THE STATE OF THE ART IN CHEMICAL ADMIXTURES

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THE STATE OF THE ART IN CHEMICAL ADMIXTURES

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Abstract

The use of chemical admixtures for modifying the plastic and hardened properties of cementitious systems continues to expand. Traditionally, these admixtures were based upon by-products from other industries and limitations in performance were compensated for by formulation with other ingredients. While this approach is still an important one, the focus has now shifted to chemistries that allow for molecular design to achieve new and improved performance.

This paper will briefly survey the performance of a number of admixtures. High-range water reducers (HRWR) based on polycarboxylate ethers (PCE) can provide such benefits as ultra high water reduction, enhanced slump retention, early strength development, accelerated setting time and enhanced viscosity. New generation viscosity modifying admixtures (VMA) are used to provide stability to self-consolidating concrete (SCC) without adverse effects on setting time, strength development and air entrainment. Cold weather admixtures (CWA) are available that can facilitate placement of concrete at air temperatures of less than –10°C, while still achieving acceptable setting time and strength development. Shrinkage reducing admixtures (SRA) provide reductions in drying shrinkage at levels up to 80% versus a control concrete. Corrosion inhibiting admixtures (CIA) are available to provide reduction in chloride permeability and/or increases in the threshold chloride level at which corrosion is initiated. Hydration control admixtures (HCA) can arrest hydration for multiple days, followed by re-activation with accelerating admixtures.

Keywords: high range water reducer, viscosity modifying agent, cold weather admixture, shrinkage reducing admixture, hydration control admixture

1. Introduction

Chemical admixtures of many different types are available to the producer, contractor and engineer to achieve concrete with a wide range of properties. For example, water reducers with extended workability retention allow the concrete producer to transport fresh concrete long
distances to the job site and still meet the slump requirements of the job. Mid range water reducers that impart enhanced finishing characteristics desired by the contractor are available, as well. In addition, a number of durability products, such as shrinkage reducing admixtures or corrosion inhibiting admixtures are available to meet the demands of the engineer and owner of a concrete structure.

This paper is intended to be only a very brief survey of this topic. Only the key classes of chemical admixtures will be addressed and with very limited depth. This is due in part to the length restrictions of this paper, but primarily because an exhaustive overview was just recently prepared by the author and a colleague on this topic [1]. Please refer to that publication for a more in-depth review and extended list of references.

2. Discussion

a. Water Reducing Admixtures (WR)
This class of admixtures is generally accepted to give at least 5% water reduction with acceptable levels of retardation. In the vocabulary of ASTM C 494, these are referred to as Type A [2]. They are still dominated by lignosulfonate (LS) and sugar based chemistries, due to their lower cost/performance characteristics. Most innovation in the field of water reducers over the last few decades has focused on lowering the sugar content and air entraining characteristics of LS. The success of achieving these goals is strongly dependent upon the tree source (hardwood versus softwood) from which the LS comes and the production conditions of preparing the LS. There have also been efforts to improve molecular weight distributions and achieve higher levels of water reduction [3].

b. Mid Range Water Reducing Admixtures (MRWR)
This class of admixtures is generally accepted to give approximately 10% water reduction with acceptable levels of retardation. While there is no specific ASTM C 494 classification for them, they are certified to a Type A, and some are able to meet the requirements of a Type F – High Range Water Reducing admixture (HRWR). In Australia there is a specific category for MRWR’s, the so called AS 1478.1-2000, which requires meeting the 10% water reduction level versus a control concrete. In the North America or Pacific regions, these products are typically based on LS, or more recently polycarboxylate ethers (PCE). In Asia, they are more often based on LS or beta-naphthalene sulfonate (BNS), with some recent emergence of PCE based types [4].

The main benefit of this class of admixtures is the ability to achieve moderate levels of water reduction with improved finishing characteristics. Prior to the introduction of these admixtures in North America in the mid 1980’s, there was a gap in performance. WR’s provided good finishing characteristics, but insufficient water reduction without retardation, while HRWR’s provided sufficient water reduction, but imparted generally poor finishing characteristics. An overview of the development of MRWR’s is given by Nmai, et al. [5].

c. High Range Water Reducing Admixtures (HRWR)
This class of admixtures is categorized by giving a minimum of 12 to 18% water reduction with acceptable levels of retardation, the former based on ASTM C 494 Type F requirements and the latter on Chinese standards. The range of chemistries used to achieve this performance is quite diverse. The earliest generations were based on sulfonated melamine formaldehyde condensates (SMF) and exhibited excellent water reduction capabilities, but generally poor slump life, hence they were used predominately in precast applications. The next generations were based on a sodium salt of BNS, which had the ability to achieve 30% water reduction, but still had insufficient slump life for many ready-mixed concrete applications. The introduction of a calcium salt of BNS in the 1980’s, which had adequate slump life, made possible the routine addition of a HRWR at the batch plant.

The main innovation in this class of admixtures has been the introduction and use of PCE’s. These materials were first introduced in Japan in the late 1980’s and have been rapidly expanding in use in many other regions in the late 1990’s and early 2000’s. These dispersants are based on a charged polymer backbone with pendant side chains and disperse using both electrostatic and steric hindrance mechanisms [6]. They are unique to this class of cement dispersants because they can be tailored chemically into an almost infinite number of possible configurations, in contrast to previous chemistries which allowed very little variation in structure. More importantly, many of these varied structures give rise to significant changes in both plastic and hardened performance when added to a cementitious system, as highlighted in Figures 1-4. As such, new levels of concrete performance can be achieved [7-8].
d. Viscosity Modifying Admixtures (VMA)

This class of admixtures is used to modify the rheological characteristics of cementitious mixtures (Fig. 5). They are generally based on natural polymers (i.e. welan gum), semi-synthetic polymers (i.e. modified cellulose ethers), or synthetic polymers (i.e. polyvinyl alcohol). Early use was in mortars and grouts to minimize bleeding and improve adhesion. In the 1990’s, versions were introduced for use in underwater concreting applications to prevent washout of fines, hence coining the term anti-washout admixtures (AWA). More recently the interest in adding them to self-consolidating concrete (SCC) has significantly expanded their use [9]. Early versions of SCC were made with a high content of fine material to maintain static and dynamic stability of the mixture. This raised concerns about creep and shrinkage of the hardened concrete. With the use of a VMA, a more conventional concrete mixture design could be used to provide stability, and minimize bleeding by providing more forgiveness to variations in water content (see Fig. 6). Additionally, VMA’s are finding application in conventional slump concrete applications to provide enhanced finishing characteristics to mixtures with poorly shaped or graded fine aggregates. The new VMA chemistries used for these applications are less retarding, more robust with respect to variations in cement chemistry, and have no adverse interaction with air entraining agents.

e. Shrinkage Reducing Admixtures (SRA)

This class of admixtures is used to minimize the effect of drying on the shrinkage of hydraulic cementitious systems. When the stresses developed during the volume change that occurs during shrinkage are higher than the tensile stress of the concrete, the effect is generally manifested in the form of cracking. Hence, the addition of the SRA helps minimize the formation of cracks in a slab or other structure. First introduced in the early 1980’s in Japan, these admixtures are based on low molecular weight polyoxyalkylene alkyl ethers. They are believed to reduce shrinkage by reducing the capillary tension inside the pore system during drying. They are applied at relatively high dosages of 0.75 to 2.0 % by cement weight and can give reductions in unrestrained drying shrinkage of as much as 80% [10]. A typical dosage response curve is shown in Figure 7. At the high end of the SRA dosage range, some reduction in compressive strength is typically observed, as well as some difficulties in obtaining an adequate air void system with rosin-based air entraining agents. Nevertheless, the consumption of SRA’s in concrete applications continues to rise in North America.

f. Corrosion Inhibiting Admixtures (CIA)

This class of admixtures is added to protect reinforced concrete structures constructed in marine environments or subjected to contact with deicing salts. They impart a reduction in the rate of corrosion and significantly extend the life of a structure, but do not completely “inhibit” corrosion as the name implies. The most common chemistry is based on calcium nitrite and is added integrally during the production of concrete. It works as an anodic inhibitor, thereby effectively elevating the chloride threshold at which corrosion initiates. It also meets the requirements of Type C – Accelerating Admixture, so it is generally used in combination with a retarder in warm/hot weather concreting. Another available corrosion inhibitor is an organic CIA based on a mixture of amines and esters and is considered a mixed inhibitor [11]. This CIA provides protection based on a dual mechanism of film formation to prevent chloride ingress, and inhibition by amine technology. A third technology is the use of the so called migrating corrosion inhibitors (MCI) which can be applied topically and consist of proprietary components.

g. Hydration Control Admixtures (HCA)

This class of admixtures is generally used to arrest the hydration of portland cement for days or even weeks, with the intention of initiating the hydration process at a later time. This “sleeping” concrete can then be “awakened” either by waiting for the effects of the HCA to wear off, or by activating it with a conventional accelerating admixture. These admixtures can be used to maintain workability during long hauls, stabilize returned concrete overnight for use the next day, or for treating wash water that is reincorporated into fresh concrete to minimize the adverse effects on time of setting and slump retention. HCA’s are a form of retarding admixtures that work on all mineral phases of the cement, in contrast to sugar based retarders, which tend to work primarily on the silicates and can make the concrete unusable if used at high dosages [12]. HCA’s are generally formulated based on carboxylic acids and/or phosphorus-containing organic acids/salts.

h. Cold Weather Admixtures

This class of admixtures is used to facilitate placement of concrete under conditions where the
concrete temperature is below the freezing point of water and would normally freeze without some form of protection. These admixtures work by providing both some level of freezing point depression and an acceleration of the hydration process. They generally contain inorganic salts and/or organic compounds and must be applied at relatively high dosages (2 to 6%), depending upon the conditions. Generally a water reducing component is included to further lower the water content and increase the salt concentration of the pore solution to minimize the chance of freezing before the concrete has set. Quite acceptable time of setting and early strength development can be achieved with the use of these admixtures, as shown in Table 1. Early versions of a CWA developed in the 1980’s have recently been improved with the use of new formulation ingredients [13].

i. Other Chemical Admixtures

Many other classes of admixtures are available, but are not discussed here. Such types as accelerating, retarding and air entraining admixtures have been around for decades and there has been relatively little innovation in these areas, except to transition away from chloride to non-chloride based accelerators. Mold release agents and curing compounds (internal and external) are available, but no significant advances have been reported recently. Admixtures for mitigating alkali-silica reaction are available, but have found limited use due to their high cost and the increased use of supplementary cementing materials to minimize the risk of expansion. Liquid dispersions of coloring admixtures are now available but require a measurable investment in dispensing equipment. Admixtures for reducing permeability, minimizing efflorescence and providing water repellency are also available, especially for applications in dry cast manufactured concrete products. Additionally, admixtures for providing germicidal, insecticidal and fungicidal control are available.

3. References

3. Reknes, K., and Gustafsson, J., “Effect of Modifications of Lignosulfonate on Adsorption on Cement and Fresh Concrete Properties,” Sixth CANMET/ACI International Conference on Superplasticizers and Other Chemical Admixtures in Concrete, SP-195, American Concrete Institute, Farmington Hills, MI, 2000, pp. 127-142.


**Figure 1.** Time of setting for concrete mixtures containing different types of dispersants. No additional formulation ingredients are used. Mix design is identical for all mixtures, except control which has a higher w/c. 380 kg/m$^3$ portland cement, w/c=0.38, s/a=0.43, slump=200 mm.

**Figure 2.** Slump flow versus mixing time under continuous rotary agitation in the laboratory for concrete mixtures containing three different PCE dispersants. Time zero corresponds to 7 minutes from initial contact of cement and water. Mix design is consistent for all mixtures with 445 kg/m$^3$ portland cement, w/c=0.35, s/a=0.43.
Figure 3. Compressive strength development for concrete mixtures containing different types of dispersants. No additional formulation ingredients are used. Mix design is identical for all mixtures, except control which has a higher w/c. 380 kg/m³ portland cement, w/c=0.38, s/a=0.43 and slump=20 cm.

Figure 4. Concrete viscosity as measured with the IBB Rheometer for concrete mixtures containing three different PCE dispersants. Mix design is consistent for all mixtures with 475 kg/m³ portland cement, w/c=0.36, s/a=0.55 and slump flow of 70 cm.
Figure 5. Increase of concrete viscosity as measured by the IBB Rheometer as a function of increased dosage of VMA.

Figure 6. Percentage of bleed water collected from the surface of an SCC mixture as a function of excess water in the mixture for concrete with and without a VMA. Excess water is reported as a percentage of the fine aggregate weight, simulating typical uncertainties encountered in practice when determining the actual water content of the fine aggregate. Mixture design at 0% additional water is 445 kg/m³ portland cement, s/a=0.45, w/c=0.40 and slump flow of 63 cm.
Figure 7. Example plot of length change (shrinkage) of concrete prisms versus days of drying at 23 C and 50% rh. Identical mixture designs were used, except for increasing dosages of SRA.

Table 1. Time of initial setting and compressive strength development for concrete made without and with two different dosages of cold weather admixture. Concrete was batched at 12 C and stored at -7 C. Cylinders were thawed at room temperature for 4 hours prior to performing compressive strength measurements. Concrete mixtures contained 350 kg/m³ portland cement and had a 15 cm slump.

<table>
<thead>
<tr>
<th>CWA Dose (ml/kg)</th>
<th>0</th>
<th>39.6</th>
<th>59.4</th>
</tr>
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<tbody>
<tr>
<td>Setting Time (hr)</td>
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<td>3.8</td>
</tr>
<tr>
<td>Compressive Strength (MPa)</td>
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<td>1</td>
<td>6.4</td>
</tr>
<tr>
<td></td>
<td>7 day</td>
<td>4.1</td>
<td>10.1</td>
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</tbody>
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