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VERDiCT: Viscosity Enhancers Reducing Diffusion in Concrete Technology

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Introduction

Increasing the service life of concrete structures has been an ever-present objective of concrete technologists [1]. Our nation's infrastructure and the containment of nuclear waste are two of the more prominent examples of concretes where an extended service life is an absolute necessity. While quite resistant to ultraviolet (solar) degradation, concrete structures are susceptible to attack by other elements of the environment, including but not limited to chloride and sulfate ions. Past attempts at increasing service life have generally focused on limiting the ingress of these deleterious species by producing a less permeable concrete. Lower water-to-cementitious material ratios (*w/cm*) 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. However, these mixture modifications 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 [2,3]. Attempts to produce a less permeable concrete can be totally compromised by the existence of just a few (through depth) cracks. But for any density concrete, diffusive transport of chloride and sulfate ions will occur through the water-filled pores. In this paper, a new approach to increasing the service life of concrete by slowing down the diffusive transport in the pore solution phase is presented. Specifically, carefully selected viscosity modifiers can be used to substantially increase the viscosity of the concrete pore solution, and proportionally decrease the rates of diffusive transport. Thus, doubling the service life of a specific concrete may be possible by doubling the viscosity of its pore solution [4]. This approach has been assigned the acronym VERDiCT: Viscosity Enhancers Reducing Diffusion in Concrete Technology.

What's the VERDiCT?

The scientific principle behind VERDiCT was presented by Gordon in 1937 [5]. In a paper on the diffusion of electrolytes, he derived equations indicating 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 relation:

$$D_o = \frac{k_B T}{6\pi \eta_o r} \tag{1}$$

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 provocatively suggests that one may slow down diffusion by increasing the solution viscosity. The same molecules that are interacting with the water to increase the solution viscosity may also be effective in serving as physical barriers that reduce ionic diffusion rates. As pointed out by Shimizu and Kenndler [6], the size of these molecules is critical to their performance as diffusion barriers. Their results indicated that larger molecules such as higher molecular mass polyethylene glycols that drastically increase solution viscosity at low concentrations have no measurable effect on diffusion rates. Conversely, for ethylene glycol and lower molecular mass polyethylene glycols, the reduction in diffusion was inversely proportional to the measured increase in viscosity (e.g., doubling the solution viscosity produced a diffusion coefficient that was half of that measured in the original solution) [6]. From these previous studies and the results that will be presented shortly, it seems that nano-sized molecules are the best candidates to serve as viscosity modifiers that also significantly reduce diffusion rates. For example, neither cellulose ether nor xanthum gum (two very large molecules that were investigated in this study) the desired effect on transport at concentrations which were adequate to more than double the solution viscosity.

Delivering the VERDiCT

As of this time, three different methods have been investigated for delivering the VERDiCT into mortars and concretes.

The VERDiCT Is In

The most conventional approach is simply to directly add the viscosity modifier as a chemical admixture into the concrete mixture. The admixture can be pre-mixed into the mixing water prior to the mixing of the concrete or added directly to the concrete mixer.

The VERDiCT Is Out

Since concretes will absorb external curing solutions during their hydration (due to the chemical shrinkage that accompanies the hydration reactions), an alternative delivery vehicle for VERDiCT is to use a topical curing solution that contains the viscosity modifier, as has been suggested previously for the delivery of shrinkage-reducing admixtures [7]. While the penetration depth of the admixture will be limited by the permeation properties (sorptivity and permeability) of the concrete, this delivery route may offer an advantage over conventional delivery when the viscosity modifier has significant detrimental influences on the cement hydration reactions (such as retarding effects) or the fresh concrete properties (such as air entrainment or detrainment).

A VERDiCT with FLAIR

A third delivery option for VERDiCT is to saturate fine lightweight aggregates (LWA) with a concentrated solution of the viscosity modifier prior to their incorporation into a concrete mixture. As the cement hydrates, this internal curing solution will be drawn from the larger pores in the LWA 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 investigated previously for the delivery of shrinkage-reducing admixtures in order to mitigate their tendency to sometimes function as air detrainers in fresh concrete mixtures [8].

Initial Evaluation of the VERDiCT

To date, two evaluations of VERDiCT have been initiated, one based on measuring the conductivity of ionic solutions containing various viscosity modifiers and the other based on measuring chloride ion ingress into mortars with and without the viscosity modifier (utilizing the three delivery mechanisms outlined above).

VERDiCT in Solutions

Taking advantage of the Nernst-Einstein relation, relative ionic diffusivities can be related directly to relative electrical conductivities. Thus, a first test of VERDiCT has been performed based on measuring the electrical conductivities of ionic solutions of different strengths, with and without the various viscosity modifiers [4]. 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 of known dimensions [4] or by using a commercial vibrational viscometer. Replicate measurements on distilled water at (23 ± 1) ºC with the latter method have yielded a mean value of 0.90 mPa·s with a standard deviation (of the sample) of 0.01 mPa·s. The same solutions were evaluated in a conductivity cell with solutions of KCl of various concentrations as indicated in Table 2. Consistent with the previous results of Shimizu and Kenndler [6], the three largest molecules (cellulose ether, xanthum gum, and polyvinyl alcohol) resulted in no measurable reduction in electrical conductivity. However, for smaller molecules such as glycerol, low molecular mass polyethylene/polypropylene glycols, and two currently employed shrinkage-reducing admixtures, 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 is to consider their performance in actual mortars and concretes.

VERDiCT in Mortars

Based on the results in Tables 1 and 2, the polyoxyalkylene alkyl ether was selected for further (ongoing) studies in a series of mortars with a water-to-cement ratio (*w/c*) of 0.4. The viscosity modifier was added at a concentration of 10 % (of total solution mass), which provided a viscosity increase of 1.5X in distilled water (Table 1). The three methods mentioned previously were each employed for delivering VERDiCT into the mortars. After curing times of

1 d (curing in molds), 7 d, and 28 d, the 50 mm diameter by 100 mm long (2" by 4") cylinders were exposed in individual sealed plastic bottles to 1 molar chloride ion solutions. For the latter two curing times, three different curing procedures were employed after demolding at 1 d: 1) curing in a solution of $NaOH/KOH/Ca(OH)_2$, 2) curing in a solution of this same hydroxide mixture along with the VERDiCT admixture, or 3) sealed curing in double plastic bags (only for the FLAIR procedure delivery of VERDiCT). For the FLAIR delivery of VERDiCT, the dry lightweight aggregates were pre-wetted with a 50 % solution of the viscosity modifier in water. The replacement of normal weight sand by lightweight aggregates in the mortar was then performed to achieve the same overall addition rate of the admixture as that used in the other mortars (per unit volume of mortar).

Table 1. Viscosity Measurements (Relative to Value for Distilled Water) [4]

Chemical Name [Molar mass (g/mol)]	**Solution Mixture**	$\eta_{solution}/\eta_{water}$
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 (≈ 400 to 1000)	10 g in 90 g of water	1.50
Polyoxyalkylene alkyl ether	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-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

Table 2. Electrical Conductivity Reductions for Solutions with Various Viscosity Modifiers [4]

Chemical Name (Concentration)	$\eta_{water}/\eta_{solution}$	**Electrical Conductivity Reduction Factor for KCl/Modifier Solutions vs. KCl/Distilled Water Solutions (moles of chloride ion per unit mass of solution) 0.1 mol/kg**
Xanthum Gum	0.43	1.00
Cellulose Ether	0.30	0.98
Polyvinyl alcohol (2/98)	0.58	0.98
Polyoxyalkylene alkyl ether (10/90)	0.67	0.67
Polyoxyalkylene alkyl ether (20/80)	0.39	0.47
Polyethylene Glycol 600 (15/85)	0.52	0.67
Polyethylene Glycol 400 (20/80)	0.44	0.56
Polypropylene Glycol P400 (10/90)	0.66	0.75
Dipropylene glycol/Propanol, [2-,1-dimethylethoxy)methylethoxy] (10/90)	0.72	0.76
Glycerol (30/70)	0.48	0.49

Various methods are being employed for quantifying the chloride ion ingress into the mortar cylinders after exposure times of 28 d, 56 d, 180 d, and 365 d. At each exposure time, two cylinders are removed from their chloride solutions and broken down the middle (lengthwise) using a universal testing machine. For each specimen, one of the two created faces is sprayed with silver nitrate ($AgNO_3$) [9,10], the specimen is photographed, and image processing software is used to visually assess the penetration depth of the chloride ions (Figure 1). 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 [11] (Figure 2). In this case, the chloride ion penetration depth is easily observed in the x-ray image for chlorine, for example (left side of Figure 2).

To date, exposures through 56 d have been completed. The results obtained with respect to the penetration depth as determined using the $AgNO_3$ spraying technique are shown in Figures 3 and 4. Within the uncertainty of the measurements, the systems employing VERDiCT do exhibit a significant reduction in chloride ion penetration depth, particularly those with the FLAIR delivery of VERDiCT. For this delivery method, additional benefits may be provided by the accompanying internal curing [12] and the elimination of a fraction of the more porous interfacial transition zones due to the reduction in the normal weight sand volume fraction [13] (interfacial transition zones surrounding lightweight aggregates are often denser than the bulk paste [14,15]).

In extrapolating the results of the solution studies presented in Tables 1 and 2 to performance in actual cement-based materials, several confounding factors must be considered. These include possible retardation of the cement hydration reactions by the viscosity modifier leading to a higher (and coarser) capillary porosity (which would somewhat offset the benefits of VERDiCT), and 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 the transport of chloride ions into the mortar cylinders. In the former case, a slight retardation of the cement hydration reactions has indeed been observed in w/c = 0.4 cement pastes containing a 10 % viscosity modifier addition (mass percent of solution), as assessed using isothermal calorimetry at 25 ºC [4]. In the latter case, the estimated penetration depths solely due to sorption of the chloride ion solution are on the order of 1 mm (0.04”) for specimens first cured for 7 d and then exposed to chlorides for 28 d, 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, an increased viscosity will result in reduced sorption rates, particularly for the viscosity modifier investigated in this study that also significantly reduces surface tension [16]. The lower absorption of the specimens with VERDiCT may also contribute to the measured overall reduction in chloride penetration depth.

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

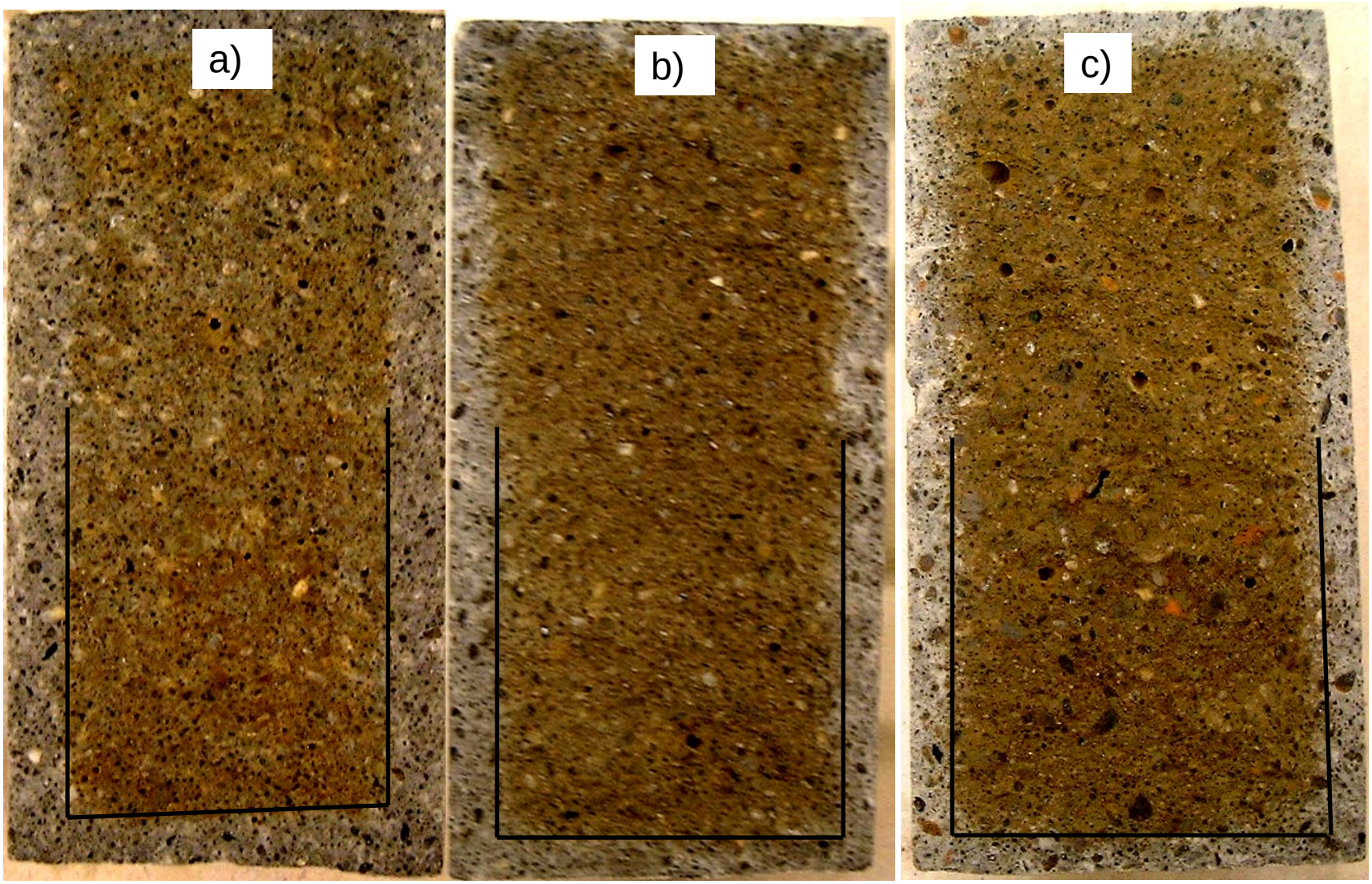

Figure 1. Split $AgNO_3$-sprayed cylinders after being cured for 7 days (either in a hydroxide solution or under sealed conditions for the FLAIR procedure) and then exposed for 28 d to a chloride solution (1 mol/L). Mixtures without VERDiCT (a), with VERDiCT added to the mixing water (b), and with VERDiCT added via the FLAIR procedure (c) are shown. Split cylinders are 50 mm by 100 mm (2" by 4"). Brown areas indicate regions of minimal chloride concentration.

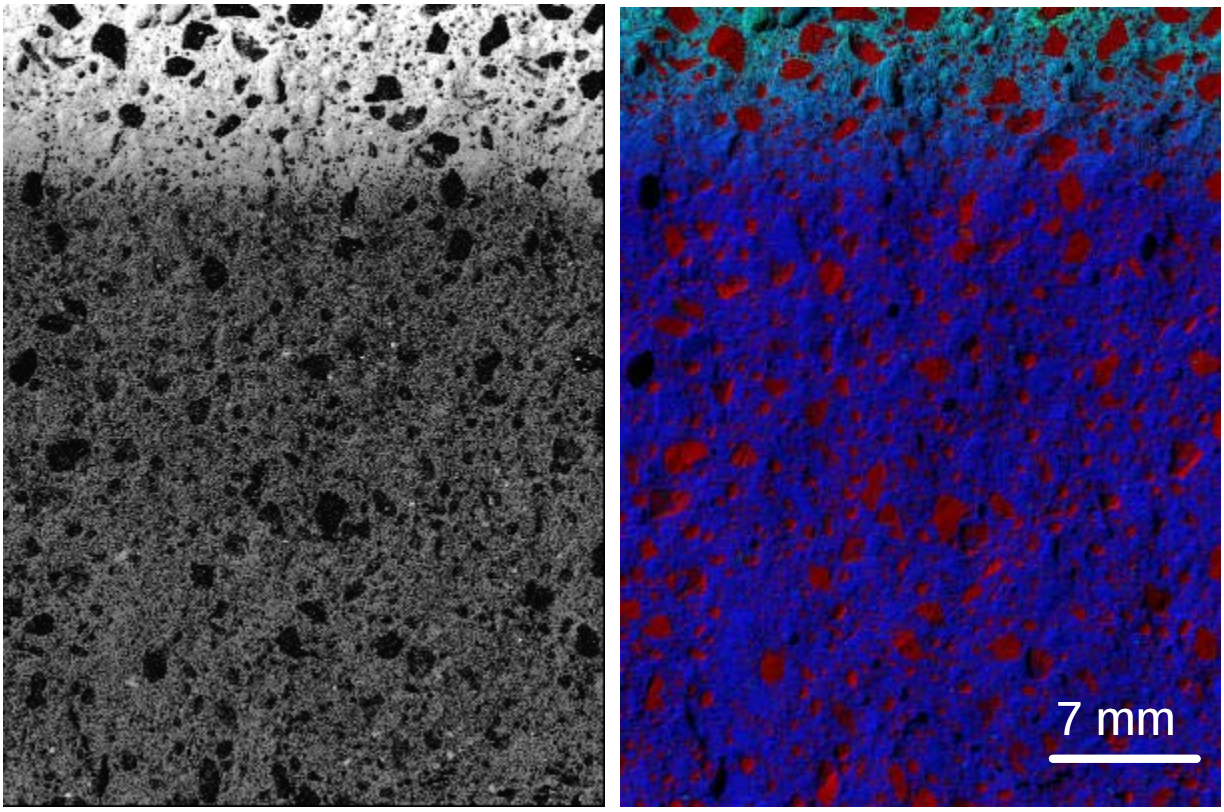

Figure 2. X-ray map for Cl (left) and a false three color image (right) for a mortar specimen. In the X-ray map image, the brightness indicates the local Cl concentration. In the false color image, the silicon X-ray signal has been mapped to red, calcium to blue, and chlorine to green. Scale bar indicates 7 mm or 0.28 in.

depth achieved after 56 d is slightly less than that after 28 d. One hypothesis for this unexpected result is that the specimens only cured for 7 d undergo significant additional hydration during their chloride ion exposure period. Continuing hydration will lead to reductions in capillary porosity (water) 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 d, where the hydration is much more complete, the expected trend of an increasing penetration depth with exposure age is generally observed.

Other Advantages of an Increased Viscosity

In VERDiCT, viscosity enhancers are being utilized to decrease the diffusion rates of ingressing ions such as chlorides and sulfates. However, an increase in the viscosity of the pore solution will also reduce other modes of ingress from the environment into the concrete, such as sorption (as mentioned above) 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 coefficient of a porous material is proportional to one over the square root of the solution viscosity; once again, a higher viscosity means a lower transport (sorption) rate [16,17], during wet/dry cycling, for example. This assumes that the admixture can precipitate and redissolve during wet/dry cycling, as supported by experimental

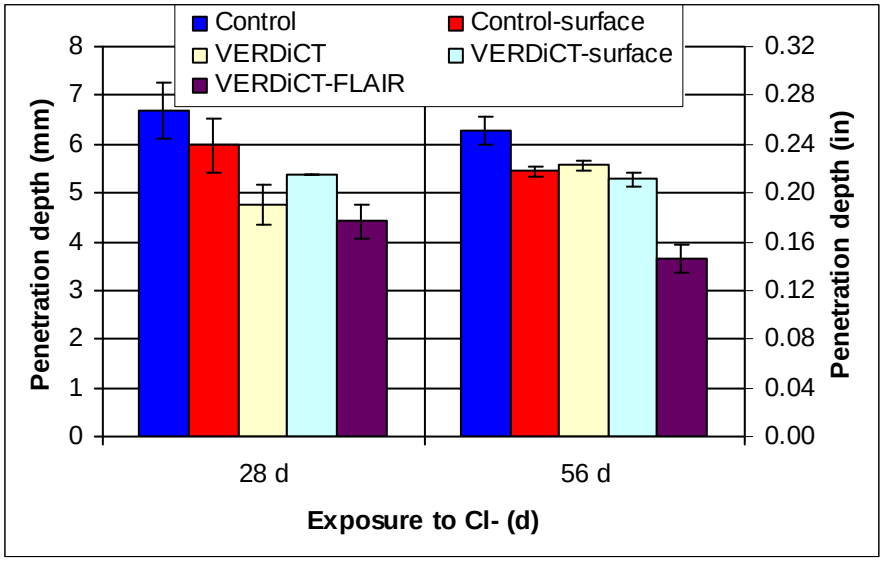

Figure 3. Penetration depth as determined by spraying with $AgNO_3$ vs. Cl^- exposure time for mortar cylinders first cured for 7 d and then exposed to chloride solutions. Labels of surface and FLAIR indicate 7 d curing in a curing solution composed of a mixture of hydroxides and the VERDiCT admixture, or cured for 7 d under sealed conditions, respectively. Error bars indicate ± one standard deviation in the measured average penetration depth.

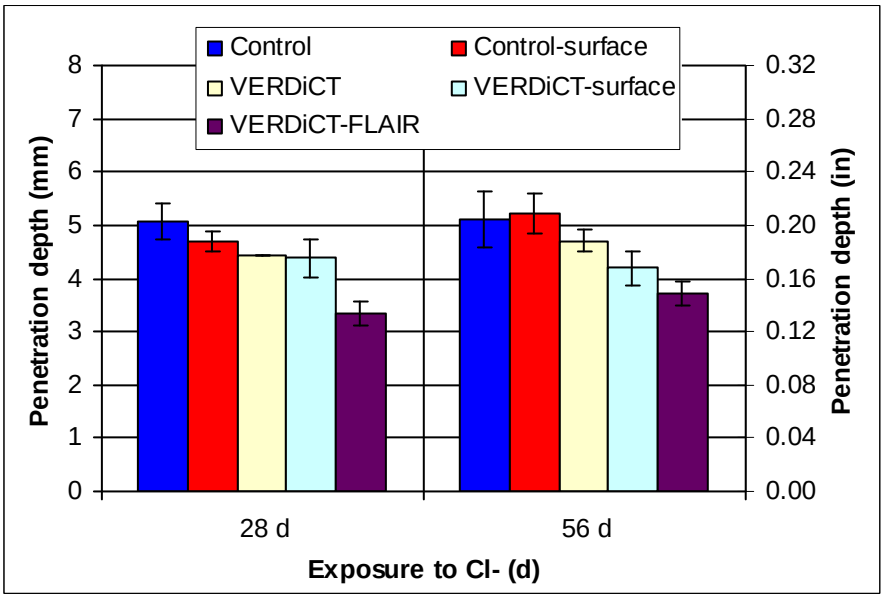

Figure 4. Penetration depth as determined by spraying with $AgNO_3$ vs. Cl^- exposure time for mortar cylinders cured for 28 d prior to chloride solution exposure.

data [16]. 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

A provisional patent application has been filed in the US on this technology. Once a non-provisional patent is filed, the technology will be available for licensing from the US government. Research continues on evaluating the performance of VERDiCT in mortars and on solution studies that are investigating alternative viscosity modifiers, both in terms of viscosity enhancements and conductivity/diffusivity reductions.

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