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Doubling the service life of concrete structures. I: Reducing ion mobility using nanoscale viscosity modifiers

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A B S T R A C T

A new approach for increasing the service life of concrete structures is presented. While conventional approaches have focused on producing a more impermeable matrix by reductions in water-to-cementitious materials ratio and the addition of fine particles such as silica fume, in the new approach, focus is shifted to the remaining pore solution through which diffusive transport will always be occurring. By adding appropriate nano-sized viscosity modifiers to the pore solution, conductive and diffusive transport can be reduced by basically the same factor as the viscosity increase relative to the viscosity of water (pore solution). Since in many degradation scenarios, service life is directly proportional to the diffusion coefficient of an ingressing ionic species such as chloride or sulfate ions, it is envisioned that a doubling of the service life of structural concrete can be achieved by increasing the pore solution viscosity by a factor of two. In part I of this series, viscosities of bulk solutions and electrical conductivities of solutions containing various concentrations of potassium chloride are examined to verify the viability of this revolutionary approach.

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1. Introduction

Many degradation scenarios for concrete structures involve the ingress of one or more deleterious species from the external environment into the concrete. Examples include sulfate attack due to external sources of sulfate ions and the ingress of chloride ions enhancing the likelihood of corrosion of steel reinforcement bars. Often, in such cases, service life models will predict that the estimated service life will be in direct proportion to the diffusion coefficient of the ingressing species in the concrete matrix [1], particularly when the service life is equated to the time necessary for a critical concentration of some deleterious species to be achieved at a specific depth within the concrete, such as the depth of the uppermost steel reinforcement layer. Past efforts have focused on reducing this diffusion coefficient by producing a denser, more impermeable matrix via reductions in the water-to-cementitious materials ratio (*w*/cm) or via the addition of fine (reactive) materials such as silica fume [2]. In this paper, a new approach that focuses instead on the properties of the remaining pore solution will be introduced. However dense the cement paste matrix in a specific concrete might be, diffusion will still occur within the water-filled pore spaces within this matrix. Hence, modifying this solution to slow down these diffusion processes should be a viable approach for increasing the service life of a wide variety of structural concretes. In focusing on the long term performance of concrete structures, it is being tacitly assumed that the early-age cracking that often drastically compromises long term performance can be eliminated by appropriate mitigation strategies [3].

An understanding of how to reduce the ion mobilities (diffusion) can only be achieved by first considering the motion of the ions at the molecular level. The motion of an individual ion in the pore solution is characterized by the particle mobility μ, which is the ratio of the particle velocity to the force on the particle. The Einstein relation expresses the self-diffusion coefficient D_0 of an ion as a function of its mobility μ [4]:

$$D_0 = \mu k_B T \qquad (1)$$

The quantities k_B and T are the Boltzmann constant and the thermodynamic temperature, respectively, and the product has units of energy. In electrical conduction, the electrophoretic mobility μ_e is the ratio of the ion drift velocity v_d and the applied electric field E ($\mu_e = e\mu$, where e is the charge of an electron). Therefore, there is a fundamental similarity between diffusion coefficients and electrical conductivity, at the molecular scale, that allows one to infer the value of one from a measurement of the other. This is the basis for estimating diffusion coefficients from electrical migration (applied electric field) tests, such as ASTM C 1202 [5].

The self-diffusion coefficient of an ion can be modified by altering the fluid it moves through. For a spherical particle having radius r in a fluid (composed of much smaller particles) having bulk viscosity η_0, the self-diffusion coefficient is given by the Stokes–Einstein relation:

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$$D_0 = \frac{k_B T}{6\pi\eta_0 r} \tag{2}$$

This relationship suggests that one can change the self-diffusion of an ion by simply changing the bulk viscosity of the solution. This relationship between self-diffusion coefficient and bulk viscosity leads to the postulation that changes in the solution viscosity η should lead to changes in the self-diffusion coefficient [6]:

$$\frac{D}{D_0} = \frac{\eta_0}{\eta} \tag{3}$$

This result provocatively suggests that if one increases the fluid viscosity, η, to be twice that of its original bulk value, η_0, the corresponding diffusion coefficient D, will decrease by a factor of two relative to its original value of D_o, thereby increasing the service life by a factor of two, all other things being equal. For example, it was previously noted that shrinkage-reducing admixtures (SRAs), in addition to significantly reducing the surface tension of pore solution, also increase its viscosity by about 50% and could thus perhaps result in reduced diffusion coefficients into concrete [7]. This approach is only valid, however, where the Stokes equation applies: diffusing particles in a fluid composed of smaller (or similar size) particles.

The practical limitation in using this approach is the boundary between changing the bulk viscosity and changing the ion mobility. There are many commercial products that can be used to change the bulk viscosity of a pore solution; these products are typically used for applying mortar to vertical surfaces [8] and in self-consolidating concretes. These viscosity modifiers, however, are typically composed of large molecules, potentially violating the applicability of the Stokes relation.

In [6], Eq. (3) was successfully applied to aqueous solutions of potassium chloride, sodium chloride, or potassium nitrate, but whether it holds in situations of practical interest for diffusion in a concentrated multi-species concrete pore solution is a question that must be addressed. Some hope for a positive answer can be found in the (seemingly unrelated to concrete) works of Caputo and Dipolo in 1973 [9] and Bobroff et al. in 1997 [10]. The former studied ionic diffusion delays in frog muscle fibers and concluded that increasing the viscosity of the bathing medium by a factor of 3.4× by adding 15% Dextran 15[1] did indeed delay the diffusion of sodium ions [9]. In the latter, it was shown that the diffusion coefficient of ammonium ions in aqueous solutions was almost inversely proportional to the relative viscosity of the solution, in direct agreement with Eq. (3) [10].

But, perhaps the deepest insights into a possible starting point for the current study are to be found in the 1999 paper of Shimizu and Kenndler [11]. These authors studied electrophoretic mobilities and diffusion coefficients of a small ion (relative molecular mass of 579) in solutions containing viscosity modifiers such as ethylene glycol and polyethylene glycols (PEG) of relative molecular masses ranging from 400 to 2,000,000. For solutions with the smaller nano-sized additives (ethylene glycol and PEG 400), indeed, the diffusion coefficient was inversely proportional to the solution viscosity. Conversely, for larger molecules, the diffusion coefficient was independent of solution viscosity and had approximately the same value as that observed for pure water [11]. So, clearly the size of the viscosity modifier molecules has a critical influence on whether or not ionic mobility is effectively inhibited in the resulting solution.

This paper presents an initial study of the effectiveness of a variety of viscosity modifiers, with potential application in concrete, in reducing ionic transport. Here, ionic transport is quantified by measuring the electrical conductivity of potassium chloride solutions of various concentrations ranging from about 0.001 M to 0.1 M, taking advantage of the relationships between conduction and diffusion for ionic solutions [12] that are commonly utilized for example in the ASTM C1202 Rapid Chloride Permeability Test [5,12,13]. This new technical approach has been given the name VERDICT (Viscosity Enhancers Reducing Diffusion In Concrete Technology). Currently, a patent application is pending for this technology.

2. Materials and experimental procedures

A variety of potential viscosity modifiers were obtained for evaluation in this preliminary solution-based study. Identifying characteristics are provided in Table 1. The last two chemicals listed in Table 1 are commercially available shrinkage-reducing admixtures that have been used in previous studies at NIST [7].

Solution viscosities were measured using a Cannon–Fenske Routine Viscometer[1] in which the time needed for the solution to flow between two marker lines is measured. Various concentration solutions were prepared, as necessary, to achieve an increase in solution viscosity ranging from about 1.4× to 3.3× that of distilled water.

The electrical conductivity of the aqueous solutions was determined using a conductivity cell having a diameter of 25 mm and an electrode separation of 150 mm [14]. The cell was calibrated using the standard potassium chloride (KCl) solutions [15] appearing in Table 2 with concentrations (per unit mass of water) of 0.01 mol/kg and 0.10 mol/kg. The resulting cell constant (the effective ratio between the apparatus length to area) was (0.31455 ± 0.00010) mm^{-1}, where the uncertainty is the difference between the two calculated cell constants. The measurements were performed in a walk-in environmental chamber that was maintained at (25.0 ± 0.4) °C; the reported uncertainty is the standard deviation of the temperature control hysteresis. Measurements were repeated until the values varied by less then 1%. The experimental method was similar to one used previously [14].

The current experiment was developed on the assumption that KCl would serve as a chloride "invader" to the aqueous viscosity modifier solutions, acting as a surrogate cementitious pore solution. These solutions were prepared and then various concentrations of KCl were added to them. The resulting bulk electrical

Table 1
Chemical names and molecular masses for viscosity modifiers used in this study

Chemical name	Estimated relative molecular mass
Cellulose ether	91,000–99,000
Xanthum gum	≈1,000,000
Glycerol ($C_3H_8O_3$)	92.1
Polyethylene glycol ($HO–(CH_2–CH_2–O)_n–H$)	≈400
Polyethylene glycol	≈600
Polyoxyalkylene alkyl ether	≈400–1000
Dipropylene glycol ($C_6H_{14}O_3$)/propanol,[2-,1-dimethylethoxy)methylethoxy] ($C_{10}H_{22}O_3$)	134–190

Table 2
Reference conductivities of solutions of various concentrations (per unit mass of water) of KCl [15]

Concentration KCl (mol/kg)	Solution conductivity (S/m)
0.001	0.0151
0.01	0.141
0.1	1.28

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[1] Certain commercial products are identified in this paper to specify the materials used and procedures employed. In no case does such identification imply endorsement by the National Institute of Standards and Technology, nor does it indicate that the products are necessarily the best available for the purpose.

conductivities were compared to those of KCl solutions prepared with distilled water only. The KCl concentrations were maintained at consistent levels per unit mass of solution (water plus viscosity modifier). This implies that in comparing field concretes, the chloride exposure conditions will be the same and the viscosity modifier will be replacing an equivalent mass of the mixing water. For many commercial liquid admixtures, it is recommended that the mixing water be reduced by some percentage (50% is typical) of the admixture dosage volume.

For large molecular mass viscosity modifiers that require very small mass fractions to achieve desired effects, the distinction between a constant water mass basis and a constant solution mass basis is unimportant. When large mass fractions of viscosity modifiers are required, the distinction becomes important. Keeping the KCl concentration constant with respect to the solution mass is a more stringent test of the viscosity modifier effect.

3. Results and discussion

Viscosity measurements are summarized in Table 3 that provides the relationship between chemical dosage and solution viscosity with respect to the viscosity of water. A typical coefficient of variation for the solution viscosity, when 10 replicate measurements are performed, is on the order of 0.5%. The general trend is that the larger the molecular mass of the additive, the lower the concentration required to double or triple the viscosity of distilled water. If increasing the viscosity were the only goal, large molecules such as cellulose ethers and xanthum gum would clearly provide the most (cost) efficient solution. However, our true interest is in decreasing conduction/diffusion by decreasing ion mobility, and not simply increasing solution viscosity.

With this goal in mind, results of the measurements of electrical conductivities are summarized in Table 4 for the various additives. A typical coefficient of variation for the solution conductivity, when 6–12 replicate measurements are performed, is on the order of 0.6%. One complication in measuring the electrical conductivities of the solutions containing both KCl and an additive is that the presence of the additive alone may increase the solution conductivity, as shown in Table 5. Thus, in determining the reduction in conductivity provided by the additive, the measured solution conductivity was divided by the sum of the conductivities of two solutions, namely a solution containing only KCl at the same concentration being examined (see Table 2) and a solution containing only the additive. Simply adding these two conductivities basically assumes that the two conductive paths through the solution exist in parallel. This adjustment has a significant effect only on the values measured for the lowest concentration KCl solution (0.001 mol/kg), as the base conductivities of the 0.01 mol/kg and 0.1 mol/kg KCl solutions (Table 2) are much larger than any of the solutions containing the viscosity enhancers (Table 5).

In Table 4, it is clear that some of the viscosity enhancers are very effective in reducing the solution conductivities, while others have almost no measurable effect on conductivity. The results are in basic agreement with those of Shimizu and Kenndler [11] in that the larger molecules such as cellulose ether and xanthum gum have basically no influence on conductivity within the solutions despite their measurable effects on viscosity. Conversely, the smaller nano-sized molecules, such as glycerol, the two PEGs, and the two commercial SRAs are highly effective in reducing conductivity. For these compounds, as shown in Table 4, the measured conductivity reduction is basically in direct proportion to the inverse of the relative viscosity factor, in agreement with Eq. (3). The glycerol molecule is on the order of 1 nm in size [16]. Based on the ratios of their respective molecular masses, it could be estimated that the low molecular mass polyethylene glycols and commercial SRAs employed in this study will be less than 20 nm in size, as the molecular backbones of each of these is based on carbon–carbon (like glycerol) and carbon–oxygen units. It is possible that a high degree of local hydrogen bonding between water and these nano-sized well-dispersed molecules is partially responsible for the observed increase in hydrodynamic friction experienced by the diffusing ions. For much larger molecules such as xanthum gum and cellulose ether, this effect is not observed.

Of course, there are numerous other practical considerations that must be addressed when introducing chemical admixtures into concrete. For example, while the polyethylene glycols appear promising in terms of their conductivity reductions, they may produce a considerable retardation of cement hydration [17]. In further support of this, results of calorimetric studies, both isothermal and semi-adiabatic, for one particular cement prepared at a water-to-cement ratio (*w*/*c*) of 0.4 with several of the different solutions investigated in this study are provided in Figs. 1 and 2. While the PEG 600 produces a significant retardation of the cement hydration, that produced by a 10:90 polyoxyalkylene alkyl ether solution is significantly less and may be acceptable from a practical

Table 3
Viscosity measurements (relative to value for distilled water)

Chemical name	Solution mixture	η/η_0
Cellulose ether	0.29 g in 100 g of water	3.30
Xanthum gum	0.4 g in 100 g of water	2.32
Glycerol	30 g in 70 g of water	2.10
Polyethylene glycol 400	20 g in 80 g of water	2.26
Polyethylene glycol 600	15 g in 85 g of water	1.93
Polyoxyalkylene alkyl ether	10 g in 90 g of water	1.50
Polyoxyalkylene alkyl ether	20 g in 80 g of water	2.58
Dipropylene glycol/propanol,[2-,1-dimethylethoxy)methylethoxy]	10 g in 90 g of water	1.40

Table 4
Electrical conductivity reductions for solutions with various viscosity modifiers

Chemical name (concentration)	η_0/η	Electrical conductivity reduction factor for KCl/modifier solutions (moles of chloride ion per unit mass of solution)		
		0.001 mol/kg	0.01 mol/kg	0.1 mol/kg
Cellulose ether	0.30	1.03	0.98	0.98
Xanthum gum	0.43	0.96	0.99	1.00
Glycerol (30/70)	0.48	0.52	0.53	0.49
Polyethylene glycol 400 (20/80)	0.44	0.49	0.55	0.56
Polyethylene glycol 600 (15/85)	0.52	0.74	0.70	0.67
Polyoxyalkylene alkyl ether (10/90)	0.67	0.83	0.69	0.67
Polyoxyalkylene alkyl ether (20/80)	0.39	0.78	0.59	0.47
Dipropylene glycol/propanol, [2-,1-dimethylethoxy)methylethoxy] (10/90)	0.72	0.89	0.79	0.76

Table 5
Base conductivities of solutions of the various viscosity enhancers

Chemical name	Solution mixture	Conductivity (S/m)
Cellulose ether	0.29 g in 100 g of water	5.49×10^{-3}
Xanthum gum	0.4 g in 100 g of water	4.69×10^{-3}
Glycerol	30 g in 70 g of water	5.52×10^{-4}
Polyethylene glycol 400	20 g in 80 g of water	6.20×10^{-3}
Polyethylene glycol 600	15 g in 85 g of water	5.86×10^{-3}
Polyoxyalkylene alkyl ether	10 g in 90 g of water	1.17×10^{-2}
Polyoxyalkylene alkyl ether	20 g in 80 g of water	1.78×10^{-2}
Dipropylene glycol/propanol,[2-,1-dimethylethoxy)methylethoxy]	10 g in 90 g of water	2.02×10^{-2}

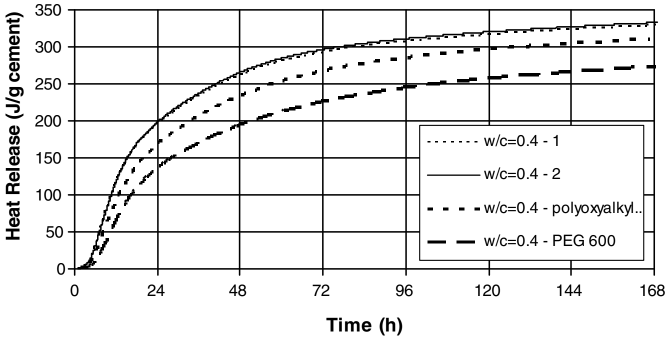

Fig. 1. Isothermal (temperature of 25 °C) calorimetry results for *w/c* = 0.4 cement pastes prepared with the indicated solutions. Results for two replicate specimens of the cement paste prepared with only water are provided to give an indication of variability.

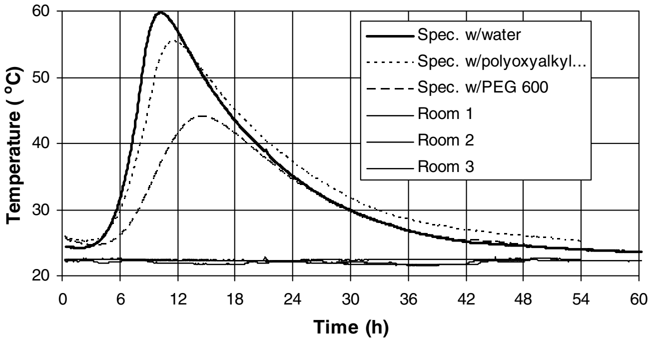

Fig. 2. Semi-adiabatic calorimetry results for *w/c* = 0.4 cement pastes prepared with the indicated solutions. Replicate specimens have indicated a standard deviation of 1.4 °C in the maximum specimen temperature achieved during a 3 day test [17].

performance standpoint. For those viscosity modifiers that do exhibit excessive retardation (or acceleration) of the cement hydration reactions, alternative methods for the delivery of VERDICT may be considered. For example, in the case of SRAs, delivery methods based on either an external application of the SRA solution once any bleeding subsides [18] or using saturated lightweight fine aggregates as a delivery vehicle [19] have been successfully employed in the past. In part II of this study, chloride diffusion into mortars prepared with and without one of these viscosity modifiers will be compared, including an evaluation of the three different delivery methods, as part of the mixing water, as part of an external "curing" solution, and as part of an internal curing solution using saturated lightweight fine aggregates. In each case, chloride ingress will be quantified by splitting open exposed (to chloride) cylindrical specimens and analyzing their open surfaces both by spraying with a solution of $AgNO_3$ [20,21] and by direct analysis using X-ray microfluorescence techniques [22].

4. Conclusions

A new approach for increasing the service life of concrete has been introduced. The basic concept of utilizing nano-sized viscosity modifiers to decrease diffusion coefficients has been demonstrated based on measurements of the electrical conductivity of solutions of KCl. It has been further demonstrated that the size of the viscosity enhancers is critical to their ability to reduce electrical conduction, as "larger" molecules, while being able to dramatically increase solution viscosity at rather low concentrations, have basically no effect on solution conductivity. Conversely, nano-sized molecules were highly successful at both increasing solution viscosity and decreasing electrical conduction. While applications of nanotechnology to concrete have previously focused almost exclusively on additions of solid nanoparticles (to the solid matrix), this study indicates that nano-engineering of the pore solution can also offer substantial benefits. From a practical viewpoint, it may indeed be possible to double the viscosity of the pore solution and thus ultimately double the service life of many concrete structures using this new approach.

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