ACI MATERIALS JOURNAL TECHNICAL PAPER

Title no. 110-M44

Viscosity Modifiers to Enhance Concrete Performance

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The hazard rate function for concrete structures is often portrayed as a "bathtub"-shaped curve, with a finite ever-decreasing probability of early-age failures being followed by a life with a relatively 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 strategy based on increasing the pore solution viscosity. This approach has 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 mortar and concrete, 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-cementitious material ratio (w/cm) concrete. 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. Herein, chloride ion diffusion coefficients are evaluated for two types of concrete 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, freezing-and-thawing 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] and 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 into the concrete (enhanced by the presence of cracks), 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[3,5-7] have verified that this theoretical relationship indeed holds for a variety of nanoscale viscosity modifiers evaluated in both bulk solutions and mortar.

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 mortar when a VERDiCT solution is used to pre-wet fine lightweight aggregates (LWAs),[6,7] effectively combining the viscosity modification with internal curing (IC). Because the previous studies[3,5-7] have mainly focused on the longer-term diffusion resistance of mortar specimens to chloride ingress, the objectives of this study were twofold: 1) to examine the early-age performance of mortar 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. This 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 this study, mortar and concrete were

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ACI Materials Journal, V. 110, No. 5, September-October 2013.

MS No. M-2011-381.R3 received October 27, 2012, and reviewed under Institute publication policies. Pertinent discussion including author's closure, if any, will be published in the July-August 2014 *ACI Materials Journal* if the discussion is received by April 1, 2014.

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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 (4.03 lb)
LWA (pre-wetted)	—	464.1 g (1.02 lb)
VERDiCT in LWA	—	48.6 g (0.11 lb)

prepared using a single VERDiCT admixture, a commercially available shrinkage-reducing admixture (SRA)—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 approximately a 55% reduction in surface tension.[9]

Mortar specimens were prepared to assess the early-age autogenous deformation properties of systems with and without the VERDiCT admixture (introduced using IC). Specifically, the VERDiCT/IC mortar was prepared with a partial substitution of fine LWA for normalweight sand, with the fine LWA being pre-wetted with a 50:50 solution of the VERDiCT admixture in distilled water. Concrete mixtures were prepared to verify the effectiveness of the VERDiCT admixture in reducing diffusive transport in typical ready mixed concrete containing supplementary cementitious materials—in this case, either 25% fly ash or 40% slag by mass. For the concrete, the VERDiCT admixture was either introduced directly in the mixing water or via the pre-wetting of fine LWA. Concrete was prepared using a No. 57 crushed stone coarse aggregate.

Mortar—Two mortars were prepared using an ASTM C150/C150M-09[10] Type I/II cement with a water-cement ratio (*w/c*) by mass 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 (a commercially available SRA) added by pre-wetting LWA with a 50:50 solution of the viscosity modifier in distilled water. This 50:50 solution has a viscosity 1200% greater than that of pure water and a surface tension 55% less than that of pure water. Because the separate influences of IC[11,12] and SRAs[11-13] on autogenous shrinkage, heat release, internal relative humidity, and compressive strength have been evaluated previously, in this 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 used to prepare the mortar. 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 normalweight 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.

Mortar was mixed in a planetary mixer and specimens were prepared for the evaluation of isothermal calorimetry to 7 days; semi-adiabatic calorimetry to 3 days; autogenous shrinkage (ASTM C1698-09[14]) on 420 mm (16.5 in.) long corrugated tubes to 28 days; and compressive strength (ASTM C109/C109M[15]) of 50.8 mm (2 in.) mortar cubes at ages of 1, 3, 7, 28, and 91 days. Approximately 8 g (0.28 oz) of mortar were used for the isothermal calorimetry specimens, while the semi-adiabatic calorimetry cells each held approximately 370 g (0.81 lb) of mortar. For the semi-adiabatic calorimetry, replicate specimens from separate batches indicated a standard deviation of 1.4°C (2.5°F) in the maximum specimen temperature achieved during a 3-day test.[16] 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 mortar 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).

Concrete—Concrete mixtures were batched and specimens were 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

Table 2—Mixture proportions in units of kg/m^3 (lb/yd^3) except where noted (assumed air content of 2% for proportioning) 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[*] (29)	—	16 (27)	—	17.4[*] (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, mm (in.)	75 (3)	165 (6.5)	180 (7)	165 (6.5)	180 (7)	180 (7)	180 (7)	190 (7.5)

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

control concretes contained either 25% Class F fly ash or 40% slag replacement for cement by mass. These replacement levels were selected based on the common practices currently employed by the industry in using Class F fly ash or slag. The water-cementitious material ratio (*w/cm*) by mass 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 IC via pre-wetted 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 to 175 mm (3 to 7 in.), with the dosage of an ASTM C494/C494M-10[17] Type F water reducer being adjusted during mixing to provide the requisite slump. Complete mixture proportions for these eight concrete mixtures can be found in Table 2. Fresh concrete was characterized with respect to slump (ASTM C143/C143M[18]), temperature (ASTM C1074[19]), and unit weight (ASTM C138/C138M).[20] While a 50% increase in mixing water viscosity due to the VERDiCT addition might be expected to negatively influence slump, for the mixtures investigated in this study, the observed impact was minimal. For example, for the slag concrete, the VERDiCT mixtures had equivalent or greater slumps than their counterpart control mixtures, even with a lower dosage of the water reducer. Hydration progress was also monitored for the first 24 hours using commercially available semi-adiabatic testing equipment.

Concrete cylinders with dimensions of 100 x 200 mm (4 x 8 in.) without LWA were demolded at 24 hours and cured in a fog room maintained at 23°C ± 1°C (73°F ± 2°F) until the time of testing or until the time of chloride exposure. Concrete cylinders with LWA were demolded at 24 hours 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, 56, and 365 days of curing. For specimens that were to be exposed to chlorides at an age of 56 days, the LWA concrete cylinders were removed from their plastic bags at 55 days and cut in half to create two 100 x 100 mm (4 x 4 in.) cylinders. Their sides were coated with epoxy and they were returned to the fog room (no bags) for 1 day 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 days before being returned to the fog room for 1 day prior to chloride exposure. All specimens were exposed to a 2.8 mol/L chloride solution (as per ASTM C1556[21]) at 56 days of age.

Resistance to chloride ingress was evaluated using both a rapid migration test (RMT) and a bulk diffusion test. The RMT is a provisional AASHTO standard (2004)—AASHTO TP 64.[22] Two 100 x 200 mm (4 x 8 in.) cylindrical specimens were cured in the fog room at 23°C (73°F) until the test ages of 56 and 365 days. The top 50 mm (2 in.) of the cylinders were cut off and used for the test. At 56 days, the specimens were evaluated from their cut surface; at 365 days, 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 hours. 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 10 locations and averaged.

In the chloride bulk diffusion test (ASTM C1556[21]), after 56 days 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 or 52 weeks. The specimen was then removed and ground off in sequential 2 mm (0.078 in.) thick layers from an exposed

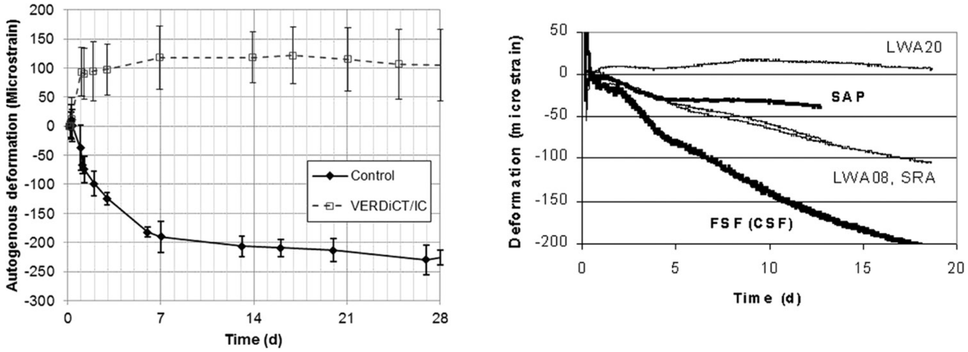

Fig. 1—Autogenous deformation versus time for w/c *= 0.35 mortar with and without VERDiCT/IC admixture (left) in comparison to previous results (right)*[11] *with either IC (LWA08 and LWA20 [LWA replacing 8% and 20% of normalweight sand by mass, respectively]), superabsorbent polymer (SAP), or SRA (SRA = VERDiCT), also contrasted against control (FSF [mortar prepared with blended cement containing fine silica fume, 8% mass fraction]). Error bars on left plot indicate ±1 standard deviation for testing of three specimens.*

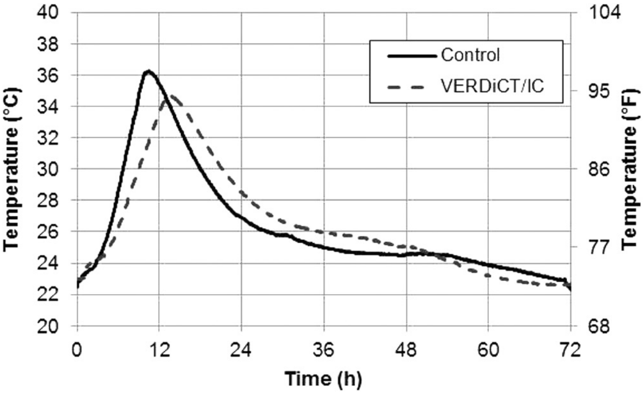

Fig. 2—Semi-adiabatic temperature versus time for mortar with and without VERDiCT admixture.

surface. After 26 weeks of exposure, these grindings were performed from a cut surface; after 52 weeks of exposure, they were performed from either a cast or 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 C1556.[21] 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/C1152M.[23] 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

Mortar—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 Fig. 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 approximately 250 $\mu\varepsilon$ was obtained at an age of 28 days. 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 the reduced surface tension of the pore solution due to the viscosity modifier being employed (for example, a conventional SRA). As illustrated by the complete autogenous deformation curves provided in Fig. 1, the VERDiCT/IC system actually initially produced expansion for the first 7 days of sealed curing, with very little, if any, subsequent shrinkage. The results generated in this study can be compared to those from a previous study that investigated IC and SRA/VERDiCT individually for a set of $w/cm = 0.35$ mortars, as included in Fig. 1.[11] The results in the present case are quite similar to those for the higher level of IC (LWA20) used in the previous study and are superior to those obtained when using only an SRA with no LWA. This significant reduction in autogenous shrinkage should translate into an increased resistance to early-age cracking.[24]

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, Fig. 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 Fig. 3. The retardation is on the order of an hour but, eventually, the two mortar mixtures have basically equivalent total heat releases (or degrees of hydration) at 7 days under isothermal conditions. Figure 3 also shows results obtained in another study of these technologies, illustrating the separate influences of IC and VERDiCT on the early-age heat release curves. In the latter case, it is clear that the retardation in the VERDiCT/IC mortar can mainly be attributed to the contribution of the VERDiCT admixture.

The influence of this retardation can also be observed in the mortar cube compressive strength results provided in Fig. 4. At an age of 1 day, due to the retardation and presence of the (weaker) LWA, the strength of the VERDiCT/IC

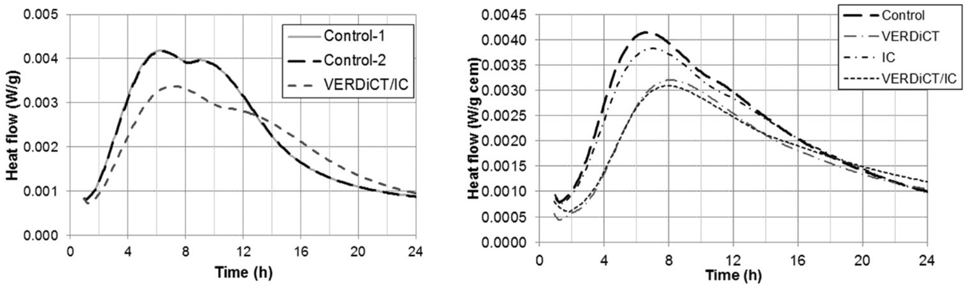

Fig. 3—Isothermal calorimetry heat flow curves for w/c *= 0.35 mortar with and without VERDiCT/IC technology in this study (left) contrasted with those from another study (right) employing three variants of VERDiCT/IC technology in* w/c *= 0.485 mortar.*[13] *Two replicate curves are provided for control (non-VERDiCT) mortar in graph on left to provide an indication of variability. (Note: 1 W/g = 1548 BTU/[h·lb].)*

mortar is approximately 70% of that of the control mortar. At ages of 3 days and beyond, however, as the effects of the retardation gradually diminish and eventually disappear, the VERDiCT/IC mortar consistently produces a strength that is approximately 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. These lower early-age strengths must be properly considered when evaluating the propensity for early-age cracking of these mixtures. The benefits provided by reduced autogenous shrinkage (Fig. 1) and a slightly reduced maximum temperature (Fig. 2) will be competing against the disadvantage of reduced early-age strength (Fig. 4), as it is nominally the strength/stress ratio (and the degree of restraint) that will ultimately determine whether cracking occurs. It should be noted, however, that previous studies employing cracking rings have indicated a reduction in cracking tendencies when either IC[24] or SRA/VERDiCT[25] is employed.

Concrete—As shown in Fig. 5, all eight concrete mixtures achieved compressive strengths greater than or equal to 40 MPa (5800 psi) by 28 days. 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 concrete without LWA was 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, likely due to a negative interaction between the VERDiCT admixture and the slag and the lower strength of the LWA relative to normalweight sand. In general, the strength increases from 28 to 56 days and from 56 to 365 days were fairly similar for all concrete 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 6 provides the average relative chloride penetration depth (all values are normalized by the penetration depth measured on the counterpart control concrete at each exposure time) measured following the RMT for the concrete with VERDiCT relative to their respective controls (fly ash or slag). The observed reductions in penetration depths for the mixtures with fly ash in Fig. 6 are in line with previous published performance results for this VERDiCT admixture in mortar.[6,7] For the RMT, much of the initial benefit of the VERDiCT/IC delivery over that of simply using VERDiCT in the initial mixing water was lost when specimens were cured for 365 days prior to the RMT. At these later ages, the LWAs will have surrendered nearly all of their initial solution to the hydrating cement paste and may therefore contribute a sorption component to the RMT in addition to

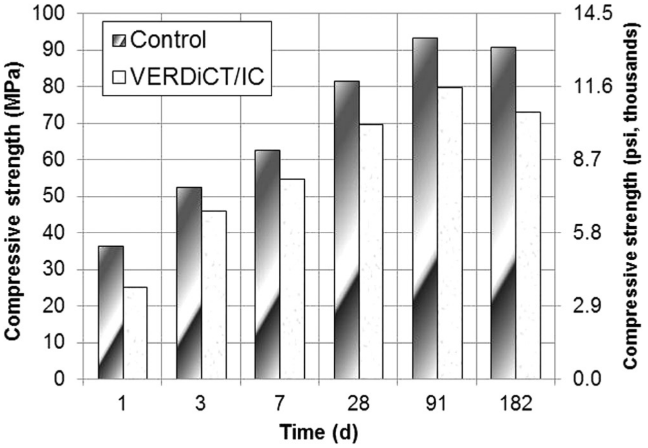

Fig. 4—Compressive strength results to 182 days for mortar with and without VERDiCT admixture. Average coefficient of variation among three replicate specimens was 4%.

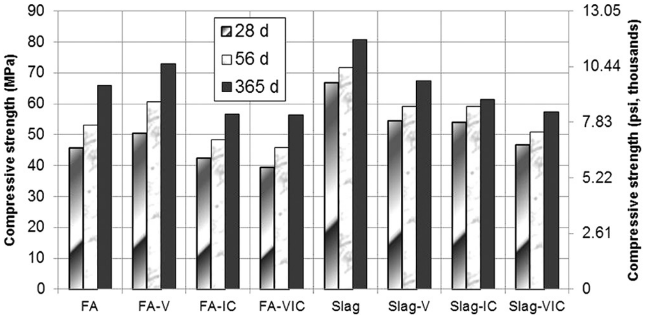

Fig. 5—Compressive strength results for concrete mixtures at ages of 28, 56, and 365 days. Average standard deviations in compressive strength for two replicate specimens for each mixture were 0.6, 1.1, and 1.2 MPa (87, 160, and 174 psi) for testing at 28, 56, and 365 days, respectively.

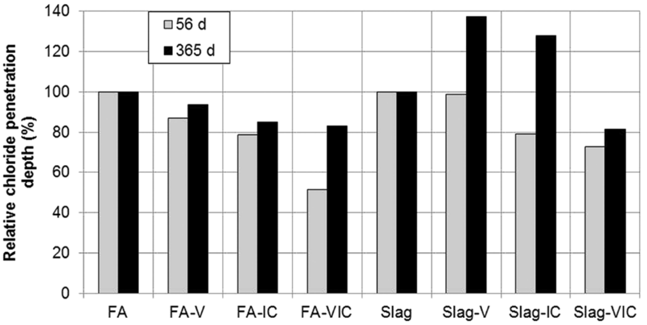

Fig. 6—Relative chloride penetration depth from RMT for eight concrete mixtures tested at ages of 56 and 365 days; controls (fly ash and slag) are assigned value of 100%. For two replicate specimens, at 56 days, coefficients of variation in average penetration ranged between 4 and 27% with an average of 14%. At 365 days, these values ranged between 1 and 38% with an average of 15%.

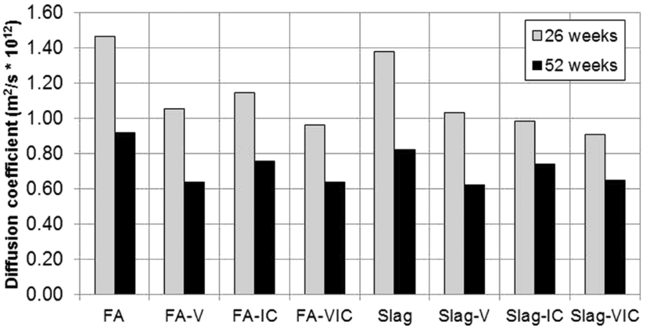

Fig. 7—Estimated chloride ion diffusion coefficients for eight concrete mixtures evaluated after 26 or 52 weeks of exposure following 56 days of curing. Coefficients of variation for eight concrete mixtures ranged between 2 and 9% with an average of 5% for 26-week data; after 52 weeks, coefficient of variation ranged between 5 and 14% with an average of 10%. (Note: 1 × 10^{-12} m^2/s = 0.049 in.^{2}/year.)

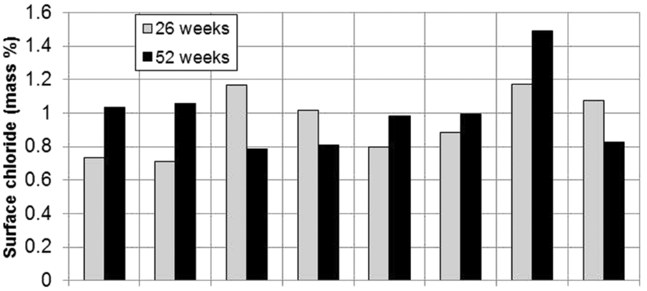

Fig. 8—Estimated surface chloride concentration for eight concrete mixtures evaluated after 26 or 52 weeks of exposure following 56 days of curing. Specimens at 26 weeks were evaluated from cut surfaces, while those at 52 weeks were evaluated from cast/finished surfaces. Coefficients of variation for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

the electrically driven diffusion. The 365-day results for the slag mixtures with VERDiCT in the mixing water (Slag-V) or IC using water (Slag-IC) exhibit quite an anomalous behavior, with a chloride penetration depth that is much higher than the control. For the mixture with VERDiCT in the mixing water (Slag-V), 10 individual measurements of penetration depth exhibited a wide disparity for one of the specimens, with values ranging between 4.2 and 13.0 mm (0.165 and 0.512 in.) (a range of 8.8 mm [0.346 in.]). For the two specimens evaluated at 365 days for the slag mixture with IC (Slag-IC), similarly, these measurement ranges for the 10 assessments of penetration depth were 5.8 and 6.2 mm (0.228 and 0.244 in.) versus the overall average range of 4.5 mm (0.177 in.) for the eight concrete mixtures. The observed inhomogeneity of the slag concrete prepared with the VERDiCT admixture, along with the significant strength reductions, should serve as a caution for using this combination of materials. Further research should be conducted prior to employing such mixtures in field structures.

The apparent chloride ion diffusion coefficients estimated from the long-term chloride ponding exposures are shown in Fig. 7, and their accompanying estimated surface chloride concentrations are provided in Fig. 8. In all cases in Fig. 7, the apparent diffusion coefficient decreased significantly (by 30 to 40%) in going from 6 months to 1 year, likely due to continuing hydration and densification of the (blended) cement paste in each mixture. The results in Fig. 7 indicate a reduction in the diffusion coefficient for the modified concrete mixtures, 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 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.[24] For the concrete mixtures investigated in this study, IC with water provided apparent diffusion coefficient reductions of approximately 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%. In each case, delivering a solution of the VERDiCT admixture instead of simply water using the LWA resulted in a further decrease in the measured diffusion coefficients, providing reductions on the order of 33% at both evaluation times.

Although the 26-week data indicate an improvement for VERDiCT/IC over VERDiCT in the mixing water for both the fly ash and slag concrete mixtures, at 52 weeks, their performance is nearly identical in both cases. This can be contrasted against previous results in ordinary portland cement mortar with a *w/c* between 0.40 and 0.45,[6,7] where 365-day 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 partially be 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 is likely more effective at depercolating the ITZs surrounding the fine normalweight aggregate in a mortar and less influential in depercolating these ITZs around both the coarse and fine normalweight aggregate in a concrete.[26]

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 Fig. 7 due to the concurrent higher measured surface concentration of chlorides, particularly for the mixtures with the LWA (Fig. 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 Fig. 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, and so on). 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 RMT were approximately 80% of those of the corresponding control mixtures, while apparent diffusion coefficients measured in the ponding test were approximately 67% of those of their corresponding control mixtures. Some of this difference may be due to the sorption effects introduced in the RMT due to the saturation state of the LWA, as noted previously. It should be noted that the previous VERDiCT studies have employed only direct chloride ponding exposures for characterizing their diffusion resistance.[6,7]

CONCLUSIONS

This paper evaluated the effects of viscosity modifiers and IC—separately and combined—on concrete performance for concrete mixtures containing either fly ash or slag. The following conclusions can be drawn:

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 mortar specimens with $w/c = 0.35$.

2. In the concrete with fly ash or slag first cured for 56 days, the VERDiCT technology provided an approximate 33% reduction in the 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.

3. IC using water provided smaller reductions in the apparent diffusion coefficients of 20% and 10% based on a 365-day chloride exposure for the fly ash and slag concrete mixtures, respectively.

4. The 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 concrete containing only normalweight aggregates contained a lower surface chloride concentration than their cast/finished counterparts.

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. In the case of slag mixtures, the reduction in compressive strength along with observed inhomogeneity in the ingressing chloride profiles would mandate further research before these mixtures could be used in practice.

ACKNOWLEDGMENTS

The authors would like to thank J. Winpigler, formerly of the Engineering Laboratory at NIST, and S. Sherman and S. 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*, John Wiley & Sons, Inc., New York, 1982, 591 pp.

2. ACI Committee 231, "Report on Early-Age Cracking: Causes, Measurement, and Mitigation (ACI 231R-10)," American Concrete Institute, Farmington Hills, MI, 2010, 46 pp.

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: Second Revised Edition*, Dover Publications Inc., Mineola, NY, 2002, 590 pp.

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," *Journal of Materials in Civil Engineering*, ASCE, V. 24, No. 8, 2012, pp. 1017-1024.

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," *Journal of Materials in Civil Engineering*, ASCE, V. 22, No. 3, 2010, pp. 277-286.

10. ASTM C150/C150M-09, "Standard Specification for Portland Cement," ASTM International, West Conshohocken, PA, 2009, 10 pp.

11. Bentz, D. P.; Geiker, M. R.; and Jensen, O. M., "On the Mitigation of Early-Age Cracking," *Self-Desiccation and Its Importance in Concrete Technology, Report* TVBM-3104, B. Persson and G. Fagerlund, eds., Lund University, Lund, Sweden, 2002, pp. 195-203.

12. Bentz, D. P.; Davis, J. M.; Peltz, M. A.; and Snyder, K. A., "Influence of Internal Curing and Viscosity Modifiers on Resistance to Sulfate Attack," *Materials and Structures*, May 2013. (in press)

13. 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.

14. ASTM C1698-09, "Standard Test Method for Autogenous Strain of Cement Paste and Mortar," ASTM International, West Conshohocken, PA, 2009, 8 pp.

15. ASTM C109/C109M-08, "Standard Test Method for Compressive Strength of Hydraulic Cement Mortars (Using 2-in. or [50-mm] Cube Specimens)," ASTM International, West Conshohocken, PA, 2008, 9 pp.

16. 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.

17. ASTM C494/C494M-10, "Standard Specification for Chemical Admixtures for Concrete," ASTM International, West Conshohocken, PA, 2010, 10 pp.

18. ASTM C143/C143M-10, "Standard Test Method for Slump of Hydraulic-Cement Concrete," ASTM International, West Conshohocken, PA, 2010, 4 pp.

19. ASTM C1074-04, "Standard Practice for Estimating Concrete Strength by the Maturity Method," ASTM International, West Conshohocken, PA, 2004, 10 pp.

20. ASTM C138/C138M-10, "Standard Test Method for Density (Unit Weight), Yield, and Air Content (Gravimetric) of Concrete," ASTM International, West Conshohocken, PA, 2010, 4 pp.

21. ASTM C1556-04, "Standard Test Method for Determining the Apparent Chloride Diffusion Coefficient of Cementitious Mixtures by Bulk Diffusion," ASTM International, West Conshohocken, PA, 2004, 7 pp.

22. AASHTO TP64-03 (2007), "Standard Method of Test for Predicting Chloride Penetration of Hydraulic Cement Concrete by the Rapid Migration Procedure," American Association of State and Highway Transportation Officials, Washington, DC, 2007.

23. ASTM C1152/C1152M-04, "Standard Test Method for Acid-Soluble Chloride in Mortar and Concrete," ASTM International, West Conshohocken, PA, 2004, 4 pp.

24. 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.

25. Pease, B.; Shah, S.; and Weiss, J., "Shrinkage Behavior and Residual Stress Development in Mortar Containing Shrinkage Reducing Admixtures (SRAs)," *Shrinkage and Creep of Concrete*, SP-227, N. J. Gardner and J. Weiss, eds., American Concrete Institute, Farmington Hills, MI, 2005, pp. 285-302.

26. 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.