

Doubling the Service Life of Concrete. 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 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.

Keywords: Building technology; Conduction; Diffusion; Nanotechnology; Service life; Viscosity.

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]. 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

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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 concrete mixtures.

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_o of an ion as a function of its mobility μ [3]:

$$D_o = \mu k_B T \quad (1)$$

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 [4].

The self-diffusion coefficient 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_o , the self-diffusion coefficient is given by the Stokes-Einstein relation:

$$D_o = \frac{k_B T}{6\pi \eta_o r} \quad (2)$$

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 [5]:

$$\frac{D}{D_o} = \frac{\eta_o}{\eta} \quad (3)$$

This result provocatively suggests that if one increases the fluid viscosity, η , to be twice that of its original bulk value, η_o , 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 [6]. 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 [7] and in self-consolidating concretes. These viscosity modifiers,

however, are typically composed of large molecules, potentially violating the applicability of the Stokes relation.

In [5], equation (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 [8] and Bobroff et al. in 1997 [9]. The former studied ionic diffusion delays in frog muscle fibers and concluded that increasing the viscosity of the bathing medium by a factor of 3.4x by adding 15 % Dextran 15¹ did indeed delay the diffusion of sodium ions [8]. 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 equation (3) [9].

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 [10]. 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 [10]. 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 [11] that are commonly utilized for example in the ASTM C1202 Rapid Chloride Permeability Test [4,11,12]. This new technical approach has been given the name VERDICT (Viscosity Enhancers Reducing Diffusion Into 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 [6].

Solution viscosities were measured using a Cannon-Fenske Routine Viscometer¹ 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 1.4x to 3.3x that of distilled water.

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.

Table 1. Chemical Names and Molecular Masses for Viscosity Modifiers Used in This Study

| Chemical Name | Estimated Relative Molecular Mass |
|--|-----------------------------------|
| Cellulose Ether | 91 000 to 99 000 |
| Xanthum Gum | ≈ 1 000 000 |
| Glycerol (C ₃ H ₈ O ₃) | 92.1 |
| Polyethylene Glycol (HO-(CH ₂ -CH ₂ -O) _n -H) | ≈ 400 |
| Polyethylene Glycol | ≈ 600 |
| Polyoxyalkylene alkyl ether | ≈ 400 to 1000 |
| Dipropylene glycol (C ₆ H ₁₄ O ₃)/ Propanol,[2-,1-dimethylethoxy)methylethoxy] (C ₁₀ H ₂₂ O ₃) | 134 to 190 |

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 [13]. The cell was calibrated using the standard potassium chloride (KCl) solutions [14] 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 $(0.31455 \pm 0.00010) \text{ mm}^{-1}$, 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 $(25.0 \pm 0.4) ^\circ\text{C}$; the reported uncertainty is the standard deviation of the temperature control hysteresis. Measurements were repeated until the values varied by less than 1%. The experimental method was similar to one used previously [13].

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 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.

Table 2. Reference Conductivities of Solutions of Various Concentrations (per unit mass of water) of KCl [14]

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

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 ten 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.

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 |

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 six to twelve 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 [10] 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

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

| | | Electrical Conductivity Reduction Factor for KCl/Modifier Solutions (moles of chloride ion per unit mass of solution) | | |
|---|---------------|---|---------------------|-------------------|
| Chemical Name (Concentration) | η_0/η | 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} |

conductivity reduction is basically in direct proportion to the inverse of the relative viscosity factor, in agreement with equation (3).

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 [15]. 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 Figures 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 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 [16] or using saturated lightweight fine aggregates as a delivery vehicle [17] 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 [18,19] and by direct analysis using X-ray microfluorescence techniques [20].

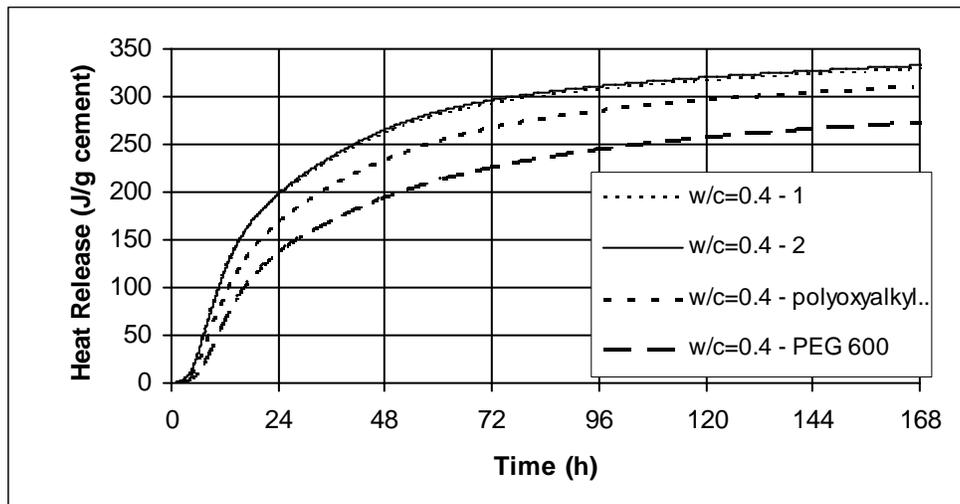


Fig. 1. Isothermal (temperature of 25 °C) calorimetry results for $w/c=0.4$ cement pastes prepared with the indicated solutions. Results for two replicate specimens of the cement paste prepared with only water are provided to give an indication of variability.

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.

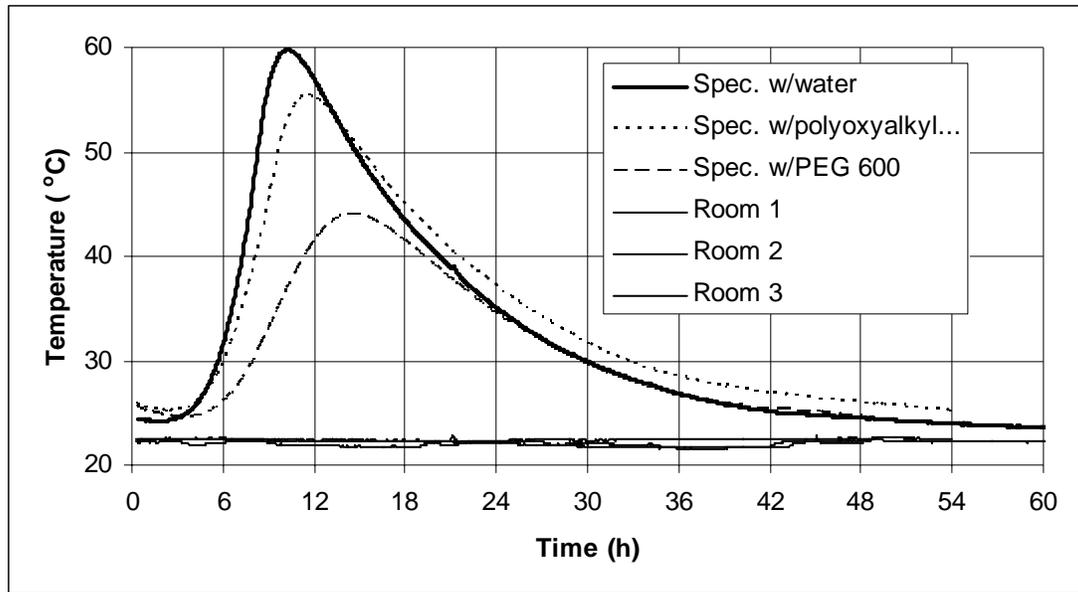


Fig. 2. Semi-adiabatic calorimetry results for $w/c=0.4$ cement pastes prepared with the indicated solutions. Replicate specimens have indicated a standard deviation of $1.4\text{ }^{\circ}\text{C}$ in the maximum specimen temperature achieved during a 3 d test [15].

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References

- 1) Bentz DP, Clifton JR, Snyder KA. Predicting service life of chloride-exposed steel-reinforced concrete. *Concrete Int* 1996; 18 (12):42-7.
- 2) Bentz DP, Jensen OM, Coats AM, Glasser FP. Influence of silica fume on diffusivity in cement-based materials. I. Experimental and computer modeling studies on cement pastes. *Cement Concrete Res* 2000; 30:953-62.
- 3) Wannier, GH. *Statistical Physics*. New York: Dover Publications; Chapter 22, 1987.
- 4) ASTM C1202. Standard test method for electrical indication of concrete's ability to resist chloride ion penetration; 1997.
- 5) Gordon AR. The diffusion constant of an electrolyte, and its relation to concentration. *J Chem Phys* 1937; 5:522-6.
- 6) Bentz DP. Influence of shrinkage-reducing admixtures on early-age properties of cement pastes. *J Adv Concrete Technol* 2006; 4 (3):423-9.
- 7) Bentz DP, Haecker, C-J, Peltz MA, Snyder, KA. X-Ray Absorption Studies of Drying of Cementitious Tile Adhesive Mortars. *Cement Concrete Comp* 2008; 30: .
- 8) Caputo C, Dipolo R. Ionic diffusion delays in the transverse tubules of frog twitch muscle fibres. *J Physiology* 1973; 229:547-57.
- 9) Bobroff S, Phillips RJ, Shekarriz A. Nuclear magnetic resonance measurement of ammonia diffusion in dense solid-liquid slurries; Pacific Northwest National Laboratory, September 1997. PNNL:-11678: 23 pp.

- 10) Shimizu T, Kenndler E. Capillary electrophoresis of small solutes in linear polymer solutions: Relation between ionic mobility, diffusion coefficient, and viscosity. *Electrophoresis* 1999; 20:3364-72.
- 11) Snyder KA, Ferraris CF, Martys NS, Garboczi EJ. Using impedance spectroscopy to assess the viability of the rapid chloride test for determining concrete conductivity. *J Res Natl Inst of Stand and Technol* 2006; 105(4):497-509.
- 12) Bentz DP. A virtual rapid chloride permeability test. *Cement Concrete Comp* 2007; 29:723-31.
- 13) Snyder, KA, Feng, X, Keen, BD, Mason, TO. Estimating the electrical conductivity of cement paste pore solutions from OH⁻, K⁺, and Na⁺ concentrations. *Cement Concrete Res* 2003; 33:793-8.
- 14) Settle, FA. *Handbook of Instrumental Techniques for Analytical Chemistry*. Upper Saddle River: Prentice Hall; 1997.
- 15) Bentz DP, Turpin R. Potential applications of phase change materials in concrete technology. *Cement Concrete Comp* 2007; 29 (7):527-32.
- 16) Bentz DP. Curing with shrinkage-reducing admixtures: Beyond drying shrinkage reduction. *Concrete Int* 2005; 27 (10):55-60.
- 17) Bentz DP. Capitalizing on self-desiccation for autogenous distribution of chemical admixtures in concrete. In: *Proceedings of the 4th International Seminar on Self-Desiccation and Its Importance in Concrete Technology*, 2005. p. 189-96.
- 18) Baroghel-Bouny V, Belin P, Maultzsch M, Henry D. AgNO₃ spray tests: Advantages, weaknesses, and various applications to quantify chloride ingress into concrete. Part 1: Non-steady-state diffusion tests and exposure to natural conditions. *Mater Struc* 2007; 40 (8):759-81.
- 19) Baroghel-Bouny V, Belin P, Maultzsch M, Henry D. AgNO₃ spray tests: Advantages, weaknesses, and various applications to quantify chloride ingress into concrete. Part 2: Non-steady-state migration tests and chloride diffusion coefficients. *Mater Struc* 2007; 40 (8):783-99.
- 20) Davis, JM, Newbury, DE, Rangaraju, P, Soundrapanian, S, Giebson, C. X-ray Microfluorescence X-ray Spectrum Imaging for Measuring Potassium Ion Intrusion into Concrete Pavements. submitted to *J Am Ceram Soc*, 2008.