

VERDiCT: Viscosity Enhancers Reducing Diffusion in Concrete Technology

A new approach to decreasing transport

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Reinforced concrete structures are susceptible to attack by elements of the environment including chloride and sulfate ions. Past attempts at increasing service life have generally focused on limiting the ingress of these deleterious elements by producing less permeable concrete. Lower water-cementitious material ratios and the addition of fine pozzolans such as silica fume contribute to a denser cement paste matrix. Such mixtures are often classified as high-performance concretes. These mixture modifications, however, also typically contribute to an increased temperature rise and increased autogenous shrinkage, both of which increase the concrete's propensity to undergo early-age cracking.^{1,2} Thus, attempts to produce less permeable concrete can be compromised by the existence of just a few through-depth cracks.

A new approach to increasing concrete service life involves the use of carefully selected viscosity modifiers to substantially increase the viscosity of the concrete pore solution and slow down diffusion through the pore solution. Doubling the service life of a specific concrete may be possible by doubling the viscosity of its pore solution.³ This approach has been assigned the acronym VERDiCT: viscosity enhancers reducing diffusion in concrete technology.

WHAT'S A GOOD VERDiCT?

The scientific principle behind VERDiCT was presented in a 1937 paper on the diffusion of electrolytes.⁴ The derived equations indicated that diffusion constants should be proportional to the ratio of the viscosity of water to that of the solution containing the electrolyte. An inverse dependency between diffusion coefficients and solution viscosity is also present in the well known Stokes-Einstein relation³

$$D_o = \frac{k_B T}{6\pi\eta_0 r} \quad (1)$$

where D_o is the self-diffusion coefficient of an ion, k_B is the Boltzmann constant, T is temperature, r is the radius of the diffusing particle, and η_0 is the bulk viscosity of the solution. This relation suggests that diffusion may be slowed down by increasing the solution viscosity. The same molecules that are interacting with the water to increase the solution viscosity may also effectively serve as physical barriers that reduce ionic diffusion rates.

Early studies showed that the size of these molecules is critical to their performance as diffusion barriers.⁵ Larger molecules, such as higher molecular mass polyethylene glycols, can drastically increase solution viscosity at low concentrations but have no measurable

TABLE 1:
VISCOSITY MEASUREMENTS RELATIVE TO VALUE FOR DISTILLED WATER³

Chemical name	Molar mass, g/mol	Solution mixture	$\eta_{\text{solution}}/\eta_{\text{water}}^*$
Xanthum gum	~ 1,000,000	0.4 g in 100 g of water	2.32
Cellulose ether	~ 100,000	0.29 g in 100 g of water	3.30
Polyvinyl alcohol	~ 10,000	2 g in 98 g of water	1.71
Polyoxyalkylene alkyl ether 10%	~ 400 to 1000	10 g in 90 g of water	1.50
Polyoxyalkylene alkyl ether 20%		20 g in 80 g of water	2.58
Polyethylene glycol 600	~ 600	15 g in 85 g of water	1.93
Polyethylene glycol 400	~ 400	20 g in 80 g of water	2.26
Polypropylene glycol P400	~ 400	10 g in 90 g of water	1.53
Dipropylene glycol/propanol, [2-(1,1-dimethylethoxy)methylethoxy]	134/190	10 g in 90 g of water	1.40
Glycerol	92.1	30 g in 70 g of water	2.10

* η_{solution} is the bulk viscosity of the solution. η_{water} is the bulk viscosity of water.

effect on diffusion rates. Smaller molecules, however, such as ethylene glycol and lower molecular mass polyethylene glycols, provide reductions in diffusion rates that are inversely proportional to the measured increase in viscosity. In other words, doubling the solution viscosity produces a diffusion coefficient that is half that measured in the original solution.⁵ In fact, previous studies and the results presented here indicate that nano-sized molecules are the best candidates to serve as viscosity modifiers that can significantly reduce diffusion rates.

DELIVERING THE VERDiCT

Currently, three different methods have been investigated for delivering viscosity modifiers into the pore solutions of mortars and concretes: internally as an admixture, topically as part of a curing compound, or internally using saturated porous lightweight aggregate as a carrier.

The most conventional approach is simply to add the viscosity modifier directly as a chemical admixture into the concrete. The admixture can be mixed in with the mixing water prior to mixing the concrete or added directly to the concrete mixer. Concrete will absorb external curing solutions during hydration due to the chemical shrinkage that accompanies the hydration reactions, however, so an alternative delivery vehicle for VERDiCT is to use a topical curing solution that contains the viscosity modifier.⁶ While the penetration depth of the solution will be limited by the sorptivity and permeability of the concrete, topical delivery may offer advantages over delivery as an admixture. If the viscosity modifier has significant detrimental influences on cement hydration reactions (such as retarding effects) or the

fresh concrete properties (such as raising or lowering air content), for example, delivery as an admixture may not be possible.

A third delivery option is to saturate fine lightweight aggregate particles with a concentrated solution of the viscosity modifier prior to adding them to a concrete mixture. As the cement hydrates, this internal curing solution will be drawn from the larger pores in the lightweight aggregate into the smaller pores in the hydrating cement paste matrix, uniformly distributing the viscosity modifier throughout the concrete. This delivery mechanism, with the acronym FLAIR (fine lightweight aggregates as internal reservoirs), has been previously investigated for the delivery of shrinkage-reducing admixtures to mitigate their tendency to sometimes function as air detrainers in fresh concrete mixtures.⁷

INITIAL EVALUATION

To date, two evaluations of VERDiCT candidates have been initiated. The first evaluation measured the conductivity of ionic solutions containing various viscosity modifiers. The second measured chloride ion ingress into mortars with and without the viscosity modifier delivered using each of the three delivery mechanisms previously outlined.

VERDiCT in solutions

Taking advantage of the Nernst-Einstein relation,⁴ relative ionic diffusivities can be related directly to relative electrical conductivities. Thus, a first test of VERDiCT has been measuring the electrical conductivities of ionic solutions of different strengths, with and without various viscosity modifiers.³ The specific viscosity

modifiers examined to date are listed in Table 1, along with the measured viscosities of their aqueous solutions relative to that of distilled water.

The viscosities were measured by determining the flow rate of the fluid through a glass capillary tube of known dimensions³ or by using a commercial vibrational viscometer. Replicate measurements on distilled water at 23 ± 1 °C (73 ± 2 °F) with the latter method yielded a mean value of 0.90 mPa·s (1.9 × 10⁻⁵ lb·s/ft²) with a standard deviation for the sample of 0.01 mPa·s (2.1 × 10⁻⁷ lb·s/ft²). The same solutions were evaluated in a conductivity cell with solutions of potassium chloride (KCl) of various concentrations, as indicated in Table 2.

Consistent with previous results,⁵ the three largest molecules (cellulose ether, xanthum gum, and polyvinyl alcohol) resulted in no measurable reduction in electrical conductivity. For smaller molecules such as glycerol, low molecular mass polyethylene/polypropylene glycols, and two currently employed shrinkage-reducing admixtures, however, the electrical conductivity reduction was indeed in direct inverse proportion to the measured viscosity increase. These results suggest that viscosity modifiers can reduce diffusion rates in solutions. The next step was to consider their performance in actual mortar and concrete.

VERDiCT in mortars

Based on the results in Tables 1 and 2, polyoxyalkylene alkyl ether was selected for an ongoing study in a series of mortars with a water-cement ratio (*w/c*) of 0.40. The viscosity modifier was added at a concentration of 10% of the total solution mass. This increased the viscosity of the solution to 1.5 times that of distilled water (Table 1). The three methods mentioned previously were each employed for delivering the VERDiCT into the mortars.

After curing times of 1 day (curing in molds), 7 days, and 28 days, the

TABLE 2:
ELECTRICAL CONDUCTIVITY REDUCTIONS FOR SOLUTIONS WITH VARIOUS VISCOSITY MODIFIERS³

Viscosity modifier*	$\eta_{water}/\eta_{solution}^{\dagger}$	Electrical conductivity reduction factor [‡]
Xanthum gum	0.43	1.00
Cellulose ether	0.30	0.98
Polyvinyl alcohol	0.58	0.98
Polyoxyalkylene alkyl ether 10%	0.67	0.67
Polyoxyalkylene alkyl ether 20%	0.39	0.47
Polyethylene glycol 600	0.52	0.67
Polyethylene glycol 400	0.44	0.56
Polypropylene glycol P400	0.66	0.75
Dipropylene glycol/propanol, [2-(1,1-dimethylethoxy)methylethoxy]	0.72	0.76
Glycerol	0.48	0.49

* Refer to Table 1 for solution concentrations.

[†] $\eta_{solution}$ is the bulk viscosity of the solution. η_{water} is the bulk viscosity of water.

[‡] Electrical conductivity reduction factor is the ratio of the electrical conductivity of the distilled water solution containing KCl and the viscosity modifier to the electrical conductivity of the distilled water solution containing KCl only. Solutions of KCl and distilled water contained 0.1 mol/kg of chloride ions.

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50 mm (2 in.) diameter by 100 mm (4 in.) long cylinders were placed in individual sealed plastic bottles and exposed to 1 molar chloride ion solutions. For the 7- and 28-day curing times, three different curing procedures were employed after demolding the specimens at 1 day: 1) curing in a solution of NaOH/KOH/Ca(OH)₂; 2) curing in this same hydroxide solution along with the VERDiCT admixture; or 3) curing in sealed double plastic bags (only for the FLAIR procedure delivery of VERDiCT). For the FLAIR delivery of VERDiCT, the dry lightweight aggregates were prewetted with a 50% solution of the viscosity modifier in water. Some of the normalweight sand in the mortar was replaced by lightweight aggregate to achieve the same overall addition rate of the admixture per unit volume of mortar as that used in the other mortars.

Various methods are being employed to quantify chloride ion ingress into the mortar cylinders after exposure times of 28, 56, 180, and 365 days. At each exposure time, two cylinders are removed from their chloride solutions and broken lengthwise down the middle using a universal testing machine. For each specimen, one of the two created faces is sprayed with silver nitrate (AgNO₃),^{8,9} the specimen is photographed, and image processing software is used to visually assess the chloride ion penetration depth (Fig. 1). As shown in Fig. 2, chloride ion ingress is also being evaluated using X-ray microfluorescence imaging of a portion of the surface exposed during the breaking of the specimens.¹⁰ In this case, the chloride ion penetration depth is easily observed in the X-ray image for chlorine.

To date, exposures through 56 days have been completed. The penetration depth results determined using the AgNO₃ spraying technique are shown in Fig. 3 and 4. Within the uncertainty of the measurements, the systems employing VERDiCT exhibit a significant reduction in chloride ion penetration depth, particularly those with the FLAIR delivery method. This delivery method may provide the additional benefits of internal curing¹¹ and eliminating a fraction of the porous interfacial transition zones due to the reduction in the normalweight sand volume fraction. Interfacial transition zones surrounding lightweight aggregate are often denser than the bulk paste.^{12,13}

Extrapolating the results of the solution studies presented in Tables 1 and 2 to performance in actual cement-based materials requires consideration of several confounding factors. These include possible retardation of the cement hydration reactions by the viscosity modifier, leading to a higher and coarser capillary porosity that would somewhat offset the benefits of VERDiCT. A slight retardation of the cement hydration reactions has been observed in $w/c = 0.4$ cement pastes containing a 10% viscosity modifier addition as assessed using isothermal calorimetry at 25 °C (77 °F).³ A second

confounding factor is the fact that during these early-age exposures to chloride solutions, both absorption (due to chemical shrinkage and self desiccation) and diffusion are responsible for transporting the chloride ions into the mortar cylinders. The estimated penetration depths solely due to sorption of the chloride ion solution are on the order of 1 mm (0.04 in.) for specimens first cured for 7 days and then exposed to chlorides for 28 days, for example.

Mass gains for the specimens measured during exposure to the curing and chloride solutions have indicated slightly lower (about 10% less) uptakes for the cylinders with VERDiCT versus those without VERDiCT. Generally, our ongoing study shows that increased viscosity will result in reduced sorption rates, particularly for a viscosity modifier that also significantly reduces surface tension. The lower absorption of the specimens with VERDiCT may also contribute to the measured overall reduction in chloride penetration depth.

As expected, in Fig. 3 and 4, the measured penetration depths (y -axis) are significantly less for all specimens that were first cured for 28 days compared with those cured for 7 days before being exposed to the chloride ion solution. This is due to the additional hydration achieved between 7 and 28 days, further densifying the mortar microstructure and reducing both its porosity and pore connectivity. For the specimens only cured for 7 days before chloride ion exposure, the penetration depths achieved after either 28 or 56 days are fairly similar, and in some cases, the penetration depth achieved after 56 days is slightly less than that after 28 days.

One hypothesis for this unexpected result is that the specimens only cured for 7 days undergo significant additional hydration during their chloride ion exposure period. Continuing hydration will lead to reductions in capillary porosity that will locally increase the concentration of chloride ions, reducing or perhaps even removing the concentration gradient that is driving the diffusion. Conversely, for the specimens cured for 28 days, where the hydration is much more complete, the expected trend of an increasing penetration depth with exposure age is generally observed.

OTHER ADVANTAGES

In VERDiCT, viscosity enhancers are used to decrease the diffusion rates of ingressing ions such as chlorides and sulfates. An increase in the viscosity of the pore solution, however, will also reduce other modes of ingress from the environment into the concrete, such as sorption and flow under pressure. While an increase in viscosity does not change the permeability coefficient of the concrete microstructure, the flow rate of a fluid within the concrete due to a pressure gradient will be inversely proportional to the viscosity of the flowing fluid. Additionally, the sorptivity

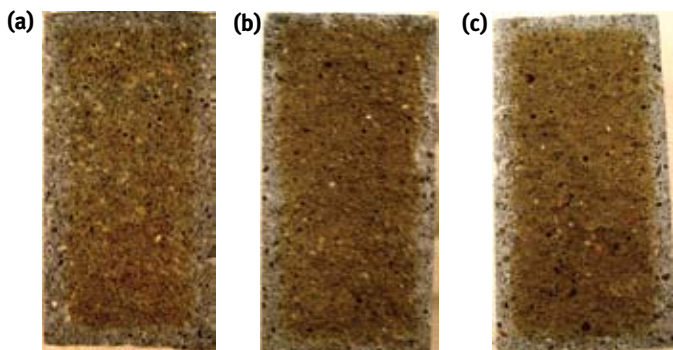


Fig. 1: Split AgNO_3 -sprayed cylinders after curing for 7 days (either in a hydroxide solution or under sealed conditions for the FLAIR procedure) and then exposed to a 1 mol/L chloride solution for 28 days. Split cylinders are 50 x 100 mm (2 x 4 in.). Brown areas indicate regions of minimal chloride concentration: (a) mixture without VERDiCT; (b) mixture with VERDiCT added to the mixing water; and (c) mixture with VERDiCT added via the FLAIR procedure

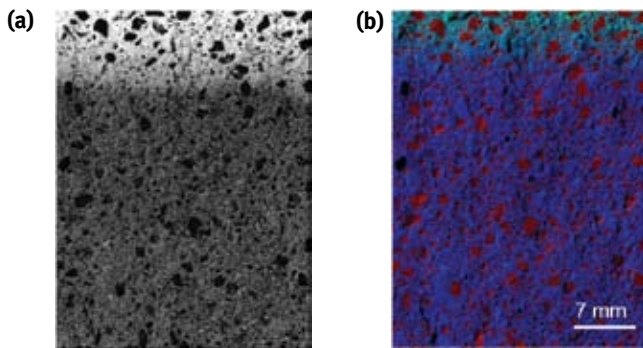


Fig. 2: X-ray microfluorescence imaging of a portion of the surface exposed during the breaking of the specimens: (a) X-ray map for chloride penetration in a mortar specimen (the brightness indicates the local chloride concentration); and (b) false three-color image for a mortar specimen (the silicon X-ray signal has been mapped to red, calcium to blue, and chlorine to green). (Note: 7 mm = 0.28 in.)

coefficient of a porous material is proportional to the inverse of the square root of the solution viscosity; once again, a higher viscosity means a lower sorption rate.¹⁴ As supported by our ongoing tests, this requires that the admixture can precipitate and redissolve during wet and dry cycling. Thus, the advantages provided by VERDiCT with respect to diffusion will also be present for flow under pressure and for sorption, two of the other common mechanisms of transport into and through concrete.

VERDiCT PROSPECTUS

We are continuing to evaluate the performance of the identified VERDiCT candidates in mortars as well as

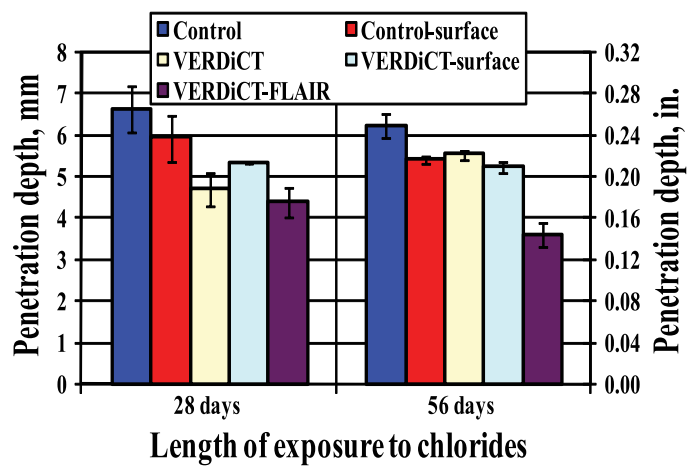


Fig. 3: Penetration depth as determined by spraying with AgNO_3 versus chloride (Cl^-) exposure time for mortar cylinders cured for 7 days prior to chloride solution exposure. Labels of surface and FLAIR indicate 7-day curing in a curing solution composed of a mixture of hydroxides and the VERDiCT admixture, or cured for 7 days under sealed conditions, respectively. Error bars indicate \pm one standard deviation in the measured average penetration depth

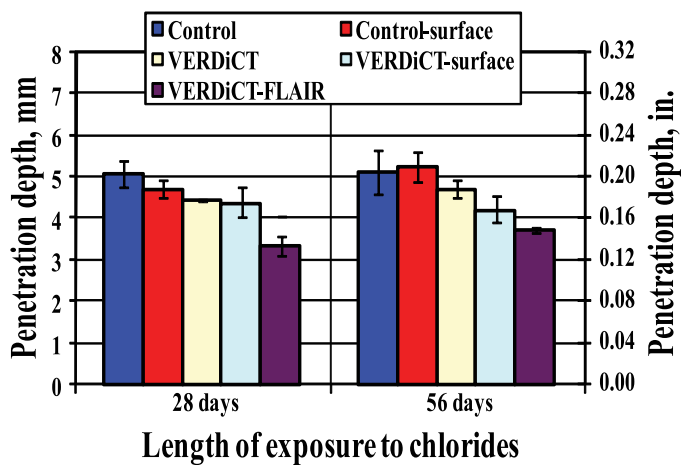


Fig. 4: Penetration depth as determined by spraying with AgNO_3 versus chloride (Cl^-) exposure time for mortar cylinders cured for 28 days prior to chloride solution exposure. Labels of surface and FLAIR indicate 28-day curing in a curing solution composed of a mixture of hydroxides and the VERDiCT admixture, or cured for 28 days under sealed conditions, respectively. Error bars indicate \pm one standard deviation in the measured average penetration depth

identify alternative viscosity modifiers capable of reducing conductivity and diffusivity. A nonprovisional patent application was filed in the U.S. on this technology in September 2008, so it is now available for licensing from the U.S. government. The National Institute of Standards and Technology Office of Technology Partnerships may be contacted for further licensing details.

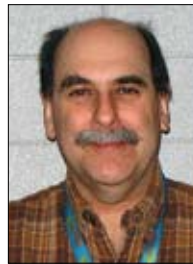
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