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REPORT ON CHEMICAL ADMIXTURES FOR CONCRETE

ACI 212.3R-10

Reported by ACI Committee 212

CHAPTER 15 – PERMEABILITY REDUCING ADMIXTURES

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Report on Chemical Admixtures for Concrete

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American Concrete Institute®

CHAPTER 15 – PERMEABILITY REDUCING ADMIXTURES

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

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

14.7—Storage

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

CHAPTER 15—PERMEABILITY-REDUCING ADMIXTURES

15.1—Introduction

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

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

15.2—Materials

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

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

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

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

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

calcium hydroxide (lime) + stearate admixture → insoluble calcium stearate + water.

The insoluble stearate created by the reaction between the admixture and the lime forms a hydrophobic layer on the walls of the concrete pores. Waxes and bituminous emulsions are other materials that can deposit hydrophobic particles in the concrete pores, although there is no chemical reaction involved in that process. Hydrophobic admixtures are effective at reducing the capillary absorption and chloride ingress of concrete under nonhydrostatic conditions as shown in Fig. 15.1 and 15.2, respectively (Aldred et al. 2001; Civjan and Crellin 2008).

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

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

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

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

Unlike hydrophobic materials, crystalline admixtures are hydrophilic, and the active ingredients react with water and cement particles in the concrete to form calcium silicate hydrates and/or pore-blocking precipitates in the existing microcracks and capillaries. The mechanism is analogous to the formation of calcium silicate hydrates and the resulting

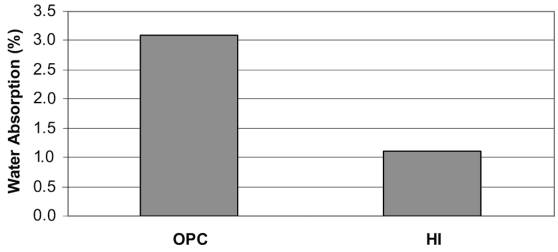

Fig. 15.1—Water absorption for ordinary portland cement (OPC) concrete with hydrophobic ingredient (BS EN 1881-122) with an age of 28 days and a w/cm *of 0.40.*

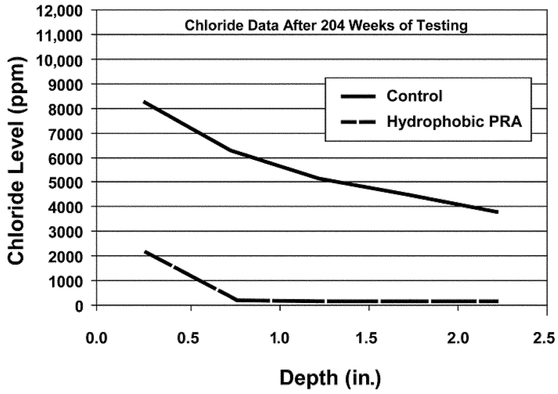

Fig. 15.2—Chloride penetration of a hydrophobic PRA subjected to ponding. Tested using modified chloride ponding protocol (not the AASHTO T259 procedure discussed in Section 15.3). Cementitious content is 690 lb/yd^3 and w/cm *is 0.40. (Note: 1 in. = 25.4 mm; 1 lb/yd^3 = 0.5933 kg/m^3.)*

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

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

(calcium silicate + crystalline promoter + water →
modified calcium silicate hydrate + pore-blocking precipitate)

Similar reactions may exist involving the calcium aluminates, but the aforementioned process is expected to predominate due to the abundance of calcium silicates.

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

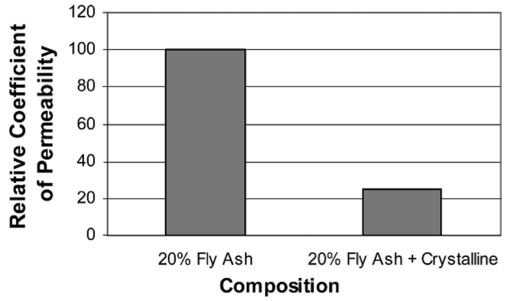

Fig. 15.3—Permeability of concrete containing 20% Type F fly ash and crystalline admixture.

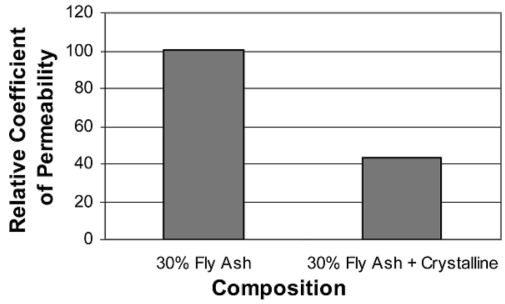

Fig. 15.4—Permeability of concrete containing 30% Type F fly ash and crystalline admixture.

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

15.3—Selection and evaluation

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

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

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

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

One widely-used indirect method for inferring permeability information is ASTM C1202. This method measures the

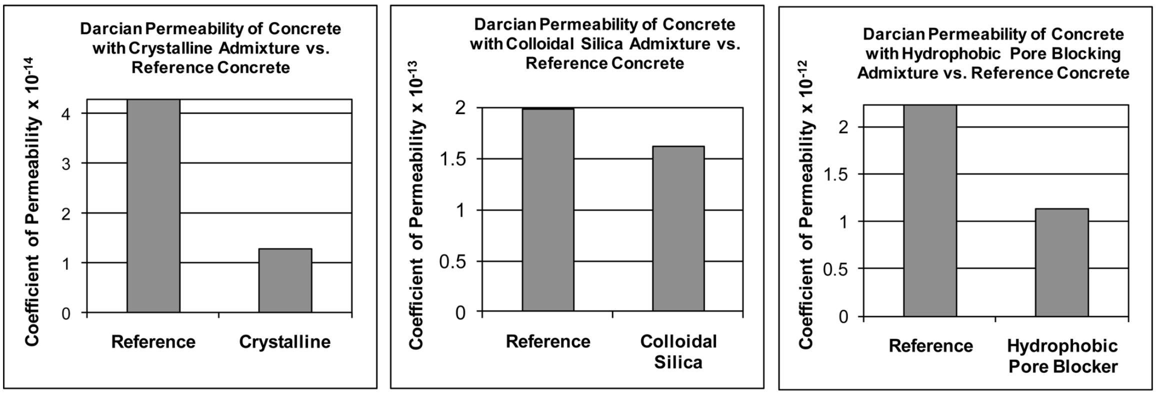

Fig 15.5—Reduction in permeability of concrete using PRAs. Tested using modified BS EN 12390-8. Pressure = 150 psi (1.0 MPa). Time = 96 hours.

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

15.4—Applications

PRAs can be incorporated into virtually any concrete mixture. Usage of these admixtures, however, is usually limited to structures that will be exposed to moisture, salt, salt water, wicking, or water under hydrostatic pressure. Prevention of water-related problems such as water migration, leaking, freezing-and-thawing damage, corrosion, carbonation, and efflorescence are reasons to choose a PRA. PRAHs are appropriate for water-containment structures, below-grade structures, tunnels and subways, bridges and dams, and recreational facilities such as aquatic centers. These materials in a properly proportioned mixture with a *w/cm* of 0.45 or less can generally withstand aggressive environments with exposure to salt spray and some chemicals.

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

Table 15.1—Reduction in permeability of concrete using PRAs

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

15.5—Proportioning concrete

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

15.6—Effects on fresh and hardened properties

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

15.7—Quality assurance

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

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

15.8—Batching

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

15.9— Storage

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

CHAPTER 16—MISCELLANEOUS ADMIXTURES

16.1—Bonding admixtures

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

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

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

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