Re-examining the influence of the inclusion characteristics on the drying shrinkage of cementitious composites

Galen Egan (^{*}), Aditya Kumar ([†]), Narayanan Neithalath ([‡]), Gaurav Sant ([§], ^{**}, ¹)

Abstract

The addition of aggregates to cement paste is known to alter its shrinkage, in relation to the aggregate stiffness and volume fraction. This study reexamines the effects of aggregate volume, and stiffness on shrinkage experienced upon 1st and 2nd drying, by cement pastes across a range of w/c (water-to-cement ratio, mass basis). Special focus is paid to understand the influence of the volume and properties of inclusions on the shrinkage response. By unifying shrinkage and mass loss relations with sorption isotherms, the moisture transport properties are extracted as a function of drying time and external relative humidity (RH).

Keywords: drying, shrinkage, moisture diffusion, inclusions, transport, elastic modulus

^{*} Laboratory for the Chemistry of Construction Materials (LC²), Department of Civil and Environmental Engineering, University of California, Los Angeles, CA 90095

[†] Department of Materials Science and Engineering, Missouri University of Science and Technology, Rolla, MO 65409

[‡] School of Sustainable Engineering and the Built Environment, Arizona State University, Tempe, AZ 85287

[§] Laboratory for the Chemistry of Construction Materials (LC²), Department of Civil and Environmental Engineering, University of California, Los Angeles, CA 90095

^{**} California Nanosystems Institute, University of California, Los Angeles, CA 90095

¹ Corresponding Author: Email: gsant@ucla.edu, Phone: (310) 206-3084, Fax: (310) 206-2222

1.0. Introduction and Background

From an economic and environmental standpoint, it is important that concrete structures achieve the longest service-life possible. However, a major drawback of this ubiquitous material is its tendency to shrink upon drying, which results in cracking, thereby accelerating the ingress of deleterious agents (water, Cl^- ions) which causes the premature degradation of structures [1,2]. Over several decades, extensive efforts have been devoted to better understand the shrinkage of cement pastes, mortars and concretes, and novel methods have been proposed to mitigate such volume changes [1,2,3,4,5,6,7,8,9,10]. For example, extensive efforts have been made to assess the effects of the paste's w/c on shrinkage [1,4]. In general, higher w/c pastes have been noted to shrink more than their lower w/c counterparts. This has been widely attributed to the higher evaporable water content and the reduced stiffness of the matrix in cement pastes prepared at higher w/c [1,2]. Other studies have attempted to describe moisture loss and shrinkage behavior of mortar and concrete as a function of the aggregate dosage and properties using "composite models", e.g., see [2,5].

While substantial insights regarding the drying and shrinkage of cementitious materials has been gained, several questions regarding aggregate permeability and its role on drying and on shrinkage remain unclear. For example, while several studies have shown a linear relationship between mass (water) loss during drying, and shrinkage developed [1,4,7,11] these relationships have not been carefully analyzed to draw inferences of inclusion permeability (and stiffness) on shrinkage during the 1st or subsequent drying cycles [5,6,11,12,13,14,15,16,17]. Therefore, this paper seeks to evaluate the following aspects:

- Re-examine the effects of stiffness, size, and volume dosage (%) of aggregates (subsequently referred to as inclusions) on shrinkage, and to assess the predictive capability of Pickett's and Hobbs models in shrinkage estimation [2,5],
- Critically assess shrinkage trends up on 1st drying, and following rewetting, up on 2nd drying, to assess the extent of shrinkage irreversibility, and its relation to inclusion properties, and,
- Assess the transport properties (e.g., diffusion coefficients, intrinsic permeability) of cement-based mixtures across drying cycles, and relate these to changes to microstructural changes.

The outcomes improve our understanding of the shrinkage behavior of cementitious materials, and thereby improve our ability for shrinkage prediction.

2.0. Methods and Materials

An ASTM C150 compliant Type I/II ordinary portland cement (OPC) with an estimated phase composition (on mass basis) of: 56.5% C_3S , 18% C_2S , 6.3% C_3A , 11.4% C_4AF and 0.5% Na_2O equivalent was used [18]. The inclusions used were "stiff" and "soft" inclusions. The stiff inclusions comprised: (a) an ASTM C778 compliant graded quartz sand, and, (b) nominally pure, limestone powder with median particle sizes of (d_{50} , μm): 3 μm , 15 μm , and 40 μm . The soft inclusions comprised a paraffin based microencapsulated phase change material (PCM), Micronal® DS 5008X supplied by BASF Corporation. The PCM is supplied as a powder and has a phase change temperature around 23°C, and a latent heat (ΔH_{PCM}) capacity of ≈ 110 kJ/kg respectively [19]. The density of the OPC, PCM, limestone and quartz inclusions were estimated as 3150 kg/m³, 300 kg/m³, 2700 kg/m³ and 2650 kg/m³ respectively. The particle size

distributions (PSDs; Figure 1) of the solids were measured using static light scattering (SLS) using a Beckman-Coulter analyzer. Isopropanol and ultra-sonication were used to disperse the powders to primary particles. The uncertainty in the SLS data was determined to be on the order of 6% based on measurements of six replicate samples.

Figure 1: The particle size distributions (PSDs) of the OPC, PCM, limestone and quartz used in this study as measured using static light scattering (SLS).

Cement paste mixtures were prepared using de-ionized water at fixed w/c (w/c = 0.45, w/c = 0.55, and w/c = 0.65, mass basis) as per ASTM C305 [20]. Mixtures containing inclusions were prepared in the form of mortars, using the PCM, limestone or quartz sand as inclusions, while keeping the w/c constant. The volume % of inclusions in the mixtures ranged between 0-to-50%. After mixing, the pastes were cast into prismatic molds maintained over deionized water for 24 hours after which they were de-molded, and placed in limewater (i.e., under immersion) until 56 days, after which further evaluations were carried out.

Unrestrained drying deformations were measured on prismatic cement paste and mortar samples per ASTM C157. The samples were maintained at $25 \pm 0.2^\circ\text{C}$ and $50 \pm 0.2\%$ RH [20]. Both length change and mass loss were recorded at drying times of: 1, 3, 7, 28, 56, 90, 135, 180, 225 and 270 days; after drying was initiated at an age of 56 days. The length change reported is the average of four specimens with a measuring accuracy of $\pm 10 \mu\text{m}$. Before drying was initiated, the prismatic samples were sealed on four sides (i.e., so that only two parallel, long sides remained open) with two layers of aluminum tape to ensure 1-D drying. Over the drying period between 1 and 270 days, the internal RH of the samples is expected to decrease progressively from $\approx 100\%$ (i.e., saturation) to $\approx 50\%$ with increasing drying time as equilibrium is attained.

Due to large differences between the ambient RH (50%) and the initial internal RH, the egress of moisture from the sample and the resulting shrinkage, particularly at short drying times is expected to occur at higher rates as compared to that occurring after longer drying times. This implies that the measurements of mass loss and shrinkage pertain to a mixture of

highly non-equilibrium (i.e., shorter drying times) and *near*-equilibrium (i.e., longer drying times) conditions. While it may be argued that the large dimensions (i.e., 1-inch thickness) of the samples would induce the development of moisture-/shrinkage-gradients, and potentially produce microcracks in the surface region; the “1 inch” geometry and the single-RH (50%) drying regime was adopted to acquire data using a standardized procedure (ASTM C157). Of course, ideally, while it would be desirable to dry thin samples (a few “mm” in thickness, e.g., [21, 22, 23]) in a step-wise manner; such examinations are beyond the scope of most laboratories. As such, this study places focus on describing overall trends in mass loss and shrinkage while acknowledging the potential existence of moisture and shrinkage gradients in the samples, especially at early-drying times.

After 270 days of drying, when shrinkage is near-equilibrium (see Figure 3 for the criteria by which mass and deformation “equilibrium” was established), the samples were unsealed and rehydrated in limewater for 28 days. After such resaturation, the samples were resealed and their mass loss and length change were recorded over the 2nd drying cycle, at the same time intervals as considered during the 1st drying cycle.

3.0. An Overview of Moisture Loss Driven Shrinkage and its Influencing Parameters

For drying at RH = 50%, capillary stresses are the primary driving force for shrinkage [24]. The capillary stress developed is described by the Kelvin-Laplace relation which is written as:

$$P_C = \frac{2\gamma_{LV} \cos \theta}{r_M} = \frac{\ln(RH / 100)RT}{V_M} \quad (1)$$

where, P_C is the capillary pressure (GPa) γ_{LV} is the surface tension of the pore-fluid at the liquid-vapor interface (72.8 mN/m for pure water), θ (degrees) is the contact angle between the solid-liquid interface at the pore meniscus (assumed to be 0°), r_M is the Kelvin radius (negative in the case of drying, m), RH is the relative humidity (50% RH), R is the gas constant (8.314 J/K.mole), T is the thermodynamic temperature (K) and V_M (m³/mole) is the molar volume of water. The linear shrinkage that develops due to the imposition of drying stresses can be described by Mackenzie’s formulation, as amended by Bentz et al., to consider the effects of partial liquid saturation of the pores, for a linear-elastic body as shown in Equation (2) [25, 26]:

$$\epsilon_L = \frac{SP_C}{3} \left(\frac{1}{K_B} - \frac{1}{K_S} \right) \quad (2)$$

where, ϵ_L is linear deformation (μm/m), S is degree of liquid saturation ($0 \leq S \leq 1$), K_B is the bulk modulus of the composite (GPa), and K_S is the bulk modulus of its solid-skeleton (GPa), i.e., not considering the porosity. It should be noted that during drying, the capillary pressure developed is tensile and thereby exerts a compressive (i.e., shrinkage inducing) stress on the pore walls. The relation between the bulk and skeletal modulus can be described by Equation (3) [27], where ϕ is the volumetric porosity (unitless, ratio of the volume of pores to the bulk volume).

$$K_B = K_S(1-j)^2 \quad (3)$$

Expectedly, Equations (2-3) can be combined to estimate the linear shrinkage (ϵ_L) of a cement paste, mortar or concrete as shown in Equation (4).

$$e_L = \frac{SP_c}{3K_S} \left(\frac{1}{(1-j)^2} - 1 \right) \quad (4)$$

Equation (4) can be analyzed to assess the influence of each variable on the shrinkage strain experienced by a body. While the interrelations are complex (e.g., see Sant et al. [8]), some cases can be discussed wherein the exposure RH is fixed (e.g., RH = 50%), thus resulting in fixed impositions of capillary pressure (and shrinkage stresses):

- A material with higher porosity will shrink more than a material having a lower porosity, in spite of having the same skeletal modulus and *similar* pore size distributions. This is because K_B degrades substantially with increasing porosity (1st order effect). Even if it is argued that at a given RH (e.g., between 10% and 90%), a more porous material would show a lower liquid saturation level (i.e., due to enhanced water removal per unit volume of solid), this 2nd order effect is more than compensated by the reduction in K_B . If differences in porosity between the two materials are negligible, it is possible that the effects of a slightly higher K_B and slightly higher liquid saturation for the less porous solid, and slightly lower K_B and lower saturation for the more porous solid may counterbalance each other. Herein, the shrinkage developed would be similar, due to compensation effects rather than the (dis)similarity in properties.
- The discussion above becomes more complex if of the two parameters, i.e., porosity (ϕ) and pore size distribution, one is similar while the other differs between two solids with similar skeletal moduli. For example: due to the impacts of the pore size distribution on both K_B and S , a material with (a higher volume fraction, but not exceedingly so of) larger pores would shrink less than a material with finer pores, despite both materials having similar K_S and ϕ ; due to the lower liquid saturation level in the former material.

As such, for high and low w/c cement pastes, under conditions of external drying, high w/c pastes will shrink more than lower w/c pastes, due to the larger porosity (i.e., lower K_B) of the former – which is far more influential in dictating shrinkage than the liquid saturation level. This assumes: (a) *similar* pore-size distribution but not total pore volumes for the high and low w/c pastes, (b) that K_S is insensitive to w/c; as noted by Grasley et al. [28], and, (c) early age self-desiccation effects are absent, a valid assumption herein since all pastes feature w/c > 0.42 [29].

4.0. Experimental Results and Discussion: Mass Loss and Drying Shrinkage

4.1. The Influence of w/c, Inclusion Properties and Model Predictions

Figures 2-3 show the evolutions of shrinkage as a function of the drying time for mixtures containing different volume fractions of limestone, quartz, and PCM inclusions for two different w/c. At a given age, pastes with a higher w/c shrink more than their lower w/c counterparts. This is due to the higher porosity, greater mass loss of water, and inferior mechanical properties of higher w/c pastes [1, 4]. When stiff inclusions (quartz and limestone) are added, shrinkage reduces with increasing inclusion concentration. This is expected since stiff inclusions restrain shrinkage of the cement paste (Figures 2a-b). On the other hand, when soft (PCM) inclusions are present, due to a lack of internal restraint, the extent of shrinkage experienced by both the paste and the mortars is similar, independent of inclusion concentration. This shows that dilution (reduction in the paste content), is by no means a cause of shrinkage reduction.

To consider the effects of inclusion stiffness more quantitatively, the drying shrinkage of mortars was estimated using Pickett's and Hobbs models shown in Equations (5-6) below [5, 30]:

$$\varepsilon_C = \varepsilon_P (1 - V_F)^n \quad (5a)$$

$$n = \frac{3(1 - m_C)}{1 + m_C + 2(1 - 2m_I)(E_C / E_I)} \quad (5b)$$

$$\varepsilon_C = \varepsilon_P - \frac{2K_I V_F (\varepsilon_P - \varepsilon_I)}{K_P + K_I + V_F (K_I - K_P)} \quad (6)$$

where, ε_C , ε_I and ε_P are the shrinkage ($\mu\varepsilon$) of the mortar (composite), inclusions, and plain paste, respectively, μ_I and μ_C are Poisson's ratios of the inclusions and mortar, respectively, E_I and E_C are the elastic moduli (GPa) of the inclusions and mortar, respectively, K_I and K_P are the bulk moduli (GPa) of the inclusion and plain paste, respectively, and V_F is the volume fraction of inclusion in the composite (unitless). The elastic moduli of the plain pastes were taken as: 17 GPa (w/c = 0.45), 12 GPa (w/c = 0.65) [31], and their Poisson's ratio (μ_P , unitless) fixed as 0.20. For quartz, E_I and μ_I are set as 64 GPa and 0.22 respectively, for limestone, E_I and μ_I are set as 75 GPa and 0.25 respectively, and for PCM inclusions, E_I and μ_I are set as 55.7 MPa and 0.49 respectively [31]. The composite elastic modulus (E_C) was calculated using Equation 8(a) while the Poisson's ratio of the composite (μ_C) represents the Reuss-Voigt-Hill average of the Poisson's ratio of the solids [32, 33].

Figure 2: The shrinkage evolution as a function of drying time for $w/c = 0.45$ mixtures with varying dosages of: (a) quartz (Q), (b) limestone (LS) and (c) PCM inclusions. The plain paste (neat cement paste) is abbreviated as “PP”. The solid and dashed lines represent the predictions of the *composite models* of Hobbs and Pickett, respectively. Here and in all subsequent figures, 1 microstrain = $10^{-6} \text{ m/m}_{\text{ref}}$, where m_{ref} is the original length of the sample in meters.

In general, Pickett’s and Hobbs models provide conservative estimates of mortar shrinkage as seen in Figures (2-3). While Hobbs model can be applied to mortars containing both stiff and soft inclusions, Pickett’s model is applicable only to composites containing stiff inclusions since this model neglects the inclusion’s compressibility, which in the case of soft inclusions (i.e., PCM’s) is substantial. For systems containing soft inclusions, good agreement between the measured and predicted shrinkage is observed so long as the shrinkage of the paste and inclusions is set to be equivalent. This implies that the high compressibility of the PCM inclusions, which are unable to resist the shrinkage of the paste; results in mortar shrinkage similar to the shrinkage of the paste. For a given inclusion volume, the predictions of the composite models are similar independent of inclusion size, which spans between $3 \mu\text{m}$ -to- $350 \mu\text{m}$ (d_{50} , Figure 1). This suggests that for the sizes of inclusions used, ITZ effects are negligible and shrinkage evolution is controlled by the paste and inclusion properties, and volume fractions. At equal dosages, quartz and limestone mortars experience dissimilar shrinkage, with the limestone mixtures shrinking less. While this is expected due to the higher stiffness of limestone inclusions, this is also related to differences in moisture transport properties of both inclusions (addressed later). Surprisingly, it is noted that while higher w/c mixtures experience higher shrinkage (Figure 3), this is not as much as may be expected given their substantially reduced bulk modulus (K_B) vis-à-vis lower w/c mixtures. This is because increasing the w/c while holding RH constant causes a reduction in liquid saturation which is far more significant for a higher than a lower w/c mixture [8]. This counterbalances the reduction in the bulk modulus, as a result of which increasing the w/c does not result in major enhancements in shrinkage [1].

Figure 3: A comparison of shrinkage evolutions for cement pastes for $w/c = 0.45$ and $w/c = 0.65$ with and without 10 volume % limestone. By 270 days, the rate of shrinkage is $\approx 0.30 \mu\epsilon/\text{day}$ across all mixtures which represents near-equilibrium shrinkage (N.B.: At this rate, the shrinkage developed in one month is similar to the measurement accuracy of the comparator). The lines represent best-fits to the data.

Figure 4 shows mass loss as a function of drying time across all inclusion types, dosages, and w/c . When normalized by the mass fraction of cement paste in the mixture, the mass loss curves overlap for all mixtures constituted at $w/c = 0.45$. This suggests that at low w/c , the paste dictates the drying response of the composite regardless of the type and volume of inclusions. Contrastingly, for $w/c = 0.65$ mixtures, while the normalized moisture loss curves for the quartz inclusions and the plain paste overlap, the drying curves of the mixtures containing limestone inclusions remain distinct. Specifically, at similar drying times, including those when the mixtures are expected to reach *near*-equilibrium conditions, limestone mixtures consistently show higher mass loss compared to quartz and plain paste mixtures. This suggests that when the inclusions are more permeable than the cement paste (i.e., when $k_L > k_p$, where k is the permeability and P , and L denote paste and limestone, respectively), they amplify moisture loss by providing lower resistance escape routes for moisture (e.g., analogous to short-circuit diffusion process [³⁴, ³⁵, ³⁶]). It is hypothesized that the water absorbed within the pores of the permeable inclusions (e.g., limestone) during curing, i.e., over and above mixing water, is released at later stages of drying, thus resulting in higher extents of moisture loss (see Figure 4b) at near-equilibrium conditions. At low w/c ($w/c = 0.45$), the permeability of the inclusion is inconsequential in terms of the drying (or shrinkage) response. This is because the paste component in such mixtures has a substantially lower permeability as compared to that of the inclusions, and, therefore, it dictates the rate and extent of moisture transport. It should be noted that the behavior of the $w/c = 0.65$ mixtures is not an inclusion size-effect, because if so, it would also be observed in the $w/c = 0.45$ mixtures.

Figure 4: Moisture loss as a function of drying time for mixtures of: (a) $w/c = 0.45$ and (b) $w/c = 0.65$ across all inclusion types and dosages. The mass loss is normalized by the paste content in the composite, since this is the paste that “dries” actively. By 270 days, the rate of mass loss is ≈ 0.002 %/day across all mixtures indicating *near-equilibrium* conditions. The dashed lines show best-fits to the data.

4.2. Shrinkage-Mass Loss Correlation

To correlate shrinkage to mass loss, measured shrinkage was plotted against the measured mass loss across all w/c . To account for differences in paste content (i.e., dilution), the measured shrinkage is normalized by the volume fraction of paste while the mass loss is normalized by the mass fraction of cement paste in the composite. From this data (Figure 6a, 6c), linear correlations are noted, although, with, steeper slopes in the case of softer inclusions. The slope is postulated to be a function of the extent of restraint provided by the inclusions, as a result of which softer inclusions or a lower inclusion dosage result in steeper slopes. Past studies [37, 38] have noted that the relationship between shrinkage and mass loss of a given cementitious system also depends on the maturity of the sample and the drying conditions (e.g., rate of drying), which in turn may influence long-term delayed (creep) deformations. However, based on the samples’ maturity (i.e., age > 56 days) and the use of identical drying conditions these factors are not expected to influence the shrinkage-mass loss trends.

To rationalize the data, the shrinkage of all mixtures is scaled using a shrinkage multiplier, M (unitless) [8] to overlay the curves for a given w/c and a given drying cycle. Following such rescaling, it is noted that while $w/c = 0.45$ systems show a single constant slope shrinkage-mass loss response, the $w/c = 0.65$ mixtures show a bi-linearity in their shrinkage-mass loss behavior (see Figure 6d). The bi-linearity suggests a switch in the size of pores losing moisture. As such, when drying initiates, water is lost dominantly from the larger capillary pores, which produce smaller capillary stresses and volume changes. However, as the large pores are depleted, and the smaller (nanoscale) pores evacuate, shrinkage stresses increase resulting in an increased rate of shrinkage with continued drying.

Figure 6: The measured drying shrinkage normalized by the volume fraction of cement paste as a function of the mass loss of the paste normalized by mass fraction of paste during 1st drying for: (a and b) $w/c = 0.45$ and (c and d) $w/c = 0.65$. In (b and d), the shrinkage is scaled using a shrinkage multiplier, M (unitless), that is discussed in the text.

While the trends shown in Figure 6 indicate the 1st drying, while 2nd drying, i.e., following rewetting, shows similar behavior, there is one difference that should be pointed out. Up on 2nd drying, mixtures of both w/c show a bilinear shrinkage-mass loss relation. It is postulated that the emergence of, or extent of bi-linearity, is more exaggerated upon 2nd drying due to the loss of water with little accompanying shrinkage from fissures and microcracks that may have formed during the 1st drying [11, 12, 13, 41, 39]. Figure 7 traces evolutions of the shrinkage multiplier across w/c and drying cycles. It is noted that the shrinkage multiplier scales linearly as a function of the inclusion dosage. In general, $M \geq 1$ for stiff inclusions, and $M \leq 1$ for soft inclusions (see Figure 8). As seen in Figure 8(b) for mixtures containing quartz inclusions, $M \approx 1$ up on 2nd drying. This indicates that no (re)scaling is needed for the normalized shrinkage-mass loss curves to overlap on 2nd drying for the quartz mixtures. It is also noted that M takes smaller values on 2nd drying, as compared to 1st drying. This suggests that for equal mass loss, less shrinkage develops during the second drying; likely due to the increased compliance (i.e., damage induced) of the sample following 1st drying.

The shrinkage multiplier as a function of inclusion dosage is described by the equation, $M = AV_F + 1$, where A is the slope of the shrinkage multiplier-inclusion volume curves ($\%^{-1}$), and

V_F is the volume % of inclusions. Since M is assumed to dominantly be a function of the restraint provided by the inclusions to the paste's shrinkage, it suggests that A is correlated with the elastic stiffness contrast of the inclusions-to-the-paste matrix, i.e., E_I/E_P , where E_I and E_P are inclusion and paste stiffnesses respectively (GPa) (e.g., see Figure 7d). While arguably, this description only considers the pristine modulus of the paste, i.e., before the 1st drying cycle initiates (i.e., which reduces following drying), the data explains why the quality of fit upon 2nd drying is poorer, than for the 1st drying cycle. Importantly, the trend shown in Figure 7(d) allows estimations of the shrinkage of a mortar for any combination of inclusion volume and stiffness across drying cycles given data acquired only on the (equivalent w/c) plain paste. It should be noted that given the *elastic* nature of shrinkage that manifests following the 1st drying cycle, the values of “ A ” thus determined can be applied to all subsequent drying cycles [40].

Figure 7: The shrinkage multiplier, M , as a function of the inclusion dosage in the composite for: (a) $w/c = 0.45$, 1st drying, (b) $w/c = 0.65$, 1st drying, (c) $w/c = 0.45$, 2nd drying and (d) The slope A as a function of the stiffness contrast of the inclusions to the matrix (E_I/E_P , unitless).

4.3. Shrinkage Irreversibility

After 270 days of drying, the samples were rewet in lime-saturated water for 28 days, after which shrinkage and mass loss measurements were reinitiated. After 28 days of rewetting, while all the samples regained mass to a level within 0.03% of their initial mass, expectedly, a full recovery in strain was not achieved. Figure 8 shows representative shrinkage curves as a function of time across 1st and 2nd drying for $w/c = 0.45$. In general, shrinkage experienced during the 2nd drying cycle is reduced, and achieves a near constant value faster than during the 1st drying cycle. Qualitatively similar observations are made in the case of $w/c = 0.65$ mixtures (not shown).

The extent of shrinkage irreversibility (S_{IR} , %) can be quantified in terms of the percentage of ultimate shrinkage experienced during 1st drying that cannot be recovered following rewetting such that: $S_{IR} = 100(\epsilon_{2initial}/\epsilon_{1final})$, where ϵ_{1final} is the drying strain at the end of the 1st drying cycle (after 270 days) and $\epsilon_{2initial}$ is the strain measured after rewetting for 28 days, respectively. The shrinkage irreversibility can be analyzed by considering factors including: (i) reorganization of the C-S-H following drying, and, (ii) damage developed following drying [5, 41]. Since (i) is a response intrinsic to the C-S-H, it is expected to be similar across all pastes independent of w/c (i.e., for $RH \geq 25\%$ [41]). On the other hand, (ii) is expected to be more substantial for higher w/c pastes due to the tendency of these mixtures to lose more water and

their lower stiffness; as compared to low w/c mixtures. Of course, this assumes a similar exposure RH (drying stress) across all systems.

Figure 8: Representative shrinkage curves across 1st and 2nd drying cycles for w/c = 0.45 for all inclusion types and dosages. The 2nd drying cycle was initiated following a rewetting period of 28 days between the two drying cycles.

Due to the more substantial shrinkage of high w/c pastes, the addition of stiff inclusions is expected to result in more restraint to the shrinkage of the paste in these mixtures (for a fixed inclusion dosage), as compared to lower w/c mixtures. As a result, more damage and shrinkage irreversibility is expected with increasing w/c [41]. The restraint offered by stiff inclusions to paste shrinkage can be written as shown in Equation 7(a-c) using a coefficient of elastic restraint (C_{RE} , unitless) that is a function of a geometry factor (C_G , unitless) and the mechanical properties of the paste and inclusions [42]. The geometry factor C_G assumes that the paste and inclusions are arranged in a hexagonal array, with the paste enclosing the inclusions (Figure 9a).

$$V_I(\%) = 100 \cdot \left(\frac{R_{OI}^2}{R_{OP}^2} \right) \quad (7a)$$

$$CRE = \frac{C_G}{\left(C_G + m_p + (1 - m_l)(E_p / E_l) \right)} \quad (7b)$$

$$C_G = \frac{\left(\frac{R_{OP}^2}{R_{OI}^2} \right) + 1}{\left(\frac{R_{OP}^2}{R_{OI}^2} \right) - 1} \quad (7c)$$

where, R_{OI} and R_{OP} are the outer radii of the inclusions and the paste (m) respectively (Figure 9a). As seen in Figure 9(b), the coefficient of elastic restraint is correlated with the ratio of the composite's elastic modulus (i.e., of paste + inclusions) to the elastic modulus of the plain

cement paste. It should be noted that the composite modulus is calculated using Hobbs model for an inclusion that shows negligible (Equation 8a [26]) or substantial (Equation 8b [26]) mismatch with respect to the Poisson's ratio of the inclusion [31, 32].

$$E_C = E_p \left[1 + \frac{2V_I(E_I - E_p)}{(E_I + E_p) - V_I(E_I - E_p)} \right] \quad (8a)$$

$$E_C = E_p \left[\frac{(1 - 2\mu_c)(1 - V_I)}{(1 - 2\mu_p)(1 + V_I)} \right] \quad (8b)$$

where, μ_c , the Poisson's ratio of the composite is determined by averaging the Reuss-Voigt values of the Poisson's ratio of the solid components.

Figure 9: (a) The paste-to-inclusion radius ratio as a function of the inclusion volume in the composite, (b) The elastic modulus (“stiffness”) ratio of the composite-to-the paste matrix as a function of the coefficient of elastic restraint, and, (c) The percentage of irreversible shrinkage as a function of the C_{RE} . The bold horizontal line indicates the percentage of shrinkage that is irreversible for: (i) plain pastes, for $w/c = 0.45, 0.55$ and 0.65 and (ii) for inclusions wherein $E_I \ll E_p$.

When the irreversible shrinkage is plot as a function of the coefficient of elastic restraint, two trends emerge. For $w/c = 0.45$, the extent of irreversible shrinkage decreases slightly or remains fixed around 35% with an increase in the C_{RE} (Figure 9c). On the other hand, for $w/c = 0.65$, the extent of irreversible shrinkage increases with the C_{RE} . This indicates that for the same level of restraint, a weak, high w/c paste experiences more irreversible shrinkage than its lower w/c counterparts. This is postulated to be on account of microstructural changes that occur in the pastes following drying. Specifically, it is hypothesized that low w/c pastes develop less damage, due to their lower shrinkage during the 1st drying cycle. On the other hand, the higher shrinkage of higher w/c pastes on 1st drying results in more extensive microstructural changes. Such damage developed, by reducing the extent of capillary stresses that are developed up on 2nd drying, mitigates shrinkage [43]. This also explains why when $E_I \ll E_p$, the extent of shrinkage irreversibility is similar to the plain paste because the inclusions are unable to restrain the paste's shrinkage. It is important to note that the extent of irreversible shrinkage of the plain

pastes remains unchanged as a function of w/c. This is because in plain paste the shrinkage is controlled by the C-S-H, which for similar impositions of drying stress experiences similar alterations (e.g., reorganizations) in its nanostructure and volume (per unit mass) following 1st drying [41].

5.0. Moisture Transport Behavior of Cement Paste and Mortar Formulations during Drying

The drying of a cementitious composite and the resulting shrinkage is a function of the rate and extent of loss of water from the material. Thus, it is valuable to establish the transport properties, i.e., the moisture diffusivity and permeability, of cementitious materials as a function of w/c, inclusion dosage etc. [13]. As the material dries from the saturated state, the egress of moisture occurs predominantly via capillary transport, as described by the permeability. However, at lower degrees of saturation, moisture removal occurs not only via capillary transport, but also diffusion; as described by the diffusivity. The drying of cementing materials is often approximated by Fick's 2nd law of diffusion which describes the diffusion of water under an evolving driving force (i.e., water activity gradients). For the case of 1D-diffusion, Fick's 2nd law can be expressed analytically using a Taylor series expansion of the error function as written by Crank [44]:

$$\frac{M_t}{M_\infty} = 1 - \sum_{n=0}^{\infty} \frac{8}{(2n+1)^2 \rho^2} \exp\left(-\frac{D(2n+1)^2 \rho^2 t}{4l^2}\right) \quad (9)$$

where, M_t is the mass loss at a given time (g), M_∞ is the mass loss at infinite time (g), D is the total diffusion coefficient (of water in the liquid and vapor states, m^2/s), t is time (s), and l is half the width of the sample (m). Here, ' l ' represents the thickness of the sample between the centerline and its exposed faces implying that diffusion is symmetric. To estimate M_∞ , the experimental mass loss data was fit using a Pearson function [45] and extrapolated to a large time, in this case 10000 days. Once M_∞ was obtained, given knowledge of $M(t)$ and l , Equation (9) was solved using MATLAB to determine the diffusion coefficient as a function of drying time [40, 44].

Figure 9 shows the evolution of the diffusion coefficient with drying time for both w/c and across 1st and 2nd drying cycles. For both drying cycles, the diffusion coefficient decreases by an order of magnitude over the duration of drying. The decrease in the diffusion coefficient is on account of the progressive removal of water from larger to the smaller pores, the latter of which are more resistant to the removal of water. Expectedly, a higher w/c features a higher diffusion coefficient (Figure 9c), due to its larger overall porosity and coarser pores. Drying increases the diffusion coefficient, i.e., from the 1st to 2nd drying cycle, by a factor of two; likely due to the formation of fissures up on drying. Importantly, the diffusion coefficient is on the same order of magnitude for all mixtures in spite of differences in w/c, and inclusion dosages; suggesting a response that is controlled by the C-S-H component of the cement pastes [46, 47].

Figure 9: The calculated total moisture diffusion coefficients during 1st and 2nd drying for: (a) $w/c = 0.45$ plain paste, and, (b) $w/c = 0.65$ plain paste. The bars indicate the maximum and minimum diffusion coefficient across all mixtures, inclusion types and dosages for a given w/c . (c) The total moisture diffusion coefficient during 1st and 2nd drying for the plain pastes across all w/c after 270 days of drying. The dashed lines represent exponential fits.

Figure 10 shows the evolution of the diffusion coefficient with liquid water saturation (S) across w/c and drying cycles. The values of S were determined via knowledge of: (a) the time-dependent mass of the (initially) water saturated mixtures, and, (b) the evaporable water content of the pastes established by oven drying for 24 hours at $110^\circ C$. The diffusion coefficients decrease with saturation [48]. This is expected because the egress of moisture is slowed after the capillary pores are emptied, and water removal occurs dominantly from the smaller gel pores. Also, the reduction in the diffusion coefficients is also linked to a decrease in the driving force for drying; the RH gradient, which reduces with time and saturation.

For both w/c , the diffusion coefficients during 2nd drying are somewhat higher compared to those determined for 1st drying; a reflection of damage that develops during the 1st drying. However, as saturation decreases, the 2nd drying diffusion coefficients decline sharply and are similar to those seen on 1st drying. This is due to water removal from the gel porosity, which remains essentially unaltered from the 1st to 2nd drying – over this RH range – as previously shown by Jennings et al. [41]. It is however expected that dissimilarities in moisture diffusion coefficients across 1st and 2nd drying cycles would magnify if the samples were subjected to yet more severe drying (i.e., $RH < 30\%$), due to significant changes in the C-S-H structure [41].

Figure 10: The total moisture diffusion coefficients as a function of liquid water saturation during 1st and 2nd drying for the: (a) $w/c = 0.45$, and, (b) $w/c = 0.65$ plain pastes.

The total diffusion coefficient (D , m^2/s) calculated from Fick's 2nd law (Equation 9) can be written as the sum of the liquid and the vapor diffusion coefficients as noted in Equation (10) [13]:

$$D = D_l(S) + D_v(S) \quad (10a)$$

$$D_v(S) = -\frac{dP_c(S)}{dS} \left(\frac{M}{\rho_l RT} \right)^2 D_{ve}(S) \frac{P_{vs}}{\phi} \exp\left(-\frac{M}{\rho_l RT} P_c(S) \right) \quad (10b)$$

$$D_{ve}(S) = D_{v0} \cdot [\phi^h \cdot (1-S)^j] \quad (10c)$$

$$P_c(S) = a(S^{-b} - 1)^{(1-\frac{1}{b})} \quad (10d)$$

where, D_l is the liquid water diffusion coefficient (m^2/s), D_v is the water vapor diffusion coefficient (m^2/s), S is the liquid saturation level ($0 \leq S \leq 1$, unitless; Equation 11a), M is the molar mass of water (18.02 g/mole), ρ_l is the density of water (kg/m^3), R is the gas constant (8.314 J/K.mole), ϕ is the porosity (unitless, as obtained from MIP [49]), p_{vs} is the saturated vapor pressure of water vapor (3.170 kPa at 25°C), D_{ve} is the effective vapor diffusion coefficient (m^2/s), D_{v0} is the free water vapor diffusion coefficient ($2.47 \times 10^{-5} m^2/s$), h and j are fitting parameters, where $h = 6.0$ and $j = 3.3$ respectively, and $p_c(S)$ is the liquid saturation dependent capillary pressure curve that is identified by fitting Van-Genuchten's equation to measured water sorption isotherms for pastes of different w/c , where a and b are fitting parameters (see Figure 11a and 11b) [50]. The diffusion coefficients noted above are a function of the liquid saturation level as the presence, or lack of water influences transport [49]. Equations 10(a-d) permit quantification of D_l , which can be used to estimate the intrinsic liquid water permeability of the composite using Equation (11):

$$K_l(S) = \frac{-D_l(S) \cdot \phi \cdot \eta}{\left(\frac{dP_c(S)}{dS} \cdot K_{rl}(S)\right)} \quad (11a)$$

$$K_{rl}(S) = \sqrt{S} [1 - (1 - S^b)^{1/b}]^2 \quad (11b)$$

where, η is the viscosity of water (0.89 mPa·s), and $k_{rl}(S)$ is liquid saturation-dependent relative permeability of the material (unitless)^[49].

Figure 11(c) shows the intrinsic permeability (K_l) of the cement pastes as a function of w/c . The intrinsic permeability scales with w/c . This is expected because of the enhancement in the overall porosity and pore-connectivity with increasing w/c , which facilitates moisture transport. It should be noted that, while the diffusion coefficient (D) changes slightly (Figure 9c), from the 1st to the 2nd drying cycle, the intrinsic permeability increases around one order of magnitude from the 1st to the 2nd drying cycle. This is on account of the intrinsic permeability being more sensitive to the presence of fissures (i.e., formed as a result of drying during the 1st drying cycle), as opposed to the diffusivity which is dictated by the movement of molecular water through the C-S-H. It is noted that the intrinsic permeability ($K_l(S)$, for $S = 1$) estimated from the mass loss curves is in very good agreement with the value determined from the Katz-Thompson equation ^[49] suggesting that so long as the gradient of the capillary pressure curve ($dP_c(S)/dS$) is known, mass loss data offers a quick means to estimate the transport properties of cementing materials.

Figure 11: (a) The capillary pressure curves established using the 1st desorption isotherm for different w/c , and its fitting using van Genuchten's equation (dashed lines). (b) The van Genuchten fits of capillary pressure curves for 1st and 2nd drying cycles for cement pastes across a range of w/c . The solid green line shows the capillary pressure developed at RH = 50% (95.4 MPa)^[49]. (c) The intrinsic permeability as a function of w/c across 1st and 2nd drying cycles. The intrinsic permeability quantified using the Katz-Thompson relation is shown for comparison^[49]. The dashed lines show exponential fits to the measured data.

6.0. Summary and Conclusions

This paper critically reexamines the influence of the inclusion size, volume and stiffness on the drying and shrinkage behavior of cementitious mixtures. It is seen that in low w/c pastes, the shrinkage of mortars is dominated by the shrinkage of the paste component, and, thereby, only dependent on inclusion dosage and stiffness. However, in pastes prepared at high(er) w/c, the permeability of inclusions also influences the shrinkage response. For example, if inclusions are more permeable than the paste, they facilitate moisture loss through their lower resistance pore network. Furthermore, it is seen that the ultimate shrinkage of the paste measured after the primary (1st) and secondary (2nd) drying cycles are dissimilar, wherein the extent of shrinkage irreversibility depends on the inclusion stiffness, as well as the paste's w/c. By offering a higher restraint to shrinkage, stiff inclusions produce a higher level of irreversible shrinkage in higher w/c pastes. This appears to be directly linked to the stiffness contrast between the cement paste and the inclusions. Significantly, the stiffness contrast is also well-correlated with the rescaling shrinkage multiplier that permits construction of unified shrinkage-mass loss curves across pastes prepared at different w/c, and using different types and volumes of inclusions.

Analyses of time-dependent mass loss (drying) curves permits determination of the key moisture transport coefficients (i.e., intrinsic permeability, and moisture diffusivity) as a function of the drying time and w/c. It is noted that both of the transport coefficients are dictated by the paste component, and increase with increasing w/c of the paste. Both permeability and diffusivity are enhanced after the first drying cycle, due to an increase in the porosity (or microcracking) in the composite. Taken together, the outcomes improve our insight into the drying and shrinkage behavior of cementitious materials, and, approaches/models for their estimation.

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