3

Chemical Admixtures

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3.1 Introduction to Chemical Admixtures

In recent decades, tremendous success has been achieved in the advancement of chemical admixtures for Portland cement concrete. Materials scientists, chemists, engineers, and manufacturers’ technical representatives have helped the concrete industry to improve our ability to control work times, workability, strength, and durability of Portland cement concrete. Most efforts have centered on improving the properties of concrete with minimal investments by ready-mix suppliers and contractors in the way of specialized equipment or special skills and education of their labor forces. This approach has resulted in construction cost reductions and universally accepted ready-made remedies for unexpected problems during construction.

The function of each admixture focuses on a specific need, and each has been developed independently of the others. Some admixtures already have chemistry that affects more than one property of concrete, and some have simply been combined for ease of addition during the batching process. Their definitions and specifications are discussed in the American Society for Testing and Materials (ASTM) C 494 and in the American Concrete Institute (ACI) Manual of Concrete Practice 212.3R and 212.4R. Retarders have been developed that allow for longer working times with minimal effect on the final cure strength. These retarders provide better finishing and higher quality concrete in the heat of the summer. Accelerators have been developed that initiate the cement hydration process much earlier in lower temperatures. Air-entraining agents were developed into commercial admixtures when it was observed that air entrainment...
improved the resistance of concrete to freezing and thawing. This is accomplished by the production of many well-distributed tiny bubbles that act as pressure-relief mechanisms in the matrix whenever water in the pores expands and contracts under freezing and near-freezing conditions.

Water reducers, or plasticizers, have allowed finishers to place and work the concrete with much less water and thus produce higher strengths and more durable concrete. High-range water reducers (HRWRs), or superplasticizers, were developed to adjust the plasticity of low-water concrete to a consistency that can easily be pumped up to higher elevations without compromising strength or durability. Later, organic polymers such as latex and epoxies were developed to modify the concrete matrix in such a way as to improve the bond of the cured concrete to a given substrate or to reduce permeability and internally reinforce the cured matrix. Often, a stronger matrix is also a result. Monomer systems have also been used to impregnate cured Portland cement concrete, filling the small pores, capillaries, and voids with a liquid that quickly hardens, leaving a less porous, higher modulus, and more chemical-resistant concrete.

All of these admixtures have been refined to provide concrete designers and builders with increasing options and greater adaptability to an expanding variety of applications and ambient conditions. It is estimated that one or more chemical admixtures, not including air-entraining agents, are present in 80% of the concrete placed today, and the figure rises to almost 100% when air-entraining agents are included (Whiting et al., 1994).

The most commercially important chemical admixtures are described in the ACI Manual of Concrete Practice (ACI Committee 212 on Admixtures for Concrete) and ASTM C 494 (Specifications for Chemical Admixtures for Concrete); in the Canadian Standards Association's admixture standards A 266.1, A 266.2 M78 (chemical admixtures), A 266.4 M78 (guidelines for the use of admixtures), 266.5 M 1981 (guidelines for use of HRWRs), and 266.6 M85 (HRWR requirements); and in the Reunion Internationale des Laboratoires d’Essais et de Recherches sur les Materiaux et les Constructions (RILEM) Guide for Use of Admixtures in Concrete. To better understand recommended usage for various applications of these chemical admixtures in concrete, a review of each functional category is presented. This review would be simpler if each of the admixtures worked independently in the matrix, but the performance of each is often affected by the presence of another. For this reason, known reactions and interactions are discussed wherever appropriate for specific materials.

### 3.2 Retarding Admixtures

Retarding admixtures are used to slow down the initial set of the concrete whenever elevated ambient temperatures shorten working times beyond the practical limitations of normal placement and finishing operations. Retarders are specified in ASTM C 494 as Type B admixtures and are used in varying proportions, often in combination with other admixtures, so that, as working temperatures increase, higher doses of the admixture may be used to obtain a uniform setting time (ACI 305R). Simple retarders typically consist of one of four relatively inexpensive materials: lignin, borax, sugars, or tartaric acids or salts. Retarders serve best to compensate for unwanted accelerations of working times due to changes in temperature or cement or due to other admixture side effects. They also are used to extend the working time required for complicated or high-volume placements and for retarding the set of concrete at a surface where an exposed aggregate finish is desired.

Retarding admixtures interfere with the critical chemical reactions of the fastest hydrating cement reactant groups, C₃A and C₃S (Collepardi, 1984). These reactants normally initiate the hydration process in the early stages. Eventually, the hydration process accelerates due to another initially slower reaction group, and the heat of reaction allows the hydration to continue at a normal rate until completion. Typical retardation effects are significant for the first 24 to 72 hours.

The intent is for concrete in its plastic state to be affected by retarders with little or no negative effect on the hardened properties. Improvements in fresh concrete properties include extended times for workability and set, better workability with less water, frequently an increase in air content, and minimal
delay in final cure time. Retarders may reduce critical physical properties when used in excess. Changes in hardened concrete properties due to retarders usually relate to delayed early strength development, which may affect early (especially plastic) shrinkage and creep (Daugherty and Kowalewski, 1976).

Dosage rates vary considerably depending on the needs of the concrete application, ambient and material temperatures, retarder type and concentration, cement type and content, and presence of other admixtures in the concrete, but it generally is best to use the least amount necessary to produce the required properties. This is typically between 2 and 7 fluid ounces per 100 pounds cement (ACI 211.1-4) added with a portion of the mixing water a few minutes after the first addition of water. This is recommended to ensure the most efficient and uniform dispersion throughout the batch (Figure 3.1). Manufacturers’ recommendations are a good place to start, but trial batches under the expected field conditions followed by a complete evaluation of effects on all critical properties should be conducted.

It should be noted that retardation may be a side effect of other chemical admixtures that are specified for the adjustment of other properties in the matrix. If the retardation effect is desirable and predictable, as in many water-reducing admixtures, the material is marketed as such (e.g., water-reducing and -retarding admixtures). Because users noticed that earlier water reducers tended to retard set times, today many retarders are meant to serve double duty as water reducers. This added functionality is discussed in the next section. If the retardation side effect is predictable but not desired, the simple addition of a compatible accelerator may be all that is necessary. If, however, the retardation side effect is not desired or predictable, an incompatibility may exist between the cement or other admixtures and the corrupting admixture (Dodson and Hayden, 1989; Johnston, 1987). Every effort must be made to determine the faulty ingredient and substitute it with a more compatible choice.

### 3.3 Water-Reducing Admixtures

Water-reducing agents, or plasticizers, are added to provide workability in the freshly mixed concrete matrix while using significantly lower amounts of mix water, thus achieving better strength and durability. These agents provide the lubricity in coarse mixes that would normally require additional paste or more water in the paste. According to ASTM C 494, these admixtures are classified as Type A and must allow at least a 5% reduction in water without changing the consistency or reducing the strength of the control batch having the higher water content without this admixture. They often are able to reduce the water demand by 10% and as much as 15% for even greater strength and durability benefits derived from lowering the water/cement ratio (Figure 3.2). This class of admixtures is typically made from relatively inexpensive lignosulfonates, hydroxylated carboxylic acids, or carbohydrates.
Several theories exist as to what mechanisms are responsible for the reduction in water demand in the plastic concrete matrix, but all agree that the improvement is mainly due to the chemical and physical effects of the water-reducing admixtures (WRAs) on the surface of the hydrating cement particles. Deflocculating and dispersion of the cement particles are the net result and allow better use of the available water for more uniform lubrication and hydration. Also, because many WRAs entrain as much as 2% air, increased lubricity is partly due to the distribution of tiny added air bubbles.

Many WRAs retard set times and are sometimes used with an accelerator for compensation. WRAs that are combined with an accelerator into one admixture are classified as Type E under ASTM C 494. Of course, retardation may be desired for higher temperature concreting conditions. Whenever the natural tendency of WRAs to retard hydration is not adequate for the desired application, additional retarders are added. Commercially available single admixtures that combine a retarder with the WRA are classified as Type D under ASTM C 494.

Many WRAs are associated with higher shrinkage rates and faster slump loss even though the water/cement ratio is reduced. Bleeding properties, too, are sometimes affected by the choice of WRA. To overcome these tendencies WRAs are often added at the batch plant along with much less of the more expensive, but more efficient, high-range (or mid-range) water reducers described in the next section.

Considerations for usage of WRAs are economically based, and strategies fall into the following three main categories (Collepardi, 1984):

1. Reduce the water/cement ratio for higher strengths and improved durability while maintaining the same workability and cement content.
2. Reduce the paste portion of the matrix, water, and cement, for the purpose of reducing shrinkage and heat development in massive placements; workability, strength, and durability are maintained at a comparative level.
3. Keep water and cement the same and maintain the same strength and durability but improve flow and workability.

Efficient dosage rates vary with chemical composition of the WRA, individual batch designs, cement types, other admixtures, environmental conditions (Kosmatka and Panarese, 1988), flow and workability constraints in the job, and end-product needs. Manufacturers’ guidelines typically recommend 2 to 7 fluid ounces per 100 pounds cement added into the mix water. These recommendations should be used as a starting place for several trial batches closely monitored for critical properties under field conditions in both the fresh and hardened states.
3.4 High-Range, Water-Reducing Admixtures

High-range water reducers (HRWRs) are also known as superplasticizers, super fluidizers, and super water reducers due to their higher efficiency than conventional WRAs in improving workability and flow of concrete mixes. They were developed for use where the amount of WRAs required to reach a desired slump or flow resulted in unacceptable reductions of other critical properties. Different chemistry enabled developers to produce an admixture that allowed contractors to place highly workable, pumpable, or even flowing concrete with higher strengths and greater durability and less shrinkage when the concrete mix was properly designed. The specifications for superplasticizers are detailed in ASTM C 494 as Type F for high-range water reduction with normal set times or Type G for high-range water reduction with retarded setting times. ASTM C 1017 specifies chemical admixtures for use in flowing concrete. HRWRs are typically one of four chemical groups: sulfonated melamine–formaldehyde condensate (SMF), sulfonated naphthalene–formaldehyde condensate (SNF), modified lignosulfonate (MLS), and others that may include sulfonic acid esters or carbohydrate esters (carboxylates). HRWRs deflocculate and disperse the cement particles in a similar manner but much more efficiently than WRAs. Superplasticizers can reduce water demand in the matrix by as much as 30%, and, because HRWRs can be added into the transit mixer at the plant and again at the jobsite, workability can continue to be customized at the site for specific application needs regardless of transit-time slump loss (Fisher, 1994) (Figure 3.3). HRWRs are often referred to as first-, second-, and third-generation superplasticizers:

1. First-generation superplasticizers are primarily anionic materials that create negative charges on the cement particles, resulting in reduced friction due to the same-charge particles repelling each other. These HRWRs have no effect on the hydration process, but using them to reduce water/cement ratios without the addition of retarders makes for quicker set times. Because of the shorter workability times, first-generation HRWRs are normally added at the jobsite. Their chemistry allows a reduction in water of 20 to 30%.

2. Second-generation superplasticizers, which are normally added at the batch plant, coat the cement particles with a thixotropic material; they lubricate the mix, allow lower water/cement ratios, and add a measure of control in the hydration process. Second-generation HRWRs can be used at higher concrete temperatures, thus reducing or eliminating the need for ice. Water demand is typically reduced 20 to 30%, and the higher workability time is extended.
3. Third-generation superplasticizers coat the cement particles and are added at the batch plant, just like the second-generation HRWRs. Third-generation superplasticizers offer the same advantages as second-generation HRWRs, plus they offer the added bonus of maintaining initial setting characteristics similar to normal concrete while producing a highly plastic mix at an extremely low water/cement ratio. Second-generation and third-generation superplasticizers are relatively expensive (typically $5 to $6 additional per yard of concrete), but they have proven themselves to be cost effective in such applications as hot weather concreting, wall placements, bucket and crane placements, slabs on grade, and pumped concrete (Guennewig, 1993). Modern trends are clearly moving toward the use of polycarboxylates over the older sulfonated lignins or melamine-based products, as they are so much more effective at deflocculating cement grains due to steric hindrance.

Strategies for the use of HRWRs include those listed in the WRA section above, but application-related considerations may dictate that HRWRs must be used and require decisions of which type and quantity are required to achieve the proper concrete placement. Determining optimal superplasticizer dosage can be a relatively complex task involving consideration of costs, rheology of the fresh concrete, mechanical properties at early ages, and long-term durability under expected service conditions. Optimal dosage is highly dependent on determination of the saturation concentration—the highest ratio of the mass of HRWR solids to the mass of cementitious materials over which any higher dosage will not significantly improve the workability of the paste (Gagné et al., 1996). This ratio is usually 0.8 to 1.2% and is affected by type and quality of superplasticizer, fineness of the cement, C₃A content, type and content of sulfates, and the speed and shearing action of the mixer employed (Baalbaki, 1990).

The ability of superplasticized concrete to flow through congested reinforcement and into otherwise inaccessible areas and a requirement for minimal vibration make it a natural choice in any applications presenting such problems. The ease with which it can be pumped and placed makes it a good choice for floors, structural and foundation slabs, pavements, bridges, and roof decks. Contractors and precasters prefer superplasticized concrete for its faster strength gain, improved surface details, and pigment dispersion in architectural applications. HRWRs are used in sprayed concrete applications, self-consolidating concrete, and tremie pipe placements because of the increased fluidity and higher strengths. High-performance concrete has been implemented primarily through the engineered concrete mix designs made possible by using HRWRs to reduce water/cement ratios and by adding high-surface fine materials such as silica fume and fly ash while maintaining good workability and minimal segregation. Consequently, higher and earlier strengths and increased durability are commonly expected and achieved.

Regular reporting of successful concrete applications relying on HRWRs has led to a tendency to think of HRWRs as a panacea for all concrete problems; however, good batch designs that consider the level of HRWRs to be added are critically important to avoid serious segregation, excessive bleeding, and needless extra expense. Normal mixes made flowable through the addition of HRWRs typically require an increase of approximately 5% more sand. Surface finishes can become mottled and irregular when too much HRWR is used. Water/cement ratios are critical to strength and durability, but, for even minimal workability and accounting for evaporation and substrate absorption, the practical lower water/cement ratio limits of concrete mixtures without HRWRs are well above the theoretical minimum required for complete hydration. Because HRWRs allow concrete to be made with the lowest water/cement ratios, care must be exercised to ensure that enough water is present in the matrix throughout the entire hydration process to fully hydrate all of the cement in the matrix.

As for WRAs, HRWRs tend to retard concrete setting times, but this effect may be compensated for or overridden by the addition of accelerating admixtures or the further addition of retarding admixtures. When a retarder is combined with a superplasticizer, the resulting admixture is classified by ASTM C 494 as Type G.

Slump loss is a problem of particular importance in high-slump or flowable concretes utilizing HRWRs. The rate of slump loss may be affected by the type and dosage of HRWR, other admixtures, order of addition, type and brand of cement, concrete temperature, and concrete batch design. Concrete that has
HRWRs added at the batch plant will tend to experience moderate to rapid slump loss, unless special slump-loss-control admixtures are also added. Normally, the higher dosage rates tend to slow down the rate of slump loss, and cement with higher levels of C₃A, as found in Type I and Type III cements, exhibit a more rapid rate of slump loss. Higher concrete temperatures also tend to accelerate the rate of slump loss (ACI Committee 212), but adherence to ACI Committee 305 hot-weather concreting procedures can minimize slump loss.

Entrained air content is initially increased by the addition of HRWRs, but redoing flowing concrete causes loss of entrainment with each dose. Also, air bubbles may have a tendency to be larger and coalesce in flowing concrete. Shrinkage and creep are generally as good as or better than control mixes, but flowing concrete may exhibit more shrinkage depending on water and cement content and the choice of HRWRs. Durability is generally better for concrete modified with HRWRs because strength is higher, cement particles are more uniformly dispersed and hydrated, and permeability of the hardened concrete is lower. Resistance to sulfate attack and abrasion should be better, and resistance to salt scaling and resistance to corrosion of reinforcing steel are comparable with control batches containing no superplasticizer (ACI Committee 212). As always, evaluation of trial batches cured under field conditions is highly recommended.

3.5 Accelerating Admixtures

Accelerators are commonly used to offset retardation effects from other admixtures, although overcoming weather-induced retardation due to colder temperatures at the job site is probably their primary application. Through the use of accelerators contractors can place concrete at much lower temperatures than would be practical without their use (ACI 306R). Accelerating admixtures are also commonly used to speed up normal set and cure times for purposes of earlier service than would be possible with an unaccelerated mix design. Such an application is most often the case for concrete repair mix designs and in prestressed or precast applications, where time delays cost customers or precasters significant amounts of money and inconvenience.

Accelerating admixtures should conform to ASTM C 494 Type C. These materials are predominantly calcium chloride or closely related salts because of their availability, relatively low costs, and more than a century of documented usage. Caution should be exercised, however, as the use of chloride accelerators will corrode reinforcement in concrete exposed to water. Other materials such as silicates, fluoroaluminates, thiocyanates, alkali hydroxides, calcium formate, calcium nitrate, calcium thiosulfate, potassium carbonate, sodium chloride, aluminum chloride, and various organic compounds, including triethanolamine, are also used as accelerating admixtures (ACI 517.2R). Calcium nitrite is frequently recommended and commercially available as an accelerator that also inhibits corrosion of reinforcing steel wherever exposure to precipitation and salt from deicing materials or seawater is likely to initiate corrosion problems. Lignosulfonate, benzoates, phosphates, hypophosphates, chromates, fluorides, Calgon®, and alkali nitrites have also been promoted as corrosion inhibitors, too, but their effectiveness is not widely accepted.

Because of the long-term usage of calcium-chloride-based accelerating admixtures, many of their effects on concrete are well known and highly touted in manufacturers’ literature. They should conform to ASTM D 98 requirements and be sampled and tested according to the procedures in ASTM D 345. Calcium chlorides are known to reduce initial and final setting times. The workability of the mix is usually improved by accelerators, and the air content of the matrix may be increased slightly with average-sized voids (Figure 3.4). Accelerators also tend to reduce the bleeding rate and bleeding capacity of concrete.

The effects of accelerators on hardened concrete are as important as they are for the fresh mix. Benefits of their use include accelerated strength development in both compression and in flexural modes, although less so in the latter. Modulus of elasticity, too, increases at a faster rate. Abrasion resistance and erosion resistance are improved with the use of accelerating admixtures, as is pore structure, due to reduced porosity. Frost resistance in concrete is better at early ages when calcium chloride accelerators are used, but performance declines with time, and resistance is actually worse at later ages. Other
disadvantages of using common calcium chloride accelerating admixtures in concrete include slight increases in drying shrinkage and creep increases from 20 to 35%, all of which may occur because rapid strength gain is usually obtained at the expense of reduced ultimate strength (Figure 3.4). Accelerators also often increase alkali–silica reactions and decrease resistance to external sulfate attack. Additionally, they are known to increase the rate of freeze–thaw scaling and of corrosion of steel reinforcement, except for those previously mentioned accelerating admixtures known as corrosion inhibitors (i.e., calcium nitrite and sodium thiocyanate) (Nmai et al., 1994). Accelerated concrete is also usually darker in color than unaccelerated concrete.

With these effects on properties in mind, the Portland Cement Association (PCA) recommends that calcium chloride and other admixtures containing soluble chlorides should not be used under the following conditions:

- Prestressed concrete, due to potential corrosion hazards
- Concrete containing embedded aluminum, due to serious corrosion problems in humid environments
- Concrete subjected to alkali–silica reactions or exposed to soil or water containing sulfates
- Floor slabs intended to receive dry-shake metallic finishes
- Hot ambient conditions or hot constituent materials such as aggregates or water
- Massive concrete placements

The PCA also recommends caution when using calcium chloride in the following applications (Kosmatka and Panarese, 1988):

- Concrete subjected to steam curing because of possible expansion problems with delayed ettringite formation
- Concrete containing embedded dissimilar metals, especially when electrically connected to reinforcing steel
- Concrete slabs supported on galvanized steel forms

The ACI 318 Committee on Building Code Requirements for Reinforced Concrete has recommended maximum allowable levels of chloride ions for corrosion protection in steel reinforced concrete under various service exposures. These levels are shown in Table 3.1. In spite of the cautions, calcium chlorides are used on a regular basis for interior concrete with predictable performance. Recommended usage rates vary with mixture designs, temperatures, and exposure conditions. As with any admixture,
though, no more should be used in the batching than is necessary to accomplish its intended purpose. Even then it is not generally used at rates higher than 2% of the weight of cement (Kosmatka and Panarese, 1988), and care must be taken to ascertain complete dissolution of all of the salt into the mixing water before adding it to the rest of the matrix to avoid popouts and serious local staining problems. Laboratory evaluations of field-cured trial batches are recommended before full-scale placements are made.

3.5.1 Accelerating Corrosion-Inhibiting Admixtures

When designers have concerns about corrosion of reinforcing steel under shallow concrete cover, corrosion-inhibiting admixtures are often prescribed as a mitigation strategy. This class of materials electrochemically interferes with the galvanic corrosion process by scavenging either electrons or protons near the steel reinforcement. The three general categories of corrosion inhibitors are:

1. **Anodic or active** corrosion inhibitors actively interfere with the corrosion process by occupying overactive electrons oxidizing rapidly dissolving ferrous oxide ions into an insoluble protective coating of ferric oxide on their way to the surface of the anodic steel reinforcement. Calcium nitrite is the primary material in this category, although sodium nitrite, sodium benzoate, and sodium chromate are also used outside the United States.

2. **Cathodic or passive** corrosion inhibitors indirectly interfere with the corrosion process by slowing down the cathodic reactions by serving as proton acceptors and thus impeding the corrosion current. They are normally highly alkaline materials that render the ferrous ions at the surface of the reinforcing steel insoluble in water and unable to participate in the corrosion current. The most commonly used materials in this category are sodium hydroxide, sodium bicarbonate, and ammonium hydroxide, although the use of organic materials such as substituted forms of aniline and mercaptobenzothiazole has been reported.

3. **Mixed or passive–active** corrosion inhibitors might be preferable over either of the previous two types by themselves, as this type attacks the problem at both ends of the reaction, interfering more completely with the corrosion process before it can begin. These materials can be in the form of more complicated organic molecules that are attracted to and tie up both cathodic and anodic sites, forming salts as they accept either the available electrons or protons. This category may also be a physical mixture of two simpler compounds where one component reacts at the cathodic reaction site while the other reacts at the anodic site.

Corrosion inhibitors are typically used at dosage rates of 1 to 4%, based on the weight of the cement. Properties of concrete are affected by the use of corrosion-inhibiting admixtures. Inorganic salts such as calcium nitrite are known accelerators, but organic corrosion inhibitors may retard set times. Workability may be improved at levels up to 2% but begins to degenerate above that. Hardened concrete strengths are often slightly diminished, and alkali–silica reaction may be aggravated by corrosion inhibitors if reactive aggregates are present in the matrix.
3.6 Air-Entraining Admixtures

Air-entrained concrete was developed in the 1930s, and it is still recommended today for nearly every commercial application. Air-entraining agents are provided already ground into the cement (air-entrained cement) or as an admixture whose addition can be adjusted for individual batch design needs. Because air-entraining agents provide extremely small and well-dispersed air bubbles in the paste, they act as localized stress reducers in the cured matrix. This is advantageous in concrete exposed to moisture and especially to wet deicing chemicals during freezing and thawing conditions (Figure 3.5). Because the bubble voids provide room for microscopically localized expansions, resistance to damage from alkali–silica reactions and sulfate attack is enhanced as well. The trade-off is that air is compressible and not strength enhancing; therefore, some loss in strength of the concrete will result. A good rule of thumb is that every 1% increase in air content reduces the strength of a well-designed concrete 2 to 4% (Kosmatka and Panarese, 1988) (Figure 3.6). Generally, manufacturers recommend between 0.3 and 2.0 mL/kg cement depending on the specific air-entraining admixture, mineral admixtures also included in the batch, batch conditions, and the amount of air required. Manufacturers’ recommendations for a specific air-entraining agent should be used as a guideline, but property evaluations should be made on several small batches before deciding on the optimum quantity required to produce the air content necessary for the batch design (Table 3.2).

Air-entraining admixtures are members of a class of chemicals known as surface-active substances or surfactants. These surfactants are made of molecules having a polar (water-attracted) head and a nonpolar (water-repulsed) tail. If the head is negatively charged, the surfactant is anionic, as represented by carboxylates, sulfonates, and sulfate esters. When the head is positively charged, the surfactant is cationic, as represented by substituted ammonium ion products. Nonionic surfactants are made of molecules with uncharged polar heads, and they are generally polyoxyethylenated compounds. Commercial air-entraining agents for concrete are inexpensive and have served the concrete industry well over time. They come from surfactants that can be categorized into the following seven groups (Dolch, 1984):

1. **Vinsol™** is the most widely used type of air-entraining admixture. It is the hyproduct of the distillation and extraction of pine stumps for other materials. The leftover insoluble residue is neutralized in sodium hydroxide, resulting in the soluble solution used to produce entrained air in concrete.

![FIGURE 3.5 Relationship between air content and expansion of concrete test specimens during 300 cycles of freezing and thawing for various maximum aggregate sizes. (From Kosmatka, S.H. and Panarese, W.C., Design and Control of Concrete Mixtures, 13th ed., Portland Cement Association, Skokie, IL, 1988.)](image-url)
2. Synthetic detergents, normally alkyl aryl sulfonates, come from petroleum-based (typically C_{12}) residues that are condensed with benzene then sulfonated and neutralized to obtain the soluble salt.

3. Salts of sulfonated lignin are byproducts of the paper industry. These tend to be relatively poor air-entraining agents but have been used extensively in concrete as water reducers and retarders.

4. Salts of petroleum acids are the leftovers from petroleum refineries. Sludge left after the extraction of white oils with sulfuric acid contains water-soluble sulfonates that are then neutralized with sodium hydroxide.

5. Salts of proteinaceous materials are products of animal- and hide-processing industries. They consist of salts from a complex mixture of carboxylic and amino acids. This group does not produce many commercial air-entraining admixtures.

6. Fatty and resinous acids and their salts are produced from various sources such as vegetable oil, coconut oil, and tall oil, another byproduct of the paper industry.

7. Organic salts of sulfonated hydrocarbons are the same water-soluble sulfonates described in group 4, except they are neutralized with triethanolamine instead of sodium hydroxide.

When determining air contents, an observant technician would note that even concrete without air-entraining admixtures contains some air. This air, however, is air that has become entrapped during the mixing process. Entrapped air is evident as much larger, irregularly spaced voids that do nothing to resist freeze–thaw stresses.
Entrained air has a significant influence on many of the properties of both fresh and cured concrete. In fresh concrete, it is known to reduce water demand and the tendency toward bleeding, as well as plastic shrinkage. It increases slump and workability. In hardened concrete, entrained air improves deicer scaling resistance and resistance to freezing and thawing degradation, although small and predictable reductions in compressive, flexural, and bond strengths are to be expected (Table 3.3).

If air is determined to be excessive, very small quantities of defoaming or air-detraining agents may be used as recommended by the manufacturer. Defoaming agents are typically composed of silicones, esters of carbonic acid (water-insoluble), octyl alcohol, dibutylphthalate, or tributylphosphate. These materials are very effective, but too much may hurt concrete properties; thus, care must be taken to use only enough defoamer or detrainer to bring concrete air into the specified range. All air-entraining admixtures that are to be added at the time of mixing should conform to ASTM C 260 specifications. Air-entraining cements should conform to ASTM C 150 and ASTM C 595 with ASTM C 226 specifications for the air-entraining additives in air-entraining cements.

Typically total air content needs are dependent on anticipated exposure conditions vs. the strength and quality of the matrix mortar and coarse aggregates. Table 3.4 illustrates target air content considerations for various coarse aggregates. It should be noted that sometimes other chemical or mineral admixtures in the matrix may detrimentally reduce the anticipated volume of entrained air. Of course, trial batching to verify the effects of air-entraining admixtures on critical properties for any proposed batch design is recommended.

### 3.7 Antifreezing Admixtures

As the name implies, this category of admixtures is employed to allow most types of concrete construction work and precasting to take place at freezing and well below freezing temperatures. These admixtures are sometimes used in conjunction with external energy and heat sources, but they are often used without

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**TABLE 3.3 Effect of Entrained Air on Concrete**

<table>
<thead>
<tr>
<th>Properties</th>
<th>Effect</th>
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</thead>
<tbody>
<tr>
<td><strong>Plastic</strong></td>
<td></td>
</tr>
<tr>
<td>Bleeding</td>
<td>Significant reduction of bleeding</td>
</tr>
<tr>
<td>Plastic shrinkage</td>
<td>Reduction</td>
</tr>
<tr>
<td>Slump</td>
<td>Increases (25 mm more slump/0.5–1% more air)</td>
</tr>
<tr>
<td>Unit weight</td>
<td>Decreases as air content increases</td>
</tr>
<tr>
<td>Water demand (for equal slump)</td>
<td>Decreases 3–6 kg/m³/1% increase in air</td>
</tr>
<tr>
<td>Workability</td>
<td>Increases as air increases</td>
</tr>
<tr>
<td><strong>Hardened</strong></td>
<td></td>
</tr>
<tr>
<td>Abrasion</td>
<td>Insignificant (only as it relates to strength and modulus)</td>
</tr>
<tr>
<td>Absorption</td>
<td>Insignificant</td>
</tr>
<tr>
<td>Alkali–silica reactivity</td>
<td>Concrete expansion decreases as air increases</td>
</tr>
<tr>
<td>Bond to steel</td>
<td>Decreases as air increases</td>
</tr>
<tr>
<td>Compressive strength</td>
<td>Typically decreases strength 2–6%/1% air increase; unusually harsh or lean mixes may gain strength</td>
</tr>
<tr>
<td>Creep</td>
<td>Insignificant (only as it relates to strength and modulus)</td>
</tr>
<tr>
<td>Deicer scaling</td>
<td>Significantly more resistant as air increases</td>
</tr>
<tr>
<td>Fatigue</td>
<td>Insignificant (only as it relates to strength and modulus)</td>
</tr>
<tr>
<td>Flexural strength</td>
<td>Decreases strength 2–4%/1% increase in air</td>
</tr>
<tr>
<td>Freeze–thaw resistance</td>
<td>Water-saturated F-T resistance improves with added air</td>
</tr>
<tr>
<td>Heat of hydration</td>
<td>Insignificant</td>
</tr>
<tr>
<td>Modulus of elasticity</td>
<td>Decreases 724–1380 MPa (1.05 × 10⁵–2.00 × 10⁵ psi) per 1% air increase</td>
</tr>
<tr>
<td>Permeability</td>
<td>Minimal; if higher air means lower w/c then lower permeability results</td>
</tr>
</tbody>
</table>

Chemical Admixtures

3.8 Antiwashout Admixtures

This class of chemical admixture was developed as a viscosity-modifying admixture that could improve the rheological properties of the cement paste. It has proved itself in the field by significantly improving the cohesiveness of concrete being placed underwater, where the exposed matrix is in jeopardy of being diluted and segregated or washed away by the surrounding water. It is most commonly used underwater in large placements and in repairs. These admixtures are also known as viscosity-enhancing admixtures.
and are sometimes used to produce self-leveling concrete or self-consolidating concrete (SCC), which is used wherever extreme congestion due to reinforcement configurations or unusual geometry of the forms requires a very fluid, cohesive concrete that resists bleeding and segregation (Khayat, 1996).

Disadvantages of antiwashout or viscosity-enhancing admixtures include the typical reductions in strength and modulus of elasticity. Depending on the base concrete batch design, water/cement ratio, and the type and dosage rate of antiwash admixture (AWA), compressive strength has been determined to be 75 to 100% of the same control mix without this admixture. Flexural strengths have been reported at 84 to 100%, and modulus of elasticity measurements are 80 to 100% of the control batch.

The two most commonly used AWAs are based on either welan gum or hydroxypropylmethylcellulose. Some AWAs are made from variations of related microbial saccharides similar to welan gum or various cellulose-based polymers such as hydroxyethylcellulose and hydroxyethylmethylcellulose. The thixotropic mechanisms that enable this admixture to work include attachment of its long molecules to water molecules. This inhibits the free displacement of the water by heavier mix constituents. The long chains can slip past each other under conditions of high shear, such as mixing and pumping and rapid flow, but when the moving concrete slows down the chains intermesh and the matrix behaves in a much more viscous state. This self-adjusting behavior minimizes segregation and bleeding. Workability is usually better, too, because the constituents of the mix are better dispersed, even with the higher additions of HRWRs.

Set time, cure time, shrinkage, and creep are not significantly affected by the presence of AWAs themselves but may be influenced by the addition of higher levels of HRWR associated with the use of AWAs. Electric current passed through cured permeability specimens is lower in concrete containing AWAs, indicating reduced chloride ion permeability. Addition levels for AWAs are totally dependent on the application needs and constraints, but the mechanism suggests that its function is based on the availability of free water. It is essential that trial batches be made and evaluated for all important properties before concrete containing AWA is placed. Known interactions include higher air-entraining admixture demand when higher levels of HRWRs are needed. Acceptable entrainment levels are easily attainable but require trial batch evaluations. Hydroxypropylmethylcellulose tends to entrap air unless a deaerating agent is added into the mixer with it; therefore, careful adherence to a specific mixing procedure may be more important than with other batch designs.

### 3.9 Shrinkage-Reducing Admixtures

Shrinkage-reducing or shrinkage-compensating admixtures promote expansion of the concrete at about the same volume that normal drying shrinkage is contracting it. The net change in length of the hardened concrete should be small enough to prevent shrinkage cracks. The typical materials used for shrinkage compensation in concrete are based on calcium sulfoaluminate or calcium aluminate and calcium oxide. Some losses in properties are typical with the introduction of these antishrinkage agents. Any ill effects on strength are minimized by the use of HRWRs, which provide good workability while allowing reduction of the water content. These admixtures can be used to great advantage in slabs, bridge decks, structures, and repair work where cracking can lead to steel reinforcement corrosion problems, but maintaining effective air entrainment for resistance to freezing and thawing damage can be difficult with shrinkage-reducing admixtures. Usage rates vary with batch designs and water content but typically range from 8 to 25%. ACI 223 (Standard Practice for the Use of Shrinkage-Compensating Concrete) specifies the best methods for utilization of this admixture.

### 3.10 Polymer Modifier Admixtures

Different types of polymers can be used in concrete as polymerizing admixtures for comatrix formation or where the hydraulic cement paste and the polymer simultaneously form into separate, but interdependent, phases in the matrix. This polymer-modified concrete (PMC) is the result of adding higher-
molecular-weight polymers to concrete batch designs for the purposes of improved adhesion, greater chemical resistance, lower permeability, lower drying shrinkage, improved tensile strength, or accelerated cure. Different chemical families and physical forms of polymers have been tried with varying degrees of success, but latex, acrylic, and epoxy additives are the most commonly used. They are available as powdered or liquid forms of resins, monomers, or emulsions, and their uses include concretes and mortars for flooring, ship decks, bridge decks overlays, repair, anticorrosive coatings, and adhesives. Improvements over the properties of normal concrete or mortar depend on the polymer phase formation and the cement hydration forming an interpenetrating network structure of polymer and hydrated cement phases. The resulting monolithic matrix exhibits properties beyond either isolated phase material.

Initially, the mixing process disperses the admixture into the fresh concrete matrix. As hydration begins and free water is lost, membrane strands of polymer begin forming either through water loss or independent polymerization. These membranes adhere to major portions of the hydrating cement particle surfaces. As the process continues, membranes interconnect and hydration progresses somewhat independently until both constituents of the matrix have cured (Figure 3.7). This modified matrix tends to arrest propagating microcracking due to local tensile or impact insults to the concrete. The mechanics

![Figure 3.7 Simplified formation model for latex-cement co-matrix. (From Ohama, Y., in Report of the Building Research Institute No. 65, Building Research Institute, Tokyo, Japan, 1973.]

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of this phenomenon seem to rely upon higher tensile strengths of the polymer network and the better bond to aggregates and hydration product. Additionally, higher curing shrinkage strains and resulting stresses in the polymer may post-tension the polymer phase, internally compressing the Portland cement concrete phase. Because of their significantly higher costs, these polymer modifiers are considered premium admixtures for concrete with special needs. The gains in tensile and flexural strength over normal concrete are primarily a function of the polymer/cement ratio rather than water/cement ratio.

Although mixing and placement of PMC are similar to normal concrete, there are some important differences, and finishing and curing may be very different. Normally, set times are delayed in PMC, and initial set times for PMC may be much more sensitive to ambient, substrate, and concrete constituent temperatures. Because of this sensitivity to temperature and unwanted additional air content from overmixing, latex-modified concrete is generally batched and mixed in mobile batching-plant trucks or trailers at the jobsite. With latex in particular, too much entrained air requires the addition of an antifoaming agent if it is not already included in the admixture. Initially, workability may be better than unmodified concrete, but as the polymer phase progresses and the surface begins to dry, finishing operations may tear the sticky or crusty surface due to polymer adhesion, so workers need to quickly place and finish PMC. Styrene–butadiene resin (SBR) concretes should be wet cured for 24 to 48 hours to permit concrete to gain adequate strength before the latex is allowed to cure and shrink.

Bleeding and segregation are also less in most PMCs because of the hydrophilic nature of the polymer modifiers used. Placement and finishing tools must be cleaned thoroughly and immediately after each use, and reusable formwork must be carefully coated with a special form release that releases from latex or epoxy as well as the cement paste. All joints should be formed, including construction joints and control joints. Sawed joints for control of cracking are not recommended (ACI 548 Committee, 1992).

Changes in hardened concrete properties are important to anticipate. Shrinkage is dependent on the batch design and the choice and amount of polymer modifier. Some PMCs exhibit the same or less shrinkage, and some exhibit more than expected from normal concrete. Creep properties from SBR latex-modified concrete are typically lower than for normal concrete, but epoxy-modified concrete may be higher, depending on the polymer loading in the matrix. The coefficient of thermal expansion for PMCs is minimally affected by the polymer, as it such a small constituent in the matrix compared to the aggregates. Although significant increases in tensile strength, flexural strength, and bond strength may be expected, compressive strengths do not necessarily increase. Cured PMC typically exhibits lower water absorption and water or water vapor permeability due to larger pores being filled with polymer (Figure 3.8, Figure 3.9, and Figure 3.10); however, some polymers can re-emulsify, which may reduce the strength.
Chemical Admixtures

of the matrix at least near the surface when it is saturated with water over time. Epoxy-modified concretes are more suitable for constantly wet conditions (Popovic, 1985).

Polymer-modified concrete strengths are normally better than for conventional concrete with similar water/cement ratios at ambient temperatures below 100°F. Due to marked decreases in the polymer’s modulus at polymer-specific glass transition temperatures ($T_g$s), usually somewhere between 100 and 120°F, the strength differences may decrease in service temperatures at or above this range. Abrasion resistance, frost resistance, chemical resistance, and bond to concrete or steel substrates are normally better in PMC than unmodified concrete.

Epoxy-modified concrete typically has a polymer/cement ratio of 20% for water-reducible resins and more than 30% for others (even more than 50% for some resins) (Ohama, 1984). This makes epoxy-modified concretes more expensive than latex-modified concretes, but all strengths are typically higher, including compressive strength, and these systems can be cured in water, whereas latex-modified concrete usually must be allowed to dry after 48 hours of moist curing.

Other commercially available polymers such as polyvinyl acetates, water-soluble unsaturated polyester resins, methylcellulose, and polyurethanes are used to modify concrete for specific applications, but latexes (particularly SBR and acrylic) and epoxies are the two that claim most of the market. PMC is used most often in protective coatings such as shotcrete (Shorn, 1985), overlays (Irvin, 1989), and large-
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surface-area repairs (Smoak, 1985), because these applications can take cost-effective advantage of the better adhesion, better abrasion resistance, and lower permeability afforded the matrix through the use of polymer modifiers. Also, crews associated with these applications generally tend to be better trained for the special batching, placing, finishing, and curing requirements of PMC. Job-specific materials, usage, and batch design recommendations from polymer modifier manufacturers should be solicited and closely followed to make trial batches under field conditions which must be tested for critical properties before large-scale use of PMC is implemented.

3.11 Alkali–Silica Reaction Prevention Admixtures

In recent years, alkali–silica reaction (ASR) has been found to be responsible for much of the premature deterioration of many concrete structures in the United States and other countries throughout the world; consequently, there has been renewed interest in using lithium compounds (lithium hydroxide, lithium carbonate, and lithium nitrate) to combat this deleterious chemical reaction. The most promising of these lithium compounds is a solution of lithium nitrate. Research efforts are increasingly focused on understanding the mechanism by which lithium materials inhibit alkali–silica reaction. Furthermore, work continues toward improving the cost effectiveness of this mitigation strategy (Folliard et al., 2006).

3.12 Conclusion

It should be noted that all of the many admixtures are intended to enhance the properties of concrete, but they are not intended to substitute for proper concrete design, batching, transport, and finishing practices. It is often more cost effective to change the mixture proportions or the aggregate than to use higher quantities of admixtures; therefore, it is recommended that a cost analysis be done on both proposed and alternative batch designs. Any change in admixtures or their quantities should be verified in trial batch evaluations for strength and any other critical properties before delivered to any jobsite. Trial batches should be mixed with all intended admixtures and cured under expected field conditions before evaluation.

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Laboratory test on long-term deterioration of concrete prisms. (Photograph courtesy of Portland Cement Association, Skokie, IL.)