as one day. Some carbonates, silicates, and aluminates are in this category. Organic accelerators, such as triethanolamine and calcium formate, appear to be sensitive in their accelerating action to the particular concrete mixture to which they are added.

The addition of 2 percent calcium chloride by weight (mass) of cement, the 77-percent dihydrate type, increases strength at one day in the range of 100 to 200 percent depending on the cement used.

The compressive strength at one day of neat cement paste, mortar, or concrete prepared with mixtures of portland and calcium-aluminate cements generally will be materially lower than those obtained with either of the two cements alone.

Seeding of portland cement with 2 percent by weight (mass) of cement with finely ground hydrated cement has been reported to increase 90-day compressive strengths by 20 to 25 percent (Baslazzs, Kelmen, and Kilian 1959, Duriex and Lezy 1956).

3.5.5 Durability

3.5.5.1 Volume change-Accelerators have been reported to increase the volume changes that occur un-

der both moist curing and drying conditions. Calcium chloride is reported to increase creep and drying shrinkage of concrete (Shideler 1942). A discussion of literature relating to the presumed association of the use of calcium chloride with increased drying shrinkage with an alternative hypothesis has been advanced (Mather 1964).

More recent work (Bruere, Newbegin, and Wilson 1971) has indicated that such changes depend on the length of curing prior to beginning measurements, the length of the drying or loading periods, and the composition of the cement used. Also, changes in the rate of deformation are greater than changes in the total amount of deformation. It has been suggested (Berger, Kung, and Young 1967) that the influence of calcium chloride in drying shrinkage may be the result of changes in the size distribution of capillary pores due to the effect of calcium chloride on hydration of the cement.

Drying shrinkage and swelling in water are higher for mixtures containing both portland and calcium-aluminate cements, and their durability may be affected adversely by use of an accelerating admixture (Feret and Venuat 1957).

3.5.5.2 Frost damage-The resistance to deterioration due to cycles of freezing and thawing and to scaling caused by the use of deicing salts may be increased at early ages by accelerators but may be decreased at later ages (see comments in previous section on air entrainment).

3.5.5.3 Sulfate resistance-The resistance to sulfate attack is decreased when portland cement concrete mixtures contain calcium chloride (USBR 1975).

3.5.5.4 Alkali-silica reaction-The expansion produced by alkali-silica reaction is greater when calcium chloride is used (USBR 1975). This can be controlled by the use of nonreactive aggregates, low-alkali cement, or certain pozzolans.

3.5.5.5 Corrosion of metals-One of the major disadvantages of calcium chloride is its tendency to support corrosion of metals in contact with concrete due to the presence of chloride ions moisture, and oxygen. In accordance with ACI 222, the maximum acid-soluble chloride contents of 0.08 percent for prestressed concrete and 0.20 percent for reinforced concrete, measured by ASTM C 114 and expressed by weight (mass) of the cement, are suggested to minimize the risk of chloride-induced corrosion.

Values for water-soluble chloride ion are given as maxima in ACI 318-83, Table 4.5.4: 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-0.30.

The user should exercise good judgment in applying these limits, keeping in mind that other factors (moisture and oxygen) always are necessary for electrochemical corrosion.

The use of calcium chloride as an accelerator will aggravate the effects of poor-quality concrete construc-

tion, particularly when the concrete is exposed to chlorides during service. Adherence to the limits just mentioned does not guarantee absence of corrosion if good construction practices are not followed.

Thus, admixtures have been sought that emulate the accelerating properties of calcium chloride without having its corrosive potential. Formulations based on calcium formate with a corrosion inhibitor have been patented (Dodson, Farkas, and Rosenberg 1965). The use of stannous chloride, ferric chloride, and sodium thiosulfate (Arber and Vivian 1961), calcium thiosulfate (Murakami and Tanaka 1969), ferric nitrite (RI-LEM 1968), and calcium nitrite (Bruere 1971) are reported to inhibit the corrosion of steel while still accelerating setting and hardening.

However, all accelerators that do not contain chloride are not necessarily noncorrosive. Manns and Eichler (1982) reported that thiocyanates may promote corrosion. Until additional published data become available, the Committee recommends that users request suppliers of admixtures containing thiocyanates to provide test data regarding the corrosion of steel in concrete made with these admixtures. The test data provided should include corrosion results associated with the dosage range.

3.5.5.6 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 alkalies and calcium chloride. The first type has light spots on a dark background and is characteristic of mixtures in which the ratio of cement alkalies 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 alkalies to chlorides is relatively high.

Available evidence indicates that the magnitude and permanence of discoloration increases as the calcium chloride concentration increases from 0 to 2 percent by weight (mass) of cement. This type of discoloration can be aggravated by high rates of evaporation during curing and improper placement of vapor barriers. Use of continuous fog spray or curing compounds can help alleviate this problem.

3.5.6 Quick-setting admixtures-Some of the admixtures in this category are used to produce quick-setting mortars or concretes suitable for shotcreting operations, sealing leaks, or other purposes. Quick-setting admixtures are believed to act by promoting the flash setting of tricalcium aluminate (Schutz 1977). Among those admixtures used (Mahar, Parker, and Wuellner 1975) or purported to produce quick set are ferric salts, sodium fluoride, aluminum chloride, sodium aluminate, and potassium carbonate. However, many proprietary formulations are mixtures of accelerators. These proprietary compounds are available in liquid or powder form to be mixed with cement.

3.5.7 Rapid accelerators for shotcrete-Rapid accelerators for shotcrete are employed extensively in both dry- and wet-process shotcrete (ACI 506-66).

Rapid shotcrete accelerators traditionally are based on soluble aluminates, carbonates, and silicates. These materials are highly caustic and are hazardous to workers. Newer neutral-pH chloride-free proprietary compounds are penetrating the market slowly.

3.6-Wet- and dry-process shotcrete

Since the wet-process shotcrete mixture is mixed with water as in conventional concrete, the rapid-setting accelerator is added at the nozzle during shooting. Generally, the shotcrete mixture quickly stiffens and reaches an initial set, with a final set occurring much later than would occur with the dry process. However, the early stiffening imparted by the accelerator aids in vertical and overhead placement.

Accelerated shotcrete is used for providing early rock support in tunneling, applying thick sections in vertical or overhead positions, sealing flowing water, and applying of shotcrete between tides. The rate of strength gain can be greatly accelerated using rapid accelerators in dry-process shotcrete. Strength in excess of 3000 psi (21 MPa) in 8 hr would be typical for a noncaustic accelerator and 2000 psi (14 MPa) with a conventional caustic accelerator.

Using dry-process shotcrete and a compatible cement and accelerator, an initial set of less than 1 min and a final set of less than 4 min can be attained.

3.7-Control of purchase

Accelerators should meet the requirements of ASTM C 494 for Type C or E. Calcium chloride also should meet the requirements of ASTM D 98, solid or liquid.

3.8-Batching and use

The amount of accelerator needed to obtain the desired acceleration of the time of setting and strength development depends on local conditions and specific materials used; for calcium chloride, generally 1 to 2 percent of the dihydrate form (77 to 80 percent) based on the weight (mass) of cement, is added.

Practice in the industry has been to equate 1 lb of the dihydrate form to represent one percent of cement by weight (mass) (Calcium Chloride Institute 1959). Various researchers (Abrams 1924; Ramachandran 1976) have studied the effects of calcium chloride on concrete using this dosage basis. For convenience and means of reference to various research data, this practice continues and prevails.

It is recognized, however, that this practice does not result in 1 percent anhydrous calcium chloride going into the mixture (1 lb dihydrate \times 77 percent minimum assay/100 lb cement = 0.8 percent CaCl_2). Multiples of this one percent (1 lb) of dihydrate are then used depending on temperatures (see Table 3.1).

In many locations, anhydrous (94 to 97 percent) solid forms or solutions of calcium chloride are more economical. Table 3.1 lists the common dosage rates of each form. The total chloride contributed to the mixture is shown in Table 3.1, and this includes chlorides

contributed by normal impurities (NaCl , KCl , MgCl_2) in technical-grade products.

Calcium chloride should be introduced into the concrete mixture in solution form. The dihydrate and anhydrous solid forms should be dissolved in water prior to use. Preparation of a standard solution from dry calcium chloride requires that the user be aware of the percent calcium chloride printed on the container. In dissolving the dry product, it should be added slowly to the water, rather than the water to the calcium chloride as a coating may form that is difficult to dissolve. The concentration of the solution may be verified by checking the density, which should be approximately 1.28 g/ml (0.17 oz/gal.) at 73 F (23 C), for a 29 percent solution. The correct density should be obtained from the supplier.

All forms of calcium chloride should conform to ASTM D 98. Accelerating admixtures based on calcium chloride should meet the requirements of ASTM C 494. The amount of water in the solution should be deducted from the water required for the desired w/c. Batching systems are available and are recommended to assure accurate and uniform addition of calcium chloride in liquid form.

3.9-Proportions of concrete

The mix proportions for concrete containing an accelerator generally are the same as for those without the accelerator. The maximum recommended chloride-ion dosage should not exceed those mentioned in the section of this chapter dealing with corrosion of metals.

3.10-Control of concrete

Performance tests should be made if adequate information is not available to evaluate the effect of a particular admixture on properties of job concrete using job materials with expected job temperatures and construction procedures. Since some accelerators contain substantial amounts of chlorides, the user should determine whether or not the admixture under consideration contains a significant amount of chlorides and, if so, the percent by weight (mass) of the cement that its use will introduce into the concrete. The in-service potential for corrosion should then be evaluated accordingly.

CHAPTER 4-WATER-REDUCING AND SET-CONTROLLING ADMIXTURES

4.1 -General

Certain organic compounds or mixtures of organic and inorganic compounds are used as admixtures in both air-entrained and non-air-entrained concrete to reduce the water requirement of the mixture for a given slump or to modify the time of setting, or both. Reduction in water demand may result in either a reduction in w/c for a given slump and cement content or an increased slump for the same w/c and cement content.

When the w/c is reduced, the effect on the hardened concrete is increased compressive strength and reduction in permeability and, in combination with adequate air entrainment, improved resistance to freezing and

thawing. The gain in compressive strength is frequently greater than is indicated by the decrease in w/c alone. This may be due to improved efficiency of hydration of the cement. Such admixtures also may modify the time of setting of concrete or grouts.

A common side effect of many water-reducing admixtures is a tendency to retard the time of setting of the concrete. Water-reducing admixtures that do not retard frequently are obtained by combining water-reducing and retarding materials with accelerators to produce admixtures that still retain the water-reducing property but are less retarding, nonretarding (sometimes called normal setting), or even somewhat accelerating. The degree of effect depends upon the relative amounts of each ingredient used in the formulation. Such formulations may contain other materials to produce or modify certain other effects such as the inclusion of an air-entraining admixture to produce air-entrained concrete, or an air-detraining admixture to reduce or eliminate air-entrainment produced by certain ingredients in the formulation when air entrainment is either not desired or the amount of air produced is excessive.

High-range water-reducing admixtures, also referred to as superplasticizers, behave much like conventional water-reducing admixtures in that they reduce the interparticle forces that exist between cement grains in the fresh paste, thereby increasing the paste fluidity. However, they differ from conventional admixtures in that they do not affect the surface tension of water significantly; therefore, they can be used at higher dosages without excessive air entrainment.

The specific effects of water-reducing and set-controlling admixtures vary with different cements, addition sequence, changes in w/c , mixing temperature, ambient temperature, and other job conditions.

4.2-Classification and composition

Water-reducing and set-controlling admixtures should meet the applicable requirements of ASTM C 494, which classifies them into the following seven types:

1. Water-reducing
2. Retarding
3. Accelerating
4. Water-reducing and retarding
5. Water-reducing and accelerating
6. Water-reducing, high-range*
7. Water-reducing, high-range, and retarding?

This ASTM specification gives detailed requirements with respect to water requirement, time of setting, strength (compressive and flexural), drying shrinkage, and resistance to freezing and thawing.

The materials that generally are available for use as water-reducing and set-controlling admixtures fall into one of eight general classes:

1. Lignosulfonic acids and their salts

2. Modifications and derivatives of lignosulfonic acids and their salts

3. Hydroxylated carboxylic acids and their salts

4. Modifications and derivatives of hydroxylated carboxylic acids and their salts

5. Salts of the sulfonated melamine polycondensation products

6. Salts of the high molecular weight condensation product of naphthalene sulfonic acid

7. Blends of naphthalene or melamine condensates with other water-reducing or set-controlling materials, or both

8. Other materials, which include: (a) inorganic materials, such as zinc salts, borates, phosphates, chlorides; (b) amines and their derivatives; (c) carbohydrates, polysaccharides, and sugar acids; and (d) certain polymeric compounds, such as cellulose-ethers, melamine derivatives, naphthalene derivatives, silicones, and sulfonated hydrocarbons.

These materials may be used singly or in combination with other organic or inorganic, active, or essentially inert substances.

4.3-Application

Water-reducing admixtures are used to produce concrete of higher strength, obtain specified strength at lower cement content, or increase the slump of a given mixture without an increase in water content. They also may improve the properties of concrete containing aggregates that are harsh or poorly graded, or both, or may be used in concrete that may be placed under difficult conditions. They are useful when placing concrete by means of a pump or tremie.

Set-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, thereby eliminating form-deflection cracks (Schutz 1959). This method is particularly valuable to prevent cracking of concrete beams, bridge decks, or composite construction caused by form deflections. Set retarders also are used to keep concrete workable long enough so that succeeding lifts can be placed without development of cold joints or discontinuities in the structural unit. Their effects on rate of slump loss vary with the particular combinations of materials used.

High-range water-reducing admixtures can be used to reduce the water content of concrete. Concrete of a very low w/c can be made to have high strength while maintaining a higher slump [over 3 in. (75 mm)] than otherwise obtainable using a w/c as low as 0.28 by weight (mass). Water reduction up to 30 percent has been achieved. Moderate water reductions (10 to 15 percent) also have been obtained at somewhat higher slumps (6 to 7 in.).

With no reduction in water content, achievement of flowing concrete with slumps in excess of 8 in. is typical (see Chapter 5). High-range water reducers also have been employed to reduce cement content. Since the w/c controls the strength of concrete, the cement

*Also covered by ASTM C 1017 as Type I.

† Also covered by ASTM C 1017 as Type II.

content may be reduced with a proportional reduction of the water content for equivalent strength concretes.

4.4-Typical usage

Expected performance of a given brand, class, or type of admixture may be projected from one or more of the following sources:

1. Results from jobs where the admixture has been used under good field control, preferably using the same material and under conditions similar to those anticipated.

2. Laboratory tests made to evaluate the admixture.

3. Technical literature and information from the manufacturer of the admixture.

The addition rate (dosage) of the admixture should be determined from information provided by one or more of the sources just mentioned. Information should be available on past performance of the proposed admixture substantiating the desired performance.

Various results can be expected with a given admixture due to differences in dosage, cements, aggregates, other materials, and weather conditions. Water-reducing and set-controlling admixtures usually are found to be more effective with respect to water reduction and strength increase when used with portland cements of lower tricalcium aluminate (C_3A) and alkali content. Differences in setting times also can be expected with different types and sources of cement as well as concrete mixtures and ambient temperatures.

These admixtures generally are used to take advantage of water reduction to increase the strength of concrete. If it is desired to provide a given level of strength, the cement content generally can be reduced, resulting in cost savings. In mass concrete, low cement content is particularly desirable since it lowers the temperature rise of the concrete. Water-reducing and set-controlling admixtures do not lower heat of hydration of concrete except as they permit a reduction in cement content. The early temperature characteristics may be modified somewhat due to the modification of the setting properties of the concrete.

In the production of high-strength concrete [above 6000 psi (41 MPa)], it has been found beneficial to increase the dosage of the admixture. This usually provides extra water reduction as well as, typically, a retarded time of setting and slower early strength gain. Concrete having slow early strength gain characteristics generally exhibits higher later strengths.

Concretes containing high-range water reducers often have shown rapid slump loss. To overcome this, a second dosage of high-range water reducer may be used to restore the slump without any apparent ill effects. Generally, more than two dosages are less effective and concrete may lose its workability faster than with a single dosage. It has been found that redosage may result in an increase or decrease in air content on the order of 1 to 2 percent for each redose. When redosages are used, the concrete may experience a greater potential

for bleeding, segregation, and possible set retardation. Therefore, trial mixtures should be conducted to determine the effects of redosing.

ASTM C 494 includes specifications for admixtures of the water-reducing and set-controlling types. It provides for evaluation of the admixture for specification compliance under controlled conditions such as temperature, fixed cement content, slump, and air content using aggregates graded within stipulated limits. This standard requires certain minimum differences in water requirement and strength of the concrete, range in time of setting, and requirements in other properties such as shrinkage and resistance to freezing and thawing.

Most water-reducing admixtures perform considerably better than the minimum requirements of ASTM C 494. Good quality water-reducing admixtures reduce the water requirement of the concrete as much as 8 to 10 percent or more and substantially increase the strength at the same cement content. High-range water reducers may reduce the water requirement by more than 30 percent in some instances.

4.5-Effects on fresh concrete

4.5.1 Water reduction-Water-reducing admixtures, ASTM C 494, Type A, reduce the water required for the same slump concrete by at least 5 percent, and in some cases up to 12 percent. Concrete containing lignosulfonate or hydroxylated carboxylic acid salts generally reduce the water content 5 to 10 percent for a given slump and cement content. High-range water reducers must reduce the water requirement at least 12 percent but may reduce the water by more than 30 percent at a given slump. They also can be used to significantly increase slump without increasing water content. They' also may be employed to achieve a combination of these two objectives- a slump increase with a water-content reduction.

As the cement content of a concrete mixture increases, the required dosage of a high-range water reducer, as a percentage by weight (mass) of cement, is reduced. The effects of these admixtures also are dependent on the calculated C_3A , C_3S , and alkali contents of the cement. Concretes made with cements meeting requirements for Type II and Type V cements require lower admixture dosages than concretes containing Type I or Type III cements. In some cases, it has been found that higher SO₃ content may be desirable when using high-range water reducers.

4.5.2 Time of setting-Lignosulfonates and hydroxylated carboxylic acids retard times of setting by 1 to 3 hr when used at temperatures of 65 to 100 F (18 to 38 C). Sugar acids, carbohydrates, zinc salts, borates, and phosphates in unmodified form retard the setting of portland cement in varying degrees. Most other materials, including high-range water reducers, do not produce appreciable retardation.

Accelerators may be incorporated in the formulation to produce acceleration or decrease or eliminate retardation. Retarders generally are not recommended for

controlling false set; water-reducing retarders have been known to contribute to premature stiffening.

4.5.3 Air entrainment-Lignosulfonates are air-entraining agents to various degrees. The amount of air entrainment generally is in the range of 2 to 6 percent, although higher amounts have been reported. This air-entrainment may consist of large unstable bubbles that contribute little to resistance to freezing and thawing. The air-entraining properties may be controlled by modifying formulations. Materials in Classes 3 through 8 (see Section 4.2) generally do not entrain air, but materials in all eight classes may affect the air-entraining capability of both air-entraining cements and air-entraining admixtures.

Materials in Classes 5, 6, and 7 (high-range water reducers) have an effect on air entrainment. The performance and effectiveness of an air-entraining admixture is strongly dependent on the nature of the high-range water-reducing admixtures with which it may be used. Certain air-entraining admixtures have been reported to be more effective with certain high-range water-reducing admixtures in the production of adequate air entrainment.

Since the key factor in producing frost-resistant concrete is the air-void system—that is, the total volume of air, spacing factor, voids per inch, and specific surface—these factors should be quantified to achieve the desired durability and that reliance is not placed wholly on the air content of the freshly mixed concrete. Therefore, different combinations of air-entraining admixtures and high-range water-reducing admixtures should be evaluated to achieve concrete that is resistant to freezing and thawing, with determination of air-void content and parameters of the air-void system in hardened concrete specimens being a desirable addition to the test program.

It is prudent to include testing for resistance to freezing and thawing in the evaluation, as in some instances spacing factors may exceed generally accepted limits [i.e., 0.20 mm (0.008 in.)] yet concrete may still be frost resistant when subjected to freezing and thawing.

4.5.4 Workability-When otherwise comparable concretes with and without a water-reducing admixture having the same slump and air content are compared, differences in workability are difficult to detect since there is no standard test for workability. However, concrete containing a water-reducing admixture generally is less likely to segregate. When vibrated, some workers detect better flowability for the concrete containing the admixture.

Concretes proportioned for high strength using high-range water reducers usually have a sufficiently high cement content to supply the fines required. Reproportioning such concrete can be accomplished by making up the volume of water reduced by increasing the volume of coarse and 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.

4.5.5 Bleeding-Admixtures affect bleeding capacity in varying degrees. For example, Class 3 admixtures (see Section 4.2) tend to increase bleeding, while certain Class 4 admixtures, which are derivatives of the Class 3 admixtures, do not. Class 1 and 2 admixtures reduce bleeding and segregation in freshly mixed concrete, in part due to the air entrainment. Class 5 through 7 admixtures, when used as high-range water reducers, generally decrease bleeding, except when at a very high slump.

4.5.6 Heat of hydration and temperature rise-Within normal w/c ranges, adiabatic temperature rise and heat of hydration are not reduced at equal cement contents with the use of set-controlling admixtures. Acceleration or retardation may alter the rate of heat generation characteristics, which may change the early rate of temperature rise under job conditions. If the use of the admixture permits a reduction in cement content, heat generated is proportionally reduced.

4.5.7 Rate of slump loss-Rate of slump loss may not be reduced and often is increased. With the low w/c attainable with high-range water reducers, the concrete may show a greater-than-normal rate of slump loss. Because of this, high-range water reducers often are added at the jobsite. Working time can be extended with the careful use of an ASTM C 494, Type B retarding admixture or a Type D water-reducing and retarding admixture. The working time depends on many factors, including the high-range water-reducer dosage, the use of other chemical admixtures, cement characteristics, concrete temperature, slump, and the age of the concrete when the high-range water reducer is introduced.

4.5.8 Finishing-The finishing characteristics of concrete containing Class 3 and 4 admixtures generally are improved.

At reduced water contents achieved with high-range water reducers, 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 may be kept from drying by fogging, use of evaporation retarder, or other procedures (see ACI 308). This should be done with caution so that the durability of the surface is not affected adversely.

4.6-Effects on hardened concrete

4.6.1 Strength-Reduction in w/c causes an increase in strength. There is a further increase in strength due to the use of a water-reducing admixture, apart from that due to reduction of w/c , due to modification of the hydration reaction and microstructure. Unless used at unusually high rates, retarding admixtures generally will produce an increase in strength at 24 hr. The retarding types may decrease the very early strength while the normal setting and accelerating types increase the very early strength.

Later strength may be increased 20 percent or more at the same cement content. Cement contents, thus, can be reduced without lowering 28-day strengths. When high-range water reducers are used to decrease the w/c

28-day compressive strength may be increased by 25 percent or more. Increases in flexural strength of concrete containing a water-reducing admixture usually are attained, but they are not proportionally as great as increases in compressive strength.

4.6.2 Shrinkage and creep—Information on the effects of these admixtures on shrinkage and creep is conflicting. Long-term shrinkage may be less, depending on the degree to which the water content of the concrete is reduced. Creep will be reduced proportional to the increase in the strength of the concrete. The degree to which the use of an admixture, in given dosages, affects shrinkage and creep may be different if cements of different compositions are used in the concrete.

4.6.3 Durability—The effect of these admixtures on resistance to freezing and thawing, including deicer scaling, is small since resistance to freezing and thawing is almost wholly a function of the air-void system in the hardened concrete. An improvement may result from a decrease in w/c and increased strength.

Some high-range water reducers cause bubble-spacing factors \bar{L} higher than typically deemed necessary to produce concrete that will survive freezing and thawing if critically saturated. A spacing factor of 0.008 in. (0.20 mm) or less generally is needed to insure resistance to freezing and thawing. Concrete made with some high-range water reducers having spacing factors of 0.010 in. (0.25 mm) or higher was found upon testing to be highly resistant to freezing and thawing. This may be a function of increased strength and density and reduced permeability, which allowed the concrete to remain less than critically saturated in the presence of water while being tested.

A small increase in resistance to freezing and thawing and to aggressive waters and soils results from water reduction. This is due largely to decreased permeability and increased strength.

4.7-Preparation and batching

Water-reducing and set-controlling 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 recommended practices.

The density of admixtures mixed on the job, or those applied as solutions, should be determined and compared with the manufacturer's standards. Determination of density can be made 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 job quality control program. Storage tanks for solutions should be plainly identified and the solutions should be protected from contamination, dilution, evaporation, and freezing.

Two or more admixtures of different types, such as a water-reducing and an air-entraining admixture, may not be compatible when mixed together. Unless it is known that admixtures can be satisfactorily mixed to-

gether, they should be added to the batch separately so that they will be adequately diluted before coming in contact with each other. The manufacturer of the admixtures should recommend proper procedures.

4.8-Proportioning

A concrete mixture may need reportioning when an admixture is used if the water content, cement content, or air content is changed. By definition, for example, the water requirement of a concrete mixture for given consistency is reduced 5 percent or more with the introduction of a water-reducing admixture. Procedures for proportioning and adjusting concrete mixtures are covered by ACI 211.1.

One fundamental rule to remember is that when a concrete mixture that is considered satisfactory in workability and finishing qualities is modified to incorporate a chemical admixture, the ratio of volumetric proportions of mortar to coarse aggregate should remain the same. Changes in water content, cement 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.

Most chemical admixtures of the water-reducing type are water solutions. The water they contain becomes a part of the mixing water in the concrete and usually is considered in the calculation of w/c ratio. 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.

4.9-Quality control

It sometimes is necessary or desirable to determine that an admixture is the same as that previously tested, or that successive lots or shipments are the same. Tests that can be used to identify admixtures include solids content, density, infrared spectrophotometry for organic materials, chloride content, pH, and others. Guidelines for determination of uniformity (variability) of chemical admixtures are given in ASTM C 494.

Job inspectors may be instructed to sample deliveries of the admixture as part of the job quality control. Density can be determined on the job by a hydrometer or volumetric flask as mentioned previously.

Admixture users should become familiar with admixtures' appearances and odors. This knowledge has sometimes prevented errors and mixups.

4.10-Precautions

If adequate information is not available, tests should be made to evaluate the effect of the admixture on the properties of concrete made with job materials under the anticipated ambient conditions and construction procedures. Tests of water-reducing admixtures and set-controlling admixtures should indicate their effect on the following properties of concrete, insofar as they are pertinent to the job: (1) water requirement, (2) air content, (3) slump, (4) bleeding and possible loss of air from the fresh concrete, (5) time of setting, (6) corn-

pressive and flexural strength, (7) resistance to freezing and thawing, (8) drying shrinkage, and (9) setting characteristics.

When admixtures are evaluated in laboratory trial batches prior to job use, the series of mixtures should be planned to provide necessary information. They need not follow ASTM C 494 procedures, although these may be a helpful guide. The trial mixtures should be made with the same materials, particularly cement, that will be used on the job and as close to job conditions as possible. Temperature is particularly important to time of setting and early strength development.

Trial mixtures can be made at midrange slump and air contents expected or specified for the job. The cement content or *w/c* ratio should be that required for the specified design strength and durability requirements for the job. Trial mixtures also can be made with a range of cement contents or *w/c* or other properties to bracket the job requirements.

Air content and time of setting of job concrete can differ considerably from laboratory concrete with the same materials and mixture proportions. All parties should be alert to this possibility at the start of a job and be ready to make adjustments in the addition rates of materials (particularly air-entraining admixtures) to achieve the specified properties of the concrete at the project site.

Admixtures of all classes may be available in either powder or liquid form. Since relatively small quantities are used, it is important that suitable and accurately adjusted dispensing equipment be employed. Refer to Chapter 1 for information on dispensing admixtures.

CHAPTER 5-ADMIXTURES FOR FLOWING CONCRETE

5.1 -General

ASTM C 1017 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 can be placed so as to be self-leveling yet remaining cohesive without excessive bleeding, segregation, or abnormal retardation.

Since production of flowing concrete by addition of water only would result in concrete of extremely low quality, flowing concrete must be obtained through the use of a plasticizing admixture, either normal (Type 1) or retarding (Type 2). These materials used as plasticizing admixtures for production of flowing concrete generally are identical to those used as high-range water-reducing admixtures (superplasticizers) and conform to ASTM C 494, Types F and G (see Chapter 4).

As an example, concrete could be delivered to the jobsite at an initial slump of 2 to 3 in. (50 to 75 mm) and the plasticizing admixture then could be added to increase the slump to 8 in. or more, or the plasticizing admixture could be added at the plant to achieve this slump level.

The plasticizing admixture, either a conventional water-reducing admixture or a high-range water-reducing admixture, is adsorbed onto the hydrating cement par-

ticles and causes a repulsion among them. The concrete loses slump at a more rapid rate than the same concrete without the plasticizing admixture.

5.2—Materials

The admixtures that are used to achieve flowing concrete should meet the requirements of ASTM C 1017, Type 1 (plasticizing) or Type 2 (plasticizing and retarding). Commonly used materials are:

1. Sulfonated naphthalene condensates, Types 1 or 2
2. Sulfonated melamine condensates, Types 1 or 2
3. Modified lignosulfonates
4. A combination of these types plus a water-reducing admixture, Type A; or water-reducing retarding admixture, Type D; or water-reducing accelerating admixture, Type E
5. High dosages of a water-reducing admixture, Type A, plus a water-reducing accelerating admixture, Type E

This latter combination requires higher water contents than are required when using a high-range water-reducing admixture (superplasticizer).

5.3-Evaluation and selection

A decision to produce and use flowing concrete should include selecting the type of admixture to use. Factors to be considered in the choice of admixture(s) include type of construction; restriction imposed on the chloride-ion content, time interval from introduction of cement and water into the mixer; availability of accurate admixture dispensing equipment at the plant, jobsite, or both; and ambient temperature.

If the decision is made to add the plasticizing admixture at the jobsite, an accurate means of introducing the admixture into the concrete mixer must be assured. Truck mixers should be equipped with admixture tanks designed to introduce the admixture into the concrete mixer so that it can be distributed evenly throughout the batch, and adequate mixing speed and revolutions should be maintained. The concrete plant must be equipped to accurately measure the admixture into the truck-mounted tanks.

Admixtures must be handled and measured properly. An admixture batching system must include a means of visual verification of the dosage.

5.4-Application

Flowing concrete commonly is used in areas requiring maximum volume placement (slabs, mats, pavements) in congested locations where the member is unusually shaped or a great amount of reinforcement is present. Proper consolidation of high-strength concrete for columns is difficult. Flowing concrete 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. Such concrete is useful for projects requiring rapid form cycling with a maximum volume of concrete required per day,

coupled with a low w/c to achieve the early strengths required for stripping or tensioning. A short time cycle often can be used on such projects.

5.5-Performance criteria

Expected performance of a given brand, class, or type of admixture may be estimated from one or more of the following sources: (a) results from jobs where the admixture has been used under good technical control, preferably using the same concreting materials and under conditions similar to those anticipated; (b) laboratory tests made to evaluate the admixture; and (c) technical literature and information from the manufacturer of the admixture.

The dosage required to increase the slump to flowing consistency varies depending upon the cement, the initial slump, w/c , temperature, time of addition, and concrete mix proportions. The dosage required to increase slump from 1 to 8 in. may be 50 percent higher than that required if the starting slump is 3 in. The proposed flowing concrete mixture should be used initially in noncritical work 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 initial slump, rate of slump loss, and setting characteristics.

Results may vary with a given admixture due to differences in cement, aggregates, other material, and weather conditions from day to day. The use of admixtures to increase slump from the 2 to 3 in. range may also allow a cement reduction with a resultant cost saving. Since very little concrete is placed at that low slump level, the additional water required to raise the slump of conventional concrete from 2 to 3 in. to 5 to 6 in. would have to be matched with an increase in the cement content if the strength and, consequently, the w/c is kept constant.

Flowing concrete is desirable for use in mass placements. The cement content may be kept low, which will minimize heat development, and the lower water content will reduce shrinkage. The plasticizing admixture does not lower the temperature rise in concrete except as a result of reducing cement content. The early temperature-rise characteristics also may be modified with the use of the retarding version of the plasticizing admixture (Type 2) or in combination with a conventional water-reducing retarding admixture (Type D).

Concrete intended to have a compressive strength higher than 6000 psi (41 MPa) may be produced as flowing concrete; since a low w/c is required, reducing the mixing water is the best approach. Flowing concrete, being easier to consolidate, also contributes to proper bond between reinforcing steel and concrete in areas where reinforcement is congested.

ASTM C 1017 is the specification for admixtures for flowing concrete. It provides for evaluation of the admixture for specification compliance under controlled conditions of temperature, fixed cement content,

slump, and air content, using aggregates graded within stipulated limits. This standard requires certain minimum differences in strength of concrete, range of times of setting, and requirements regarding other aspects of performance such as shrinkage and resistance to freezing and thawing.

It is preferable to keep the cement content constant, allowing the significant slump increase to assist in placement. When admixtures are evaluated in laboratory trial mixtures prior to job use, the series of mixtures should be planned to provide the necessary information. Assuming specification compliance has been established, the tests need not follow ASTM C 1017 procedures such as slump, air content, and cement content; however, consistency of procedures should be maintained.

The trial mixtures should be made with the same materials, particularly cement, that will be used on the job, and simulate the job conditions as closely as possible. Temperature is particularly important to times of setting 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 admixture can be varied to achieve various slump increases. If allowed, the starting slumps also may be varied. The specified w/c should be maintained in each case, and a range of slump can be reviewed. In this manner, the optimum mixture proportions can be selected and the required results achieved.

Air content and time of setting of job concrete can differ considerably from laboratory concrete with the same materials and mixture proportions. Therefore, adjustment of the proposed mixture on the jobsite prior to its use in the required locations usually is beneficial.

5.6-Proportioning of concrete

A concrete mixture usually needs reportioning when a plasticizing admixture is added to achieve flowing concrete. Procedures for proportioning and adjusting concrete mixtures are covered in 211.1. The fine aggregate-coarse aggregate ratio may require adjustment to assure that sufficient fines are present to allow a flowable consistency to be achieved without excessive bleeding or segregation. It also may be necessary to increase the cement content or add other fine materials such as pozzolan or slag.

Since 0.5 gal. or larger volume of plasticizing admixture is customarily used per yd^3 (m^3) of concrete to produce flowing concrete, the water in the admixture must be accounted for in calculating w/c and the effect on mixture volume.

5.7-Effect on fresh concrete

5.7.1 Times of setting—ASTM C 1017 Type 1 admixtures do not have much effect on times of setting. Therefore, flowing concrete with a water content that would give a 2 to 4 in. slump if an admixture were not used will set as quickly as if the admixture had not been used. Type 2 admixtures can reduce slump loss significantly and retard the initial times of setting of the con-

crete. At concrete temperatures below 60 F (15 C), the time of setting of concrete containing the Type 1 admixture may be increased.

5.7.2 Workability and finishing-When concrete mixtures are properly proportioned, flowing concrete is extremely workable without bleeding and segregation. The fine-to-coarse aggregate ratio often has to be adjusted by an increase in fine aggregate content to prevent segregation at high slump. Flowing concrete should be vibrated to achieve proper consolidation.

The characteristics of flowing concrete at the time it is being machine floated or troweled will be similar to those of conventional concrete with the same ingredients. Properly proportioned flowing concrete should not exhibit objectionable bleeding even at high slump. Proper timing is imperative in the finishing operation.

If a concrete is over-sanded or the air content is too high, or both, the surface of the concrete tends to dry before it sets. This condition may cause the concrete to feel rubbery or jelly-like and cause finishing problems by its stickiness and rolling. The problem of excessive air entrainment in concrete used in floor slabs is particularly apparent when the initial machine-finishing operations begin.

5.7.3 Bleeding and segregation-Properly proportioned concrete mixtures should not bleed excessively or segregate. The upper slump limit of cohesive yet flowable concrete varies and it can be determined from testing the mixture prior to its use. Segregation and bleeding may be reduced by increasing the fine-to-coarse aggregate ratio, or by the addition of other fine materials.

5.7.4 Rate of slump loss-The rate of slump loss may be altered by many factors such as concrete temperature, type and amount of cement, water content, time of admixture addition, and amount of admixture employed. Therefore, an acceptable rate of slump loss can be achieved by monitoring these conditions and by changing the initial time of setting characteristics of the concrete.

5.7.5 Additional dosages-Additional dosages 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. In general, the compressive strength level is maintained or increased and the air content decreased. Therefore, if air entrainment is of concern, it must be checked after the concrete has been redosed and returned to its intended slump.

5.8-Effect on hardened concrete

5.8.1 Heat of hydration and temperature rise-Heat of hydration is not reduced if the cement content is not reduced. If the use of flowing concrete involves the use of a lower cement content, the heat evolved will be reduced. If the rate of hydration is not changed, the temperature rise will not be changed if the cement content is not reduced.

5.8.2 Strength-Since concrete that is intended to be flowing often is batched with a water content that would result in a slump of 2 to 4 in. (51 to 102 mm),

the w/c is lower than that of conventional concrete of similar cement content at a 5-in. (127-mm) slump, and strength improvement therefore is realized. Flowing concrete with no water reduction, as compared to conventional concrete, often shows strength increases. When concrete strengths above 6000 psi (41 MPa) at 28 days are desired, a high-range water-reducing admixture often is added to achieve a low w/c . It then may be added 'again in the field as a plasticizing admixture to increase the slump in order to obtain the flowing concrete required for the placing conditions.

When flowing concrete is used, the flexural strength is not changed significantly from that of the initial concrete of the same w/c at a lower slump.

5.8.3 Drying shrinkage and creep-When low-slump concrete and flowing concrete are compared, the drying shrinkage will be approximately the same if the water contents are virtually identical. If, in conjunction with producing flowing concrete, the water content of the mixture at equal cement content is lowered, then the drying shrinkage may be reduced. There seems to be little change in the creep characteristics of concrete with the use of these admixtures when comparisons are made on the basis of equal w/c concretes.

5.8.4 Air entrainment-Higher dosages of air-entraining admixture usually are required for flowing concrete to maintain proper air content as compared to conventional concrete. As with any air-entrained concrete, the air content in the field must be checked so that the air-entraining admixture dosage can be modified as required to keep the air content in the specified range.

5.8.5 Resistance to freezing and thawing-Flowing concrete exhibits degrees of resistance to freezing and thawing similar to conventional concrete with a similar w/c and air-void system. The air-void structure may have larger spacing factors and a decrease in the number of voids per inch compared to the control concrete; however, satisfactory resistance to freezing and thawing has been achieved in most cases. Lucas (1981) indicated that concrete made with a high-range water-reducing admixture (superplasticizer) has a smaller tendency to absorb chloride than do untreated concretes of the same w/c .

5.8.6 Permeability-Flowing concrete has resistance to chloride penetration similar to, if not slightly greater than, that of conventional concrete with the same w/c . When the admixture is used to reduce the w/c , the resistance of the concrete to chloride penetration is even greater. Flowing concrete tends to be of lower permeability because of better consolidation, reduced bleeding, and increased cement hydration.

Low permeability results from low w/c concrete when it is properly placed and cured. Flowing concrete with a low w/c can be placed and consolidated easily. This allows concrete with a w/c below 0.40 to be placed easily; therefore, the resultant concrete, if properly cured, can be of extremely low permeability and have good resistance to the penetration of aggressive solutions.

5.8.7 Bond-Flowing concrete can improve bond strength to reinforcing steel when compared to similar concrete with a 100-mm (4-in.) slump (Collepari and Corradi 1979) conventional and flowing concrete. Brettman, Darwin, and Donahey (1986) found that in reinforced concrete beams bond strength of concrete of equal w/c was decreased as the slump was increased and was decreased the longer the concrete remained unhardened. Proper vibration is required for both concretes. Proper consolidation around the reinforcing is more easily achieved with flowing concrete.

5.9-Quality assurance

It is desirable and sometimes necessary to determine that an admixture is the same as that previously tested or that successive lots or shipments are the same. Tests that can be used to identify admixtures include solids content, density, infrared spectrophotometry for organic materials, chloride content, pH, and others. Admixture manufacturers can recommend which tests are most suitable for their admixtures and the results that should be expected. Guidelines for determining uniformity of chemical admixtures are given in ASTM C 1017.

5.10-Control of concrete

5.10.1 Concrete mixture proportioning-Concrete should be proportioned with flowing characteristics in mind; therefore, sufficient fines must be present in the mixture to allow the desired slump to be achieved without excessive bleeding and segregation. Trial batches usually are prepared to confirm concrete characteristics. The mixture is adjusted in the field to verify flowing characteristics.

Necessary adjustments can be made to assure the user of the optimum mixture with regard to slump, workability, rate of slump loss, and setting characteristics. Verification of early strengths can be accomplished if required. The rate of slump loss should be noted and adjusted as required. The mixture proportions also should conform to the procedures indicated in ACI 211.1 or ACI 211.2. Flowing concrete should be placed in accordance with ACI 304 and consolidated in accordance with ACI 309.

5.10.2 Field control-Flowing concrete control requires checking the initial slump or water content prior to the addition of the admixture to assure that the water content and the w/c are as required. After the plasticizing admixture is added and thoroughly mixed into the batch, the resulting slump should be in the specified range. For air-entrained concrete, the air content also must be checked at the point of discharge into the forms.

Rate of slump loss, initial setting characteristics, and both early and final strength results may require mixture adjustments. Slump loss and setting characteristics may be adjusted by changes in the plasticizing admixture dosage or by concurrent use of accelerating or retarding admixtures. When the concrete placement is

abnormally slow or the temperature is high, or both, the USC of a Type 2 admixture may be desirable.

Changes in cement composition or in aggregate grading, or both, can cause significant variations in the flowing concrete characteristics. Therefore, these changes should be minimized.

CHAPTER 6-MISCELLANEOUS ADMIXTURES

6.1 -Gas-forming admixtures

6.1.1 Introduction-The gas-void content of concrete can be increased by the use of admixtures that generate or liberate gas bubbles in the fresh mixture during and immediately following placement and prior to setting of the cement paste. Such materials are added to the concrete mixture to counteract settlement and bleeding, thus causing the concrete to retain more nearly the volume at which it was cast. They are not used for producing resistance to freezing and thawing; any such effect is incidental. Air-entraining admixtures are discussed in Chapter 2.

6.1.2 Materials-Admixtures that produce these effects are hydrogen peroxide, which generates oxygen; metallic aluminum (Menzel 1943; Shideler 1942), which generates hydrogen; and certain forms of activated carbon from which adsorbed air is liberated.

Only aluminum powder is used extensively for gas formation. An unpolished powder usually is preferred, although polished powder may be used when a slower reaction is desired. The rate and duration of gas evolution of the cement (particularly alkali content), temperature, w/c , and fineness and particle shape of the aluminum powder.

The effectiveness of the treatment is controlled by the duration of mixing, handling, and placing operations relative to the speed of gas generation. The addition rate may vary from 0.006 to 0.02 percent by weight (mass) of cement under normal conditions, although larger quantities may be used to produce low-strength cellular concrete. Approximately twice as much aluminum powder is required at 40 F (4 C) as at 70 F (21 C) to produce the same amount of expansion.

Because of the very small quantities of aluminum powder generally used [a few grams per 100 lb (45 kg) of cement], and because aluminum powder has a tendency to float on the mixing water, it generally is premixed with fine sand, cement, or pozzolan, or incorporated in commercially available admixtures having water-reducing set-retarding effects.

In cold weather, it may be necessary to speed up the rate of gas generation by the addition of such caustic materials as sodium hydroxide, hydrated lime, or trisodium phosphate. This may be done to insure sufficient gas generation before the mixture has set and hardened.

6.1.3 Effectiveness-The release of gas, when properly controlled, causes a slight expansion of freshly mixed concrete. When such expansion is restrained, there will be an increase in bond to horizontal reinforcing steel without excessive reduction in compressive

strength. Too much gas-producing material may produce large voids, seriously weakening the matrix. To a considerable extent, the effect on compressive strength depends on the degree to which the tendency of the mixture to expand is restrained; therefore, it is important that confining forms be tight and adequately closed. Gas-forming agents will not overcome shrinkage after hardening caused by drying or carbonation.

6.2-Grouting admixtures

6.2.1 Introduction-Many of the admixtures used for specific purposes in concrete are used as grouting admixtures to impart special properties to the grout. Oil-well cementing grouts encounter high temperatures and pressures with considerable pumping distances involved. Grout for preplaced-aggregate concrete requires extreme fluidity and nonsettling of the heavier particles. Nonshrink grout requires a material that will not exhibit a reduction from its volume at placement. Installation of tile subjects bonding and joint-filling grout to very fast drying or loss of water through absorption by the substrate and the tile. A wide variety of special purpose admixtures are used to obtain the special properties required.

6.2.2 Materials-For oil-well cementing grouts, retarders, as described in Chapter 4, are useful in delaying setting time. Bentonite clays may be used to reduce slurry density, and materials such as barite and iron filings may be used to increase the density (Hansen 1954). Tile grouts and certain other grouts use materials such as gels, clays, pregelatinized starch, and methyl cellulose to prevent the rapid loss of water.

Grout fluidifiers for preplaced-aggregate concrete grouts usually contain water-reducing admixtures along with admixtures to prevent settlement of heavy constituents of the grout. Nonshrink grouts may contain gas-forming or expansion-producing admixtures, or both.

Special grout applications may require such admixtures as accelerators and air-entraining materials as described in other sections. Tests should be conducted to determine the compatibility of admixtures with the cement to be used.

6.2.3 Effect-Retarders may be used to keep a grout fluid at temperatures up to 400 F (204 C) and pressures as high as 18,000 psi (124 MPa) for 1 hr or more. Grouting is a highly specialized field, usually requiring material properties not necessary for ordinary concreting operations. The admixture manufacturer's suggestions on addition rates should be followed; however, tests must be performed on the grout to determine if the properties of the grout meet the project requirements.

6.3-Expansion-producing admixtures

6.3.1 Introduction-Admixtures that expand during the hydration period of the concrete or react with other constituents of the concrete to cause expansion are used to minimize the effects of drying shrinkage. They are used both in restrained and unrestrained concrete placement.

6.3.2 Materials-The most common admixture for this purpose is a combination of finely divided or granulated iron and chemicals to promote oxidation of the iron. Expansion is greatest when the mixture is exposed alternately to wetting and drying. Expansive cements are used on large projects where a predetermined uniform degree of expansion is required (Klein and Troxell 1958). Materials are available (calcium sulfoaluminates) that can be added to portland cements to produce useful amounts of expansion. These materials are part of the cementitious component and, therefore, not admixtures. For additional information regarding these cements refer to ACI 223.

6.3.3 Effect of expansion on concrete-The controlled expansion produced by these admixtures may be of about the same magnitude as the drying shrinkage expected at later ages or it may be slightly greater. For a given application, the extent of expansion and the time interval during which it takes place are very important and must be under control for the most satisfactory results.

For unrestrained concrete, the expansion must not take place before the concrete gains sufficient tensile strength, or else the concrete will be disrupted. For restrained applications, the concrete must be strong enough to withstand the compressive stresses developed. It is reported that restraint in only one direction (Klein, Karby, and Polivka 1961) creates some degree of compression in the other two orthogonal directions.

6.4-Bonding admixtures

6.4.1 Introduction-Admixtures specifically formulated for use in portland cement mixtures to enhance bonding properties generally consist of an organic polymer emulsion commonly known as latex (Goeke 1958; Ohama 1984). In general, latex forms a film throughout the concrete.

6.4.2 Materials-A wide variety of types of latex is used in paints, paper coatings, textile backing, etc. 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. An unstable emulsion will coagulate in the mixture, rendering it unsuitable for use.

6.4.3 Function-When used as admixtures in the quantities normally recommended by the manufacturers (5 to 20 percent by weight [mass] of the cement), different latexes may affect the unhardened mixture differently. For example, a film-forming latex may feel tacky in contact with air.

Water still is necessary to hydrate the portland cement of the cement-polymer system. The polymer component becomes effective only when the emulsion is broken through a drying out process. The polymer emulsion carries a portion of the mixing water into the mixture, the water being released to the cement during the hydration process.

At the same time, this release of water sets the emulsion. Hence, after an initial 24 hr of moist curing to eliminate chances of cracking, additional moist curing

is not necessary and actually is undesirable since the emulsion will not have an opportunity to dry and develop the desired strength. The only exception to this is when a very low w/c is used (less than 0.3 by weight [mass]).

Upon drying or setting, the polymer particles coalesce into a film, adhering to the cement particles and to the aggregate, thus improving the bond between the various phases. The polymer also fills microvoids and bridges microcracks that develop during the shrinkage associated with curing (Isenberg et al. 1971). This secondary bonding action preserves some of the potential strength normally lost due to microcracking.

Greater strength and durability are associated with the lower w/c of latex mixtures. The polymer particles act as a water replacement, resulting in more fluidity than in mixtures without latex, but having a similar w/c ratio.

The compressive strength of moist-cured grouts, mortars, and concrete made with these materials may be greater or less than that of mixtures of the same cement content without the admixture, depending on the admixture used (Grenley 1967). However, the increase in bond, tensile, and flexural strengths far outweigh the possible disadvantage of slight compressive-strength reduction. Latex-modified concrete has better abrasion resistance, better resistance to freezing and thawing, and reduced permeability.

6.4.4 Limitations-Surfactants present in latex emulsions can entrap air and may require that a foam-suppressing agent be used. Dosage rates for air-entraining agents will be affected. Some types of polymers will soften in the presence of water; therefore, these types should not be used in concrete that will be in contact with water during service. The ultimate result obtained with a bonding admixture is only as good as the surface to which the mixture is applied. The surface must be clean, sound, and free from such foreign matter as paint, grease, and dust.

6.5-Pumping aids

6.5.1 Introduction-Pumping aids for concrete are admixtures with the sole function of improving concrete pumpability. They normally will not be used in concrete that is not pumped or in concrete that can be pumped readily.

The primary purpose of using admixtures to enhance pumpability of concrete is to overcome difficulties that cannot be overcome by changes in the concrete mixture proportions. As in the use of many ingredients in concrete, the objective is economic.

6.5.2 Materials-Many pumping aids are thickeners that increase the cohesiveness of concrete. The Standards Association of Australia* identified five categories of thickening admixtures for concrete and mortar as follows:

1. Water-soluble synthetic and natural organic polymers that increase the viscosity of water-cellulose derivatives (methyl, ethyl, hydroxyethyl, and other cellulose gums); polyethylene oxides; acrylic polymers; polyacrylamides; carboxyvinyl polymers; natural water-soluble gums; starches; and polyvinyl alcohol,

2. Organic flocculants-carboxyl-containing styrene copolymers, other synthetic polyelectrolytes, and natural water-soluble gums.

3. Emulsions of various organic materials-paraffin, coal tar, asphalt, and acrylic and other polymers.

4. High-surface-area inorganic materials-bentonites and organic-modified bentonites and silica fume.

5. Finely divided inorganic materials that supplement cement in cement paste-fly ash and various raw or calcined pozzolanic materials, hydrated lime, and natural or precipitated calcium carbonates and various rock dusts.

This list does not include all of the materials listed in McCutcheon's *Functional Materials* (McCutcheon Division 1975). Classifications may be misleading since the performance of a given admixture can change drastically with change of dosage rates, cement composition, mixing temperature and time, and other factors. An example is provided by the polyethylene oxides. When used in small amounts of 0.01 to 0.05 percent of cement weight (mass), they improve pumpability. Larger amounts produce thickening that may or may not disappear upon prolonged mixing.

Other examples are provided by synthetic polyelectrolytes, which act as flocculants or thickeners depending upon dosage levels. It would appear to be highly undesirable to induce flocculation and increase bleeding in pumped concrete. Nevertheless, these admixtures are considered effective in pumped concrete because they lower bleeding capacity or total bleeding despite causing increases in initial rates of bleeding.

Other problems with the listing given previously occur with the natural gums (algins, tragacanth, arabic). They can function as thickeners or flocculants depending upon dosage levels and other factors. These agents and some of the synthetic materials also can have dispersing or water-reducing effects. Gum arabic is a powerful water reducer for calcium-sulfate plasters, but in portland cement pastes, it can produce a glue-like stickiness.

Factors to consider in the use of emulsions (paraffins, polymers) are whether they function in the desired way in cement paste by remaining stable or by breaking of the emulsion. Both types of paraffin emulsion are considered to be useful in Australian concrete technology*.

The listing given previously does not include such air-entraining agents or surface-active agents widely used in concrete as hydroxylated carboxylic acid derivatives, lignosulfonates and their derivatives, formaldehyde-condensed naphthalene sulfonates, melamine polymers, and other set-retarding or water-reducing admixtures. The omission here is deliberate because a substantial proportion of concrete that is to be pumped

*Information on Thickening Admixtures for Use in Concrete and Mortar, "Draft for Comment, *Miscellaneous Publication* No. DR 73146, Standards Association of Australia, Committee BD/33, Oct. 1973, unpublished.

in North America will be specified as air-entrained concrete, and probably also will contain a water-reducing or set-retarding admixture. Therefore, such admixtures may be considered to be normal constituents of concrete.

Evaluation of and experience with these admixtures are well known. In this chapter, these types of admixtures are not considered specifically as pumping aids. They will be present in many cases in combination with other agents introduced for the specific purpose of improving pumpability. In such cases, evaluation of effects of such combinations on pumpability and other properties of concrete will be required to determine whether or not adverse interactions occur between admixtures.

6.5.3 Effects on concrete—A side effect of a concrete pumpability-enhancing admixture is any effect it may have on fresh concrete other than that on pumpability, and any effect that changes the characteristics of the hardened concrete. Since the main effect of a water thickener is to increase viscosity, substantial thickening can increase water requirements with the usual consequences of reduced strength. By using a suitable dispersant in combination with a thickening agent, no increase in water may be required. At certain dosage levels, some thickeners act as dispersants of solid particles. Many of the thickening agents cause entrainment of air. To control air content, a defoamer (for example, tributyl phosphate) may be needed, especially when higher concentrations of pumping aid are used in mortars and concretes.

Many of the synthetic and natural organic thickening agents retard the setting of portland cement pastes. For dosages of methyl or hydroxyethyl cellulose of 0.1 percent or more by weight (mass) of portland cement, retardation may be substantial. In any case, the particular concrete system in which a pumpability-enhancing admixture is incorporated must be evaluated in terms of side effects upon the fresh and hardened concrete in addition to assessing the effectiveness of the admixture in performing its intended function.

6.6-Coloring admixtures

6.6.1 Introduction—Pigments specifically prepared for use in concrete and mortar are available both as natural and synthetic materials. They are formulated to produce adequate color without materially affecting the desirable physical properties of the mixture. They are covered by ASTM C 979.

6.6.2 Materials—The pigments listed in Table 6.6.2 may be used to obtain a variety of colors.

6.6.3 Effects on concrete properties—The addition rate of any pigment to concrete normally should not exceed 10 percent by weight (mass) of the cement (Wilson 1927); however, some pigments, such as carbon black, should be used at lesser quantities. Natural pigments usually are not ground as finely as, and often are not as pure as, synthetic materials and generally do not produce as intense a color per unit of addition. Except for carbon black, additions of less than 6 percent of

Table 6.6.2 — Colors produced by various pigments

Shades of color	Pigment
Grays to black	Black iron oxide Mineral black Carbon black
Blue	Ultramarine blue
Bright red to deep red	Red iron oxide
Brown	Brown iron oxide Raw and burnt umber
Ivory, cream, or buff	Yellow iron oxide
Green	Chromium oxide Phthalocyanine green
White	Titanium dioxide

pigment generally have little or no effect on the physical properties of the fresh or hardened concrete. Larger quantities may increase the water requirement of the mixture to such an extent that the strength and other properties, such as abrasion resistance, may be adversely affected.

The addition of an unmodified carbon black will increase considerably the amount of air-entraining admixture needed to provide resistance of the concrete to freezing and thawing (Taylor 1948). However, most carbon blacks available for coloring concrete do contain air-entraining materials in sufficient quantity to offset the inhibiting effect of the carbon black.

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. Stronger colors can be obtained if white rather than grey cement is used. If bright colors are required, a surface coating should be specified in lieu of pigment admixtures.

6.7-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 understood fully, it is believed that these compounds, containing highly charged groups in their chains, are adsorbed 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 floc.

6.8-Fungicidal, germicidal, and insecticidal admixtures

6.8.1 Introduction—Certain materials have been suggested as admixtures for concrete or mortar to impart fungicidal, germicidal, and insecticidal properties. The primary purpose of these materials is to inhibit and control the growth of bacteria and fungus on concrete floors and walls or joints. They may not always be completely effective.

6.8.2 Materials—The materials that have been found to be most effective are: polyhalogenated phenols (Le-

vowitz 1952), dieldrin emulsion (Gay and Wetherly 1959), and copper compounds (Robinson and Austin 1951; and Young and Talbot 1945).

6.8.3 Effectiveness—Addition rates vary from 0.1 to 10 percent by weight (mass) of the cement, depending on the concentration and composition of the chemical. The higher rates, above 3 percent, may have an adverse effect on the strength of the concrete. The effectiveness of these materials, particularly the copper compounds, is reported to be of a temporary nature. This probably will vary with the type of wear and cleaning methods employed.

6.9-Dampproofing admixtures

6.9.1 Introduction—The term “dampproofing” implies prevention of water penetration of dry concrete or stoppage of water transmission through unsaturated concrete. However, admixtures have not been found to produce such effects and the term has come to mean a reduction in rate of penetration of water into dry concrete or in rate of transmission of water through unsaturated concrete.

When some concrete dams, retaining walls, tanks, and other structures show evidence of leakage, it usually is the result of faulty production and placement of concrete. When properly proportioned concrete mixtures are used and placed with high-quality workmanship under qualified inspection, the concrete in a structure should be virtually impermeable, although leakage still may occur through cracks. Dampproofing admixtures cannot be expected to be as reliable or effective as applying a moisture-barrier system to the concrete.

Dampproofing may reduce the rate of penetration of aggressive chemicals found in water; however, it will not stop them. Dampproofing admixtures also 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.

An admixture described as a dampproofer may have a secondary effect on the properties of fresh concrete not directly indicated by the name. For example, it may promote entrainment of air; thus, it may more properly be considered an air-entraining admixture.

This section deals with those effects directly implied by the word “dampproofing” on the properties of hardened concrete.

6.9.2 Materials—Admixtures for dampproofing are used to render the concrete hydrophobic and therefore capable of repelling water that is not under hydrostatic pressure.

Admixtures for dampproofing include soaps, butyl stearate, and certain petroleum products (Dunagan and Ernst 1934; Uppal and Bahadur 1958).

1. The soaps are composed of salts of fatty acids, usually calcium or ammonium stearate or oleate. The soap content usually is 20 percent or less, the remainder being calcium chloride or lime. Total soap added should not exceed 0.2 percent by weight (mass) of concrete. Soaps cause entrainment of air during mixing.

2. Butyl stearate reportedly performs better than soap as a water repellent. It does not entrain air and has a negligible effect on strength. It is added as an emulsion with the stearate being 1 percent by weight (mass) of the cement.

3. Among petroleum products are mineral oils, asphalt emulsions, and certain cutback asphalts. Heavy mineral oil is effective as a water repellent for concrete and in reducing its permeability. The petroleum product must be a fluid and have a viscosity approximately equal to SAE60, with no fatty or vegetable oils.

4. In addition, there is a group of miscellaneous materials sometimes advertised as dampproofing agents. All of these are usually detrimental to concrete strength, and none are truly dampproofers. These include barium sulfate and calcium and magnesium silicates, finely divided silica and naphthalene, colloidal silica and fluosilicate, petroleum jelly and lime, cellulose materials and wax, silica and aluminum, coal tar cut with benzene, and sodium silicate.

6.9.3 Effectiveness—Dampproofing admixtures may aid in shedding or repelling water from the surface of the concrete. Some dampproofing admixtures also may aid in reducing the ability of rain to penetrate the surface of the concrete or reducing the wicking or wetting properties of concrete. These admixtures, by reducing penetration of the visible pores, may retard penetration of rain into concrete block made of nonplastic mixtures. Test data show that they also reduce the rate of penetration of moisture into the micropores of dry concrete, but there is no indication that there are comparable effects on the transmission of moisture through unsaturated concrete, except when the concrete contains paste with relatively high porosity.

A paste of high porosity results from low cement content and correspondingly high w/c , lack of curing, or from both factors. If the concrete has a sufficiently low porosity, such as that obtained by producing a well-cured paste having w/c not over 0.6 by weight (mass), dampproofing agents give no appreciable improvement.

The Building Research Advisory Board (1958) reported that in the opinion of the majority of 61 observers, dampproofing admixtures are not “... effective or acceptable in controlling moisture migration through slabs-on-ground.”

A special advisory committee to the Building Research Advisory Board reached the following conclusion on the basis of data from tests of moisture transmission through unsaturated concrete slabs: “The Committee does not find adequate data to demonstrate the effectiveness of any admixture to reduce the transmission of moisture through concrete slabs-on-ground in a manner sufficient to replace either a vapor barrier or granular base, or both, under conditions where such protection would be needed.”

6.10-Permeability-reducing admixtures

Permeability refers to the rate at which water is transmitted through a saturated specimen of concrete

under an externally maintained hydraulic gradient. Admixtures of the kinds discussed in the previous section do not reduce the permeability of saturated concrete. However, mineral powders (essentially fly ash, raw or calcined natural pozzolans, and silica fume), properly proportioned, reduce the permeability of mixtures in which the cement content of the paste is relatively low. This is due to the production of additional cementitious material, primarily calcium silicate hydrates and calcium aluminum silicate hydrates, which form by the combination of lime from the cement and silica and other components in the mineral powder.

The reduction of total water content by means of a water-reducing admixture should reduce the total porosity slightly, but there are no adequate data to demonstrate that permeability is reduced materially. However, decreased permeability with the use of high-range water reducers at equivalent w/c has been reported.

Polymer-emulsion admixtures have been used to reduce permeability of concrete overlays for bridge decks and parking decks. The polymer particles coalesce into a continuous film, which reduces permeability by sealing air voids and blocking microcracks (Isenburg et al. 1971; Whiting 1981).*

Accelerating admixtures such as calcium chloride increase the rate of hydration (see Section 3.2.2), thereby reducing the length of time required for a concrete mixture to attain a given fraction of its ultimate degree of impermeability (see Section 3.2.1). However, any advantage attained this way is likely to be temporary since, if conditions are such that water is being transmitted through the concrete, they also are conducive to continued hydration of cement.

6.11 -Chemical admixtures to reduce alkali-aggregate expansion

6.11.1 Introduction-The use of pozzolans to reduce expansion caused by alkali-aggregate reaction has been studied widely and reported (Stanton 1950). As early as 1950, reports began to appear on admixtures other than pozzolans to reduce expansion caused by alkali-aggregate reaction. Since that time there has been little new information added in the form of meaningful research of field practice (see ACI Committee 212's 1963 report).

6.11.2 Materials-Soluble salts of lithium, barium, and certain air-entraining and some water-reducing set-retarding admixtures have been reported to produce reduction in expansion of laboratory mortar specimens. Outstanding reductions have been obtained in such specimens using 1 percent additions of the lithium salts and 2 to 7 percent additions by weight (mass) of cement of certain barium salts. The lithium salts are very expensive.

Salts of proteinaceous materials and water-reducing set-retarding materials have shown moderate reductions in expansion. Data on the protein air-entraining

admixtures are based on the use of 0.2 percent by weight (mass) of concrete. Some laboratories have reported on the use of calcium chloride with the barium salts to counteract strength loss.

Air entrainment, regardless of the admixture used, has been shown to lower the expansion slightly.

6.11.3 Effectiveness-Limited laboratory data on the use of chemical admixtures to reduce expansion resulting from the alkali-silica reaction are available; therefore, no recommended practices are presented. Any user of these materials should test them thoroughly before proceeding to field use.

6.12-Corrosion-inhibiting admixture

6.12.1 Introduction-Many investigators have studied the corrosion of iron and steel with particular reference to protective coatings. It has been found that concrete furnishes ample protection to the steel embedded in it, although a limited number of cases have been reported in which infiltrating or percolating waters find a way through the concrete, removing or carbonating the calcium hydroxide (Cushman 1909; Cushman and Gardener 1910). Reports indicate that the use of small quantities of bentonite in the mixing water reduces corrosion by reducing the permeability of the concrete.

The major contributor to corrosion of reinforcing steel is the presence of chlorides in the concrete. The chlorides may come from circumstances such as exposure of the concrete to saline or brackish waters, exposure to saline soils from which chlorides can reach the steel by diffusion through the concrete, by entrance of deicer solutions through cracks or pores in the concrete, or use of calcium chlorides as an admixture constituent (see Chapter 3).

Corrosion caused by the inclusion or infiltration of chlorides in concrete is difficult to control once it has started. Numerous chemicals have been evaluated as potential corrosion-inhibiting admixtures for concrete (Verbeck 1975; Clear and Hay 1973; Griffin 1975). These include chromates, phosphates, hypophosphorites, alkalies, nitrites, and fluorides. Recently, calcium nitrite has been reported as an effective corrosion inhibitor (Rosenberg et al. 1977). Studies of this material are continuing (Virmani, Clear, and Pasko 1983).

6.12.2 Materials-The use of sodium benzoate at a rate of 2 percent in the mixing water or a 10 percent benzoate-cement slurry painted on reinforcement, or both, have been described as effective (Lewis, Mason, and Brereton 1956). Analysis showed that the sodium benzoate remained in the concrete after five years' exposure. It also accelerates compressive strength development.

Calcium lignosulfonate reduces the tendency for corrosion of steel in concrete containing calcium chloride (Kondo, Takeda, and Hideshima 1959).

Sodium nitrite has been investigated by Moskvin and Alekseyev (1958) as an inhibitor of corrosion of steel in autoclaved products. These authors suggest that the high alkalinity, which normally is present in concrete and which serves to passivate the steel, may be reduced

*Also, Grenley, Dallas G., Michalyschin, J., and Molodovan, D., Mar. 1983, "Effect of Certain Concrete Admixtures on the Chloride Permeability of Concrete," Dow Chemical Company, Inc., presented at the Annual Meeting of the American Concrete Institute, Los Angeles.

and Brereton 1956). Analysis showed that the sodium benzoate remained in the concrete after five years' exposure. It also accelerates compressive strength development.

Calcium lignosulfonate reduces the tendency for corrosion of steel in concrete containing calcium chloride (Kondo, Takeda, and Hideshima 1959).

Sodium nitrite has been investigated by Moskvina and Alekseyev (1958) as an inhibitor of corrosion of steel in autoclaved products. These authors suggest that the high alkalinity, which normally is present in concrete and which serves to passivate the steel, may be reduced considerably by autoclave treatment, especially when siliceous admixtures are present. Two to 3 percent sodium nitrite by weight (mass) of cement was found to be an efficient inhibitor under these conditions.

Sarapin (1958) found by storage tests that 2 percent sodium nitrite was effective in preventing corrosion of steel in concrete containing calcium chloride under certain conditions of storage. Low-solubility salts such as certain phosphates or fluosilicates and fluoaluminates are beneficial, according to limited reports. Dosage should be limited to 1 percent by weight (mass) of cement.

6.12.3 Effect-Warnings have been sounded against the use of inhibitors. For example, the South African National Building Research Institute (1957) made the following statement, "Integral additives: although certain inert and reactive materials have shown promise, their use cannot be recommended at this stage, as insufficient evidence of their effectiveness or possible dis-effects from the inhibitor addition might reasonably be expected, if the steel surface is clean and chlorides absent; but under such conditions, there is unlikely to be serious trouble without added inhibitor."

CHAPTER 7-REFERENCES

7.1-Recommended references

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

American Concrete Institute

116R	Cement and Concrete Terminology	212.2R	Guide for Use of Admixtures in Concrete
201.2R	Guide to Durable Concrete	222R	Corrosion of Metals in Concrete
211.2	Standard Practice for Selecting Proportions for Normal, Heavyweight, and Mass Concrete	223	Standard Practice for Use of Shrinkage-Compensating Concrete
212.1R	Admixtures for Concrete	304R	Guide for Measuring, Mixing, Transporting, and Placing Concrete
		306R	Cold Weather Concreting
		308	Standard Practice for Curing Concrete
		309R	Guide for Consolidation of Concrete
		311.1R	Manual of Concrete Inspection (SP-2)
		311.4R	Guide for Concrete Inspection
		318	Building Code Requirements for Reinforced Concrete
		506R	Guide to Shotcrete
		523.1R	Guide for Cast-in-Place Low Density Concrete
		548R	Polymers in Concrete
<i>ASTM</i>			
		C 94	Standard Specification for Ready-Mixed Concrete
		C 114	Standard Methods for Chemical Analysis of Hydraulic Cement
		C 125	Terminology Relating to Concrete and Concrete Aggregates
		C 138	Standard Test Method for Unit Weight, Yield, and Air Content (Gravimetric) of Concrete
		C 150	Standard Specification for Portland Cement
		C 173	Standard Test Method for Air Content of Freshly Mixed Concrete by the Volumetric Method
		C 231	Standard Test Method for Air Content of Freshly Mixed Concrete by the Pressure Method
		C 233	Standard Test Method for Air-Entraining Admixtures for Concrete
		C 260	Standard Specification for Air-Entraining Admixtures for Concrete
		C 457	Standard Practice for Microscopical Determination of Air Void Content and Parameters of the Air Void System in Hardened Concrete
		C 494	Standard Specification for Chemical Admixtures for Concrete
		C 595	Standard Specification for Blended Hydraulic Cements
		C 666	Standard Test Method for Resistance of Concrete to Rapid Freezing and Thawing
		C 979	Standard Specification for Pigments, for Integrally Colored Concrete

- C 1017 Standard Specification for Chemical Admixtures for Use in Producing Flowing Concrete
- D 98 Standard Specification for Calcium Chloride

These publications may be obtained from the following organizations:

American Concrete Institute
P. O. Box 19150
Detroit, MI 48219-0150

ASTM
1916 Race Street
Philadelphia, PA 19103

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This report was submitted to letter ballot of the committee and was approved in accordance with ACI balloting procedures.