Influence of Shrinkage-Reducing Admixtures on Moisture Absorption in Cementitious Materials at Early Ages

Gaurav Sant\(^1\); Arnd Eberhardt\(^2\); Dale Bentz\(^3\); and Jason Weiss\(^4\)

Abstract: The water-absorption behavior of cement pastes (w/c=0.30) containing varying concentrations (i.e., 0, 0.2, and 5%) of a shrinkage-reducing admixture (SRA) was measured. Moisture ingress was monitored using X-ray absorption. A decrease in both the depth of water penetration and the rate of water absorption was observed with increasing specimen maturity and admixture concentration. This agrees with theoretical considerations that suggest water sorption is a function of the surface tension and the viscosity of the fluid ingressing into the pores. The Boltzmann-Matano method was successfully employed to determine the moisture content dependent moisture diffusivity of the material, which exhibited a dependence on both the pore structure (specimen maturity) and the SRA concentration.

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Introduction and Background

Shrinkage-reducing admixtures (SRAs) are being increasingly used in concrete construction (Weiss and Berke 2002). SRAs work by reducing the surface tension of the pore fluid which in turn reduces the capillary stress developed and the shrinkage of concrete (Ai and Young 1997; Shoya et al. 1990). Several studies have demonstrated that SRAs can substantially reduce shrinkage (both drying and autogenous) while having a minimal impact on mechanical properties such as strength or elastic modulus (Shah and Weiss 2000; Weiss et al. 1998, 2008; Bentz et al. 2001; Sant 2007). Several researchers have shown that reducing shrinkage results in a reduction or elimination of cracking in concrete elements (Shah et al. 1992; Ribeiro et al. 2006; See et al. 2003; D’Ambrosia et al. 2001).

While the majority of research has focused on assessing the influence of SRAs on volume change, the impact of these admixtures on material durability has received less attention [Shah and Weiss 2000; Sant et al. 2006b; Sant 2007; Pease et al. 2005; American Concrete Institute (ACI) 2009; Weiss et al. 2008; Bentz 2006a]. Schissel et al. assessed the electrical properties and rapid chloride penetrability of concrete mixtures containing SRAs and observed them to provide a greater resistance to ionic transport than conventional mixtures (Schissel et al. 2000). This may be due in part to the reduction in the conductivity of solutions containing SRAs (Rajabipour 2006; Bentz et al. 2008). Furthermore, Bentz et al. (2008) demonstrated that additions of SRAs may reduce the diffusion rate of ionic species due to the increase in the viscosity of the pore solution. Berke et al. (1997) showed that reinforced concrete containing a SRA may also have a lower potential for corrosion related damage as compared to concrete containing such an admixture.

Other researchers have investigated the influence of SRAs on the freeze-thaw resistance of concrete. While some have suggested that the SRA may in some cases interact with the air entraining admixture resulting in a reduction in the stability of the air system (Cope and Ramey 2001; Schemmel et al. 1999) or reduce the scaling performance under freeze-thaw loading (B. Bissonnette, personal communication, November 2006), others have shown that it is possible to make concretes with a sufficient air-void system. It has often been anecdotally observed that concrete containing SRAs can be even more resistant to freezing and thawing than conventional concrete after some drying is permitted before exposure to freeze-thaw cycling (W. J. Weiss, unpublished results, 2004; N. S. Berke, personal communication, 2005). This can be explained by observations that water is absorbed less quickly into concrete containing SRAs (Weiss and Berke 2002; Weiss 1999). This has been previously attributed to the reduction in surface tension of the pore fluids (Ai and Young 1997; Pease 2005; Weiss et al. 2008).

A need exists for the development of more comprehensive approaches for quantifying the water-absorption behavior of concretes containing SRAs. This has implications on the interpreta-
tion of laboratory tests like chemical shrinkage, chloride ingress or freeze-thaw, and can also have a substantial impact on the field performance and service-life modeling of concretes containing SRAs. Specifically, this could include considerations of water absorption during curing, saturation leading to freeze-thaw damage, or the ingress of aggressive ionic agents.

Research Significance

This paper quantifies how SRAs reduce water absorption and relates this to a moisture diffusivity coefficient. The diffusivity coefficient is related to considerations of specimen age (maturity), and surface tension and the viscosity of the pore fluid. The results demonstrate a benefit of SRAs in reducing moisture ingress and enable this effect to be incorporated from a fundamental perspective in service-life models which aim to predict the durability performance of structures.

Materials and Mixing Procedures

Three cement paste mixtures were prepared as per the mixture proportions shown in Table 1. An ASTM C 150 Type I ordinary portland cement was used. The cement had a Blaine fineness of 360 m²/kg and a Bogue potential phase composition (mass fraction) of 60% C₃S, 12% C₂S, 12% C₃A, and 7% C₄AF, with a Na₂O equivalent of 0.72%. A high-range water reducing admixture (HRWRA) (Glenium 3000NS, BASF Construction Chemicals, Cleveland) was used. A commercially available SRA (Tetraguard AS20, BASF Construction Chemicals, Cleveland) was added at 0, 0.2, and 5% concentration (based on the initial water to SRA replacement rates by mass) of the initial mixing water. The mixture compositions (SRA concentrations) were specifically selected to evaluate the moisture transport performance of mixtures having three distinct values of liquid-vapor surface tensions (72 × 10⁻³, 54 × 10⁻³, and 38 × 10⁻³ N/m). Further details are provided in the following sections. While Tetraguard AS20 was the SRA used in this study; the results and conclusions presented can be extended to other surface tension or the ingress of aggressive ionic agents.

The cement paste slurry was placed in the specimen molds using external vibration (Sant et al. 2006a; G. Sant and W.J. Weiss, unpublished results, 2006).

General Information on the X-Ray Absorption Equipment

The equipment used is an X-ray absorption system produced by GNI (GNI 2007). The system consists of a modified type 9120 X-ray source (tube) contained in an environmentally controlled (temperature and humidity) chamber (Nielsen 2007). For the X-ray settings (power=2.5 W; 50 KeV and 50 μA) used in this study, the spot size of the source was approximately 0.0055 mm (Nielsen 2007). The X-ray beam output by the source exhibits a conical spread (Nielsen 2007).

The X-ray intensity is measured using a charge-coupled device (CCD) (i.e., X-ray camera). The 16-bit CCD camera records the cumulative X-ray intensity at each pixel, for a total surface of 252 × 256 pixels (Paradis and Weiss 2007). The X-ray source and camera can be moved simultaneously using an X-Y positioning table with a precision of ±0.001 mm. The focus to detector distance (FDD) (Fig. 1), can be adjusted from 10 to 500 mm; however, for this study the FDD was fixed at 500 mm. The object to detector distance (ODD) was fixed at 100 mm for this study (Fig. 1).

The specimens analyzed in this study are mounted on a fixed stage, which allows the user to perform repetitive imaging, ensuring a fixed specimen position. An illustration of the experimental setup is provided in Fig. 1. A single-pixel size and spatial resolution (refer to “Spatial and moisture content resolution of the X-ray absorption equipment”) of 0.08 mm has been determined for the geometry used in this investigation.

Analytical Assessment of Moisture Movement Using X-Ray Absorption

The intensity of X-ray radiation transmitted at any time through a dry element can be described using Eq. (1) (Als-Nielsen and McMorrow 2006; Hansen et al. 1999)

\[ I_{DRY} = I_0 \exp\left(-\frac{\mu_{eff} \cdot t}{\delta}\right) \]  

while the intensity of radiation transmitted through the same element that contains moisture can be described by Eq. (2) (Als-Nielsen and McMorrow 2006; Hansen et al. 1999)
where \( I_{\text{WET}} \) = intensity of radiation transmitted through a dry element; \( \mu_{\text{Eff}} \) and \( \ell = \) effective linear attenuation coefficient and thickness of the dry volume element; \( I_{\text{DRY}} \) = intensity of radiation transmitted through an element containing moisture; and \( \mu_w \) and \( t_w = \) linear attenuation coefficient and the thickness of the volume of water present in the material (Sant and Weiss 2009). In each case, \( I_0 = \) intensity of radiation incident on the specimen.

To describe the influence of moisture ingress on the transmitted X-ray behavior, the ratio of the wet and dry transmitted intensities can be compared. This can be done by rearranging and reducing Eqs. (1) and (2). Eq. (3) describes this ratio as

\[
\frac{I_{\text{WET}}}{I_{\text{DRY}}} = \exp[\mu_w t_w]
\]

The moisture content (MC) of a porous specimen (m³/m³) can be expressed as a ratio of the volume of water (m³) absorbed to the total (solid) volume of the dry material (m³). This can be written as shown in Eq. (4)

\[
MC = V_i = \frac{I_w}{t}
\]

where \( V_i = \) volume fraction of water contained in the specimen (Sant and Weiss 2009).

Eqs. (3) and (4) can then be rearranged to represent the moisture level that exists in the material as a function of the natural logarithm of the ratio of the transmitted intensities in the wet and the dry states, the attenuation coefficient of water (at a specified energy level) and the thickness of the material in the dry state as shown in Eq. (5); assuming the specimen volume remains constant upon wetting (Sant and Weiss 2009)

\[
\ln \left( \frac{I_{\text{WET}}}{I_{\text{DRY}}} \right) = -\mu_w t_w
\]

### Spatial and Moisture Content Resolution of the X-Ray Absorption Equipment

A critical consideration in moisture movement studies is the need to resolve the spatial position and moisture resolution of the equipment with the settings used. While the spatial resolution is crucial to identify the position of the moisture front and to account for mismatch of the attenuation coefficients encountered at the specimen-air interface (Wagenaar et al. 1991), the moisture resolution is necessary to describe the in situ MC of the specimen.

Fig. 2(a) shows the spatial resolution of the X-ray absorption equipment as a function of the magnification level determined using Eq. (6) (Roels and Carmeliet 2006; Mouze 1996). The spatial resolution can be calculated as

\[
R_s = \frac{S_p}{M} + \left(1 - \frac{1}{M}\right)S_s + \frac{(M - 1)\ell(x^2 + y^2)}{\text{ODD}}
\]

where \( R_s = \) spatial resolution (mm); \( S_p = \) single-pixel size on the camera (0.08 mm in this study); \( M = 1 + \text{ODD/FOD} = \) level of magnification (1.25x in this study); \( S_s = \) spot size of the X-ray beam at the source (0.0055 mm); \( \ell = \) specimen thickness (12.7 mm in this study); and \( x \) and \( y = \) dimensions from the center of the specimen to its visible edges in the horizontal and vertical directions (mm). Fig. 2(a) illustrates that increasing the magnification increases the spatial resolution. For the setup used in this study and a specimen thickness of 12.7 mm, a spatial resolution of \( \approx 0.08 \) to \( \approx 0.39 \) mm was determined, at the center and visible edges of the specimen, respectively.

The MC resolution (%) of the X-ray equipment can be determined from the coefficient of variation (COV) of the transmitted intensity for a dry specimen (or a specimen containing a specific fixed level of moisture). Multiple measurements (three) on a single specimen tested in the dry state with an incident beam power of 2.5 W (50 KeV and 50 μA) demonstrate a measurement (intensity) variability (COV) of 0.55%. Using the ratio of the transmitted intensity of a wet specimen (containing a variable level of moisture), the transmitted intensity of a dry specimen, the effective attenuation coefficient of water at a specific energy level (cm⁻¹), and the thickness of the specimen (cm), the relationship between the normalized X-ray intensity and the MC can be determined using Eq. (5). This relationship is graphically illustrated in Fig. 2(b) (Sant and Weiss 2009). The volumetric MC resolution is then determined to be 0.0055 (m³/m³) which for the material tested (\( \rho = 2100 \) kg/m³) is equivalent to a mass-based MC resolution of 0.26% (kg/kg).

### Experimental Procedures

#### Fluid Surface Tension and Viscosity Measurements

The surface tension of solutions of SRA and DI water and SRA and synthetic pore solution [(0.35 KOH+0.05 NaOH)–molar concentration] were measured using the du Nöy ring method at 23 ± 0.5°C (Adamson 1990). The method is based on determining the force that is required to detach a wire ring from the surface of a solution. The ring used was made of a platinum-iridium alloy and was cleaned according to ASTM D971 prior to each measurement. The measured surface tension of distilled water (0.0723 N/m) was used as a standard reference in determining the change in surface tension caused by the addition of the SRA (Weast et al. 2007). The average of three measurements was used in the representation of each data point, with a typical COV being 0.50%. A more detailed description of the surface tension measurements can be found elsewhere (Pease et al. 2005; Rajabipour 2006).

The viscosities of solutions of SRA and DI water were measured using a Hydromotion 700 portable viscometer (Hydromotion Ltd., York, U.K.), at a temperature of 23 ± 0.5°C, with an
uncertainty of 0.02 mPa·s. The measured viscosity of distilled water (0.89 mPa·s) was used as a standard reference in determining the change in viscosity that occurs due to the addition of the SRA. Measurements were performed at water-SRA mass concentrations of 0, 2, 5, and 10%.

**Moisture Ingress Assessment Using X-Ray Absorption**

Cement paste samples (25.4 × 25.4 × 12.7 mm, ρ=2,100 kg/m³) were used to measure water absorption. A dimensional tolerance of ±0.5 mm was noted between samples. At degrees of hydration evaluated using chemical shrinkage measurements (Sant 2007; Sant et al. 2006a,b) of ≈10 and ≈47% (equivalent ages of 8 and 24 h, respectively, for the plain mixture; w/c=0.30) the samples were demolded and weighed. At this time, the samples were placed in an oven at 50°C for 2 days to remove the majority of the evaporable water contained in the sample, while minimizing the influence of drying on the pore structure. After 2 days of drying, the samples were weighed and the evaporable water content was measured (≈30% and ≈20% at 10% and 47% hydration, respectively, on a volumetric basis of the sealed samples). The initial water content of the plain cement paste (w/c=0.30) is approximately 48% by volume.

At the time of testing, the oven-dried samples were wrapped in two uniform layers of aluminum tape to seal the sample and enable one-dimensional water absorption. Consequently, the measured intensity of X-ray radiation transmitted through the overall specimen would be a function of the thickness of the cement paste and the aluminum tape. After the samples were sealed, they were exposed to X-rays having energy of 2.5 W (50 KeV and 50 μA), for a camera integration (exposure) time of 5 s per image. Multiple (three imaging cycles, which acquired 10 images each cycle for a total of 30 images) X-ray images were acquired for the dry samples, to develop a baseline calibration profile in the dry state. This profile was then used to track the time-dependent ingress of moisture into the samples using Eq. (5), assuming a uniform moisture front and degree of hydration (reaction) through the specimen volume (Sant and Weiss 2009; Sant 2009). After testing of the dry samples was completed, water was ponded on the top of the paste samples. X-ray measurements were then performed periodically over a duration of 1 h after water addition to monitor moisture ingress.

**Experimental Results**

**Fluid Surface Tension and Viscosity Measurements**

Fig. 3(a) shows the measured surface tension of the DI-water solutions and synthetic pore solutions (0.35 KOH with 0.05 NaOH–molar concentration) containing various concentrations of a SRA. As observed in Fig. 3, dramatic reductions in surface tension are noted at even very low concentrations of SRA addition. However, a plateau in the reduction in surface tension is achieved when the SRA concentration reaches a critical level of between 10 and 15% (Pease et al. 2005; ACI 2009; Rajabipour et al. 2008). A similar response is noted for SRA addition in pore solution; however, the plateau in surface tension reduction is reached at a lower SRA concentration due to the presence of salts in the pore solution (Rajabipour et al. 2008).

Fig. 3(b) shows the measured viscosity of solutions containing various concentrations of a SRA normalized to the viscosity of DI-water solutions. As observed in Fig. 3(b), the solution viscosity increases linearly with increasing SRA concentration, and is ≈55% higher than DI-water at a SRA concentration of 10%.

**Moisture Ingress Assessment Using X-Ray Absorption**

Fig. 4 shows the time-dependent moisture penetration profiles for the plain and 5% SRA mixtures at 10% hydration. In Fig. 4, a ratio of X-ray intensity (transmitted) less than 1 indicates a region where water has penetrated from the top surface (depth=0), while a value near 1.0 indicates a dry (original) region. It is seen while water rapidly penetrates the plain mixture [Fig. 4(a)], water penetration is significantly slower in the 5% SRA system, with approximately one-half the extent (depth) of penetration being achieved in this system over the same time interval [Fig. 4(b)].

The moisture ingress trends noted at 10% hydration are also applicable at higher degrees of hydration (e.g., 47% hydration).

**Discussion of Experimental Results**

**Influence of Surface Tension and Fluid Viscosity on Water Sorption: Experimental Observations and Theoretical Modeling**

It is common to consider the parameter sorptivity (the rate of water absorption) to describe the moisture sorption behavior of a porous material (Hall and Hoff 2002). The sorptivity is determined from the slope of the plot of volume of water absorbed as
Penetration ensuring a negligible hydraulic head contribution to moisture the shallow reservoir with water periodically during the test, thus vapor diffusion. An unlimited supply of water is ensured by filling one-dimensional flow while minimizing concerns related to surface the infiltration of water water content; of the system sureillary suction, the reduction in surface tension a function of the square root of the time from ponding, or in the case of spatially sensitive studies from a plot of the depth of penetration of water as a function of the square root of the time from ponding. Since water absorption is a process driven by capillary suction, the reduction in surface tension (and capillary pressure), and the increase in viscosity effected by the addition of a SRA would have significant implications on the sorption behavior of the system (Figs. 5 and 6).

Measurements of sorptivity require fulfillment of certain considerations to be valid/comparable including: (1) a uniform initial water content; (2) one-dimensional flow and an unlimited supply of water at the ponding surface; (3) a homogenous material; and (4) a material which is structurally and chemically unaltered by the infiltration of water (Hall and Hoff 2002). While Conditions (1) and (3) can be ensured by oven drying and assuming that at the scale tested the cement paste is homogenous, Condition (2) is ensured by sealing all the faces of the specimen except the top surface (where water is ponded) using aluminum tape thus ensuring one-dimensional flow while minimizing concerns related to vapor diffusion. An unlimited supply of water is ensured by filling the shallow reservoir with water periodically during the test, thus ensuring a negligible hydraulic head contribution to moisture flow. Condition (4) presents difficulties especially in the case of early-age testing when a large proportion of unhydrated cement exists in the system. To minimize microstructural changes and any anomalies induced due to continuing hydration (i.e., changes in the permeability and capillary forces due to pore refinement), ingress studies in this project were performed for a duration of only 1 h (Hall and Hoff 2002).

The reduction in surface tension and the increase in pore-fluid viscosity effected by addition of a SRA would exert a considerable influence on the water-absorption behavior of materials dosed with a SRA (Bentz et al. 2008; Weiss 1999; Hall and Hoff 2002; Pease 2005; Reinhardt 1997). To comprehensively evaluate changes in water absorption induced by the addition of a SRA, experimental observations of ingress (Fig. 4) were complemented by theoretical modeling of water absorption using a formulation developed by Kelham [Eq. (7)] (Weiss 1999; Kelham 1998)

\[
x(t) = \sqrt{\frac{4k \gamma \cos(\theta) t}{\phi \mu r}}
\]

where \( x(t) \) = depth of penetration (m) at any time \( t \) (s); \( k = \) intrinsic permeability of the material (m²); \( \gamma \) (N/m) = liquid-vapor surface tension of fluid; \( \theta = \) liquid-solid contact angle (radians); \( \Phi = \) porosity of the material (fraction); \( \mu = \) viscosity of the fluid [kg/(m·s)]; and \( r \) (m) = radius of the pore (capillary). In this study, the liquid-solid contact angles were not measured directly but rather they were determined using a linear interpolation of values reported previously for 0% and 10% DI-water-SRA solutions (concentration expressed on a mass basis); 7° and 28°, respectively (Bentz 2006a).

Considering that each mixture displays a similar pore structure at an equivalent degree of hydration, one can assume similar values of porosity and intrinsic permeability for these systems (Sant 2007; G. Sant and W.J. Weiss, unpublished results, 2006). Furthermore, considering a ratio of surface tension values of 1.00:0.75:0.53 [Fig. 3(a)], and a ratio of fluid viscosities values of 1.00:1.01:1.27 [Fig. 3(b)] for pure water, 0.2 and 5% SRA solutions, the depth of penetration (arbitrary units) and the sorptivity (slope of the depth of penetration versus square root of time curve) can be modeled for each mixture evaluated in this project. The results of this analysis are described in Fig. 5(b) and summarized in Table 2. The sorptivity values determined from theoretical modeling for each of these systems, pure water, 0.2% SRA and 5% SRA scale as 1.00:0.84:0.61, respectively. It is seen that the ratio of the sorptivities determined from theoretical modeling are in good agreement with the scaled values of sorptivity determined from experimental measurements (Fig. 6 and Table 2). The difference observed in the measured (Fig. 6) and modeled sorption [Fig. 5(b)] coefficients may be attributed to the change in the SRA concentration with increasing hydration (as water is consumed the concentration of SRA in the pore-fluids increases; refer to Rajabipour et al. 2008) and water absorption into the microstructure, which would exert a larger influence on the results at higher SRA concentrations as evidenced in Table 2.

**Table 2. Experimentally Measured and Theoretically Modeled Sorption Coefficients**

<table>
<thead>
<tr>
<th>Cement paste mixture</th>
<th>Scaled experimental coefficient</th>
<th>Scaled theoretical coefficient</th>
</tr>
</thead>
<tbody>
<tr>
<td>w/c=0.30</td>
<td>1.00</td>
<td>1.00</td>
</tr>
<tr>
<td>w/c=0.30+0.2% SRA</td>
<td>0.75</td>
<td>0.79</td>
</tr>
<tr>
<td>w/c=0.30+5% SRA</td>
<td>0.45</td>
<td>0.49</td>
</tr>
</tbody>
</table>

**Fig. 5.** (a) Capillary pressure as a function of the pore radius computed using the Young-Laplace equation; the dashed line indicates the thermodynamic stability limit of the liquid-vapor meniscus (Weiss et al. 2008; Christenson 1985; Fisher and Israellaivili 1981a,b; Digilov 2000); (b) theoretical water sorption profiles for solutions containing different concentrations of a SRA computed using Eq. (7)

**Fig. 6.** Measured depth of penetration and the sorption coefficients evaluated for cement paste mixtures at: (a) 10% hydration; (b) 47% hydration

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It is noted that a linear fit of the experimental water-absorption measurements displays a small nonzero intercept. This may be explained due to air-trapping and surface and edge effects in the specimen (Hall and Hoff 2002). The agreement between experimental and modeling approaches is significant in that, for measurements performed over a short-time scale, it would allow estimation of the sorptivity for various mixtures and ingressing fluids, permitting determination of the fluid-saturation level in the material. While in this study the ingressing fluid was the DI-water solution and the SRA was supplied from within the paste, previous measurements of the ingress of both DI-water and a 10% SRA solution into hardened paste specimens (containing no SRA) have also supported the validity of the \( \sqrt{\gamma/\mu} \) scaling of sorption coefficients (Bentz 2006b).

The results of theoretical modeling and experimental observations of water sorption illustrate an important point; even upon cycles of drying (desorption) and wetting (absorption), the SRA is observed to persist in the material and is capable of altering the progressive drying, the SRA is adsorbed/absorbed onto the pore walls and maintains this state until a cycle of rewetting is experienced, when the SRA goes back into the pore solution. This has significant implications on the durability performance of materials containing SRAs and is discussed further in “Influence of SRA addition and specimen maturity on the moisture diffusivity.”

**Boltzmann-Matano Method for Assessment of the Moisture Diffusivity**

Neglecting gravitational effects, one-dimensional moisture diffusion in an unsaturated porous medium can be described using a differential equation in the case of a single-phase isothermal moisture transport as shown in Eq. (8) (Fick 1855; Hall and Hoff 2002; Richards 1931)

\[
\frac{\partial w}{\partial t} = \frac{\partial}{\partial x} \left( D(w) \frac{\partial w}{\partial x} \right) \tag{8}
\]

where \( w = MC \) (fraction) which is a function of time and spatial position; \( D(w) = MC \) dependent moisture diffusivity (units of \( \text{m}^2/\text{s} \)); and \( x \) and \( t \) denote variables for spatial position and time, respectively. In the case of moisture transport in a seminfinite, isotropic, and homogenous medium that has a uniform initial moisture \( w_i \) and a constant (far-field) MC \( w_f \) at the boundary furthest from the wetting end [i.e., \( w(x,0) = w_i \), \( w(\infty,t) = w_f \), \( w(0,t) = w_i \), which is the water content at saturation, and \( w(x,t) = w_i \)], the diffusivity function can be computed using transient ingress profiles in a unique closed form using a procedure known as the Boltzmann transformation [Eq. (9)] (Besienn et al. 2002; Boltzmann 1894; Bruce and Klute 1956; Cranck 1975; Hall and Hoff 2002; Matano 1933). A key consideration of the Boltzmann-Matano method is to choose the zero-flux plane (ZFP or Matano plane) to ensure mass conservation (balance) conditions; such that water lost from the reservoir equals water absorbed by the paste (Mehrer 2007). As a first approximation, the ZFP is positioned at the specimen-water interface \( (x = 0 \text{ mm}) \). The exact position of the ZFP is then determined by analyzing the terminal moisture ingress profiles to quantify if a volume change in the paste (induced due to wetting) may result in a displacement of the ZFP (Cranck 1975; Dayananda and Kim 1979; M.A. Dayananda, personal communication, 2009). The analysis indicates a maximum displacement of \( \approx 3.5\% \) \((\approx 0.88 \text{ mm})\) for a 25-mm specimen of the ZFP for the plain cement paste \( (w/c = 0.30) \) at 10% hydration (this will be even smaller for materials which absorb less water). Given the uncertainties involved, this displacement was determined to be negligible, and the calculations were performed while maintaining the ZFP at the specimen surface \( (x_M = 0 \text{ mm}) \)

\[
\lambda = \frac{x - x_M}{\sqrt{t}} \tag{9}
\]

where \( \lambda = \text{Boltzmann variable (mm}/\sqrt{\text{h}}) \) and \( x_M = \text{spatial coordinate corresponding to the position of the Matano plane (x=0 mm)} \). By substituting Eq. (9) in Eq. (8) while applying the chain rule, Eq. (8) can be transformed to an ordinary differential equation [Eq. (10)] in which the Boltzmann variable is the only independent parameter

\[
- \frac{\lambda}{2} \frac{dw}{dx} = \frac{d}{dx} \left( D(w) \frac{dw}{dx} \right) \tag{10}
\]

Eq. (10) can then be solved by the method of variable separation and direct integration over the initial and final boundary conditions \( (\lambda_i, \lambda_f, \text{and } w_i \text{ to } w_f) \) to describe the Boltzmann-Matano relation [Eq. (11)] which permits direct computation of the MC dependent (nonlinear) moisture diffusivity of the cementitious material under evaluation

\[
D(w) = - \frac{1}{2} \left[ \left( \frac{dx}{d\lambda} \right)_{w_f} \right] \int_{w_i}^{w_f} \lambda dw \tag{11}
\]

A primary consideration for the validity of the Boltzmann transformation dictates that the wetting front should not reach the bottom of the specimen (the region having a fixed MC) to ensure the semiinfinite criterion. For measurements which satisfy the criteria of the Boltzmann method, when the wetting profiles are represented as a function of the Boltzmann variable, \( \lambda \), all the experimental measurements collapse onto a single master curve, known as the characteristic moisture profile which describes the MC (normalized X-ray intensity) as a function of the Boltzmann variable.

Fig. 7 shows wetting profiles for two cement paste mixtures \( (w/c = 0.30 \text{ and } w/c = 0.30+5\% \text{ SRA}) \) at 10% hydration which have been subjected to the Boltzmann transformation (i.e., characteristic moisture profiles). The fitted Boltzmann-Matano curve is seen to provide a good representation of the measured ingress profiles within a small region of scatter (Fig. 7).

The characteristic curve shows four distinct stages which correspond to regions having four different MCs in the specimen [Fig. 7(a)], Stage I is the surface zone, closest to the water source...
Moisture transport in porous materials can be comprehensively predicted (Lockington et al. 1999; Carmeliet et al. 2003).

The moisture diffusivity of a porous material can be calculated from transient moisture transfer measurements, shown in Fig. 5 (Carmeliet et al. 2003; Pel 1995). The Boltzmann-Matano approach can then be used to yield the characteristic moisture profile shown in Fig. 7 (Hall and Hoff 2002; Pel et al. 1996). Traditionally, the MC dependent moisture diffusivity (for absorption, imbibition or infiltration type processes) for concretes has been represented as an exponential function [Eq. (12)] (Hall and Hoff 2002; Pel 1995; Leech et al. 2003; Hall 1989; Daian 1988)

\[
D(w) = D_0 \exp(\beta w)
\]  

where \(D_0\) and \(\beta\)=constants which depend upon the properties of the material and the ingressing fluid. In this work, the exponential function has been fit over the linear range of the moisture diffusivity function due to the difficulties associated with accurately describing the diffusivity at very low and very high moisture levels (Mehrer 2007); from 0.01–0.24 \(m^3/m^2\) for specimens at 10% hydration and from 0.01–0.12 \(m^3/m^3\) for specimens at 47% hydration.

Fig. 8 shows the moisture diffusivity of cement pastes at 10 and 47% hydration computed using an averaging and curve-fitting procedure and Eq. (11) (Sant 2009). It is seen [Fig. 8(a)] that pastes containing SRA (0.2 and 5%) exhibit lower moisture diffusivity \(D_0\) and higher \(\beta\) values as compared to the plain cement paste (Table 3). This behavior can be explained by the reduction in surface tension of the pore fluid and increase in fluid viscosity, induced by the addition of the SRA which reduces capillary suction (and water absorption) and the tendency of the material to transmit fluids due to capillarity (refer to “Influence of surface tension and fluid viscosity on water sorption: Experimental observations and theoretical modeling”). The point at which the diffusivity dramatically increases corresponds to the surface zone, closest to the water source, where porosity saturation is achieved. Furthermore, the assumption of plain and SRA mixtures exhibiting similar porosities is validated as the moisture diffusivity dramatically increases at similar MCs, corresponding to porosity saturation at the specimen surface.

In addition to changes in the fluid properties, pore structure refinement with increasing hydration would also influence the moisture diffusivity of the material. This influence is evident in Table 3 which shows a reduction in the moisture diffusivity, \(D_0\) with increasing hydration. This is reasonable considering that a less porous microstructure would exert a larger resistance to the movement of moisture. Furthermore, it is interesting to note the \(\beta\) parameter increases with increasing maturity (structure densification), and exhibits an opposing trend to the \(D_0\) value (which decreases with increasing hydration). The value of the \(\beta\) calculated compares well with the value (\(\beta=4–9\)) reported in the

<table>
<thead>
<tr>
<th>Moisture diffusivity parameters</th>
<th>(10^%) hydration</th>
<th>(47^%) hydration</th>
</tr>
</thead>
<tbody>
<tr>
<td>(w/c=0.30)</td>
<td>(3.0 \times 10^{-9})</td>
<td>(2.7 \times 10^{-10})</td>
</tr>
<tr>
<td>(w/c=0.30+0.2%) SRA</td>
<td>(4.1 \times 10^{-10})</td>
<td>(3.6 \times 10^{-10})</td>
</tr>
<tr>
<td>(w/c=0.30+5%) SRA</td>
<td>(3.8 \times 10^{-10})</td>
<td>(9.9 \times 10^{-11})</td>
</tr>
</tbody>
</table>

Table 3. Moisture Diffusivity Parameters for Cement Pastes at 10% and 47% Hydration

**Influence of Shrinkage-Reducing Admixtures Addition and Specimen Maturity on the Moisture Diffusivity**

Isothermal moisture transport in porous materials can be adequately represented using a nonlinear diffusion equation [Eq. (8)] (Hall and Hoff 2002). In Eq. (8), all mechanisms of moisture movement distribution and transfer (liquid and vapor) are represented by a single moisture diffusivity, \(D(w)\), which is dependent upon the local MC of the material. The moisture diffusivity increases with increasing MC, showing a dramatic increase at saturation (Fig. 8). When the moisture diffusivity is combined with the initial and boundary conditions of the element under evaluation, the moisture transfer performance of building materials can be comprehensively predicted (Lockington et al. 1999; Carmeliet et al. 2003).

Stage II is a region of almost uniform MC (constant intensity) and corresponds to a diffuse-moisture zone preceding the wetting front. The movement of moisture in the diffuse zone is driven by capillary forces which suck moisture into the sample. Issues of air-trapping in the diffuse and wetting zones are crucial, with saturation not being achieved until all the entrapped air is able to diffuse out.

Stage III corresponds to the wetting front that penetrates progressively deeper into the specimen with increasing time. This region shows the largest variability in MC (intensity), as a function of increasing depth (and the Boltzmann variable). Stage IV corresponds to the region having uniform MC \((w_f)\) throughout the course of the imbibition experiment which satisfies the semi-infinite medium diffusion criteria of the Boltzmann-Matano approach.

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The change in the moisture diffusivity achieved by the addition of a SRA has powerful implications on curing, the freeze-thaw performance, and ion migration in concretes containing SRAs. The reduced moisture diffusivity and sorptivity of SRA mixtures suggests the depth of fluid penetration in these mixtures at short-time scales would be less than in plain mixtures. This may imply less water absorption during curing in these mixtures over short curing durations. The reduced sorptivity and moisture diffusivity could indicate a longer time to saturation and the reduction in surface tension may indicate greater drying (i.e., lower saturation levels) which may enhance the performance of these mixtures when subjected to freeze-thaw loadings (Fagerlund 1972; Lura et al. 2007; Weiss et al. 2008). Furthermore, the decrease in the moisture diffusivity may indicate better durability performance in concretes containing SRAs due to decreased moisture movement and consequently aggressive ion migration in these materials (Bentz et al. 2008).

Summary and Conclusions

This paper has described the water-absorption behavior of cement pastes containing various concentrations of a SRA. X-ray absorption measurements were used to provide high resolution spatial information on the movement and depth of penetration of moisture. The Boltzmann-Matano concentration dependent nonlinear diffusion approach was used to profile the characteristic moisture curve, which enabled the determination of the wetting moisture diffusivity of the material. The addition of a SRA results in a reduction in surface tension and an increase in fluid viscosity. Furthermore, the addition of a SRA reduces the sorptivity and wetting moisture diffusivity of the material. The reduction in the sorptivity, measured for mixtures containing a SRA, compared well with theoretical modeling of the sorption coefficient. The sorptivity and moisture diffusivity both decreased with increasing maturity and pore structure refinement (hydration).

The outcome of this investigation has implications on the durability and moisture transfer performance of concretes containing admixtures that alter the surface tension and viscosity of the pore solution (e.g., SRAs). The reduction in the sorptivity and moisture diffusivity that occurs due to the addition of a SRA influences the durability of cementitious materials. This would include considerations of curing (reduction in the depth of curing water), fluid absorption (reduced chloride and deleterious ion absorption), and ionic diffusivity (reduced chloride and deleterious ion migration).

Since fluid transport is primarily attributed to the pore structure and pore-fluid properties the benefits of SRAs scale to mortar and concrete mixtures. The transport properties of concretes containing SRAs should be evaluated considering the concepts outlined in this paper. This may indicate that in addition to reducing shrinkage, SRAs may have other benefits that may improve the performance of concrete. This could include improved corrosion resistance (decreased chloride-ion penetration rates) and improved freeze-thaw (decreased fluid saturation levels) performance of the system if a period of initial drying is permitted.

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