

CHAPTER 7

Chemical Admixtures for Concrete

Chemical admixtures are those ingredients in concrete other than hydraulic cement, supplementary cementitious materials (SCMs), water, aggregates, and fiber reinforcement that are added to the mixture immediately before or during mixing (Figure 7-1). There are a variety of chemical admixtures available for use in concrete mixtures to modify fresh and hardened concrete properties. Chemical admixtures can be classified by function as follows:

1. Air-entraining
2. Normal, Mid-range, and High-range water-reducing
4. Set accelerating
5. Set retarding
6. Hydration-control
7. Rheology modifying
8. Corrosion inhibitors
9. Shrinkage reducers
10. Permeability reducing admixtures
11. Alkali-silica reactivity inhibitors
12. Coloring admixtures
13. Miscellaneous admixtures such as workability, bonding, grouting, gas-forming, anti-washout, foaming, and pumping admixtures



Figure 7-1. Liquid admixtures, from far left to right: antiwashout admixture, shrinkage reducer, water reducer, foaming agent, corrosion inhibitor, and air-entraining admixture.

The major reasons for using chemical admixtures in concrete mixtures are:

1. To achieve certain properties in concrete more effectively than by other means;
2. To maintain the quality of concrete during the stages of mixing, transporting, placing, finishing, and curing (especially in adverse weather conditions or intricate placements);
3. To overcome certain emergencies during concreting operations; and
4. Economy.

Despite these considerations, no admixture of any type or amount is a substitute for good concreting practice.

The effectiveness of an admixture depends upon factors such as its composition, addition rate, time of addition; type, brand, and amount of cementing materials; water content; aggregate shape, gradation, and proportions; mixing time; slump; and temperature of the concrete.

Chemical admixtures considered for use in concrete should meet applicable specifications as presented in Table 7-1. Trial mixtures should be made with the admixture and the other concrete ingredients at the temperature and relative humidity anticipated during placement. Then, observations can be made on the compatibility of the admixture with other ingredients, as well as its effects on the properties of the fresh and hardened concrete. The amount of admixture recommended by the manufacturer should be used, or the optimum dosage should be verified by laboratory testing. For more information on chemical admixtures for use in concrete see ACI Committee 212 (2004 and 2010), Thomas and Wilson (2002), Hewlett (1998), and Ramachandran (1995).

Table 7-1. Concrete Admixtures by Classification

Type of admixture	Desired effect	Material
Accelerators (ASTM C494 and AASHTO M 194, Type C)	Accelerate setting and early-strength development	Calcium chloride (ASTM D98 and AASHTO M 144) Triethanolamine, sodium thiocyanate, calcium formate, calcium nitrite, calcium nitrate
Air detrainers	Decrease air content	Tributyl phosphate, dibutyl phthalate, octyl alcohol, water-insoluble esters of carbonic and boric acid, silicones
Air-entraining admixtures (ASTM C260 and AASHTO M 154)	Improve durability in freeze-thaw, deicer, sulfate, and alkali-reactive environments Improve workability	Salts of wood resins (Vinsol resin), some synthetic detergents, salts of sulfonated lignin, salts of petroleum acids, salts of proteinaceous material, fatty and resinous acids and their salts, alkylbenzene sulfonates, salts of sulfonated hydrocarbons
Alkali-aggregate reactivity inhibitors	Reduce alkali-aggregate reactivity expansion	Barium salts, lithium nitrate, lithium carbonate, lithium hydroxide
Antiwashout admixtures	Cohesive concrete for underwater placements	Cellulose, acrylic polymer
Bonding admixtures	Increase bond strength	Polyvinyl chloride, polyvinyl acetate, acrylics, butadiene-styrene copolymers
Coloring admixtures (ASTM C979)	Colored concrete	Modified carbon black, iron oxide, phthalocyanine, umber, chromium oxide, titanium oxide, cobalt blue
Corrosion inhibitors (ASTM C1582)	Reduce steel corrosion activity in a chloride-laden environment	Amine carboxylates aminoester organic emulsion, calcium nitrite, organic alkydicarboxylic, chromates, phosphates, hypophosphites, alkalis, and fluorides
Dampproofing admixtures	Retard moisture penetration into dry concrete	Soaps of calcium or ammonium stearate or oleate Butyl stearate, Petroleum products
Foaming agents	Produce lightweight, foamed concrete with low density	Cationic and anionic surfactants Hydrolyzed protein
Fungicides, germicides, and insecticides	Inhibit or control bacterial and fungal growth	Polyhalogenated phenols Dieldrin emulsions, Copper compounds
Gas formers	Cause expansion before setting	Aluminum powder
Grouting admixtures	Adjust grout properties for specific applications	See Air-entraining admixtures, Accelerators, Retarders, and Water reducers
Hydration control admixtures	Suspend and reactivate cement hydration with stabilizer and activator	Carboxylic acids Phosphorus-containing organic acid salts
Permeability-reducing admixture: non-hydrostatic conditions (PRAN)	Water-repellent surface, reduced water absorption	Long-chain fatty acid derivatives (stearic oleic, caprylic capric), soaps and oils, (tallows, soya-based), petroleum derivatives (mineral oil, paraffin, bitumen emulsions), and fine particle fillers (silicates, bentonite, talc)
Permeability reducing admixture: hydrostatic conditions (PRAH)	Reduced permeability, increased resistance to water penetration under pressure	Crystalline hydrophilic polymers (latex, water-soluble, or liquid polymer)
Pumping aids	Improve pumpability	Organic and synthetic polymers Organic flocculents Organic emulsions of paraffin, coal tar, asphalt, acrylics Bentonite and pyrogenic silicas Hydrated lime (ASTM C141)
Retarding admixtures (ASTM C494 and AASHTO M 194, Type B)	Retard setting time	Lignin, Borax Sugars, Tartaric acid and salts
Shrinkage reducers	Reduce drying shrinkage	Polyoxyalkylene alkyl ether Propylene glycol
Superplasticizers* (ASTM C1017, Type 1)	Increase flowability of concrete Reduce water-cement ratio	Sulfonated melamine formaldehyde condensates Sulfonated naphthalene formaldehyde condensates Lignosulfonates, Polycarboxylates

Table 7-1. Concrete Admixtures by Classification (Continued)

Type of admixture	Desired effect	Material
Superplasticizer* and retarder (ASTM C1017, Type 2)	Increase flowability with retarded set Reduce water–cement ratio	See superplasticizers and also water reducers
Water reducer (ASTM C494 and AASHTO M 194, Type A)	Reduce water content at least 5%	Lignosulfonates Hydroxylated carboxylic acids Carbohydrates (Also tend to retard set so accelerator is often added)
Water reducer and accelerator (ASTM C494 and AASHTO M 194, Type E)	Reduce water content (minimum 5%) and accelerate set	See water reducer, Type A (accelerator is added)
Water reducer and retarder (ASTM C494 and AASHTO M 194, Type D)	Reduce water content (minimum 5%) and retard set	See water reducer, Type A (retarder is added)
Water reducer—high range (ASTM C494 and AASHTO M 194, Type F)	Reduce water content (minimum 12%)	See superplasticizers
Water reducer—high range—and retarder (ASTM C494 and AASHTO M 194, Type G)	Reduce water content (minimum 12%) and retard set	See superplasticizers and also water reducers
Water reducer—mid range	Reduce water content (between 6 and 12%) without retarding	Lignosulfonates Polycarboxylates

* Superplasticizers are also referred to as high-range water reducers or plasticizers. These admixtures often meet both ASTM C494 (AASHTO M 194) and ASTM C1017 specifications.

Air-Entraining Admixtures

One of the greatest advances in concrete technology was the development of air-entrained concrete in the mid-1930s. Air-entrainment dramatically improves the durability of concrete exposed to cycles of freezing and thawing and deicer chemicals (see [Chapter 11](#)). There are also other important benefits of entrained air in both freshly mixed and hardened concrete (see [Chapter 9](#)).

Air-entraining concrete is produced by using either an air-entraining cement or by adding an air-entraining admixture during batching, or a combination of these approaches. Air-entraining cement is a portland cement with an air-entraining addition interground with the clinker during manufacture (see [Chapter 3](#)). An air-entraining admixture, on the other hand, is added directly to the concrete materials either before or during mixing. Regardless of the approach used, adequate control and monitoring is required to ensure the proper air content at all times.

Specifications and methods of testing air-entraining admixtures are given in ASTM C260, *Standard Specification for Air-Entraining Admixtures for Concrete*, and C233, *Standard Test Method for Air-Entraining Admixtures for Concrete* (AASHTO M 154 and T 157). Air-entraining additions for use in the manufacture of air-entraining cements must meet requirements of ASTM C226, *Standard Specification for Air-Entraining Additions for Use in the Manufacture of*

Air-Entraining Hydraulic Cement. Applicable requirements for air-entraining cements are given in ASTM C150, *Standard Specification for Portland Cement* and AASHTO M 85. See [Chapter 11](#), Klieger (1966), and Whiting and Nagi (1998) for more information.

Air-Entraining Materials

The primary ingredients used in air-entraining admixtures are listed in Table 7-1. Numerous commercial air-entraining admixtures, manufactured from a variety of materials, are available. Most air-entraining admixtures consist of one or more of the following materials: wood resin (Vinsol resin), sulfonated hydrocarbons, fatty and resinous acids, and synthetic materials. Chemical descriptions and performance characteristics of common air-entraining agents are shown in Table 7-2. Air-entraining admixtures are usually liquids and should not be allowed to freeze. Admixtures added at the mixer should conform to ASTM C260 (AASHTO M 154).

Air-entraining cements comply with ASTM C150 and C595 (AASHTO M 85 and M 240). To produce such cements, air-entraining additions conforming to ASTM C226 are interground with the cement clinker during manufacture. Air-entraining cements generally provide an adequate amount of entrained air to meet most job conditions; however, a specified air content may not necessarily be obtained in the concrete. If an insufficient volume of air is entrained, it may also be necessary to add an air-entraining admixture at the mixer.

Table 7-2. Classification and Performance Characteristics of Common Air-Entraining Admixtures

Classification	Chemical description	Notes and performance characteristics
Wood derived acid salts Vinsol® resin	Alkali or alkanolamine salt of: A mixture of tricyclic acids, phenolics, and terpenes.	Quick air generation. Minor air gain with initial mixing. Air loss with prolonged mixing. Mid-sized air bubbles formed. Compatible with most other admixtures.
Wood rosin	Tricyclic acids-major component.	Same as above.
Tall oil	Tricyclic acids-minor component. Fatty acids-major component. Tricyclic acids-minor component.	Slower air generation. Air may increase with prolonged mixing. Smallest air bubbles of all agents. Compatible with most other admixtures.
Vegetable oil acids	Coconut fatty acids, alkanolamine salt.	Slower air generation than wood rosins. Moderate air loss with mixing. Coarser air bubbles relative to wood rosins. Compatible with most other admixtures.
Synthetic detergents	Alkyl-aryl sulfonates and sulfates (e.g., sodium dodecylbenzenesulfonate).	Quick air generation. Minor air loss with mixing. Coarser bubbles. May be incompatible with some HRWR. Also applicable to cellular concretes.
Synthetic workability aids	Alkyl-aryl ethoxylates.	Primarily used in masonry mortars.
Miscellaneous	Alkali-alkanolamine acid salts of ligno- sulfonate. Oxygenated petroleum residues. Proteinaceous materials. Animal tallows.	All these are rarely used as concrete air-entraining agents in current practice.

Mechanism of Air Entrainment

Air-entraining admixtures are surfactants (surface-active agents) which concentrate at the air-water interface and reduce the surface tension encouraging the formation of microscopic bubbles during the mixing process. The air-entraining admixture stabilizes those bubbles, enhances the incorporation of bubbles of various sizes, impedes bubble coalescence, and anchors bubbles to cement and aggregate particles.

The air-entraining admixture acts at the air-water interface. Air-entraining admixtures typically have a negatively charged head which is hydrophilic and attracts water, and a hydrophobic tail which repels water. As illustrated in Figure 7-2; the hydrophobic end is attracted to the air within bubbles generated during the mixing process. The polar end, which is hydrophilic, orients itself towards water (A). The air-entraining admixture forms a tough, water-repelling film, similar to a soap film, with sufficient strength and elasticity to contain and stabilize the air bubbles. The hydrophobic film also keeps water out of the bubbles (B). The stirring and kneading action of mechanical mixing disperses the air bubbles. The charge around each bubble leads to repulsive forces, that prevent the

coalescence of bubbles (C & D). The surface charge causes the air bubble to be adhered to the charged surfaces of cement and aggregate particles. The fine aggregate particles also act as a three-dimensional grid to help hold the bubbles in the mixture (E). This improves the cohesion of the mixture and further stabilizes the air bubbles (F).

Entrained air bubbles are not like entrapped air voids, which occur in all concretes as a result of mixing, handling, and placing. Entrapped air voids are largely a function of aggregate characteristics. Intentionally entrained air bubbles are extremely small in size, between 10 to 1000 μm in diameter, while entrapped voids are usually 1000 μm (1 mm) or larger. The majority of the entrained air voids in normal concrete are between 10 μm and 100 μm in diameter. As shown in Figure 7-3, the bubbles are not interconnected. They are well dispersed and randomly distributed. Non-air-entrained concrete with a 25-mm (1-in.) maximum-size aggregate has an air content of approximately 1.5%. This same mixture air entrained for severe frost exposure would require a total air content of about 6%, made up of both coarse entrapped air voids and fine entrained air voids. However, it is the finely entrained air system that is most effective at providing frost resistance.

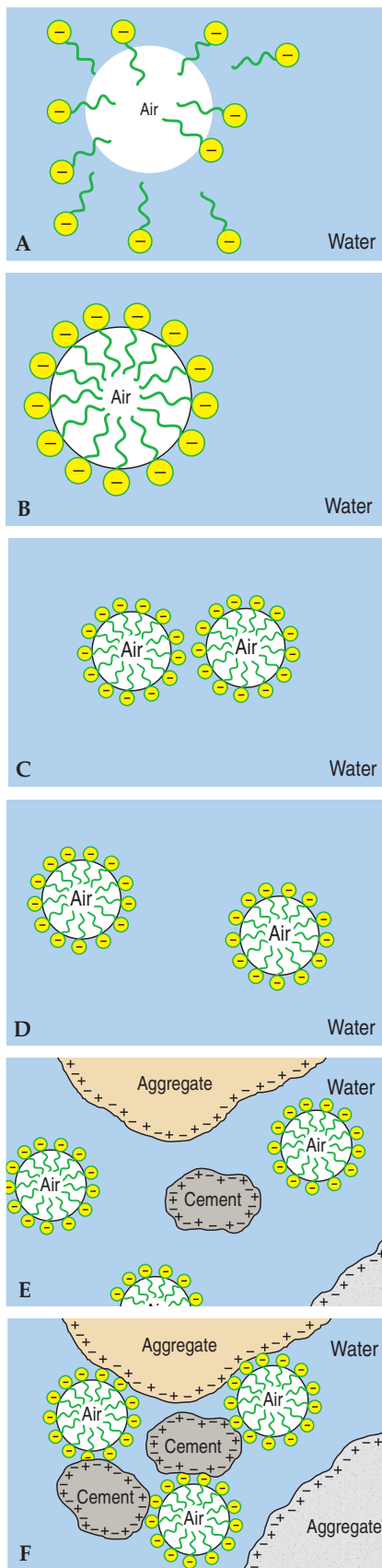


Figure 7-2. Mechanism of air-entraining surfactants (Thomas and Wilson 2002).

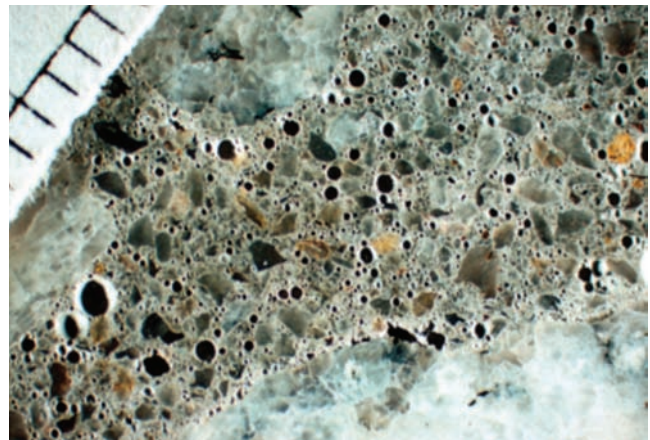


Figure 7-3. Polished concrete surface shows air voids clearly visible as dark circles.

Control of Air Content

The amount of air entrained in concrete for a given dose of admixture depends on materials, mixture proportions, methods of transport, placing and finishing methods, and curing. Variations in air content can be expected with variations in aggregate proportions and gradation, mixing time and intensity, temperature, and slump. The order of batching and mixing concrete ingredients when using an air-entraining admixture can also have a significant influence on the amount of air entrained. The late addition of water and extended retempering can cause clustering of air bubbles around aggregate resulting in strength reduction (Kozikowski and others 2005 and Camposagrado 2006). Therefore, consistency in batching is needed to maintain adequate control. For more information on the effects of constituent materials, mixture proportions, and placing and finishing operations on air content see [Chapter 9](#).

When entrained air is excessive, it can be reduced by using one of the following defoaming (air-detraining) agents: tributyl phosphate, dibutyl phthalate, octyl alcohol, water-insoluble esters of carbonic acid and boric acid, and silicones. Only the smallest possible dosage of defoaming agent should be used to reduce the air content to the specified limit. An excessive amount might have adverse effects on concrete properties (Whiting and Stark 1983).

Impact of Air Content on Properties of Concrete

The presence of a finely distributed network of bubbles has a significant impact on the properties of plastic concrete. Entrained air improves the workability of concrete. It is particularly effective in lean (low cement content) mixtures that otherwise might be harsh and difficult to work. In one study, an air-entrained mixture made with natural aggregate, 3% air, and a 37-mm (1.5-in.) slump had about the same workability as a non-air-entrained concrete with 1% air and a 75-mm (3-in.) slump, even though less cement was required for the air-entrained mix (Cordon 1946). Workability of concrete mixtures with angular and poorly graded aggregates is similarly improved.

Because of improved workability with entrained air, water and sand content can be reduced significantly as shown in Figure 7-4. A volume of air-entrained concrete requires less water than an equal volume of non-air-entrained concrete of the same consistency and maximum size aggregate. Water reductions in the range of 15 L/m³ to 25 L/m³ (25 lb/yd³ to 40 lb/yd³) may be achieved with adequate air entrainment (Figure 7-4). Freshly mixed concrete containing entrained air is cohesive, looks and feels “fatty” or workable, and can usually be handled with ease. On the other hand, high air contents can make a mixture sticky and more difficult to finish. Furthermore, the air bubbles reduce the tendency for segregation and bleeding.

Improvements in the performance of hardened concrete obviously include improved resistance to freezing and thawing, and deicer-salt scaling. Furthermore, the incorporation of air also results in a reduced permeability and possibly improved resistance to sulfate attack and alkali-silica reactivity (see Chapter 11).

The single detrimental effect is that an increase in air content results in a decrease in the strength of the concrete. When the air content is maintained constant, strength varies

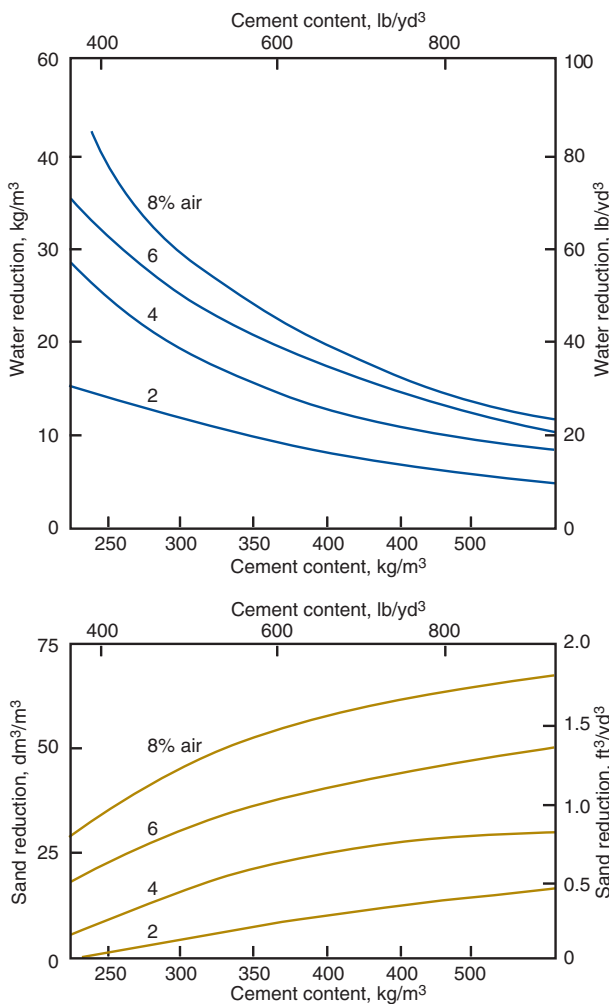


Figure 7-4. Reduction of water and sand content obtained at various levels of air and cement contents (Gilkey 1958).

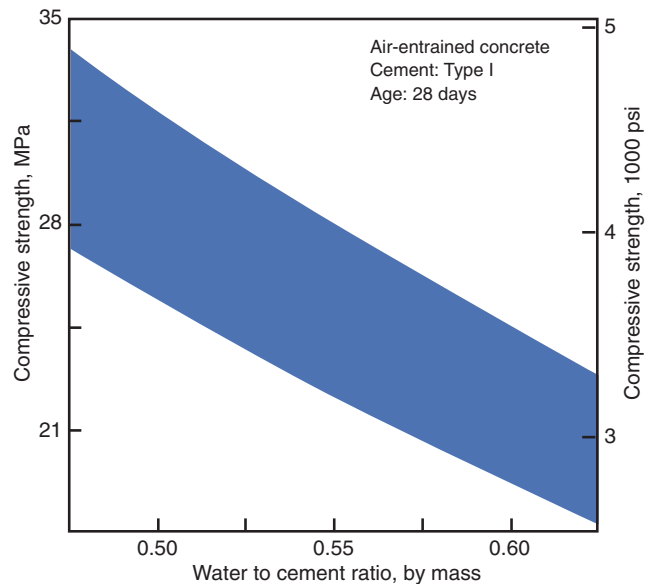


Figure 7-5. Typical relationship between 28-day compressive strength and water-cement ratio for a wide variety of air-entrained concretes using Type I cement.

inversely with the water-cement ratio (see Figure 7-5). A good rule of thumb is that each 1% increase in air content is accompanied by 5% to 6% reduction in strength. More information on the impact of air content on fresh and hardened properties of concrete can be found in Chapter 9.

Water-Reducing Admixtures

A water-reducing admixture is an admixture that increases workability without increasing the water content of concrete, or that permits a decrease in water content without decreasing the slump and conforms to ASTM C494, *Standard Specification for Chemical Admixtures for Concrete* (AASHTO M 194). Some water-reducing admixtures, typically high-range, are also plasticizers conforming to ASTM C1017, *Standard Specification for Chemical Admixtures for Use in Producing Flowing Concrete* (AASHTO M 194).

When used as a water-reducer, the water content is reduced while maintaining the slump; this reduces the water-cement ratio of the concrete and increases its strength and durability. When the same chemical is used as a plasticizer, the workability is increased while the water content is kept constant. This can improve the placing characteristics of the concrete without adversely affecting the strength and durability.

If the flow is maintained, the water content can be reduced. The conditions are ideal for the strength and durability of concrete. Here the admixture is used as a true water-reducer; allowing concrete to be produced with low water-to-cement ratios and good workability. Advantage

may be taken for both purposes of a water-reducing admixture when designing concrete; producing concrete with improved fresh and hardened properties (Figure 7-6) (see Chapter 12).

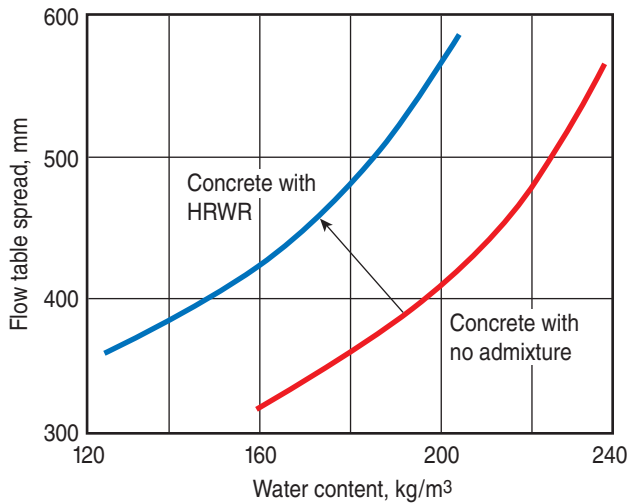


Figure 7-6. Advantage may be taken for both purposes of a water-reducing admixture (lowering w/cm, and increasing flow) when designing concrete. (Adapted from Neville 1995)

Normal (Conventional) Water Reducers

When used as a water reducer, normal range, or conventional water reducers can reduce the water content by approximately 5% to 10%. Alternatively, they may be used as plasticizers to provide a moderate increase in workability. Normal water reducers are intended for concretes with slumps up to 100 mm or 125 mm (4 in. or 5 in.), but they are also used in combination with mid-range and high-range water reducers in higher slump concrete mixtures.

Mid-Range Water Reducers

Mid-range water reducers were first introduced in 1984 to bridge the gap between normal range water reducers and high-range water reducers (superplasticizers). These admixtures provide significant water reduction (between 6% and 12%) for concretes with slumps of 125 mm to 200 mm (5 in. to 8 in.) without the retardation associated with high dosages of conventional (normal) water reducers. Mid-range water reducers can be used to reduce stickiness and improve finishability, pumpability, and placeability of concretes containing silica fume and other supplementary cementing materials. Some can also entrain air and be used in low slump concretes (Nmai, Schlagbaum, and Violetta 1998).

High-Range Water Reducers

High-range water reducers, ASTM C494 (AASHTO M 194) Types F (water reducing) and G (water reducing and retarding), can be used to impart properties induced

by regular water reducers, only much more efficiently. They can greatly reduce water demand and cement contents and make low water-cement ratio, high-strength concrete with normal or enhanced workability and to generate slumps greater than 150 mm (6 in.). A water reduction of 12% to 40% can be obtained using these admixtures. The reduced water content and water-cement ratio can produce concretes with: (1) ultimate compressive strengths in excess of 70 MPa (10,000 psi), (2) increased early strength gain, (3) reduced chloride-ion penetration, and (4) other beneficial properties associated with low water-cement ratio concrete.



Figure 7-7. High-range water reducers, also known as superplasticizers, produce flowing concrete with slumps greater than 150 mm (6 in.).

When the same chemicals used for high-range water reducers are used to make flowing concrete, they are often called plasticizers or superplasticizers meeting ASTM C1017. This specification has provisions for two types of admixtures: Type 1 – plasticizing, and Type 2 – plasticizing and retarding. These admixtures are added to concrete with a low-to-normal slump and water-cement ratio to make high-slump flowing concrete (Figures 7-6 and 7-7). Flowing concrete is a highly fluid but workable concrete that can be placed with little or no vibration or compaction while still remaining essentially free of excessive bleeding or segregation. Applications where flowing concrete is used include: (1) thin-section placements (Figure 7-8), (2) areas of closely spaced and congested reinforcing steel (Figure 7-9), (3) tremie pipe (underwater) placements, (4) pumped concrete to reduce pump pressure, thereby increasing lift and distance capacity, (5) areas where conventional consolidation methods are impractical or can not be used, and (6) for reducing handling costs. The addition of a plasticizer to a 75-mm (3-in.) slump concrete can easily produce a concrete with a 230-mm (9-in.) slump. Flowing concrete is defined by ASTM C1017 as a concrete having a slump greater than 190 mm (7.5 in.), yet maintaining cohesive properties.



Figure 7-8. Plasticized, flowing concrete is easily placed in thin sections such as this bonded overlay that is not much thicker than 1.5 diameters of a quarter (shown).



Figure 7-9. Flowable concrete with a high slump (top) is easily placed (middle), even in areas of heavy reinforcing steel congestion (bottom).

Composition of Water-Reducing Admixtures

The classifications and components of water reducers are listed in Table 7-1. The chemistry of water-reducing or superplasticizing admixtures falls into broad categories: lignosulfonates, hydroxycarboxylic acid, hydroxylated polymers, salts of melamine formaldehyde sulfonates or naphthalene formaldehyde sulfonic acids, and polycarboxylates. The use of organic materials to reduce the water content or increase the fluidity of concrete dates back to the 1930s. The most recent breakthrough in this technology is the development of high-range water-reducers based on polycarboxylates – which occurred in the late 1980s.

Mechanisms of Water Reducers

Water reducers and plasticizers function as cement dispersants primarily through electrostatic and steric repulsive forces. Acidic groups within the polymer neutralize the surface charges on the cement particles (Ramachandran 1998 and Collepardi and Valente 2006). These groups bind to positive ions on the cement particle surfaces. These ions attach the polymer and give the cement a slight negative charge as well as create a layer on the surface. This negative charge and layer of adsorbed compounds create a combination of electrostatic and steric repulsion forces between individual cement particles, dispersing them,

thus releasing the water tied up in agglomerations and reducing the viscosity of the paste and concrete (Figures 7-10 and 7-11). A melamine-based, naphthalene-based, or lignin-based superplasticizer uses a molecule that has a size of about 1 to 2 nm. The effect of the water reducer depends on the dosage level, sequence of addition, and molecular weight. The water reducer will also contribute to dispersion by repelling negatively charged aggregate particles and air-entrained bubbles. The electrostatic repulsion for these materials is affected far more by dissolved ions (as compared to polycarboxylates) and rapidly diminishes as the hydrating cement releases more ions into the mixture.

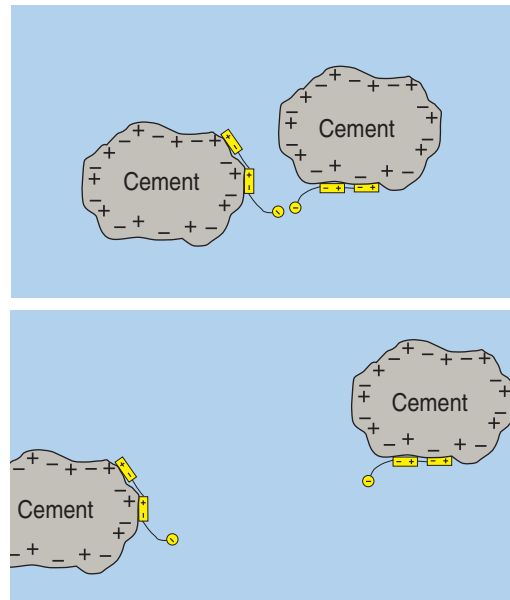


Figure 7-10. Mechanism of dispersive action of water-reducing admixtures (Thomas and Wilson 2002).

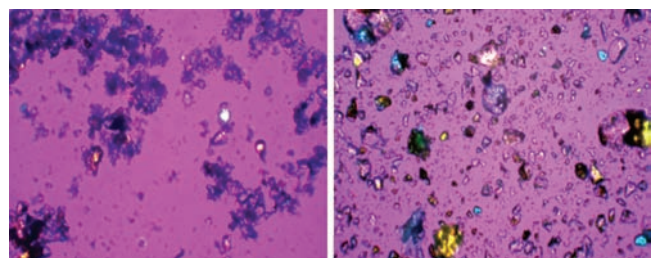


Figure 7-11. Dispersive action of water-reducing admixtures.

Polycarboxylate Technology. Polycarboxylate derivatives are the newest generation of high-range water reducers and superplasticizers. These polymers are comprised of a main carbon chain with carboxylate groups and polyethylene oxide (PEO) side chains. The number of carboxylate groups and the number and length of PEO side chains can be adjusted to change the properties of the plasticizer. The PEO side chains extend out from the cement particles and add the mechanism of steric hindrance to the typical electrostatic repulsion (Li and others 2005 and Nawa 2006).

The mechanism of steric hindrance is illustrated in Figure 7-12 (a-d). As with typical superplasticizers, the water reducer is dissolved in water, and the polar chain is absorbed at the solid-water interface (A). The long side chains physically help hold the cement grains apart allowing water to totally surround the cement grains (steric hindrance) (B). Additionally, the polar chain imparts a slight negative charge causing the cement grains to repel one another (electrostatic repulsion) (C). As the electrostatic repulsion dispersing effect wears off due to cement hydration, the long side chains still physically keep the cement dispersed (D).

The PEO chains prevent particles from agglomerating through physical separations on the order of 10 nm (Nawa 2006). This physical separation is still great enough to allow fluid to flow between the particles. This inhibition of agglomeration disperses the cement particles and allows the concrete to flow more easily. Because steric

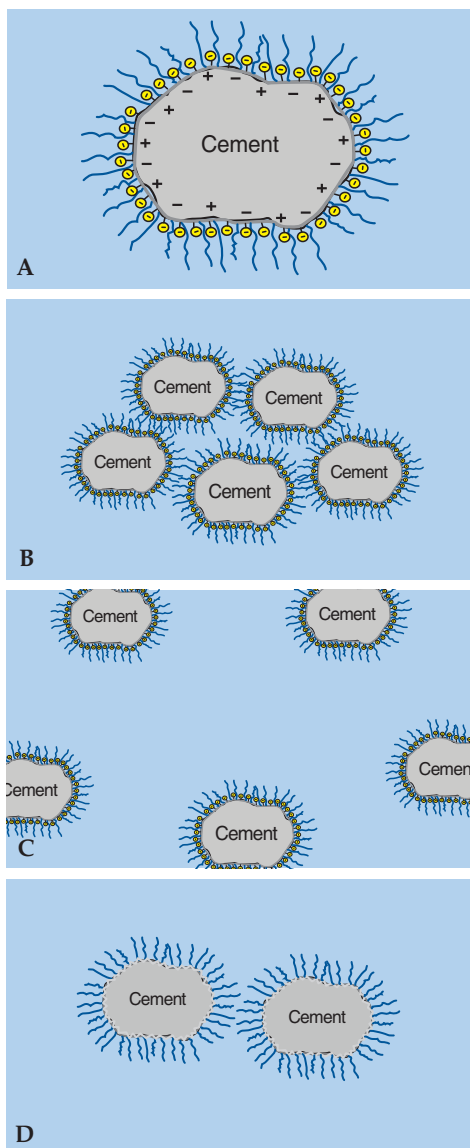


Figure 7-12. Mechanism of steric hindrance of polycarboxylate water-reducing admixtures (Thomas and Wilson 2002).

hindrance is a physical mechanism, it is not as sensitive to dissolved ions as an electrostatic repulsion mechanism. Concrete mixtures with polycarboxylate additions tend to retain fluidity for longer periods and they tend to require less water than concrete mixtures using other water reducers (Jeknavorian and others 1997). Polycarboxylate admixtures are commonly used in self-consolidating concrete (see Chapter 19 and Szecsy and Mohler 2009 for more information on self-consolidating concrete.)

Impact of Water Reducers on Properties of Concrete

Adding a water-reducing admixture to concrete without also reducing the water content can produce a mixture with a higher slump. The rate of slump loss, however, is not reduced and in most cases is increased (Figures 7-13 and 7-14), with the exception of polycarboxylate technology. Rapid slump loss results in reduced workability and less time to place concrete.

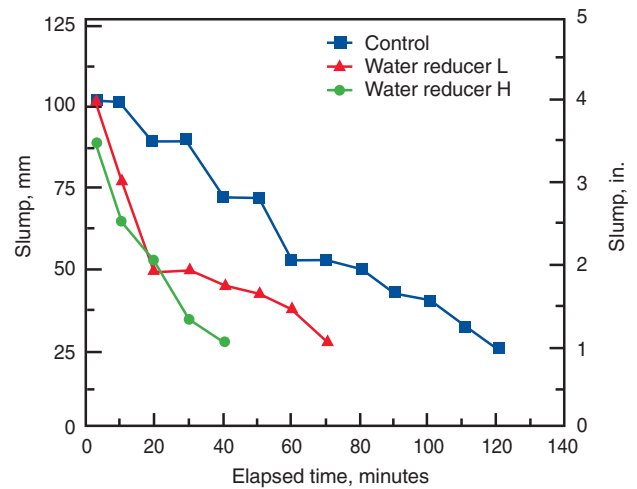


Figure 7-13. Slump loss at 23°C (73°F) in concretes containing conventional water reducers (ASTM C494 and AASHTO M 194 Type D) compared with a control mixture (Whiting and Dziedzic 1992).

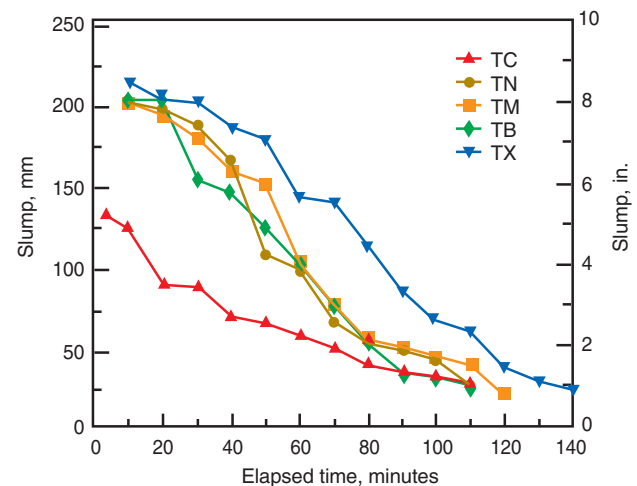


Figure 7-14. Slump loss at 32°C (90°F) in concretes with high-range water reducers (TN, TM, TB, and TX) compared with control mixture (TC) (Whiting and Dziedzic 1992).

High-range water reducers are generally more effective than regular water-reducing admixtures in producing workable concrete. The effect of certain plasticizers in increasing workability or making flowing concrete is short-lived, 30 to 60 minutes. This period is followed by a rapid loss in workability or slump loss. High temperatures can also aggravate slump loss. Due to their propensity for slump loss, these admixtures are sometimes added to the concrete mixer at the jobsite. They are available in liquid and powder form. Extended-slump-life plasticizers added at the batch plant help reduce slump-loss problems.

An increase in strength is generally obtained with water-reducing admixtures as the water-cement ratio is reduced. For concretes of equal cement content, air content, and slump, the 28-day strength of a water-reduced concrete containing a water reducer can be 10% to 25% greater than concrete without the admixture. Using a water reducer to reduce the cement and water content of a concrete mixture, while maintaining a constant water-cement ratio, can result in equal or reduced compressive strength, and can increase slump loss by a factor of two or more (Whiting and Dziedzic 1992).

Water reducers decrease, increase, or have no effect on bleeding, depending on the chemical composition of the admixture. A significant reduction of bleeding can result with large reductions of water content; this can result in finishing difficulties on flat surfaces when rapid drying conditions are present (see Chapter 16). Tests have shown that some plasticized concretes bleed more than control concretes of equal water-cement ratio (Figure 7-15); but plasticized concretes bleed significantly less than control concretes of equally high slump and higher water content.

Despite reduction in water content, water-reducing admixtures may cause increases in drying shrinkage. Usually the effect of the water reducer on drying shrinkage is small when compared to other more significant factors that affect shrinkage cracking in concrete. High-slump, low-water-

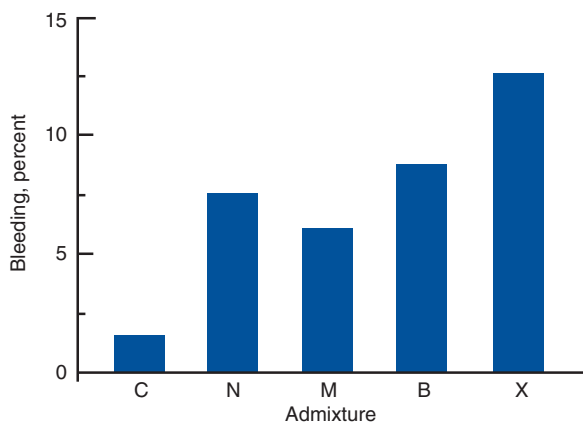


Figure 7-15. Bleeding of flowing concretes with plasticizers (N, M, B, and X) compared to control (C) (Whiting and Dziedzic 1992).

content, plasticized concrete tends to develop less drying shrinkage than a high-slump, high-water-content conventional concrete. However, high slump plasticized concrete has similar or higher drying shrinkage than conventional low-slump, low-water-content concrete (Whiting 1979, Gebler 1982, and Whiting and Dziedzic 1992).

Water reducers can be modified to give varying degrees of retardation while others do not significantly affect the setting time. ASTM C494 (AASHTO M 194) Type A water reducers can have little effect on setting time at their typical dosages, while Type D admixtures provide water reduction with retardation, and Type E admixtures provide water reduction with accelerated setting. Type D water-reducing admixtures usually retard the setting time of concrete from one to four hours (Figure 7-16). Some water reducers meet the requirements of more than one category depending on the dosage rate. For example, a Type A water reducer may perform as a Type D water reducing and set retarding admixture as the dosage rate is increased. Setting time may be accelerated or retarded based on each admixture's chemistry, dosage rate, and interaction with other admixtures and cementing materials in the concrete mixture.

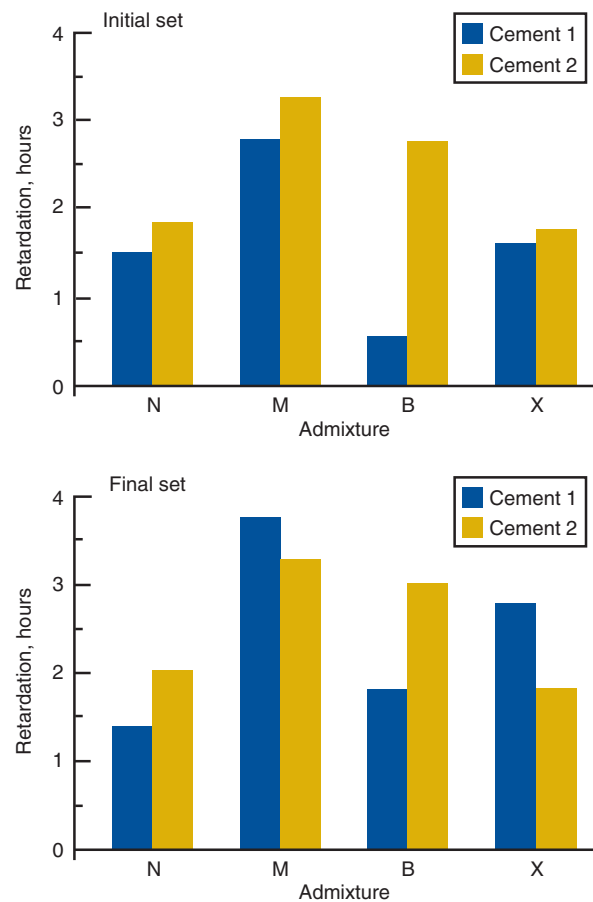


Figure 7-16. Retardation of set in cement-reduced mixtures relative to control mixture. Concretes L and H contain conventional water reducer, concretes N, M, B, and X contain high-range water reducer (Whiting and Dziedzic 1992).

Some water-reducing admixtures may also entrain some air in concrete. Lignin-based admixtures can increase air contents by 1% to 2%. Concretes with water reducers generally have good air retention. Concretes with high-range water reducers or plasticized flowing concrete can have larger entrained air voids and higher void-spacing factors than normal air-entrained concrete. Air loss can also be significant when compared to concretes without high range water reducers held at constant water-cement ratios (reduced cement and water contents) (Table 7-3). Some research has indicated poor frost- and deicer-scaling resistance for some flowing concretes when exposed to a continuously moist environment without the benefit of a drying period (Whiting and Dziedzic 1992). However, laboratory tests have shown that concretes with a moderate slump using high-range water reducers have good freeze-thaw durability, even with slightly higher void-spacing factors. This may be the result of the lower water-cement ratios often associated with these concretes.

Table 7-3. Loss of Air from Cement Reduced Concrete Mixtures

Mixture	Initial air content, %*	Final air content, %†	Percent air retained	Rate of air loss, %/minute
C Control	5.4	3.0	56	0.020
L } Water	7.0	4.7	67	0.038
H } reducer	6.2	4.6	74	0.040
N } High-range	6.8	4.8	71	0.040
M } water	6.4	3.8	59	0.065
B } reducer	6.8	5.6	82	0.048
X }	6.6	5.0	76	0.027

* Represents air content measured after addition of admixture.

† Represents air content taken at point where slump falls below 25 mm (1 in.).

(Whiting and Dziedzic 1992)

The effectiveness of water reducers on concrete is a function of their chemical composition, concrete temperature, cement composition and fineness, cement content, and the presence of other admixtures.

See Whiting and Dziedzic (1992) for more information on the effects of water reducers on concrete properties.

Set Retarding Admixtures

Set retarding admixtures are used to delay the rate of setting of concrete. Retarders are sometimes used to: (1) offset the accelerating effect of hot weather on the setting of concrete (see Chapter 16); (2) delay the initial set of concrete or grout when difficult or unusual conditions of placement occur, such as placing concrete in large piers and foundations, cementing oil wells, or pumping grout or concrete over considerable distances; (3) delay the set for special finishing techniques, such as an exposed aggregate surface, or anticipating long transport time or delays between batching and placement.

A set retarder extends the period during which concrete remains plastic. This allows a large placement to be completed before setting occurs, which helps eliminates cold joints in large or complex pours and extends the time allowed for finishing and joint preparation. The reduced hydration rate is also helpful in reducing early temperature rises, which can induce internal stresses and cracking in concrete.

Types of Set Retarding Admixtures

The classifications and components of set retarders are listed in Table 7-1. Compounds used as set retarders fall into four general categories: lignosulfonates, hydroxy-carboxylic acids, sugars and their derivatives, and selected inorganic salts.

Mechanism of Set Retarders

Set retarders function by slowing the normal cement hydration through complex processes such as inhibiting the growth of certain crystalline hydration products (nucleation). Earlier research has suggested the formation of a shell of initial hydration products, which diminishes the access of water to the inner anhydrous cement surfaces. For example, lignosulfonate molecules can adsorb to the surface of calcium silicates and calcium aluminates and form a coating that slows down the dissolution of calcium from the anhydrous grains. This in turn retards the formation of the hydration products, C-S-H and ettringite, which are discussed in Chapter 3. Eventually, osmotic rupturing of the coating allows the silicates and aluminates to resume hydration.

Effects of Set Retarders on Concrete Properties

The use of a set retarding admixture delays both the initial and final set of concrete. The extent of the delay is dependent on admixture composition, dosage, time of addition, and the temperature of the concrete. Retarders do not decrease the initial temperature of concrete. The effectiveness of a set retarder can also depend when it is added to the concrete mixture.

The amount of water reduction for an ASTM C494 (AASHTO M 194) Type B retarding admixture is normally less than that obtained with a Type A water reducer. Type D admixtures provide both water reduction and retardation.

In general, some reduction in strength at early ages (one to three days) accompanies the use of retarders. However, increased long-term strength may result from retarding the initial rate of hydration. Excessive addition rates of a retarding admixture may permanently inhibit the hydration of the cement.

The effects of these materials on the other properties of concrete, such as shrinkage, may be unpredictable. The incorporation of retarders can affect some of the other properties of concrete including slump, bleeding, and

early-age strength development. Therefore, acceptance tests of retarders should be made with actual job materials under anticipated job conditions.

Set Accelerating Admixtures

A set accelerating admixture is used to accelerate the rate of hydration (setting) and strength development of concrete at an early age. The strength development of concrete can also be accelerated by other methods: (1) using Type III or Type HE high-early-strength cement, (2) lowering the water-cement ratio by adding 60 kg/m³ to 120 kg/m³ (100 lb/yd³ to 200 lb/yd³) of additional cement to the concrete, (3) using a water reducer (provided it does not contribute significantly to set retardation), or (4) curing at higher temperatures. Accelerators are designated as Type C admixtures under ASTM C494 (AASHTO M 194).

Types of Set Accelerating Admixtures

Calcium chloride (CaCl₂) is the most common material used in set accelerating admixtures, especially for non-reinforced concrete. It should conform to the requirements of ASTM D98 (AASHTO M 144), *Standard Specification for Calcium Chloride*, and should be sampled and tested in accordance with ASTM D345, *Standard Test Method for Sampling and Testing Calcium Chloride for Roads and Structural Applications*.

Calcium chloride is highly effective in this role; however, it is limited to a dosage of 2% or less (by mass of cement) for non-reinforced concrete. Specifications may restrict its use in concrete as chlorides will accelerate corrosion of the reinforcing steel. Calcium chloride is generally available in three forms – as flake, pellets, or in solution.

The amount of calcium chloride added to concrete should be no more than is necessary to produce the desired results and in no case should be permitted to exceed 2% by mass of cementing material. When calculating the chloride content of commercially available calcium chloride, it can be assumed that regular flake contains a minimum of 77% CaCl₂; and concentrated flake, pellet, or granular forms contain a minimum of 94% CaCl₂.

A more appropriate accelerator for reinforced concrete is a non-chloride containing accelerator. These include organic compounds such as triethanolamine (TEA) and inorganic salts such as sodium and calcium salts of formate, nitrate, and nitrite (see Table 7-1). The inorganic salts tend to be less effective than calcium chloride and are used at higher dosages. TEA is not generally used on its own as an accelerating admixture, but is often used in other chemical admixtures such as normal and mid-range water reducers. There it acts as a set balancer to compensate for possible retarding effects. Certain non-chloride set accelerators are specially formulated for use in cold weather applications with ambient temperatures down to -7°C (20°F).

Mechanism of Set Accelerating Admixtures

Calcium chloride and calcium or alkali salts catalyze the hydration of the calcium silicates by weakening the barrier of initial hydration products that may form on the cement surface. In contrast to those inorganic salts, TEA, acts on the C₃A component of the cement accelerating its reaction with gypsum and the production of ettringite and also promoting the subsequent conversion to monosulfate (see Chapter 3). At high dosage levels, TEA may cause flash set to occur. It can also retard, even permanently, the hydration of C₃S leading to reduced long-term strength. Calcium formate, another organic compound, works by accelerating the hydration of C₃S.

Effects of Set Accelerators on Concrete Properties

Set accelerators cause a reduction in the time to both the initial and final set, the effect generally increasing with admixture dosage. There will also typically be an increase in the early-age strength development dependant on the admixture dosage, composition, and time of addition. The increase in strength due to the addition of calcium chloride is particularly noticeable at low temperatures and early ages.

The widespread use of calcium chloride as an accelerating admixture has provided much data and experience on the effect of this chemical on the properties of concrete. Besides accelerating strength gain, calcium chloride causes an increase in potential reinforcement corrosion and may lead to discoloration (a darkening of concrete). The incorporation of calcium chloride can also affect other properties of concrete including shrinkage, long-term strength and resistance to freezing and thawing, sulfates, and ASR.

An overdose of calcium chloride can result in placement problems and can be detrimental to concrete. It may cause: rapid stiffening, a large increase in drying shrinkage, corrosion of reinforcement, and loss of strength at later ages (Abrams 1924 and Lackey 1992).

Applications where calcium chloride should be used with caution:

1. Concrete reinforced with steel
2. Concrete subjected to steam curing
3. Concrete containing embedded dissimilar metals, especially if electrically connected to steel reinforcement
4. Concrete slabs supported on permanent galvanized-steel forms
5. Colored concrete

Calcium chloride or admixtures containing soluble chlorides should not be used in the following:

1. Construction of parking garages

2. Prestressed concrete because of possible steel corrosion hazards
3. Concrete containing embedded aluminum (for example, conduit) since serious corrosion of the aluminum can result, especially if the aluminum is in contact with embedded steel and the concrete is in a humid environment
4. Concrete containing aggregates that, under standard test conditions, have been shown to be potentially deleteriously reactive
5. Concrete exposed to soil or water containing sulfates
6. Floor slabs intended to receive dry-shake metallic finishes
7. Hot weather
8. Massive concrete placements

The maximum chloride-ion content for corrosion protection of prestressed and reinforced concrete as recommended by the ACI 318 building code is presented in **Chapter 11**. Resistance to the corrosion of embedded steel is further improved with an increase in the depth of concrete cover over reinforcing steel, and a lower water-cement ratio. Stark (1989) demonstrated that concretes made with 1% $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ by mass of cement developed active steel corrosion when stored continuously in fog. When 2% $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ was used, active corrosion was detected in concrete stored in a fog room at 100% relative humidity. Risk of corrosion was greatly reduced at a lower relative humidity (50%). Gaynor (1998) demonstrates how to calculate the chloride content of fresh concrete and compare it with recommended limits.

Calcium chloride is not an antifreeze agent. When used in allowable amounts, it will not reduce the freezing point of concrete by more than a few degrees. Attempts to protect concrete from freezing by this method are not effective. Instead, proven reliable precautions should be taken during cold weather (see **Chapter 14**).

Calcium chloride should be added to the concrete mixture in solution form as part of the mixing water. If added to the concrete in dry flake form, all of the dry particles may not completely dissolve during mixing. Undissolved lumps in the mixture can cause popouts or dark spots in the hardened concrete.

Hydration-Control Admixtures

Hydration controlling admixtures became available in the late 1980s. They consist of a two-part chemical system: (1) a stabilizer or retarder that essentially stops the hydration of cementing materials, and (2) an activator that reestablishes normal hydration and setting once added to the stabilized concrete. The stabilizer can suspend hydration for

extended periods (for example, 72 hours). A set activator is added to the mixture just before the concrete is ready for use. These admixtures make it possible to reuse concrete returned in a ready-mix truck by suspending setting overnight. The admixture is also useful in maintaining concrete in a stabilized non-hardened state during long hauls. The concrete is reactivated when it arrives at the project. This admixture presently does not have a standard specification (Kinney 1989).

Workability-Retaining Admixtures

Workability retaining admixtures provide varying degrees of workability retention without affecting the initial set of concrete or early-age strength development, as is the case with retarding admixtures. These admixtures can be used with mid-range or high-range water reducers to provide desired levels of workability retention in moderate to high slump concrete mixtures, including self-consolidating concrete (SCC). Their main benefit is reducing the need for slump adjustments prior to concrete placement, thus helping to maintain consistency in concrete performance throughout a project. Workability-retaining admixtures should meet the requirements of ASTM C494/C494M, Type S.

Corrosion Inhibitors

Corrosion inhibitors are chemical admixtures that are added to concrete to limit the corrosion of steel reinforcement. Corrosion inhibitors are used in concrete for parking structures, marine structures, and bridges where chloride salts are present. Chlorides can cause corrosion of steel reinforcement in concrete (Figure 7-17).



Figure 7-17. The damage to this concrete parking structure resulted from chloride-induced corrosion of steel reinforcement.

Commercially available corrosion inhibitors include: calcium nitrite, sodium nitrite, dimethyl ethanolamine, amines, phosphates, and ester amines as listed in Table 7-1.

Corrosion-inhibiting admixtures chemically arrest the corrosion reaction and reinstate the passive layer, which provides protection to the steel. When calcium nitrite is used as an admixture, nitrite anions are in solution with hydroxyl and chloride ions. The nitrite-ions cause the ferric oxide of the passivation layer around the steel reinforcement to become more stable. This ferric oxide film is created by the high pH environment in concrete. In effect, the chloride-ions are prevented from penetrating the passive film and making contact with the steel. A certain amount of nitrite can stop corrosion up to some level of chloride-ion. Therefore, increased chloride levels require increased levels of nitrite to stop corrosion.

Organic inhibitors, based on a combination of amines and esters in a water medium, act in two ways. First, the esters provide some water repellency (see section on PRAN-type permeability reducing admixtures), thereby restricting the ingress of water soluble chlorides. Second, the amines adsorb onto the steel surface forming a tight film which repels moisture and acts as a barrier to chemical attack. The result of this dual action is an increase in the time to corrosion initiation and a decrease in the rate of corrosion once it has started.

Cathodic inhibitors react with the steel surface to interfere with the reduction of oxygen. The reduction of oxygen is the principal cathodic reaction in alkaline environments (Berke and Weil 1994). Corrosion inhibitors should conform to ASTM C1582, *Standard Specification for Admixtures to Inhibit Chloride-Induced Corrosion of Reinforcing Steel in Concrete*.

Shrinkage-Reducing Admixtures

Shrinkage-reducing admixtures (SRAs), introduced in the 1980s, have potential uses in bridge decks, critical floor slabs, and buildings where cracks, curling, and warping must be minimized for durability or aesthetic reasons (Figure 7-18). As concrete dries, water is removed from the capillary pores and a meniscus is formed at the air interface due to surface tension. Surface tension forces also act on the solid phases and tend to draw the walls of the pore together. As the water meniscus recedes into smaller and smaller pores the surface tension forces increase, causing the concrete to shrink more. Shrinkage reducing admixtures reduce the surface tension of the liquid phase, which reduces the forces exerted on the pore walls thereby producing less drying shrinkage.

Propylene glycol and polyoxyalkylene alkyl ether have been used as shrinkage reducers. Drying shrinkage reductions between 25% and 50% have been demonstrated in laboratory tests. These admixtures have negligible effects on slump, but can impact air content and may possibly require an increase in the dose of air-entraining admixture to achieve a target air content. A delay in time of set and

slower bleed rate may also result from the use of SRAs. They are generally compatible with other admixtures (Nmai and others 1998 and Shah, Weiss, and Yang 1998). The manufacturer's recommendations should be followed, particularly when used in air-entrained concrete. Due to their potential effects on bleeding and setting time, caution and proper planning are required when SRAs are used in slabs that receive a hard-trowelled finish. Premature finishing of a SRA-treated concrete slab can trap bleed-water and, subsequently, lead to delamination of the concrete surface. Because of their effectiveness in reducing drying shrinkage, SRAs are also generally effective in reducing curling and cracking in slabs. SRAs should meet the requirements of ASTM C 494/C 494M, Type S.



Figure 7-18. Shrinkage cracks, such as shown on this bridge deck, can be reduced with the use of good concreting practices and shrinkage reducing admixtures.

Permeability Reducing Admixtures

The ingress of water and water borne chemicals into concrete can have many undesirable effects; including damp, leaking structures, corrosion of steel reinforcement, and concrete deterioration. Water can enter concrete through two primary mechanisms; capillary absorption under non-hydrostatic conditions (often referred to as wicking) and the direct ingress of water under pressure. Technically, the term permeability only refers to concrete exposed to water under pressure. However, permeability is often used informally to describe any passage of water through concrete, whether by pressure driven ingress or by wicking.

Considering these two mechanisms of water ingress, permeability reducing admixtures (PRAs) can be divided into two categories; Permeability Reducing Admixture – Non-Hydrostatic (PRAN) and Permeability Reducing Admixtures – Hydrostatic (PRAH) (ACI 212.3R-10).

Permeability Reducing Admixture – Non-Hydrostatic (PRAN)

Permeability reducing admixtures that are non-hydrostatic (PRAN) have traditionally been referred to as “damp-proofers”. Most PRANs are hydrophobic in

nature. PRANs give concrete a water repellent property and they provide reduced absorption (wicking). Common materials include soaps such as stearates and other long chain fatty acids, or their derivatives, as well as petroleum products. These PRANs are sometimes used to reduce the transmission of moisture through concrete in contact with water or damp soil. However, hydrophobic admixtures are usually not effective when the concrete is in contact with water under pressure. Some PRANs contain finely divided solids such as bentonite or siliceous powders that restrict water absorption. Often referred to as “densifiers”, finely divided solids may reduce permeability slightly, although the effect is relatively small. In practice, fine solid fillers are usually used for non-hydrostatic applications similar to hydrophobic admixtures.

Permeability Reducing Admixtures – Hydrostatic (PRAH)

Hydrostatic permeability reducing admixtures (PRAH) have often been referred to as “waterproofers”, although permeability reducing admixture for hydrostatic conditions is a more technically correct term. PRAHs contain materials that act to block the pores and capillaries in concrete. These materials have been shown to be effective in reducing permeability to water under pressure. They have also been shown to reduce concrete corrosion in chemically aggressive environments. Products usually consist of hydrophilic crystalline materials that react in concrete to produce pore blocking deposits, or polymeric materials that coalesce in the concrete’s pores. Reactive PRAHs have also been shown to increase the autogenous sealing of leaking, hairline cracks.

Additional Considerations

Permeability reducing admixtures will not correct for a poorly designed concrete mixture. Proper proportioning, placement, and curing are needed for effective performance from a PRA. Concrete joints should be treated with a suitable waterstop. Also, the selection of a PRA must take into account the expected service conditions as well as the features of the admixture (PRAN or PRAH). PRANs are usually evaluated using an absorption based test method such as ASTM C1585, *Standard Test Method for Measurement of Rate of Absorption of Water by Hydraulic-Cement Concretes*. PRAHs are best evaluated using a pressure driven penetration test such as the U.S. Army Corp of Engineers CRC C48-92, *Standard Test Method for Water Permeability of Concrete*, or the European standard BS EN 12390-8, *Testing Hardened Concrete – Depth of Penetration of Water under Pressure*. PRAs are discussed in detail in ACI 212.3R-10, *Report on Chemical Admixtures for Concrete*.

Alkali-Aggregate Reactivity Inhibitors

In the 1950s, McCoy and Caldwell discovered that lithium based compounds when used in sufficient quantity were capable of inhibiting damage due to alkali-silica reactivity (ASR).

The use of lithium nitrate, lithium carbonate, lithium hydroxide, lithium aluminum silicate (decrepitated spodumene), and barium salts have shown reductions of alkali-silica reaction (ASR) in laboratory tests (Figure 7-19) (Thomas and Stokes 1999 and AASHTO 2001). Some of these materials may have potential for use as an additive to cement (Gajda 1996).

As discussed in Chapter 11, ASR gel has a great capacity to absorb moisture from within the concrete pores. This can cause a volumetric expansion of the gel, which in turn leads to the build up of internal stresses and the eventual disruption of the cement paste surrounding the aggregate particle. If lithium nitrate is used as an admixture, the pore solution will contain lithium and nitrate ions in addition to sodium, potassium, and hydroxyl ions. Likewise the reaction product (ASR gel) that forms will also contain appreciable quantities of lithium. The reduction in ASR by lithium salts appears to result from an exchange of the lithium ion with sodium and potassium. The resulting lithium-bearing reaction product does not have the same propensity to absorb water and expand.

There has been considerable research in the last 20 years in the use of lithium to combat ASR in concrete – including a major study conducted under the support of the Federal Highway Administration (Thomas and others 2007). Alkali-aggregate reactivity inhibitors should meet the requirements of ASTM C494/C494M, Type S.

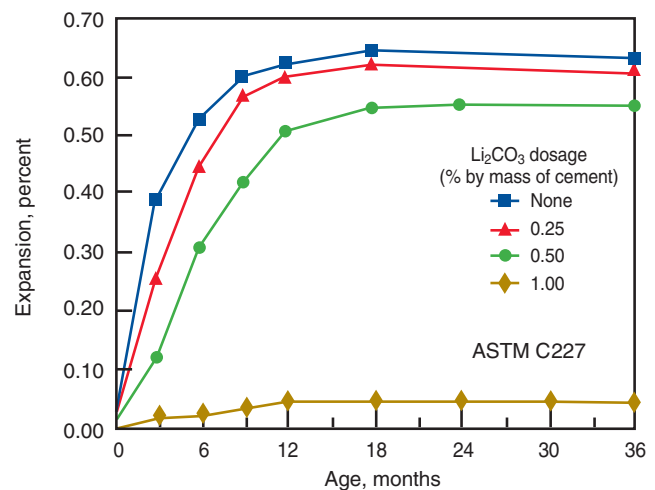


Figure 7-19. Expansion of specimens made with lithium carbonate admixture (Stark 1992).

Coloring Admixtures (Pigments)

Natural and synthetic materials are used to color concrete for aesthetic and safety reasons (Figure 7-20). Pigments used in amounts less than 6% generally do not affect concrete properties. Unmodified carbon black substantially reduces air content. Most carbon black for coloring



Figure 7-20. Red and blue pigments were used to color this terrazzo floor.

concrete contains an admixture to offset this effect on air. Generally, the amount of pigments used in concrete should not exceed 10% by weight of the cement.

Before a coloring admixture is used on a project, it should be tested for color fastness in direct sunlight and autoclaving, chemical stability in cement, and effects on concrete properties. To avoid color distortions, calcium chloride should not be used with pigments. Pigments should conform to ASTM C979, *Standard Specification for Pigments for Integrally Colored Concrete*.

Pumping Aids

Pumping aids are added to concrete mixtures to improve pumpability. Pumping aids are not a cure-all; they are best used to make marginally pumpable concrete more pumpable. These admixtures increase viscosity or cohesion in concrete to reduce dewatering of the paste while under pressure from the pump.

Some pumping aids may increase water demand, reduce compressive strength, cause air entrainment, or retard setting time. These side effects can be corrected by adjusting the mixture proportions or by adding another admixture to offset the side effect.

A partial list of materials used in pumping aids is given in Table 7-1. Some admixtures that serve other primary purposes but also improve pumpability are air-entraining admixtures and some water-reducing and retarding admixtures.

Bonding Admixtures and Bonding Agents

Bonding admixtures are usually water emulsions of organic materials including rubber, polyvinyl chloride, polyvinyl acetate, acrylics, styrene butadiene copolymers, and other polymers. They are added to portland cement mixtures to increase the bond strength between old and

new concrete. Flexural strength and resistance to chloride-ion ingress are also improved. They are added in proportions equivalent to 5% to 20% by mass of the cementing materials; the actual quantity depending on job conditions and type of admixture used. Some bonding admixtures may increase the air content of mixtures. Non-reemulsifiable types are resistant to water and are better suited to exterior applications and in applications where moisture is present.

A bonding admixture is only as good as the surface to which the concrete is applied. The surface must be dry, clean, sound, free of dirt, dust, paint, and grease, and at the proper temperature. Organic or polymer-modified concretes are acceptable for patching and thin-bonded overlayment, particularly where feather-edged patches are desired.

Bonding agents should not be confused with bonding admixtures. Admixtures are an ingredient in the concrete; bonding agents are applied to existing concrete surfaces immediately before the new concrete is placed. Bonding agents help “glue” the existing and the new materials together. Bonding agents are often used in restoration and repair work; they consist of portland cement or latex-modified portland cement grout or polymers such as epoxy resins (ASTM C881, *Standard Specification for Epoxy-Resin-Base Bonding Systems for Concrete*, or AASHTO M 235, *Standard Specification for Epoxy Resin Adhesives*) or latex (ASTM C1059, *Standard Specification for Latex Agents for Bonding Fresh to Hardened Concrete*).

Grouting Admixtures

Portland cement grouts are used for a variety of purposes: to stabilize foundations, set machine bases, fill cracks and joints in concrete work, cement oil wells, fill cores of masonry walls, grout prestressing tendons and anchor bolts, and fill the voids in preplaced aggregate concrete. To alter the properties of grout for specific applications, various air-entraining admixtures, accelerators, retarders, and nonshrink admixtures are often used.

Gas-Forming Admixtures

Aluminum powder and other gas-forming materials are sometimes added to concrete and grout in very small quantities. These materials cause a slight expansion of the mixture prior to hardening. This may be of benefit where the complete grouting of a confined space is essential, such as under machine bases or in post-tensioning ducts of prestressed concrete. These materials are also used in larger quantities to produce autoclaved cellular concretes. The amount of expansion that occurs is dependent upon the amount of gas-forming material used, the temperature of the fresh mixture, the alkali content of the cement, and

other variables. Where the amount of expansion is critical, careful testing through trial batching and jobsite control of mixtures and temperatures must be exercised. Gas-forming agents will not overcome shrinkage once hardening caused by drying or carbonation occurs.

Air Detrainers

Air-detraining admixtures reduce the air content in concrete. They are used when the air content cannot be reduced by adjusting the mixture proportions or by changing the dosage of the air-entraining admixture and other admixtures. Air-detrainers are rarely used and their effectiveness and dosage rate should be established on trial mixtures prior to use in actual job mixtures. Materials used in air-detraining agents are listed in Table 7-1.

Fungicidal, Germicidal, and Insecticidal Admixtures

Bacteria and fungal growth on concrete surfaces or in hardened concrete may be partially controlled through the use of fungicidal, germicidal, and insecticidal admixtures. The most effective materials are polyhalogenated phenols, diel-drin emulsions, and copper compounds. The effectiveness of these materials is generally temporary. In high dosages they may reduce the compressive strength of concrete.

Viscosity Modifying Admixtures

Another group of chemical admixtures important to self-consolidating concrete production is viscosity modifying admixtures (VMA). These are also used as antiwashout admixtures for concrete placed underwater. Antiwashout admixtures increase the cohesiveness of concrete to a level that allows limited exposure to water with little loss of cement paste. This cohesiveness allows placement of concrete in water and under water without the use of tremies. These admixtures increase the viscosity of water resulting in a mixture with increased thixotropy and resistance to segregation. VMAs usually consist of water soluble cellulose ethers, acrylic polymers, or high molecular weight biogums. Viscosity modifying admixtures should meet the requirements of ASTM C494/C494M, Type S.

The two basic types of VMAs include thickening type and binding type VMAs. The thickening type increases the viscosity through molecular obstruction. The technology is based on an addition of a large polymer molecule into the paste. Thickened paste then translates to increased cohesion of the mortar system and the concrete as a whole. The binding type of VMA is much more effective than the thickening type (Bury and Buehler 2002a). A binding type VMA chemically combines with water molecules, as opposed to just obstructing them. Binder VMAs are typically inorganic

materials that produce a gel. The gel promotes thixotropic behavior. In both types, the increase in viscosity may also be accompanied by an increase in yield stress. VMAs dampen the changes in viscosity potentially caused by material and process variations. However, VMAs should not be considered a substitute for good concrete quality control (EFNARC 2006).

VMAs can be used to replace fines or to supplement them. Trial batch evaluation, using the recommended dosage from the manufacturer as a starting point, is the best method to determine the appropriate use for each mixture. An increase in high-range water reducer dosage may be necessary when a VMA is used to counteract an increase in yield stress.

Compatibility of Admixtures and Cementitious Materials

Fresh concrete problems of varying degrees of severity are encountered as a result of cement-admixture incompatibility and incompatibility between admixtures. Incompatibility between supplementary cementing materials and admixtures or cements can also occur. Slump loss, air loss, early stiffening, and other factors affecting fresh concrete properties can result from incompatibilities. While these problems primarily affect the plastic-state performance of concrete, long-term hardened concrete performance may also be adversely affected. For example, early stiffening can cause difficulties with consolidation of concrete which may also compromise strength.

When incompatibility is encountered, it can often be solved by changing the admixture dosage rate or the sequence of addition to the mixture. However, some incompatibility issues may be solved by modifying the composition of the cement, particularly the C_3A , alkali or sulfate content; or modifying the composition of the admixture. In practice, changing the source of the cement or the admixture may be the most direct solution to achieving the desired performance.

Taylor and others (2006 and 2006a) have developed protocols for testing the compatibility of various combinations of materials. This preconstruction testing can reduce the likelihood of performance problems in the field. However, reliable test methods are not available to adequately address all incompatibility issues due to variations in materials, mixing equipment, mixing time, and environmental factors. When incompatibility is discovered in the field, a common solution is to simply change admixtures or cementing materials. For more information on incompatibility of cement and chemical admixtures refer to Taylor, Kosmatka, and Voight 2008, Helmuth and others 1995, Tagni-Hamou and Aitcin 1993, and Tang and Bhat-tacharja 1997.

Less-Than Expected Water Reduction

If the water reduction achieved using an admixture is less than expected based on previous experience with the same admixture, this may be caused by: the composition of the cementitious materials, the presence of other set-control admixtures, the temperature of the concrete, clay minerals in the aggregates, and the dose of the admixture itself.

Slump loss. High-range water reducers are only effective for a limited period before they are overwhelmed by the hydration products (particularly ettringite) in the very early stages of hydration. The rate of loss depends on: C_3A , SO_3 and alkalis, temperature, and fineness of cement and pozzolans.

Slump loss can often be offset by delaying the time of addition of the admixture. For example, a high-range water reducer is often added on site rather than during batching. Concrete batched from a remote location, such as in municipal paving projects that employ a stationary ready-mix source are a prime example.

Incompatibility between some high-range water-reducers and cementing materials can result in very rapid losses in workability, shortly after mixing. While this can often be attributed to the temperature of the concrete, the reactivity of the cement and the continuous availability of admixture to disperse the hydrating cement grains is a key factor.

Certain minerals found in various aggregate sources such as expansive clays, have been found to rapidly adsorb polycarboxylate-type superplasticizers, thus significantly reducing their effectiveness (Jeknavorian and others 2003).

Cement admixture compatibility, with regards to slump loss, can be examined in the laboratory by testing the flow properties of pastes. A suitable test (Tang and Bhattacharja 1997) is the mini-slump test. This test gives an indication of how long the plasticizing action of a high-range water reducer can be maintained.

Another test used for this purpose is the Marsh cone method (ASTM D6910 and API 13B-1). This test can also be used to gauge the saturation point for a particular cement/admixture combination. The saturation point is the level at which further admixture addition will no longer produce any benefit.

ASTM C1679, *Standard Practice for Measuring Hydration Kinetics of Hydraulic Cementitious Mixtures Using Isothermal Calorimetry*, may be another useful approach to evaluate the compatibility of cementitious mixtures containing chemical admixtures. Changes in the thermal power curve obtained from this practice may indicate changes in a material property.

Less-Than Expected Retardation

If the length of retardation is less than expected, this may be due to an increase in the C_3A content of the cement. Abnormally retarded set may be caused by: a low C_3A content or low cement reactivity, excessive admixture with retarding properties, high levels of SCMs, or low temperature. Testing an admixture over a range of addition rates can often identify a critical dosage above or below which unacceptable set performance can result.

Problems on site can be avoided by trial batching with the actual materials in environments that are as close as possible to field conditions.

The performance of concrete produced with cements of abnormally low C_3A and SO_3 content should be carefully observed when water-reducing or set retarding admixtures are used. Any changes in the alkali content of the cement should alert the concrete producer to potential changes in admixture performance.

Storing and Dispensing Chemical Admixtures

Liquid admixtures can be stored in barrels or bulk tankers. Powdered admixtures can be placed in special storage bins and some are available in premeasured plastic bags. Admixtures added to a truck mixer at the jobsite are often in plastic jugs or bags. Powdered admixtures, such as certain plasticizers, or an admixture drum or barrel may be stored at the project site.

Dispenser tanks at concrete plants should be properly labeled for specific admixtures to avoid contamination and avoid dosing the wrong admixture. Most liquid chemical admixtures should not be allowed to freeze; therefore, they should be stored in heated environments. Consult the admixture manufacturer for proper storage temperatures. Powdered admixtures are usually less sensitive to temperature restrictions, but may be sensitive to moisture.



Figure 7-21. Liquid admixture dispenser at a ready mix plant provides accurate volumetric measurement of admixtures.

Liquid chemical admixtures are usually dispensed individually in the batch water by volumetric means (Figure 7-21). Liquid and powdered admixtures can be measured by mass, but powdered admixtures should not be measured by volume. Care should be taken to keep certain admixtures separate before they are dispensed into the batch. Some combinations may neutralize the effects desired. Consult the admixture manufacturer concerning compatible admixture combinations or perform laboratory tests to document performance.

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