Viscosity Modifiers to Enhance Concrete Performance

Dale P. Bentz, Kenneth A. Snyder, Max A. Peltz
Engineering Laboratory
National Institute of Standards and Technology
100 Bureau Drive, Stop 7313
Gaithersburg, MD 20899
E-mail: dale.bentz@nist.gov, kenneth.snyder@nist.gov, max.peltz@nist.gov

Karthik Obla, Haejin Kim
National Ready-Mixed Concrete Association
900 Spring Street
Silver Spring, MD 20910
E-mail: kobla@nrmca.org, hkim@nrmca.org

Abstract

The hazard rate function for concrete structures often is portrayed as a “bathtub”-shaped curve, with a finite ever-decreasing probability of early-age failures being followed by a life with a relative low, constant probability of failure that ultimately increases dramatically as the end of service is reached. Ideally, new concrete technologies should reduce the failures occurring at both ends of this service life spectrum. VERDiCT (Viscosity Enhancers Reducing Diffusion in Concrete Technology) is one such technology, having the potential to reduce the propensity for early-age cracking, while also reducing long-term transport coefficients of deleterious ions such as chlorides. In this paper, the performance of a typical VERDiCT admixture, a viscosity modifier/shrinkage-reducing admixture, is investigated in mortars and concretes, both as an addition to the mixing water and as a concentrated solution used to pre-wet fine lightweight aggregates. A reduction in early-age cracking is achieved by eliminating autogenous shrinkage stresses that typically develop in lower water-to-cementitious materials ratio concretes. By substantially increasing the viscosity of the pore solution in the concrete, the resistance to ionic diffusion is proportionally increased relative to a control concrete without the VERDiCT admixture. Here, chloride ion diffusion coefficients are evaluated for two types of concretes containing typical substitution levels of supplementary cementitious materials, namely either 25 % fly ash or 40 % slag by mass. For the eight concrete mixtures investigated, the effective diffusion coefficient was reduced by approximately 33 % by adding the VERDiCT admixture, which, in practice, may imply a 50 % increase in their service life, while the autogenous shrinkage was virtually eliminated. However, these benefits in early-age cracking resistance and long-term durability are tempered by up to a 20 % reduction in compressive strength that may need to be accounted for at the design stage.

Keywords: Autogenous deformation; diffusion; durability; service life; strength; viscosity.

Introduction

Concrete, like many widely employed construction materials, typically follows the classic bathtub hazard rate function curve [1]. A measurable fraction of concrete structures exhibit problems with early-age cracking [2]. Those that perform well at these early ages often provide a long and generally service-free life, followed by end-of-life failures, due to the material's most common degradation mechanisms including sulfate attack, chloride-induced corrosion, freeze-thaw attack or degradation, and/or alkali-silica reaction. While most new concrete technologies are intended and designed to address either the early-age performance or the longer term durability of concrete, those that provide benefits in both arenas would offer significant advantages, such as reduced concrete mixture complexity.

In 2008, a new strategy was developed for reducing diffusive transport in concrete [3], as well as reducing the propensity for early-age cracking caused by autogenous stresses. Rather than densifying the binder matrix in the concrete (which sometimes leads to early-age cracking issues), the new approach focused on appropriately increasing the viscosity of the solution that fills the pores within a concrete. Because the most common long-term degradation mechanisms involve diffusive transport through the pore solution followed by destructive chemical reactions, the service life of a concrete is often inversely proportional to the diffusion coefficient. Based on Walden's rule [4], the ionic diffusion coefficient should be inversely proportional to the solution viscosity. Therefore, doubling the viscosity halves the diffusion rate, thus potentially doubling the service life of the concrete. Previous studies have verified that this theoretical relationship indeed holds for a variety of nanoscale viscosity modifiers evaluated in both bulk solutions and in mortars [3, 5-7].

The new technology has been assigned the acronym of VERDiCT = Viscosity Enhancers Reducing Diffusion in Concrete Technology. While the VERDiCT admixture can be added directly to the mixing water, enhanced performance has been achieved in mortars when a VERDiCT solution is used to pre-wet fine lightweight aggregates (LWA) [6,7], effectively combining the viscosity modification with internal curing (IC). Since the previous studies [3, 5-7] have focused mainly on the longer term diffusion resistance of mortar specimens to chloride ingress, the objectives of the present study were twofold: 1) to examine the early-age performance of mortars with and without the VERDiCT admixture and 2) to evaluate the performance of the viscosity modifier in actual concrete mixtures containing commonly used quantities of representative supplementary cementitious materials, namely fly ash and slag.

Research Significance

The decaying state of U.S. infrastructure requires that new construction and repair materials provide increased service life. New concrete construction for transportation infrastructure is frequently plagued by early-age cracking and premature deterioration of joints, for example. New technologies that reduce early-age cracking while also increasing service life [8] would be a significant improvement. Using chemical admixtures that increase pore solution viscosity, while also reducing its surface tension, is one potential paradigm for providing such performance. The present study demonstrates the efficacy of this technology to reduce early-age stresses and strains, while also significantly reducing long-term chloride ion diffusion coefficients.

Materials and Experimental Procedures

While several VERDiCT admixtures have been evaluated in past studies [3, 5-7], in the present study, all mortars and concretes were prepared using a single VERDiCT admixture, a commercially available shrinkage-reducing admixture, specifically a polyoxyalkylene alkyl ether. An aqueous solution containing 10 % by mass of this viscosity modifier has a viscosity that is 50 % greater than that of pure water [3]. Such a solution also provides about a 55 % reduction in surface tension [9].

Mortars were prepared to assess the early-age autogenous deformation properties of systems with and without the VERDiCT admixture (introduced using IC). Specifically, the VERDiCT mortar was prepared with a partial substitution of fine LWA for normal weight sand, with the fine LWA being pre-wetted with a 50:50 solution of the VERDiCT admixture in distilled water. Concretes were prepared to verify the effectiveness of the VERDiCT admixture in reducing diffusive transport in typical ready-mixed concretes containing supplementary cementitious materials, in this case, either 25 % fly ash or 40 % slag by mass. For the concretes, the VERDiCT admixture was either introduced directly in the mixing water or via the pre-wetting of fine LWA.

Mortars

Two mortars were prepared using an ASTM C150 [10] Type I/II cement, with a water-to-cement ratio by mass (*w/c*) of 0.35 and 55 % sand (a blend of four silica sands) by volume. One mortar was prepared without any viscosity modifier and the other with the viscosity modifier added by pre-wetting lightweight aggregate (LWA) with a 50:50 solution of the viscosity modifier in distilled water. Since the separate influences of IC [11] and shrinkage-reducing admixtures [12] on autogenous shrinkage have been evaluated previously, in the present study, only their evaluation as an integrated system was performed. A blend of four silica sands, each with a specific gravity of 2.61, was utilized to prepare the mortars. In the mortar with the VERDiCT admixture and IC, an LWA (expanded clay) sand with a pre-wetted specific gravity of 1.5, an absorption of 26.5 % water by dry mass, and a desorption of 90 % of this water at a relative humidity of 93 % was employed. This desorption was determined by drying the pre-wetted LWA to constant mass over a saturated salt slurry of KNO_3. The LWA sand replaced an equal volume of normal weight silica sand. The dosage of the LWA sand was such that when pre-wetted with a 50:50 solution of the VERDiCT admixture, the readily available admixture (accounting for the 90 % desorption factor) was equivalent to 10 % of the mass of the mixing water contained in the mixture. This VERDiCT dosage is thus in line with that employed in previous studies [3, 5-7]. Complete mortar mixture proportions are provided in Table 1.

Mortars were mixed in a planetary mixer and specimens were prepared for the evaluation of isothermal calorimetry to 7 d, semi-adiabatic calorimetry to 3 d, autogenous shrinkage (ASTM C1698 [13]) to 28 d, and compressive strength (ASTM C109 [10]) at ages of 1 d, 3 d, 7 d, 28 d and 91 d. For the semi-adiabatic calorimetry, replicate specimens from separate batches have indicated a standard deviation of 1.4 °C (2.5 °F) in the maximum specimen temperature achieved during a 3 d test [14]. Prior to compressive strength testing, the control mortar cubes were stored in saturated limewater, while the VERDiCT/IC mortar cubes were stored in a sealed container and located directly above (but not touching) a small supply of saturated limewater; preventing direct contact between the VERDiCT/IC mortars and limewater promoted migration of the viscosity modifier solution from the LWA to the surrounding cement paste during curing. Both sets of mortar cube specimens were stored in an environmental chamber maintained at 23 °C ± 1 °C (73 °F ± 2°F).

Table 1. Mixture proportions for mortar mixtures.

Component	*w/c* = 0.35 control	*w/c* = 0.35 VERDiCT in LWA
Cement	1250 g (2.75 lb)	1250 g (2.75 lb)
Water	437.5 g (0.96 lb)	437.5 g (0.96 lb)
Sand	2626.3 g (5.78 lb)	1828.7 g (5.78 lb)
LWA (pre-wetted)	---	464.1 g (1.02 lb)
VERDiCT in LWA		48.6 g (0.11 lb)

Concretes

Concretes were batched and specimens prepared using the research laboratory facilities of the National Ready Mixed Concrete Association (NRMCA), to ensure that the new VERDiCT technology can be implemented following typical industry practice. To evaluate the performance of the VERDiCT admixture in mixtures containing supplementary cementitious materials, the two control concretes contained either 25 % Class F fly ash or 40 % slag replacement for cement by mass. The water-to-cementitious materials ratio by mass (*w/cm*) for the two types of concrete was set at a value commonly employed in transportation applications (0.41 to 0.42). For each of these two concrete types, four mixtures were designed and prepared: a control mixture, a mixture with the VERDiCT admixture in the mixing water (10 % solution), a mixture with internal curing via pre-wetted lightweight aggregate (LWA) sand containing distilled water, and finally a mixture with the same LWA that was pre-wetted by a 50:50 solution of the VERDiCT admixture in distilled water. For the concrete, the LWA sand (an expanded shale) had a pre-wetted specific gravity of 1.7, an absorption of 25 % by dry mass, and a desorption of 93 % at a relative humidity of 93 %. Mixtures were designed to provide a slump in the range of 75 mm (3 in.) to 175 mm (7 in.), with the dosage of an ASTM Type F water reducer [13] being adjusted during mixing to provide the requisite slump. Complete mixture proportions for these eight concrete mixtures can be found in Table 2. Fresh concretes were characterized with respect to slump (ASTM C143), temperature (ASTM C1074), and unit weight (ASTM C138) [13]. Hydration progress was monitored for the first 24 h, using commercially available semi-adiabatic testing equipment.

Concrete cylinders, 100 mm (4 in.) by 200 mm (8 in.), without LWA were demolded at 24 h and cured in a fog room maintained at 23 °C ± 1 °C (73 °F ± 2 °F) until the time of testing or until their time of chloride exposure. Concrete cylinders with LWA were demolded at 24 h and stored in the same fog room in double plastic bags, once again to better promote the migration of the water/VERDiCT solution contained in the LWA into the surrounding hydrating cement paste. Cylinder strength testing was performed after 28 d, 56 d, and 365 d of curing. For specimens that were to be exposed to chlorides at an age of 56 d, the LWA concrete cylinders were removed from their plastic bags at 55 d and cut in half to create two 100 mm (4 in.) x 100 mm (4 in.) cylinders. Their sides were coated with epoxy and they were returned to the fog room (no bags) for 1 d, before finally being submerged in individual containers of the chloride exposure solution. The sides of the non-LWA concrete half-cylinders were also coated at 55 d, before returning them to the fog room for 1 d prior to their chloride exposure. All specimens were exposed to a 2.8 mol/L chloride solution (as per ASTM C1556 [13]) at 56 d of age.

Table 2. Mixture proportions in units of kg/m^3 (lb/yd^3) except where noted (assumed air content of 2 %) and fresh properties.

Designation	FA	FA-V	FA-IC	FA-VIC	Slag	Slag-V	Slag-IC	Slag-VIC
Cement	270 (454)	262 (442)	266 (449)	268 (452)	220 (371)	219 (370)	217 (365)	222 (374)
Fly ash	90 (151)	88 (147)	89 (150)	90 (151)	---	---	---	---
Slag	---	---	---	---	146 (246)	146 (247)	145 (244)	148 (250)
Coarse Aggregate	1141 (1923)	1111 (1872)	1127 (1899)	1136 (1915)	1138 (1917)	1141 (1922)	1127 (1899)	1155 (1946)
Fine aggregate	777 (1310)	757 (1275)	506 (854)	511 (861)	795 (1339)	797 (1343)	526 (886)	539 (908)
Pre-wetted LWA sand	---	---	170 (287)	172 (289)	---	---	170 (287)	174 (294)
Water	151 (254)	147 (247)	149 (251)	150 (253)	150 (253)	151 (254)	149 (251)	152 (257)
VERDiCT admixture	---	16 (27)	---	17.2[A] (29)	---	16 (27)	---	17.4[A] (29)
Type F water reducer L/m^3 (fl. oz./yd^3)	0.97 (25.2)	1.58 (40.8)	0.72 (18.6)	0.73 (18.8)	1.46 (37.7)	1.22 (31.5)	0.94 (24.3)	0.80 (20.7)
w/cm	0.42	0.42	0.42	0.42	0.41	0.41	0.41	0.41
Unit weight	2440 (4120)	2380 (4010)	2320 (3910)	2340 (3940)	2460 (4150)	2470 (4160)	2350 (3950)	2400 (4050)
Slump	75 mm 3 in.	165 mm 6.5 in.	180 mm 7 in.	165 mm 6.5 in.	180 mm 7 in.	180 mm 7 in.	180 mm 7 in.	190 mm 7.5 in.

[A] VERDiCT admixture added as a 50:50 solution used to pre-wet the LWA sand, accounting for the 93 % desorption efficiency measured for the LWA.

Resistance to chloride ingress was evaluated using both a rapid migration test and a bulk diffusion test. The Rapid Migration test (RMT) is a provisional AASHTO standard (2004), AASHTO TP 64. Two 100 mm x 200 mm (4 in. x 8 in.) cylindrical specimens were cured in the fog room at 23 °C (73 °F) until the test ages of 56 d and 365 d. The top 50 mm (2 in.) of the cylinders were cut off and used for the test. At 56 d, the specimens were evaluated from their cut surface, while at 365 d, they were evaluated from their cast/finished surface. The vacuum saturation step in the standard test was omitted, to avoid possibly saturating the unsaturated

LWA present in some of the concrete mixtures. A constant voltage of 60 V was applied to the test specimen for a period of 18 h. The specimen was then fractured along its diameter and sprayed with silver nitrate solution. Silver nitrate reacts with the chloride ions (turns white) to provide a visible depth of penetration of the chlorides. The depth of penetration of chlorides was measured at ten locations and averaged.

In the chloride bulk diffusion test (ASTM C 1556 [13]), after 56 d of moist curing, the top and bottom 75 mm (3 in.) of the concrete cylinders were cut and sealed on their sides. Each test specimen was immersed in a 2.8 mol/L sodium chloride solution with its unsealed faces exposed to the solution until attaining an age of either 26 weeks or 52 weeks. The specimen was then removed and ground off in sequential 2 mm (0.078 in.) thick layers from an exposed surface. After 26 weeks exposure, these grindings were performed from a cut surface, while after 52 weeks exposure, they were performed from either a cast or a cast/finished surface. The acid soluble (total) chloride content was measured at each depth, from which an apparent chloride diffusion coefficient was calculated in accordance with ASTM C 1556. The chloride diffusion coefficient is referred to as "apparent" because no corrections are made for chloride binding within the cement hydration products; these bound chlorides would not be available to initiate corrosion. The acid soluble chloride content was measured using potentiometric titration in accordance with ASTM C1152 [13]. The apparent chloride diffusion coefficient is typically used in service life prediction models to estimate the service life of concrete structures exposed to chlorides. For the chloride diffusion, two replicate specimens were tested for each mixture.

Results

Mortars

The primary objective of the mortar testing was to evaluate the early-age performance of mixtures with and without the VERDiCT/IC technology. As shown in Figure 1, the combination of the viscosity modifier with additional curing water provided via the pre-wetted LWA sand virtually eliminated autogenous shrinkage by comparison with the control mixture where an autogenous shrinkage of about 250 microstrain was obtained at an age of 28 d. In this case, the reduction in autogenous shrinkage is due to both the IC provided by the 50 % distilled water in the solution used to pre-wet the LWA and by the reduced surface tension of the pore solution due to the viscosity modifier being employed (e.g., a conventional shrinkage-reducing admixture). As illustrated by the complete autogenous deformation curves provided in Figure 1, the VERDiCT/IC system actually initially produced expansion for the first 7 d of sealed curing, with very little if any subsequent shrinkage. This significant reduction in autogenous shrinkage should translate into an increased resistance to early-age cracking [15].

Another contribution to early-age (cracking) performance is the temperature rise that occurs in a concrete under field conditions. For the two mortars examined in this study, Figure 2 indicates that their laboratory semi-adiabatic temperature rise behaviors are quite similar. There is an indication of a slight retardation and a lower temperature rise in the VERDiCT/IC mortar, most likely due to the presence of the viscosity modifier [3, 5-7], also supported by the isothermal calorimetry heat flow curves provided in Figure 3. The retardation is on the order of an hour, but as indicated by the cumulative heat flow curves in Figure 3, the two mortar mixtures have basically equivalent total heat releases (or degrees of hydration) at 7 d under isothermal conditions.

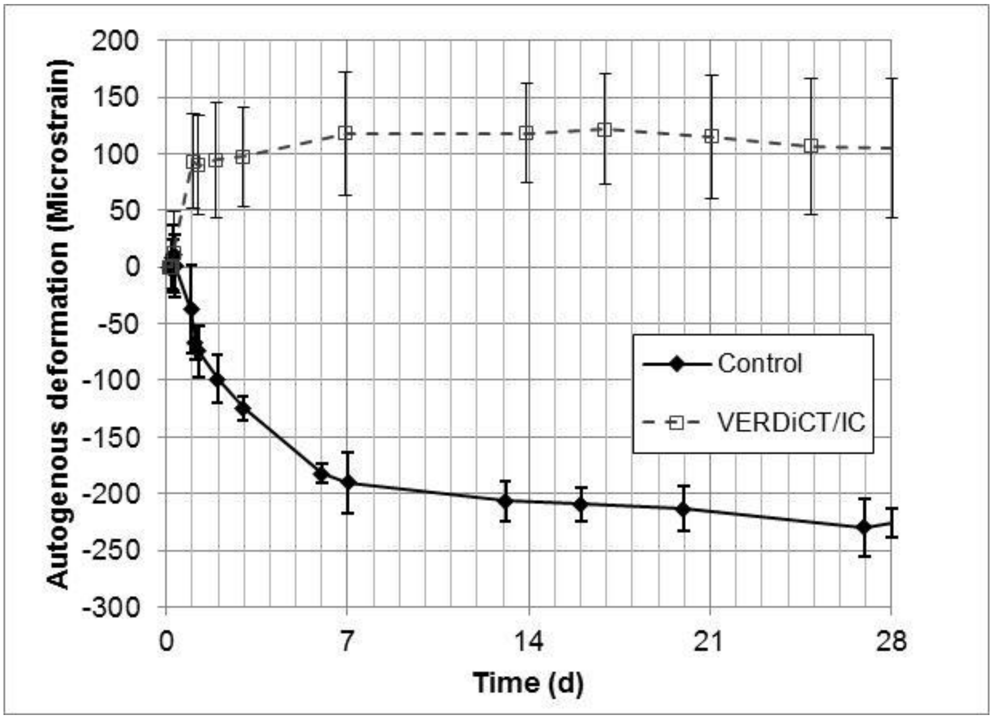

Figure 1. Autogenous deformation vs. time for mortars with and without the VERDiCT admixture. Error bars indicate ± one standard deviation for the testing of three specimens.

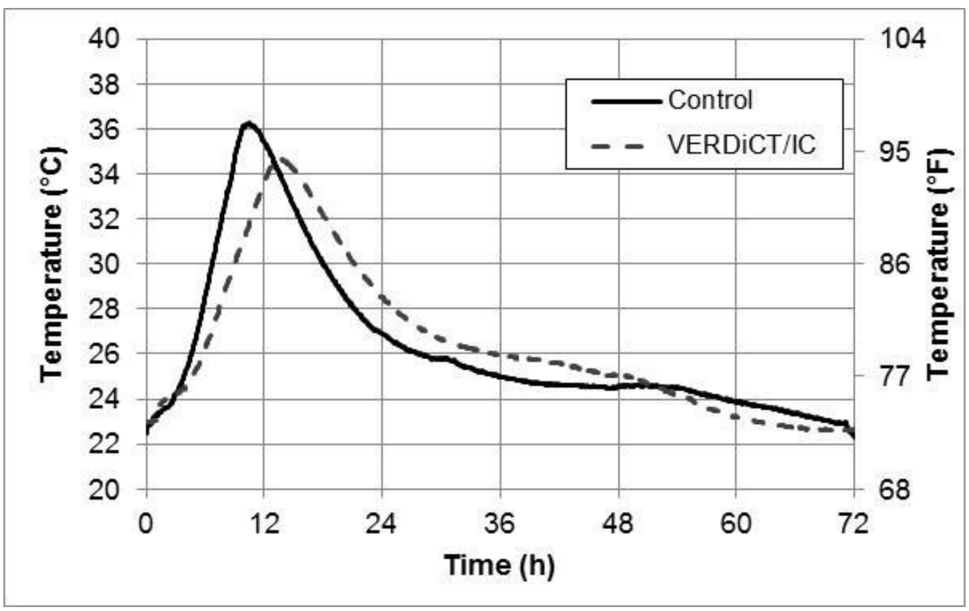

Figure 2. Semi-adiabatic temperature vs. time for mortars with and without the VERDiCT admixture.

The influence of this retardation can also be observed in the mortar cube compressive strength results provided in Figure 4. At an age of 1 d, due to the retardation and the presence of the (weaker) LWA, the strength of the VERDiCT/IC mortar is approximately 70 % of that of the control mortar. At ages of 3 d and beyond, however, as the effects of the retardation gradually diminish and eventually disappear, the VERDiCT/IC mortar consistently produces a strength that is about 80 % to 85 % of that of the control mortar. Similar results are seen in the concrete samples studied, indicating that mortar tests should be sufficient for developing concrete mixtures containing LWA to meet strength requirements.

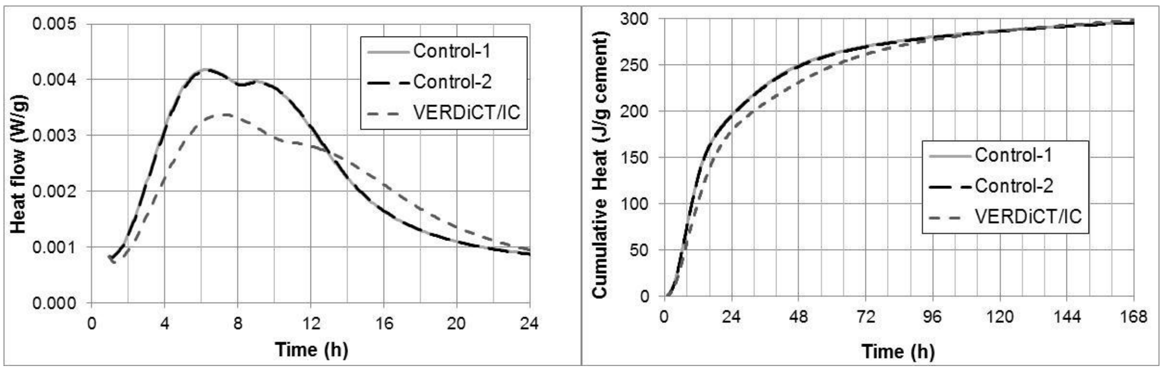

Figure 3. Isothermal calorimetry heat flow (left) and cumulative heat release (right) curves for mortars with and without the VERDiCT admixture. Two replicate curves are provided for the control (non-VERDiCT) mortar to provide an indication of the variability.
1 W/g= 1548 BTU/(h·lb) and 1 J/g=0.4299 BTU/lb.

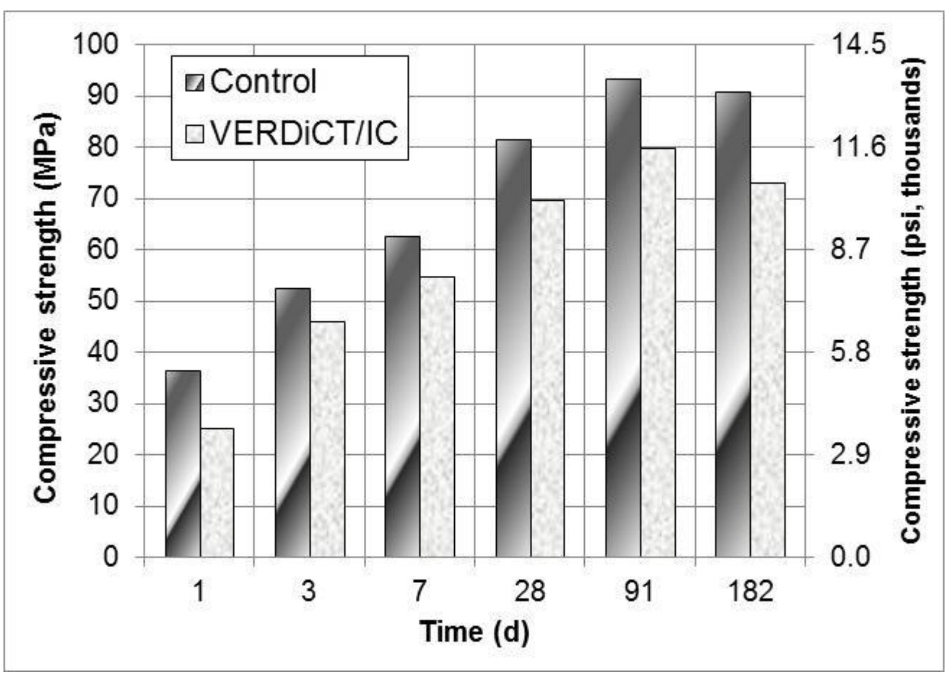

Figure 4. Compressive strength results to 182 d for mortars with and without the VERDiCT admixture. Average coefficient of variation amongst three replicate specimens was 4 %.

Concretes

As shown in Figure 5, all eight concretes achieved compressive strengths greater than or equal to 40 MPa (5800 psi) by 28 d. For the fly ash concrete, the mixture with the VERDiCT admixture in the mixing water actually produced increased strengths relative to the control mixture, while the mixtures with LWA for IC containing either water or a VERDiCT solution produced lower strengths, keeping in mind that the latter were cured under sealed conditions, while the concretes without LWA were cured directly in the fog room. For the slag mixtures, the mixtures with IC and/or the VERDiCT admixture all failed to achieve the strength levels attained by the control, providing only 70 % to 84 % of the strengths measured for the control cylinders. In general, the strength increases from 28 d to 56 d and from 56 d to 365 d were fairly similar for all concretes in a given class (fly ash or slag) regardless of LWA/VERDiCT, with the slag mixtures generally showing slightly less strength gain than their fly ash counterparts.

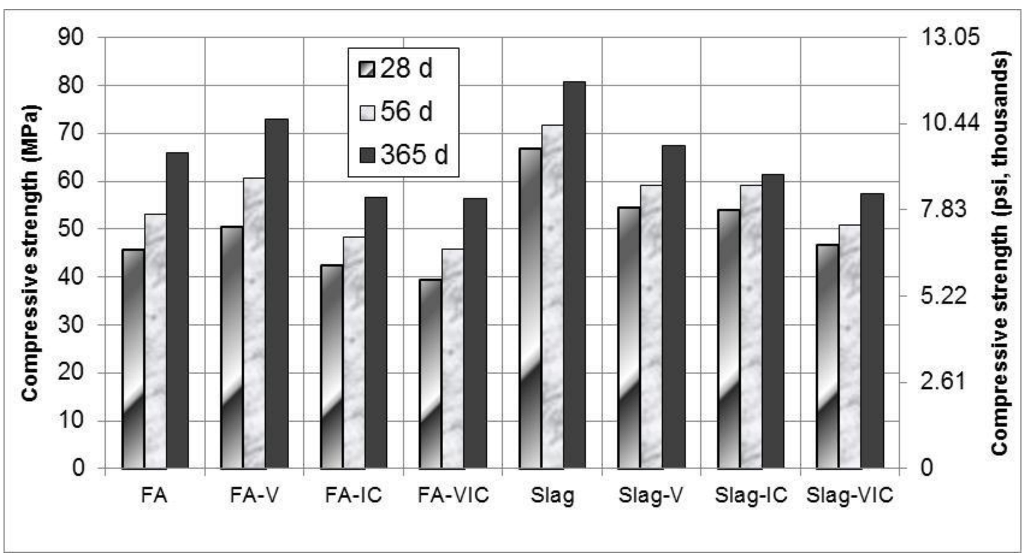

Figure 5. Compressive strength results for the concrete mixtures at ages of 28 d, 56 d, and 365 d. Average standard deviations in compressive strength for two replicate specimens for each mixture were 0.6 MPa (87 psi), 1.1 MPa (160 psi), and 1.2 MPa (174 psi), for testing at 28 d, 56 d, and 365 d, respectively.

Figure 6 provides the average relative chloride penetration depth measured following the rapid migration test for the concretes with VERDiCT relative to their respective controls (fly ash or slag). The observed reductions in penetration depths for the mixtures with fly ash in Figure 6 are in line with previous published performance results for this VERDiCT admixture in mortars [6, 7]. For the rapid migration test, much of the initial benefit of the VERDiCT/IC delivery over that of simply using VERDiCT in the initial mix water was lost when specimens were cured for 365 d prior to the rapid migration test. At these later ages, the LWA will have surrendered nearly all of their initial solution to the hydrating cement paste and may therefore contribute a sorption component to the rapid migration test, in addition to the electrically-driven diffusion. The 365 d results for the slag mixtures with VERDiCT in the mix water (Slag-V) or IC (Slag-IC) using water exhibit a quite anomalous behavior, with a chloride penetration depth that is much higher than the control. For the mixture with VERDiCT in the mix water (Slag-V), the ten individual measurements of penetration depth exhibited a wide disparity for one of the specimens, with values ranging between 4.2 mm (0.165 in.) and 13.0 mm (0.512 in.) (range of 8.8 mm or 0.346 in.). For the two specimens evaluated at 365 d for the slag mixture with IC (Slag-IC), similarly, these measurement ranges for the ten assessments of penetration depth were 5.8 mm (0.228 in.) and 6.2 mm (0.244 in.), versus the overall average range of 4.5 mm (0.177 in.) for the eight concrete mixtures.

The apparent chloride ion diffusion coefficients estimated from the long-term chloride ponding exposures are shown in Figure 7 and their accompanying estimated surface chloride concentrations are provided in Figure 8. In all cases in Figure 7, the apparent diffusion coefficient decreased significantly (by 30 % to 40 %) in going from 6 m to 1 yr, likely due to continuing hydration and densification of the (blended) cement paste in each mixture. The results in Figure 7 indicate a reduction in the diffusion coefficient for the modified concretes, whether via VERDiCT addition to the mixing water, IC, or VERDiCT addition via pre-wetted aggregates (VIC). While the reduction produced by VERDiCT is explained by the increase in

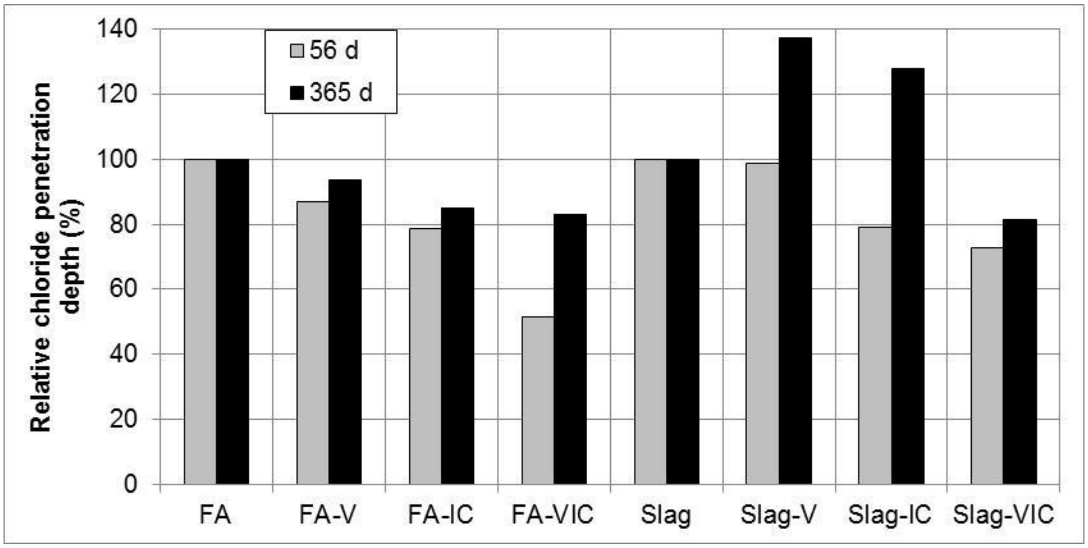

Figure 6. Relative chloride penetration depth from the rapid migration test for the eight concrete mixtures tested at ages of 56 d and 365 d; the controls (FA and Slag) are assigned a value of 100 %. For two replicate specimens, at 56 d, coefficients of variation in average penetration ranged between 4 % and 27 %, with an average of 14 %. At 365 d, these values ranged between 1 % and 38 %, with an average of 15 %.

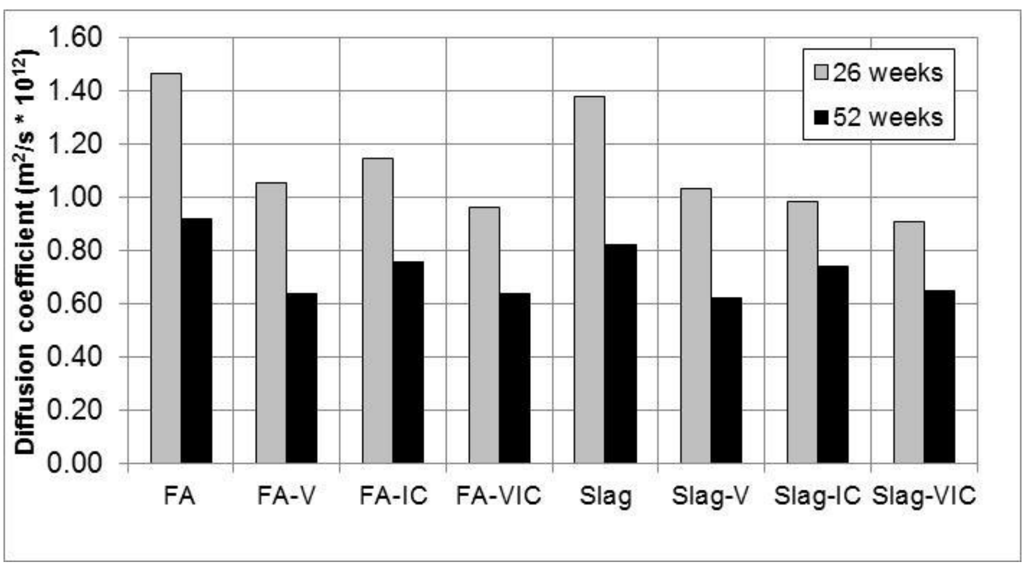

Figure 7. Estimated chloride ion diffusion coefficients for the eight concrete mixtures evaluated after 26 weeks or 52 weeks of exposure following 56 d of curing. Coefficients of variation (CoV) for the eight concrete mixtures ranged between 2 % and 9 %, with an average of 5 % for the 26 week data, while after 52 weeks, the CoV ranged between 5 % and 14 %, with an average of 10 %. $1*10^{-12}$ m^2/s = 0.049 in^2/yr.

pore solution viscosity, that achieved by the IC is due both to the provision of additional curing water to promote the hydration and pozzolanic reactions, and to the potentially superior interfacial transition zone (ITZ) microstructures that may be produced in a system with pre-wetted LWA [16]. For the concretes investigated in this study, IC with water provided apparent diffusion coefficient reductions of about 20 % and 30 % at an exposure age of 26 weeks for the fly ash and slag concretes, respectively. For an exposure age of 52 weeks, these corresponding reductions were 20 % and 10 %.

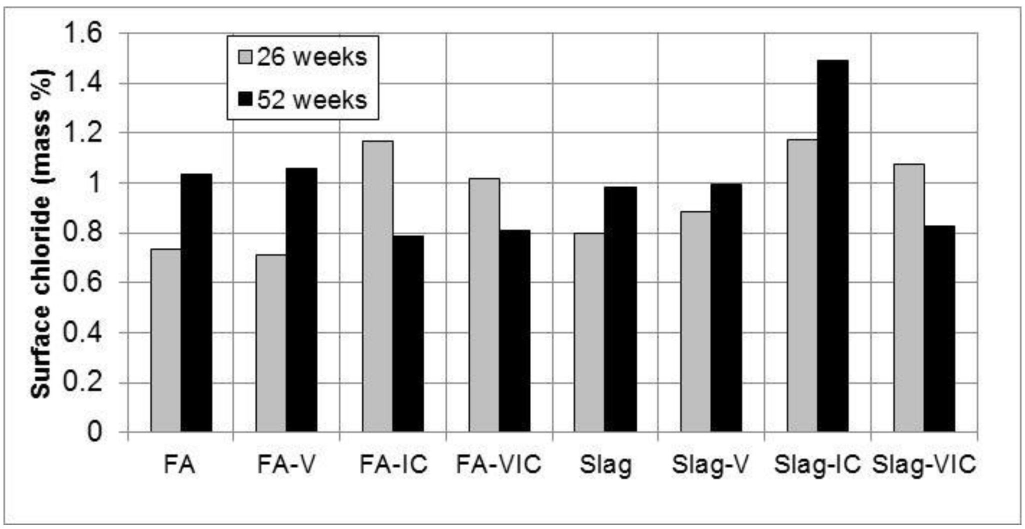

Figure 8. Estimated surface chloride concentration for the eight concrete mixtures evaluated after 26 weeks or 52 weeks of exposure following 56 d of curing. Specimens at 26 weeks were evaluated from cut surfaces while those at 56 weeks were evaluated from cast/finished surfaces. Coefficients of variation (CoV) for the eight concrete mixtures ranged between 1.4 % and 7.6 %, with an average of 4.7 % for the 26 week data, while after 52 weeks, the CoV ranged between 0.34 % and 19 %, with an average of 6.8 %.

Although the 26-week data indicates an improvement for VERDiCT/IC over VERDiCT in the mixing water for both the fly ash and slag concretes, at 52 weeks, their performance is nearly identical in both cases. This can be contrasted against previous results in ordinary portland cement mortars with *w/c* between 0.40 and 0.45 [6, 7], where 365 d exposure results continued to show a significant performance enhancement when the VERDiCT admixture was introduced via the LWA. This performance difference between mortar and concrete could be partially due to the presence of coarse aggregates and the higher total aggregate volume fraction in the latter (55 % in mortar, 70 % in concrete), as the fine LWA are likely more effective at depercolating the ITZs surrounding the fine normal weight aggregate in a mortar and less influential in depercolating these ITZs around both the coarse and fine normal weight aggregate in a concrete [16].

In several cases, the actual chloride profiles measured from cut surfaces at 26 weeks did not indicate the level of reduction in chloride penetration that would be suggested solely by the reduced apparent diffusion coefficients in Figure 7, due to the concurrent higher measured surface concentration of chlorides, particularly for the mixtures with the LWA (Figure 8). It appears that cutting the specimens from the mixtures containing LWA exposed porous LWA surfaces that increased the measured surface chloride concentration relative to the non-LWA mixtures. For this reason, at 52 weeks, specimens belonging to all of the mixtures were evaluated from their cast/finished surfaces instead of their cut surfaces. In Figure 8, it is clear that for the four mixtures that do not contain LWA, the cast/finished surfaces have a higher surface chloride concentration than the cut surface counterparts, most likely due to the higher paste/mortar content (wall effect, finishing effects, etc.). Conversely, for the mixtures that contain LWA (IC and VIC), the cut surfaces (at 26 weeks) generally had a much higher surface chloride concentration than their cast/finished counterparts. In this case, exposing the porous LWA in the cutting process overwhelms any difference in paste/mortar content between the two types of surfaces. The one exception to this is the slag IC mixture, where the cast/finished surfaces still had a higher surface concentration than the cut surfaces. In this case, both specimens evaluated at 52 weeks were cast/finished top surfaces, suggesting that for this particular mixture, the finishing process may have dramatically increased the paste/mortar content at the top surface.

Improvements in transport resistance achieved with the VERDiCT admixture were different depending on the measurement technique used for their assessment in this study. For the VERDiCT/IC introduction of the admixture, penetration depths measured in the rapid migration test were about 80 % of those of the corresponding control mixtures, while apparent diffusion coefficients measured in the ponding test were about 67 % of those of their corresponding control mixtures. Some of this difference may be due to the sorption effects introduced in the rapid migration test due to the saturation state of the LWA, as noted earlier. It should be noted that the previous VERDiCT studies have employed only direct chloride ponding exposures for characterizing their diffusion resistance [6, 7].

Conclusions

Based on the results presented in this paper, the following conclusions can be drawn concerning the addition of viscosity modifiers directly to the mixing water or via the pre-wetting of LWA:

1) The combination of IC via pre-wetted LWA and the surface tension reduction provided by the viscosity modifier employed in this study essentially resulted in the elimination of autogenous shrinkage in sealed *w/c*=0.35 mortar specimens,

2) IC using water provided reductions in apparent diffusion coefficients of 20 % and 10 % based on a 365 d chloride exposure for the fly ash and slag concretes, respectively,

3) In the concretes with fly ash or slag first cured for 56 d, the VERDiCT technology provided an approximate 33 % reduction in estimated apparent chloride diffusion coefficients, whether

introduced directly into the mixing water or via pre-wetted LWA, when assessed by a long-term chloride ponding exposure with subsequent grinding and titration,

4) Cut surfaces of the specimens containing LWA generally exhibited a higher surface concentration of chlorides than the cast/finished surfaces, somewhat offsetting the positive effects of their reduced diffusion coefficients when considering overall chloride penetration; conversely, the cut surfaces of the concretes containing only normal weight aggregates contained a lower surface chloride concentration than their cast/finished counterparts, and

5) The VERDiCT technology, whether added directly to the mixing water or via pre-wetted LWA, produces up to a 20 % reduction in measured compressive strength in most cases, with the exception of the addition of VERDiCT to the mixing water of the fly ash concrete investigated in this study, where a slight increase was observed.

Acknowledgements

The authors would like to thank Mr. John Winpigler, formerly of the Engineering Laboratory at NIST, and Mr. Stuart Sherman and Mr. Soliman Ben-Barka of the NRMCA for their assistance with the experimental program. The provision of materials by BASF, Big River Industries, Inc., Holcim, Lehigh Cement Corporation, Northeast Solite Corporation, and Separation Technologies, LLC is gratefully acknowledged.

References

[1] Lawless, J.F., Statistical Models and Methods for Lifetime Data, Wiley & Sons, New York, 1982.

[2] Report on Early-Age Cracking: Causes, Measurement, and Mitigation, ACI 231 R-10, American Concrete Institute, Farmington Hills, MI, Jan. 2010.

[3] Bentz, D.P., Snyder, K.A., Cass, L.C., and Peltz, M.A., "Doubling the Service Life of Concrete. I: Reducing Ion Mobility Using Nanoscale Viscosity Modifiers," *Cement and Concrete Composites*, V. 30, No. 8, 2008, pp. 674-678.

[4] Robinson, R.A., and Stokes, R.H., Electrolyte Solutions (2nd Revised Edition), Dover Publications Inc., Mineola, NY, 2002.

[5] Bentz, D.P., Peltz, M.A., Snyder, K.A., and Davis, J.M., "VERDiCT: Viscosity Enhancers Reducing Diffusion in Concrete Technology," *Concrete International*, V. 31, No. 1, Jan. 2009, pp. 31-36.

[6] Bentz, D.P., Snyder, K.A., and Peltz, M.A., "Doubling the Service Life of Concrete Structures. II: Performance of Nanoscale Viscosity Modifiers in Mortars," *Cement and Concrete Composites*, V. 32, No. 3, 2010, pp. 187-193.

[7] Snyder, K.A., Bentz, D.P., and Davis, J.M., "Using Viscosity Modifiers to Reduce Effective Diffusivity in Mortars," accepted by *ASCE Journal of Materials in Civil Engineering*, 2011.

[8] Cusson, D., Lounis, Z., and Daigle, L., "Benefits of Internal Curing on Service Life and Life-Cycle Cost of High-Performance Concrete Bridge Decks – A Case Study," *Cement and Concrete Composites*, V. 32, No. 5, 2010, pp. 339-350.

[9] Sant, G., Eberhardt, A., Bentz, D., and Weiss, J., "The Influence of Shrinkage-Reducing Admixtures (SRAs) on Moisture Absorption in Cementitious Materials at Early Ages," *ASCE Journal of Materials in Civil Engineering*, V. 22, No. 3, 2010, pp. 277-286.

[10] ASTM Annual Book of Standards. Vol. 04.01 Cement; Lime; Gypsum. ASTM International, 2009.

[11] Geiker, M.R., Bentz, D.P., and Jensen, O.M., "Mitigating Autogenous Shrinkage by Internal Curing," High-Performance Structural Lightweight Concrete, ACI SP-218, Eds. J.P. Ries and T.A. Holm, American Concrete Institute, Farmington Hills, 143-154, 2004.

[12] Bentz, D.P., Geiker, M.R., and Hansen, K.K., "Shrinkage-Reducing Admixtures and Early Age Desiccation in Cement Pastes and Mortars," *Cement and Concrete Research,* V. 31, No. 7, 2001, pp. 1075-1085.

[13] ASTM Annual Book of Standards. Vol. 04.02 Concrete and Aggregates. ASTM International, 2009.

[14] Bentz, D.P., and Turpin. R., "Potential Applications of Phase Change Materials in Concrete Technology," *Cement and Concrete Composites*, V. 29, No. 7, 2007, pp. 527-532.

[15] Henkensiefken, R., Bentz, D., Nantung, T., and Weiss, J., "Volume Change and Cracking in Internally Cured Mixtures Made with Saturated Lightweight Aggregates under Sealed and Unsealed Conditions," *Cement and Concrete Composites,* V. 31, No. 7, 2009, pp. 426-437.

[16] Bentz, D.P., "Influence of Internal Curing Using Lightweight Aggregates on Interfacial Transition Zone Percolation and Chloride Ingress in Mortars," *Cement and Concrete Composites,* V. 31, No. 5, 2009, pp. 285-289.