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

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ABSTRACT

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]:

$$D_0 = \mu k_B T \tag{1}$$

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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$$D_0 = \frac{k_B T}{6\pi\eta_0 r} \quad (2)$$

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]:

$$\frac{D}{D_0} = \frac{\eta_0}{\eta} \quad (3)$$

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

[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.