Moisture Diffusion in Unsaturated Self-Desiccating Concrete with Humidity-Dependent Permeability and Nonlinear Sorption Isotherm

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Abstract: A nonlinear diffusion model for the drying of concrete, previously developed at Northwestern University and embedded in some design codes, was improved and calibrated on the basis of recent more extensive experimental data from the literature as well as theoretical considerations. The improvements include a new equation for the dependence of the self-desiccation rate on pore humidity and hydration degree; an updated equation for the decrease of moisture permeability at decreasing pore humidity; new equations to predict the permeability and diffusivity parameters from the water-cement and aggregate-cement ratios, hydration degree, the type of concrete; and new equations to capture the nonlinearity of the sorption isotherm as a function of pore humidity and water-cement ratio. Furthermore, the recent idea that the pore humidity drop is the driving force, rather than a side effect, of the autogenous shrinkage is verified. DOI: 10.1061/(ASCE)EM.1943-7889.0001591. © 2019 American Society of Civil Engineers.

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Introduction

By now it is generally accepted that correct calculation of the spatial distribution and time evolution of the pore humidity in concrete structures is necessary for realistic prediction of creep, shrinkage, and thermal dilation, along with their effects on deflections, crack formation, and various degradation processes (Bažant and Jirásek 2017; Bažant and Dommez 2016; Rahimi-Aghdam et al. 2019). The relative humidity in the pores has a major effect on the moisture permeability, the rate of hydration (or aging), and the rate of strength-degrading chemical reactions such as the alkali-silica reaction (ASR). It plays a large role in the assessments of durability, fire resistance, and radiation shielding. It matters for the age-old question of uplift in dams, and it must be considered in formulating the stress-strain law for concrete.

Studies of nuclear reactor structures in the 1960s led to the discovery (Bažant and Najjar 1971, 1972) that the diffusion equation for concrete is highly nonlinear because the permeability and the diffusivity decrease by more than an order of magnitude as the relative humidity, \( h \), in the pores decreases. This means that the linear diffusion theory is unable to fit the measurements of pore relative humidity, which is, for example, documented by the poor optimum fits of the experimental data in Fig. 1.

The Bažant-Najjar (BN) nonlinear diffusion model worked quite well for concretes half a century ago, and has been embedded in various recommendations and design codes, e.g., in the Model Code of fib (2012). Recently, though, it became clear that a generalization and improvement of the BN model is necessary to meet several broader objectives:

1. For modern concretes, the foremost objective is to take into account the self-desiccation, which drives the autogenous shrinkage. The self-desiccation was negligible in old concretes but became significant in modern high-strength and high-performance concretes. The causes are (1) a low water-cement ratio (w/c), and (2) admixtures such as silica fume (SF) and blast furnace slag (Baroghel-Bouny et al. 2006; Jiang et al. 2006). Baroghel-Bouny et al. (2006) showed that, in sealed specimens of high-strength concrete with a high content of silica fume, the self-desiccation can decrease the relative humidity in the pores to as low as 65%. Such a humidity decrease may be beneficial because most of the deteriorative reactions in concrete stop or drastically slow when the relative humidity in pores drops below 80%. For instance, the destructive alkali-silica reaction virtually stops at \( h < 75\% \) (Bažant and Rahimi-Aghdam 2016; Rahimi-Aghdam et al. 2017a). During the last 2 decades, several self-desiccation models were proposed (Benzt 1997; van Breugel 1997; Hubler et al. 2015b), but they fit long-term data poorly, and were complicated by a number of empirical parameters requiring experimental calibration for different concretes, or were computationally too expensive for use in finite-element analysis. In addition, the existing models were not conceived as part of a general model for water transport in concrete. Such a model must combine self-desiccation with a simultaneous exposure to drying environment, and this is the main goal of this study.

2. The second objective is to use the existing database, significantly extended since 1972, to recalibrate the decrease of permeability with decreasing \( h \). Better fits of test data can be obtained when the permeability decrease with \( h \) is more gradual than in the original BN model, and continues even for \( h < 50\% \).

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Fig. 1. Best possible fits of midcylinder evolutions and transverse distributions of relative humidity in pores, achievable with linear diffusion theory (characterized by constant permeability and diffusivity). \( y = \) distance from drying surface; and \( t' = \) drying exposure time. [Humidity data measured by (a) Kim and Lee 1999; (b) Abrams and Monfore 1965; (c) Abrams and Orals 1965; (d) Hanson 1968.]

3. The third objective is to improve the desorption isotherm. Its slope in the BN model was considered to be constant for \( h \) greater than about 30%, but recent tests (Nilsson 2002; Nielsen 1991; Xi et al. 1994) showed that this is not true for high w/c. Models to capture it exist (Xi et al. 1994; Daian 1988) but appear to be unnecessarily complicated, inaccurate, and computationally demanding. It is sufficiently accurate and simpler to consider the isotherm to consist of two straight-line segments, the upper one being much steeper than the lower one and having a length depending on the type of concrete, particularly on the w/c. The steepness and length of the initial straight segment of the isotherm near \( h = 1 \) are particularly important for calculating the self-desiccation.

4. The fourth objective is to propose a simple approximate formula for predicting the four parameters of the equation giving the moisture permeability as a function of \( h \). This is needed to enable realistic calculation of the pore humidity field in a structure, which must be known for predicting autogenous shrinkage, drying shrinkage, creep, rate of aging, and various deteriorative reactions such as the ASR. Furthermore, this is needed to extract more useful information from the existing creep and shrinkage data, for example, from the worldwide database of about 4,000 creep and shrinkage tests assembled at Northwestern University (Bažant and Li 2008; Hubler et al. 2015a).

In the literature, the autogenous shrinkage and the drying shrinkage due to environmental exposure have generally been regarded as separate additive phenomena, the former caused directly by a volume change in the chemical reaction. But were this true, it would be impossible to explain, e.g., that (1) the lowest rather than the highest w/c leads to the greatest autogenous shrinkage, or that (2) under water immersion, concrete swells. From such arguments it was concluded (Bažant et al. 2015) that

1. Contrary to prevailing opinion, the hydration reaction per se is always expansive, beginning as soon as the solid nanoskeleton of C-S-H is formed (i.e., after the first day of hydration). Swelling can be due to several hydration reaction–related phenomena such as ettringite formation, portlandite formation, crystallization pressure, C-S-H shells pushing each other apart, disjoining pressure, and nanoscale creep.

2. Like the drying shrinkage (caused by external drying), the autogenous shrinkage also is caused by a decrease of pore humidity (or of the corresponding chemical potential of water) (Hua et al. 1995; Lura et al. 2003; Gawin et al. 2006; Grasley and Leung 2011; Luan and Ishida 2013). Therefore, both must follow the same law.

When external drying occurs, the self-desiccation cannot be modeled independently. Rather, it must be considered as coupled. For clarification, consider the right half of a concrete slab of width 2 L, exposed to drying at environmental humidity \( h_{\text{env}} \) that is below the maximum possible humidity decrease due to self-desiccation. All four sides of the slab are assumed to be sealed, so that the drying would be unidirectional.

Before exposure to drying, the relative humidity in the pores decreases uniformly due to self-desiccation [Figs. 2(a and e)]. In this study, the initial humidity value minus the humidity decrease due to self-desiccation is called the self-desiccation humidity. After drying exposure, the humidity profile of drying propagates into the slab, whereas the self-desiccation humidity decreases only in that portion of cross section where its relative humidity has not yet reached the relative humidity at which hydration stops, \( h_s \) [Figs. 2(b, c, e, and f)]. Eventually, the drying front reaches the slab center [Figs. 2(c, d, and h)]. After that, the humidity due to external drying separates from the self-desiccation humidity and decreases slower than the drying humidity profile, which causes a growing separation of the profiles of self-desiccation and of external drying [Figs. 2(d and h)].

The area between the aforementioned two profiles, multiplied by the inverse isotherm slope (and weighted for axisymmetry), represents the amount of water lost to the environment, and the area above the upper profile, multiplied and weighted similarly, represents the amount of water consumed by the hydration reaction. When \( h_{\text{env}} \) is not smaller than the minimum possible humidity
reachable by self-desiccation, $h_{st}$, the stages in Figs. 2(c, d, and h) are never reached.

**Moisture Transport**

Thermodynamic equilibrium of moisture in concrete is achieved when the chemical potential of water, $\mu$ (i.e., the Gibbs free energy per unit mass), is the same in all phases of water and throughout the structure volume. Therefore, in principle, the mass flux of water, $j_w$, should be proportional to grad $\mu$. Such a diffusion model, however, seems inconvenient and apparently has never been developed.

Until the 1960s, one approach was to consider the flux of moisture to obey Fick’s law and to be proportional to grad $w_e$, where $w_e$ is the evaporable water mass per unit volume of concrete. Bažant and Najjar (1971) proposed and Bažant and Najjar (1972) elaborated a model in which the pore relative humidity, $h$, is considered as the primary unknown, whose gradient drives the diffusion (and is proportional to both grad $\mu$ and grad $p_v$, times a factor dependent on $h$, where $p_v$ is the vapor pressure).

The use of grad $h$ has three advantages

1. It is simpler, especially when the self-desiccation is mild, for dealing with the effect of hydration, which acts as a sink withdrawing a great deal of evaporable water from the pores;
2. It is more direct for formulating the environmental boundary condition; and
3. It can be verified and calibrated more directly, because of the recent development of good pore humidity gauges (Nguyen et al. 2018).

The Bažant-Najjar model, which has been embodied in the Model Code 2010 (Fédération internationale du béton 2012), directly postulates that, under uniform temperature, the total moisture flux is

$$ j_w = -c_p(h)\nabla h $$

where $c_p$ is moisture permeability (kg/m · s); and $j_w$ is mass flux of water (kg/m$^2$ · s).

To ensure water mass conservation, the rate of change of moisture content, $\dot{w}_i$, must balance the influx of water mass, that is

$$ \dot{w}_i = -\nabla \cdot j_w + \dot{w}_s $$

where $\dot{w}_i$ = water mass that has been withdrawn from the pores and combined chemically by the hydration process; and $\dot{w}_s$ = distributed sink and is the cause of self-desiccation.

Under local isothermal equilibrium conditions, the pore humidity rate is a function of the rate of specific evaporable water content, $w_e$ (kg/m$^3$ concrete). This function differs between drying and wetting conditions, due to the capillary and hindered adsorption hysteresis. In the literature, the functions describing the dependence of $h$ on $w_e$ for drying and wetting are called the desorption and resorption isotherms. Only the desorption isotherm is considered here, and is formulated as

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Fig. 2. Schematic evolution of profiles of relative humidity (RH) caused by self-desiccation and by drying in the right half of a thin specimen: (a) uniform profile prior to drying exposure; (b) soon after that; (c) later; and (d) very long after drying exposure; and by drying in the right half of a thick specimen: (e) uniform profile prior to drying exposure; (f) soon after that; (g) later; and (h) very long after drying exposure.
where \( k(\alpha, h) = \text{reciprocal moisture capacity (m}^3/\text{kg}) \), i.e., the inverse slope of the isotherm, whose evolution depends on the pore relative humidity and hydration degree, \( \alpha \) (characterizing the age of concrete); and \( k \) varies with \( h_c \), more so for concretes with high \( w/c \) (see section “Sorption Isotherm”).

Incorporating Eqs. (1), (2), and (3) gives the governing moisture diffusion equation for concrete

\[
\frac{\partial h}{\partial t} = k(\alpha, h) \nabla \cdot (c_p \nabla h) + \frac{\partial h_c}{\partial t}
\]

where the last term on the right-hand side is a distributed sink representing the self-desiccation. It can be calculated using Rahimi-Aghdam et al.’s (2017b) hydration model, and it can continue for many years. As in the Bažant-Najjar (1972) model, the dependence of moisture permeability \( c_p \) on \( h_c \) may be expressed as follows (Fig. 3(a)):

\[
c_p(h, \alpha) = c_1 \left( \beta + \frac{1 - \beta}{1 + \frac{(h - h_c)}{r}} \right)
\]

although the values of parameters \( c_1, \beta, h_c, \) and \( r \) are somewhat different, because they are obtained by the fitting of more-extensive experimental data.

The data needed to calibrate Eq. (5) should ideally include the time evolution of relative humidity in the pores and of the humidity profiles throughout the cross section at subsequent times, for various specimen sizes, various environmental humidities, and various ages at exposure to drying atmosphere. Such comprehensive data, unfortunately, do not usually exist for one concrete, and the parameters change significantly from one concrete to another. To be able to extract information from data for different concretes, the equations for the dependence of unknown material parameters in Eq. (5) had to be judiciously assumed and then empirically calibrated.

The basic parameter is \( c_1 \), i.e., the permeability at saturation (\( h = 1 \)). It is mainly a function of the pore size distribution. Two factors that affect the distribution most are the water-cement ratio, \( w/c \), and the hydration degree, \( \alpha \). The fitting test data led to the following empirical relation:

\[
c_1 = 60[1 + 12(w/c - 0.17)^2] \alpha/\alpha_u
\]

The second important parameter is the transitional humidity, \( h_c \), at which the steep permeability decrease is centered. When \( w/c \) increases, the pore-size distribution shifts toward larger pores. As the drying starts, the larger pores are emptied first (because larger pores empty at a higher humidity). Therefore, for a higher \( w/c \), for which the pores are larger, the permeability begins to decrease at a higher relative humidity. The hydration reaction causes the pore sizes to decrease as a function of age or, more precisely, the hydration degree. The data fitting led to the following empirical relation:

\[
h_c = 0.77 + 0.22(w/c - 0.17)^{1/2} + 0.15 \left( \frac{\alpha}{u} - 1 \right), \quad \alpha_u < 0.99
\]

The curing condition can also affect the value of \( h_c \), whereas Eq. (7) is calibrated for the sealed curing condition. This value should be modified if the specimen is cured in a fog room or immersed in water, because in the immersed condition, for the same hydration degree (and approximately the same pore structure), the relative humidity is higher. In this study, for simplicity, for water immersion, the \( h_c \) value is increased by the same amount as the \( h_c \) increase at the start of drying, compared with the sealed condition. For instance, if, at a certain drying time, the relative humidity at sealed condition is 0.96 and for water immersion is 1, the value of \( h_c \) is also increased 0.04 (1 − 0.96). This modification is more pronounced for lower \( w/c \) and is almost negligible for high \( w/c \).

Parameter \( \beta \) gives the maximum relative decrease of permeability as \( h \) decreases. Based on more limited data, Bažant and Najjar (1972) assumed its value as 0.05, which was reached as \( h \) decreased to approximately 0.7. Later experiments, however, indicated that permeability decreases further as \( h \) decreases below 0.7 (Fig. 4). Therefore, \( \beta \) is now changed to a variable parameter defined as follows:

\[
\beta = c_f/c_1
\]

\[
c_f^0 = 60[1 + 12(w/c - 0.17)^2] \alpha/\alpha_u
\]

\[
c_f = \begin{cases} 
0.1c_f^0 & (h > h_u) \\
0.9c_f^0 + 0.1c_f^0(h/h_u)^4 & (h < h_u)
\end{cases}
\]

where \( \alpha_u \) = ultimate hydration degree in sealed concrete, which is a function of \( w/c \); it is estimated as

\[
\alpha_u = 0.46 + 0.95(w/c - 0.17)^{0.6}, \quad \alpha_u < 1
\]
The predictions of pore humidity and drying shrinkage are quite sensitive to the shape of permeability law [Eq. (5)]. Figs. 5(a and b) presents the humidity profiles and shrinkage strain evolutions, in which two of the four parameters of permeability law are changed in correspondence to the values commonly used in the literature. This makes a large difference.

**Sorption Isotherm**

The sorption isotherm is defined as the dependence of specific evaporable water content, \( w_e \) (kg/m\(^3\) concrete at constant temperature), on the relative pore humidity, \( h \). Drying depends on the desorption isotherm. Because of pronounced capillary hysteresis, the resorption (or adsorption) isotherm, which governs wetting, lies significantly below the desorption isotherm. We focus on drying and seek a simple equation for the desorption isotherm. To be applicable to concretes of different porosities, the isotherm is described in a dimensionless form by the saturation degree, \( S = w_e / w_s \), as a function of \( h \) (where \( w_s \) is the \( w_e \) at \( h = 1 \)).

The desorption isotherm is nonlinear (Nilsson 2002; Nielsen 1991; Xi et al. 1994; Bažant and Jirásek 2017), and highly so when \( h \) is near 0 and near 1. Its shape depends on the concrete type. The most important parameters are the water-cement ratio and the age. Some tests showed that certain admixtures affect the desorption isotherm significantly. Adding silica fume fills the nanopores and thus makes the matrix more uniform, which in turn makes the isotherm slope near \( h = 1 \) less steep (Baroghel-Bouny et al. 2006; Jiang et al. 2006). Various methods to measure the desorption isotherm have been proposed, but they either are too complicated to use or necessitate several calibration parameters that are hard to determine.

Based on numerous experimental studies, the desorption isotherm may be approximated by a linear asymptote dropping from \( h = 1 \) with a steep slope, \( m_1 \), followed by a long linear segment of milder slope \( m_2 \) [Fig. 6(a)], extending down to about \( h = 50\% \).

**Fig. 4.** Dependence of permeability on relative humidity. [Data from (a) Sørensen et al. 1979; (b) Nilsson 1980.]

**Fig. 5.** Bažant-Najjar model for estimating humidity evolution and shrinkage using two different sets of calibration parameters: (a) predicted relative humidity; and (b) predicted shrinkage.

**Fig. 6.** Desorption isotherm: (a) considered simplified desorption isotherm; and (b) experimental versus simulated desorption isotherm (experimental data from Nilsson 2002). Lines = authors’ simulated results; and points = experimental results.
The proposed isotherm is a smooth transition between two linear asymptotes [Fig. 6(a)]

\[
\frac{dS}{dh} = \frac{dh}{k(h, \alpha)} \quad (12)
\]

\[
\frac{1}{k(h, \alpha)} m_2 + \frac{m_1 - m_2}{1 + \left(\frac{c_S \cdot C}{C_3\cdot H}\right)^2} \quad (13)
\]

where \(k(h, \alpha)\) is the inverse slope of the desorption isotherm; and \(h^*\) is the intersection point of the two linear asymptotes. These parameters can be empirically estimated using experimental desorption isotherms. To do so, we use the tests of Nilsson (2002), who reported the desorption isotherm for various \(w/c\) ratios at different ages. Their fitting by the present model yields the following empirical relations:

\[
m_1 = f_a^{csf} \left[2.4 + (5.26 \cdot w/c - 0.68)^{1.5}\right] \quad (14)
\]

\[
m_2 = c_{sf}^{0.5} 1.18 (w/c)^{0.4} \quad (15)
\]

\[
h^* = 1 - f c_{sf} \left(w/c\right)^{0.4} \quad (16)
\]

\[
f_a = \frac{a_u - a_0}{a - a_0} \quad (17)
\]

Parameter \(c_{sf}\) accounts for the silica fume, in the absence of which \(c_{sf} = 1\). More generally, for a finite specific content \(\xi_{sf}\) of silica fume (mass of silica fume/mass of cement)

\[
c_{sf} = 1 + 2 \xi_{sf} \quad (18)
\]

Fig. 6(b) compares the preceding equations (solid curves) with Nilsson’s (2002) test data. The agreement was satisfactory. The effect of temperature on the isotherm reported in some studies (McLaughlin and Magee 1998; Poyet 2009) was minor, except at high temperatures, and is here neglected.

### Self-Desiccation

According to RILEM TC 196-ICC (Jensen 2007), the self-desiccation is defined as the reduction in the relative humidity of sealed concrete. It is explained by removal of water for hydration and doubtless leads to enlargement of already existing vapor-filled pore space (as the capillary menisci recede into narrower pores) rather than cavitation of new vapor bubbles within liquid water. The volume and size of the empty pores depends chiefly on the water-cement ratio, the degree of hydration, the particle-size distribution of cement, and the type of admixtures. For lower \(w/c\) and finer cements, the microstructure is denser and the average pore size is smaller. A smaller pore size intensifies self-desiccation, i.e., causes a higher rate and a lower final value of the average porosity of C-S-H, \(\phi_{gc}\). The reason is that, in smaller pores, the meniscus curvature is higher and thus the pressure, given by the Laplace equation, is higher, which makes the desorption isotherm at high relative humidity values less steep. The decrease of pore size also explains why adding fine admixtures, such as silica fume, intensifies the self-desiccation.

To calculate the self-desiccation correctly, one should begin with the amount of water consumed by hydration. Ordinary Portland cement (OPC) consists of various phases such as alite (C\(_3\)S), belite (C\(_2\)S), calcium aluminate (C\(_{2}\)A), tetracalcium aluminoferrite (C\(_4\)AF), and gypsum, as well as minor other phases [we use cement chemistry notation in which C, S, A, and F denote, respectively, CaO, SiO\(_2\), Al\(_2\)O\(_3\), and Fe\(_2\)O\(_3\) (Taylor 1997)]. C\(_3\)S and C\(_2\)S are two major components of OPC, and their ratio depends on the cement type. To quantify the amount of water consumed by hydration, we consider, for simplicity, only C\(_3\)S and C\(_2\)S and we assume the cement to be composed of 80% C\(_3\)S and 20% C\(_2\)S. Chemically, the hydration reaction of C\(_2\)S and C\(_3\)S is summarized as follows (Qomi et al. 2014):

\[
C_2S + 2.1H \rightarrow C_{1.7}SH_{1.8} + 0.3CH
\]

\[
C_3S + 3.1H \rightarrow C_{1.7}SH_{1.8} + 1.3CH
\]

where C\(_{1.7}SH_{1.8}\) and \(H\) constitute the typical C-S-H and water found in OPC pastes. Table 1 summarizes the molar volumes and densities of different components in the hydration reactions. When analyzing the aforementioned hydration reactions, the C-S-H pores are assumed to be empty, and so it is necessary to include additional water that is trapped in the nanopores of C-S-H.

<table>
<thead>
<tr>
<th>Phase</th>
<th>Molar volume (cm(^3)/mol)</th>
<th>Density (g/cm(^3))</th>
</tr>
</thead>
<tbody>
<tr>
<td>C(_3)S</td>
<td>72.9</td>
<td>3.15</td>
</tr>
<tr>
<td>C(_2)S</td>
<td>52.7</td>
<td>3.28</td>
</tr>
<tr>
<td>H(_2)O</td>
<td>18.0</td>
<td>1.0</td>
</tr>
<tr>
<td>C-S-H</td>
<td>110.1</td>
<td>2.05</td>
</tr>
<tr>
<td>CH</td>
<td>33.1</td>
<td>2.24</td>
</tr>
</tbody>
</table>

Constantinides et al. (2003), Jennings (2000), and Tennis and Jennings (2000) established that the hydration reaction produces two types of C-S-H: low-density C-S-H (LD), with porosity 36%; and high-density C-S-H (HD), with porosity 26%. Tennis and Jennings (2000) showed that, for different \(w/c\) values, the ratio of these two C-S-H types varies. For instance, their model predicted that, for \(w/c = 0.45\), the proportions are 50% HD and 50% LD and, for \(w/c = 0.25\), the proportions are 80% HD and 20% LD. Therefore, the average porosity of C-S-H, \(\phi_{gc}\), depends mainly on \(w/c\). Here, for simplicity, we assume a linear relation limited by lower and upper bounds, as follows:

\[
0.27 < \phi_{gc} = 0.28 + 0.20(w/c - 0.3) < 0.35
\]

The lower and upper bounds on \(\phi_{gc}\) are introduced because it does not suffice to consider only the LD or HD phases.

Having quantified the hydration relation and calculated the porosity of C-S-H, we can calculate the total volume of water, \(\xi_{wec}\), per unit volume of cement that is consumed by hydration to produce a C-S-H gel with the empty pores, \(\xi_{bwc}\), and the volume of water that fills the gel pores, \(\xi_{fwe}\).

\[
\xi_{wec} = \xi_{bwc} + \xi_{fwe}
\]

\[
\xi_{bwc} = w_{C_3S}S_{bwc}^{C_3S} + w_{C_2S}S_{bwc}^{C_2S}
\]

\[
\xi_{fwe} = \phi_{gc}S_{wc}^{C_3S}
\]
Because the gel pores are much smaller than the capillary pores, in the literature they have always been considered as saturated. However, Rahimi-Aghdam et al. (2017b) showed that this cannot be true and that at least some of the gel pores must be considered as unsaturated. Because gel pores are smaller than capillary pores, their average saturation degree should be higher than that of normal capillary pores. To calculate the average saturation degree of gel pores, we assume 33\% of gel pores to have the same degree of saturation as the capillary pores, and 67\% to have the same degree of saturation as the nanoparticles (which, at high relative humidities, are always saturated). Accordingly, for a high relative humidity, we assume the saturation degree of gel pores to be

$$S_{gp} = 0.67 + 0.33S_{cp} \quad (24)$$

### Hydration Model

Although several experimental studies (Halamičková et al. 1995; Ji 2005) demonstrated a significant effect of aging on concrete permeability, this effect has usually been omitted from the equations for drying. This omission may be acceptable when the environmental exposure begins at a late age and high hydration degree, but it can cause a considerable error for concretes that begin to dry at an early age.

Therefore, the effect of the age at drying exposure is here taken into account. Although several hydration models took the age effect into account (Jennings and Johnson 1986; Bentz 1997; van Breugel 1997; Lin and Meyer 2009), they were, unfortunately, too complicated and computationally demanding for use in finite-element structural analysis. In addition, the previous hydration models applied only to concrete that is sealed or immersed in water.

The only model that is computationally undemanding and usable for all environmental conditions and ages appears to be the model of Rahimi-Aghdam et al. (2017b). This was achieved by considering the relative pore humidity, $h$, or the corresponding chemical potential $\mu = \mu_0 + (RT/M) \ln h$, as the driving force of the hydration process (where $T$ is absolute temperature, $M$ is molecular mass of water in moles, $R$ is the universal gas constant, and $\mu_0$ is reference chemical potential). In addition, this model is able to predict the self-desiccation without any extra calibration parameter.

Therefore, we adopt here the model by Rahimi-Aghdam et al. (2017b), albeit with a slight modification for multidecade hydration, which is needed to describe multidecade autogenous shrinkage and swelling. The model is general, can be applied to different cement types upon adjusting only a few parameters, and takes into account the temperature and cement fineness. The algorithm of this new model, with the aforementioned modification, is presented in the Appendix.

Fig. 7 shows the predicted evolution of hydration degree using the presently modified version of Rahimi-Aghdam et al.’s (2017b) hydration model. The model predicts the hydration degree well, both short-term and long-term. In addition, this model, unlike previous models, predicts the hydration reaction to be a long-lived phenomenon decaying roughly logarithmically (even for decades, if $h$ does not decrease). This agrees with the long-term self-desiccation experiments.

Fig. 8 demonstrates the experimental versus simulated comparisons for the relative humidity change due to the hydration reaction in sealed specimens. The results again agree with the experiments quite well. By virtue of the varying slope of the desorption isotherm, they predict correctly the initial relative humidity, which is important for autogenous shrinkage and swelling. The calculated relative humidity change due to hydration depends strongly on the $w/c$ and is greater for concretes with a low water content. On the other hand, the self-desiccation of concretes with a high $w/c$ at early ages is predicted to be mild, as expected.

The aforementioned self-desiccation curves are true predictions; no parameter had to be calibrated. In addition, considering various C-S-H gel porosities for concretes with different $w/c$ helped significantly in matching the observed self-desiccation.

As the preceding figures show, the proposed hydration model predicts well both the hydration degree and the self-desiccation. Because the present model is time consuming to code, and because precise hydration predictions often are not necessary for obtaining the correct humidity profiles, simplified empirical relations are here proposed and calibrated using the experimental results of Bentz (2006), as follows:

$$d\alpha = c_u (\alpha_u - \alpha)^2 (h - h_f) dt \quad (25)$$

$$h_s = h_{sf} \left( \frac{\alpha - \alpha_{set}}{\alpha_u - \alpha_{set}} \right)^{n_{wc}} \quad (26)$$

where $n_{wc} = 25(w/c - 0.1)$;

$$h_{sf} = 0.5(w/c)^{-0.26} - 0.53; \quad \text{and} \quad \alpha_u = 0.46 + 0.95(w/c - 0.17)^{0.6} < 1 \quad (27)$$

where $h_f$ = relative humidity at which the hydration reaction stops, and for normal concretes it can be set to $h_f = 0.75$; and $\alpha_{set}$ = hydration degree at the time of set, which can be calculated as $\alpha_{set} = 0.05 + 0.2(w/c - 0.3)$ (according to the hydration model, for normal temperature and normal cement). These empirical relations are calibrated for concretes without admixtures, the presence of which changes the hydration reaction.

\[\text{Fig. 7. Experimental versus predicted hydration degree. Lines = present simulated results; and points = experimental results. [Experimental data from} \text{ Bentz 2006; (b) Danielson 1962.]}\]
of which changes the rates of hydration degree and of self-desiccation significantly.

The proposed simple equations can be integrated numerically by any method and suffice for capturing the effect of relative humidity on the rate of hydration. Fig. 9 shows that these equations predict correctly the evolutions of hydration degree and self-desiccation. However, they do not suffice for predicting the autogenous shrinkage. The reason is that the autogenous shrinkage is highly sensitive to an initial decrease of relative humidity, and a small error in predicting the self-desiccation and hydration can cause a large error in predicting the autogenous shrinkage (Bažant and Najjar 1972; Ali and Urgessa 2014). To avoid major errors, the complete hydration model must be used for that purpose.

### Boundary Conditions

Unless the specimen or structure is very large, the surface moisture transmission between the concrete and environment cannot be considered as instantaneous. The relative humidities in the environment and in the concrete pores at the surface are different. In terms of relative humidity, the boundary condition is (Bažant and Najjar 1972)

\[
\dot{j}_w = \eta(h_c - h_{env}) \tag{28}
\]

where \(j_w\) = moisture flux across the surface; and \(\eta\) = surface emissivity (kg/m²s). Various values of \(\eta\) are found in the literature.

For instance, Bažant and Najjar (1972) suggested \(85 \times 10^{-6}\) kg/m²s for indoor (or still) air and \(350 \times 10^{-6}\) kg/m²s for outdoor (moving) air. Ali and Urgessa (2014) used \(6 \times 10^{-6}\) kg/m²s for indoors and \(9 \times 10^{-6}\) kg/m²s for an isolated space. West and Holmes (2005) used a boundary condition of slightly different form, \(\frac{C(h)[\partial h/\partial r]}{h_c} = f_s(h - h_{env})\), where the surface factor, \(f_s\), was considered to be approximately \(10^{-8} - 10^{-7}\) m/s. This is roughly equivalent to an evaporation rate of \(1.1 \times 10^{-6}\) to \(11 \times 10^{-6}\) kg/m²/s.

Parameter \(\eta\) has a rather uncertain value. Furthermore, it adds complexity and hardly leads to better predictions. Therefore, Bažant and Najjar (1972) proposed replacing Eq. (28) for the boundary condition with a certain equivalent extra surface thickness, \(\delta h_{eq}\), of an imagined added layer of concrete on whose surface the pore humidity equals the environmental value. Comparing analytical and experimental results, they adopted the value \(\delta h_{eq} \approx 0.75\) mm. This method also was used to calculate the shape factors for concrete shrinkage and drying creep (Dönmez and Bažant 2016). For simplicity, \(\delta h_{eq}\) is also used here, but with a different value of about 4 mm, as estimated from the present calculations. The error of this approximation was found to have little effect and decreases as drying continues.

### Comparison of Numerical and Experimental Results

The numerical results of the present model were first compared with the humidity profiles from the classical tests originally used for calibration by Bažant and Najjar (1972) (Figs. 10 and 11), and had a rather close agreement. The properties of the concrete used in these tests are given in Table 2. In Fig. 11, the humidity profile indicated a decreasing humidity near the center. These experiments were performed under unidirectional drying (two parallel faces exposed and four faces sealed). The decrease of relative humidity near the center was probably caused by breakage of the seal near the center.
Next, we consider the comprehensive experiments of Kim and Lee (1999). Concrete specimens were exposed to drying at ages of 3 and 28 days. Fig. 12 demonstrates again a satisfactory agreement with the pore humidity profiles for different depths below the drying surface, \(y\), and for both exposure times. The specimens were cured under water immersion before drying exposure, and thus the relative humidity prior to drying exposure was higher than in the sealed specimens. The equation proposed in this study for calculating \(h_c\), Eq. (7), was calibrated for the sealed condition. However, in the case of curing under water immersion, it needs to be modified. Here, for simplicity, the value of \(h_c\) in Eq. (7) was simply increased by an amount equal to the humidity difference between the sealed and immersed conditions. This change was negligible for drying that began 3 days after mixing, but for drying that began after 28 days, the initial increase of \(h_c\) at 28 days was about 2% for the finite elements near the surface.

All the preceding simulations of experimental data used the permeability law [Eq. (5)] with the same coefficient values. However, permeability varies widely, depending on the aggregate size and type, cement type, casting technique, and so on. It was clearly quite different in some reported experiments, as seen from the time evolution of pore humidity in, e.g., Laurens et al.’s (2002) experiments. Fortunately, to fit other data, it is not necessary to change all the coefficient values. Mere scaling of the permeability law is sufficient. The data of Laurens et al. (2002) can be closely matched if the permeability is reduced by 35% compared with the preceding simulations (Fig. 13).

Furthermore, consider pore humidity predictions for concretes with silica fume (SF) as an admixture, which has a major effect on permeability (Jiang et al. 2006; Baroghel-Bouny et al. 2006) by refining the pore structure due to filling the pores and pozzolanic effect (Bentz et al. 2000). Refining pores causes the pore humidity to decrease faster and to lower values. In addition, SF reacts with portlandite, producing more C-S-H and a denser structure, which results in a faster decrease of pore relative humidity. Fig. 14(a) compared to the self-desiccation for concretes with and without the SF. The SF effect on the self-desiccation was predicted correctly. The SF effect is modified in specimens exposed to the environment. This is evident from the plots of predicted versus measured relative humidity in Fig. 14. They indicate a good agreement.

Table 2. Material parameters for analyzed experiments

<table>
<thead>
<tr>
<th>Figure</th>
<th>Study</th>
<th>(w/c)</th>
<th>(a/c)</th>
<th>Shape</th>
<th>Thickness or diameter</th>
<th>Exposure time, (t')</th>
<th>Environmental humidity, (h_{env})</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fig. 10</td>
<td>Hanson (1968)</td>
<td>0.66</td>
<td>6.95</td>
<td>Cylinder</td>
<td>6 in.</td>
<td>7 days</td>
<td>0.5</td>
<td>Elgin sand and gravel</td>
</tr>
<tr>
<td>Fig. 11</td>
<td>Abrams and Monfore (1965)</td>
<td>0.45</td>
<td>4.36</td>
<td>Slab</td>
<td>12 in.</td>
<td>7 days</td>
<td>0.1</td>
<td>7 bags cement/yd³</td>
</tr>
<tr>
<td>Fig. 12</td>
<td>Kim and Lee (1999)</td>
<td>0.28, 0.4, 0.68</td>
<td>3.15, 4.14, 5.6</td>
<td>Slab</td>
<td>20 cm</td>
<td>3 and 28 days</td>
<td>0.6</td>
<td>Moist cured</td>
</tr>
<tr>
<td>Fig. 13</td>
<td>Laurens et al. (2002)</td>
<td>0.66</td>
<td>6.95</td>
<td>Slab</td>
<td>7 cm</td>
<td>2 days</td>
<td>0.55</td>
<td>Small aggregates</td>
</tr>
<tr>
<td>Fig. 14</td>
<td>Grasley and Lange (2004)</td>
<td>0.44</td>
<td>0.44</td>
<td>Slab</td>
<td>20 cm</td>
<td>1 day</td>
<td>0.5</td>
<td>Silica fume has added</td>
</tr>
</tbody>
</table>

Fig. 10. Relative humidity profiles in the cross-section for different drying times (\(t'\)): (a) \(t' = 3, 28, \) and 365 days; (b) \(t' = 7, 90, \) and 730 days; and (c) \(t' = 14, 180, \) and 1,100 days. Lines = present simulated results; and points = experimental results from Hanson (1968).

Fig. 11. Relative humidity profiles in the cross-section for different drying times (\(t'\)): (a) \(t' = 40 \) and 130 days; and (b) \(t' = 50 \) and 270 days. Lines = present simulated results; and points = experimental results from Abrams and Monfore (1965).
Fig. 12. Evolution of relative humidity versus drying time ($t'$) for different depths below the drying surface ($y$): (a–c) specimens immersed in water for 3 days and then exposed to drying; and (d–f) specimens immersed in water for 28 days and then exposed to drying. Lines = present simulated results; and points = experimental results from Kim and Lee (1999).

Fig. 13. Relative humidity profiles in the cross section for different drying times ($t'$): (a) $t' = 15, 48,$ and $139$ days; and (b) $t' = 26, 100,$ and $187$ days. Lines = simulated results; and points = experimental results from Laurens et al. (2002).

Fig. 14. Evolution of relative humidity versus drying time ($t'$): (a) comparison of self-desiccation for specimens with and without silica fume (experiment by Jiang et al. 2006); and (b) evolution of relative humidity versus drying time for specimens at different depths from the drying surface ($y$), all with silica fume. Lines = simulated results; points = experimental results from Grasley and Lange (2004).
Fig. 15. Predictions of humidity evolution in exposed specimens using: (a) complete hydration model; and (b) simplified hydration model. Lines = simulated results; and points = experimental results from Kim and Lee (1999).

Some experimenters (e.g., Jiang et al. 2006) studied admixtures other than the SF. However, their effect was found to be very small, and is here neglected.

Finally, the validity of the simplified hydration model for exposed specimens needs to be checked. This model was able to predict closely the self-desiccation and hydration degree in sealed concrete (Fig. 9). Checking the model for exposed concrete, the simplified hydration model yielded almost the same predictions as the full model, except for a small error during the initial days (Fig. 15). The reason for this error was the slope change of the desorption isotherm due to the drying process. This change cannot be captured by the simplified linear isotherm. Overall, however, the predictions were quite good, and thus the present simplified hydration relation appears to be satisfactory.

Summary and Conclusions

1. An improved equation for the dependence of self-desiccation rate on pore humidity and hydration degree was here formulated and calibrated by experimental data;
2. The 1972 Bažant-Najjar model for the strong decrease of moisture permeability with decreasing pore humidity was improved and calibrated with recent experimental data;
3. Equations to predict the four parameters for the permeability variation from the material composition, water-cement ratio, and hydration degree were formulated and calibrated with experimental data; and
4. The desorption isotherm as a function of pore relative humidity was improved by a nonlinear isotherm with a steep top segment whose slope and length depend on the water-cement ratio, according to experimental calibration.

Appendix. Algorithm for Evolution of Hydration, Autogenous Shrinkage, and Swelling

1. For cement paste or concrete with known water-cement and aggregate-cement ratios, calculate the initial volume fraction of cement $V_0^c$ and water $V_0^w$:

$$V_0^c = \frac{\rho_a \rho_c}{\rho_a + \rho_c \rho_w / c + \rho_c \rho_a w / c}$$

$$V_0^w = \frac{\rho_a \rho_w / c}{\rho_a + \rho_c \rho_w / c + \rho_c \rho_a w / c}$$

where $\rho_a$, $\rho_c$, and $\rho_w$ = specific mass of water (1,000 kg/m$^3$), cement (here considered as 3,150 kg/m$^3$), and aggregates (1,600 kg/m$^3$ for gravel and sand combined), respectively.

2. Calculate the average cement particle size (i.e., particle radius) $a_0$, based on the cement type. In this study, the Blaine fineness of cement, $f_{bl}$, 350 m$^2$/kg, was considered to correspond to a particle radius of 6.5 $\mu$m. Then calculate the number of cement particles, $n_g$, per unit volume of cement

$$a_0 = 6.5(\mu m) \frac{350}{f_{bl}}$$

$$n = \frac{V_0^c}{\frac{4}{3} \pi a_0^3}$$

3. Choose a reasonable hydration degree for setting the time $\alpha_{set}$, and the time $\alpha_c$ at which the C-S-H barrier will be completed, i.e., the critical hydration degree at which a complete C-S-H barrier will form around the anhydrous cement grains (about 1 day). For a normal cement with $a_0^c = 6.5 \mu m$, $w/c = 0.3$, and $T = 20^\circ C$, the values $\alpha_{set} = 0.05$ and $\alpha_c = 0.36$ are good approximations. For specimens with different $T$, $w/c$ and cement type, reasonable values may be calculated as follows:

$$\alpha_c = \alpha_0^c f_1(a) f_2(w/c) f_3(T) < 0.65$$

$$f_1(a) = \frac{a^0_n}{a}$$

$$f_2(w/c) = 1 + 2.5(w/c - 0.3)$$

$$f_3(T) = \exp \left[ \frac{E_a}{R} \left( \frac{1}{273 + T_0} - \frac{1}{273 + T} \right) \right]$$

$$\frac{\alpha_{set}}{\alpha_c^0} = \frac{\alpha_c}{\alpha^n_0}$$

4. Calculate the volume fraction of cement, $V_{set}^c$; portlandite, $V_{set}^{CH}$, and gel (C-S-H plus ettringite), $V_{set}^g$. Using these fractions, calculate the radius of the anhydrous cement remnants, $a_{set}$, and the outer radius of C-S-H barrier, $z_{set}$. To describe the chemical reaction of hydration, use the volume ratios $\zeta_{CH} = 1.52$ and $\zeta_{CHC} = 0.59$ in the following equations:

$$V_{set}^c = (1 - \alpha_{set}) V_0^c$$

$$V_{set}^{CH} = \zeta_{CH} \alpha_{set} V_0^c$$

$$V_{set}^g = \zeta_{CHC} \alpha_{set} V_0^c$$

$$a_{set} = \left( \frac{V_{set}^c}{\frac{4}{3} \pi n_g} \right)^{1/3}$$

$$z_{set} = \left( \frac{V_{set}^c + V_{set}^g}{\frac{4}{3} \pi n_g} \right)^{1/3}$$

5. In each time step, use the hydration degree $\alpha$ and humidity $h$ from previous step to calculate the water diffusivity $B_{eff}$.
9. In each time step, use the calculated $d\tilde{h}$.

10. At each time step calculate the increment of gel barrier $dz_i$

$$dz_i = \frac{dV_i^g}{4\pi\tilde{a}_i^2}$$ for $\alpha_i > \alpha_c$ (48)

11. Finally, calculate the self-desiccation increment of relative humidity, $dh_i^t$, of saturation degree, $dS_{it}^{cap}$, and of interparticle porosity, $d\phi_{it}^{cap}$

$$dh_i^t = K_h \left( \frac{dV_i^g(\zeta_{bw} + \phi_{np}\zeta_{gc})}{\phi_{it}^{cap}S_{it}^{cap}} \right)$$ (49)

where

$$d\phi_{it}^{cap} = -\left( dV_i^g + dV_i^{CH} + dV_i^t \right) + (\phi_{gp} - \phi_{np})\zeta_{gc}$$ (50)

where $\phi_{np}$ is nanopore part of gel porosity, in which the pores are too small to obey the Kelvin relation. These pores are assumed to be always saturated. In this study, $2/3$ of gel pores were assumed to be nanopores.

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