EARLY-AGE EVOLUTION OF THE MASS TRANSFER PROPERTIES IN MORTAR AND ITS INFLUENCE UPON ULTIMATE SHRINKAGE

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Abstract

In order to predict accurately the local shrinkage strains and eventually the shrinkage-induced stresses in concrete, it is necessary to determine in the first place the moisture distribution within the material. The knowledge of the two basic relationships that rule the mass transfer behavior of cementitious materials is required for that matter, namely the sorption isotherms and the diffusion coefficient as a function of the water content. While both of these relationships have been studied rather extensively for well hydrated materials, their evolution during the first few days after casting, which might be quite significant in practice, is poorly documented. This paper presents test results yielded in a research program undertaken to fill this gap. The moisture transfer properties and ultimate shrinkage values of a Portland cement mortar having a w/c ratio of 0.40 were characterized starting from 1 day, 3 days, 7 days and 28 days. The series of experiments performed include the monitoring of weight change during desorption above saturated salt solutions and ultimate length change measurements at different R.H. levels between 50% and saturation, pressure membrane desorption tests, dynamic weight change measurements of specimens having different thicknesses (50% R.H.), mercury intrusion porosimetry and degree of hydration assessment. Using classical assumptions, the coefficient of diffusion for the different levels of maturity is determined as a function of moisture content. The results are discussed in view of their dependency upon maturity, especially the extent to which drying shrinkage is affected by the curing regime duration.

Keywords: concrete; curing; degree of hydration; diffusion coefficient; drying shrinkage; early-age; moisture content; mortar; Portland cement; sorption isotherm.
1. Introduction

Porous materials interact with their environment. In a more specific way, variable thermal and hygrometric conditions lead to shrinkage or swelling. If these variations are not uniform or restricted, stresses are induced, which can lead to cracking of the material. Therefore, the knowledge of the moisture distribution and its evolution within concrete is important because moisture has a predominant influence on the volumetric stability of cement based-materials [1].

The moisture distribution in a cementitious material element exposed to an environment under given hygro-thermal conditions is related to the porosity and transfer properties of the material. The evolution of transfer properties has often been studied on well cured materials [2, 3, 4, 5]. Since the duration of sorption experiments up to equilibrium is generally rather important, they are mostly performed on mature materials where additional hydration during hydration is likely to be negligible. Various studies have permitted to characterize the texture of different materials from experiments like adsorption-desorption isotherms, mercury intrusion porosimetry (MIP) and determination of the degree of hydration. These tests results provide useful information allowing a better identification of the causes of deterioration of cementitious materials, such as drying shrinkage.

The drying process can begin very quickly when the structure becomes in hygrometric imbalance with its environment. Under certain drying conditions, not only the excess water needed to put the material into shape, but also some of the water needed for the cement hydration will evaporate. Therefore, the natural drying of concrete has significant consequences on the mechanical behavior and durability of structures. More or less important cracking is often caused by drying shrinkage because the material is not allowed to deform freely.

Determination of the water content and of its distribution within the concrete microstructure is necessary for the development and assessment of predictive models. Unfortunately, the evolution of moisture transfer properties of cementitious materials during the first days of hydration is almost unknown.

The results presented in this article show the evolution of moisture transfer properties such as the relationship between moisture content and relative humidity (sorption isotherm), and the coefficient of diffusion as a function of the moisture content for a 0.40 W/C Portland cement mortar after various water curing regimens, 1, 3, 7 and 28 days. In addition, experiments intended to evaluate the influence of the curing period on drying shrinkage are also reported.
2. Materials and methodology

Drying of a humid porous material exposed to hygro-thermal changes is related to its sorption isotherm, i.e. the relationship between equilibrium moisture content, temperature and relative humidity. Nevertheless, it should be emphasized that these hygro-thermal (hygrometric) conditions result from the application of boundary conditions to the structure.

The study of the evolution of the moisture content profiles in the material must be performed and associated to the material microstructural characteristics. The difficulty here is to determine these parameters for an early-age material, because of the ageing nature of cementitious materials. The difficulty is even greater when the hydration degree is low.

2.1 Experimental program

All tests were performed on the same mortar mixture. The water/cement ratio of the studied mortar was 0.40, the sand/cement ratio was 1.9, and the mix was made with CSA type 10 cement. Table 1 presents the characteristics of the mixture composition. The sand has been sieved to remove the fraction larger than 1 mm. The mixing operations were performed under vacuum to minimize the entrapment of air bubbles. Air void spacing measurements have revealed an air percentage of about 2%. The mixture was poured into 200 x 35 x 35-mm and 50 x 50 x 50-mm plastic moulds which were then covered with a plastic sheet during 24 hours. Afterwards, the specimens were withdrawn from the moulds and immersed into a lime-saturated water solution. The specimens to be used for the tests at 1 day were sawn at 26 hours and the tests were started 36 hours after the initial water-cement contact. The specimens to be used for the tests at 3, 7 and 28 days were kept in the lime-saturated water solution until the beginning of the experiments, except for a short period where they were then sawn, some 10 hours prior to drying. Further in the text, the number of days refer to the curing duration before the beginning of the tests.

Table 1: Mortar composition

<table>
<thead>
<tr>
<th>W/C ratio</th>
<th>Cement kg/m³</th>
<th>Water kg/m³</th>
<th>Sand kg/m³</th>
<th>Air content (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.40</td>
<td>693</td>
<td>277</td>
<td>1316</td>
<td>2.5</td>
</tr>
</tbody>
</table>

2.2 Mercury intrusion porosimetry

Mercury intrusion porosimetry tests were performed to characterize the porosity after the different curing regimens investigated (1, 3, 7 and 28 days). Samples of mortar which had a mass between 4 and 11 g were dried out by replacing the interstitial water with propan-2-ol. The samples were immersed in alcohol for 3 months. During that time, the propan-2-ol solution was renewed every day in the first week, and once a week until the end of the 3-month period. The samples saturated with propan-2-ol were then dried out.
in the oven during 10 days at 60°C. The principle behind this method is that propan-2-ol having a lower surface tension than that of water, the drying stresses due to capillary tension induced during the process are lower. The extend of damage to the microstructure is then lower than it would be for a direct oven-drying.

2.3 Degree of hydration
Degree of hydration measurements were performed on samples pounded into pieces taken from mortar plaquettes (35 x 35 x 3-mm) previously dried out in the oven at 105°C. Small samples were then weighted and placed in the oven at 1000°C for 30 minutes. Afterwards, the samples were allowed to cool down inside the oven until they reached a temperature of about 150°C. In order to obtain the heated sample weight, the samples were then brought back to ambient temperature inside a desiccator. The latter operation prevents any humidity gain.

The degree of hydration ($\alpha(t)$) is calculated as the ratio between the quantity chemically bound at time t ($W_n(t)$) and the total quantity of water chemically bound ($W_n(t \rightarrow \infty)$). The amount of chemically bound water, at a given time ($W_n(t)$), was evaluated by measuring the weight loss between 105°C and 1000°C. At a temperature of 105°C, free water is evaporated, and, at 1000°C, water bound to hydrates is driven out. Corrections must be made for the loss on ignition of the sand and of the anhydrous cement since such a thermal treatment causes a weight loss of these components, in addition to a water loss. The following equation gives the quantity of water chemically bound at time t [7](taken from [8]):

$$W_n(t) = \frac{w_{105^\circ C} - w_{1000^\circ C} - x \cdot w_{105^\circ C} \cdot g \cdot (1 + g)^{-1} - y \cdot w_{105^\circ C} \cdot (1 + g)^{-1}}{w_{1000^\circ C} - w_{105^\circ C} \cdot g \cdot (1 + g)^{-1} + x \cdot w_{105^\circ C} \cdot g \cdot (1 + g)^{-1}}$$

where:
- $w_{105^\circ C}$ = dried sample weight
- $w_{1000^\circ C}$ = heated sample weight
- $x$ = loss on ignition of the sand
- $y$ = loss on ignition of the cement
- $g$ = sand/cement ratio

The total amount of chemically bound water ($W_n(t \rightarrow \infty)$), and that corresponding to a full hydration, was assumed to be 25% of the unhydrated cement weight.

2.4 Sorption tests over saturated salt solutions
During wetting, and drying, two phenomena are involved in the equilibrium of water: physical adsorption and capillary condensation. These phenomena are associated to the amount of evaporable water in the system [8]. The chemically bound water is not affected by these processes (wetting, drying).
In order to determine the adsorption and desorption isotherms of the investigated mortar, sorption tests over saturated salt solutions were performed. For that purpose, small slabs (35 x 35 x 3-mm) were sawn from 200 x 35 x 35-mm prisms. The specimens used for desorption tests were brought to a saturated surface-dry (ssd) state after 1, 3, 7 and 28 days of curing in lime-saturated water. The specimens used for adsorption were immersed in propan-2-ol during 3 months and then oven-dried for 10 days in the oven at 60°C. After their respective conditioning, the specimens were stored over selected saturated salt solutions in small CO₂-free chambers.

The salts used for the tests and the corresponding relative humidities are listed in Table 2. Tests were undertaken 1, 3, 7 and 28 days under each of the 4 selected R.H. conditions. Therefore, there were 16 combinations of maturity – R.H. Series of 20 specimens were placed in baskets in order to weigh the average mass of several specimens and reduce the risk of error. Moreover, the baskets were weighed without opening the sealed boxes to avoid temperature and relative humidity disturbances in the test vessels. The chambers were located in a room at 21°C and nitrogen was regularly introduced into the chambers to avoid carbonation of the specimens.

<table>
<thead>
<tr>
<th>Salt</th>
<th>R.H. (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>K₂SO₄</td>
<td>97</td>
</tr>
<tr>
<td>KCl</td>
<td>84</td>
</tr>
<tr>
<td>NaCl</td>
<td>75</td>
</tr>
<tr>
<td>Mg(NO₃)₂</td>
<td>53</td>
</tr>
</tbody>
</table>

2.5 Pressure membrane desorption experiments

The pressure membrane technique has been used to determine the moisture content-relative humidity relationship of the investigated mortar for relative humidities above 95%. This method was developed in the geotechnical science field and applied to other hygroscopic porous materials such as wood [9]. The method is based on the principle that the pores of the membrane, made of cellulose acetate, are small enough to retain water because of the capillary forces involved, even under the pressure applied. The membrane is thus permeable to water, but impermeable to air. Under the effect of gas pressure, the humid mortar samples in contact with the porous membrane lose water until they reach equilibrium with the imposed water potential. In order to ensure a good hydraulic contact between the porous membrane and the samples, they are placed on a 2 mm-thick saturated clay bed laying on a cellulose acetate membrane previously saturated under vacuum, and a blotting paper. Details on the pressure membrane apparatus can be found in [9]. The total extracted volume of water is then measured and the moisture content of the samples at equilibrium is evaluated. The applied pressures correspond to specific relative humidities or water potentials.
The following equation relates a given applied gas pressure to its corresponding water potential (Table 3):

$$\psi_m = \psi_m - V_w P_m$$

(2)

where:

- $\psi_m$ = matric potential (J kg$^{-1}$)
- $V_w$ = specific volume of water (kg m$^{-3}$)
- $P_m$ = applied gas pressure equivalent to the matric pressure resulting from the capillary and sorptive forces due to the wood matrix.

Table 3: Relation of water potential to relative humidity and test duration

<table>
<thead>
<tr>
<th>Pressure applied (kPa)</th>
<th>Water potential $\psi$ (J/kg)</th>
<th>Relative humidity (%)</th>
<th>Test duration (days)</th>
</tr>
</thead>
<tbody>
<tr>
<td>-199.66</td>
<td>-200</td>
<td>99.852</td>
<td>3-4</td>
</tr>
<tr>
<td>-998.30</td>
<td>-1000</td>
<td>99.263</td>
<td>10</td>
</tr>
<tr>
<td>-1996.6</td>
<td>-2000</td>
<td>98.532</td>
<td>15</td>
</tr>
<tr>
<td>-4991.5</td>
<td>-5000</td>
<td>96.37</td>
<td>21</td>
</tr>
</tbody>
</table>

The following equation relates a given relative humidity to the corresponding water potential:

$$\psi_{m+o} = \frac{RT}{M_w} \ln \left( \frac{p}{p_s} \right)$$

(3)

where:

- $\psi_{m+o}$ = sum of the matric and osmotic potentials (J kg$^{-1}$)
- $R$ = gas constant (8.3143 J/mol.K)
- $T$ = absolute temperature (Kelvin)
- $M_w$ = molecular weight of water (18.0153 x 10$^{-3}$ kg/mol.)
- $p$ = partial pressure of water vapor in equilibrium with water in concrete (Pa)
- $p_s$ = partial pressure of water vapor in equilibrium with pure free water (Pa)

Equilibrium can be reached at very high relative humidity levels using this method, which is impossible to achieve with saturated salt solutions. The specimens subjected to this test were identical to those used in the sorption tests (35 x 35 x 3-mm slabs). A set of 12 specimens was placed inside the pressure membrane apparatus. The pressure was increased at a rate of 100 kPa/day for the first 1000 kPa, then 200 kPa/day for the next 1000 kPa and, finally, 500 kPa/day beyond 2000 kPa. However, these rates could vary depending on the time taken by the samples to reach equilibrium with the pressure applied. At the beginning of the test, a lot of water is extracted from the samples. This explains there is sometimes a delay before increasing the pressure rate.
2.6 Ultimate length change measurements
Length-change measurements were performed in order to determine the effect of initial maturity and relative humidity on ultimate shrinkage, and to study the relationship between the shrinkage behavior and the transfer properties. The specimens used were small 70 x 15 x 3-mm beams sawn from the 200 x 35 x 35-mm prisms. To perform length-change measurements on such small specimens, two tiny brass plugs have been glued 50 mm apart on both sides of the beams. Both the parameters investigated and the test conditions were identical to those of the desorption tests described previously. An initial reading was recorded immediately before storing each specimen in the chambers. A subsequent reading was performed after 16-17 months of exposure under the various relative humidities.

2.7 Dynamic weight change measurements
The diffusion coefficient was determined using a differential method which relies on the evolution of the weight of specimens having the same cross-section but different thicknesses, and exposed to uniaxial drying. Yet, the moisture content distribution inside a specimen can be found from techniques such as gammadensimetry or nuclear magnetic resonance. However, these techniques are not always readily available and they are not necessarily suited for very early measurements on young cementitious materials, which require the use of very shallow pieces to reduce as much as possible additional hydration.
For certain materials, wood for instance, it is possible to submit several specimens to
drying and actually determine after different periods of time the water content
distribution by sawing a specimen in pieces and then measure the water content in each
of them. Unfortunately, this simple method is not suited for most cementitious materials,
because the sawing process will affect the water content of the samples, either because
of heating if no cooling water is used or by re-wetting if cooling water is used. In both
cases, the moisture content measured on the sawed slabs is inaccurate.

A simple alternative is to prepare specimens having various thicknesses and sealed on all
except one surface (figure 2). Provided that the cross-section of each specimen has the
same geometry and dimension, it is assumed that the distribution of moisture at a given
distance from the drying surface is the same without regard to the thickness of the
specimen [10]. Then, the water concentration \( C_i(x, t) \) at time \( t \) and at a distance \( x \) from
the surface \( S \), in a layer located between the depths \( l_{i-1} \) and \( l_i \), is given by the following
equation:

\[
C_i = \frac{m_i - m_{i-1}}{(l_i - l_{i-1}) \cdot S}
\]

\[
= w_i \cdot \frac{l_i}{l_i - l_{i-1}} - w_{i-1} \cdot \frac{l_{i-1}}{l_i - l_{i-1}}
\]

(4)

where \( w_i \) is the average concentration of a material slab located between the outer
surface and depth \( l_i \) (figure 3), so the water weight contained in each slab is:

\[
m_i = w_i \cdot l_i \cdot S
\]

(5)

The water contained in the layer \( l_{i-1} \) of this slab will be:

\[
m_{i-1} = w_{i-1} \cdot l_{i-1} \cdot S
\]

(6)

It should be noted that, if the profile were uniform:

\[
w_i = w_{i-1}
\]

(7)
Besides, the concentration $C$ in kg water/m$^3$ moist concrete is given by the following equation [11]:

$$C = G_m \cdot \rho_w \cdot \frac{M}{100}$$  \hspace{1cm} (8)

where:
- $G_m =$ specific gravity of mortar (kg$_{oven-dry\ mortar}$/m$^3$ moist mortar / kg$_{water}$/m$^3$ water)
- $\rho_w =$ density of water (kg$_{water}$/m$^3$ water)
- $M =$ moisture content expressed in percentage (kg$_{water}$/kg$_{oven-dry\ mortar} \cdot 100$)

Using the hypothesis defined above, the parameter $w_i$ can be determined from samples of thickness $l_i$ (drying on one side and sealed on the other, or of thickness $2l_i$ and drying on both sides). The moisture content profile of a sample of thickness $L$ can then be evaluated by following its weight loss along with that of thinner slabs drying under the same conditions (figure 2).

For the purpose of this study, the tests have been performed on series of specimens cured for 1, 3, 7 and 28 days respectively and each set of specimens contained 35 x 35 mm...
slabs, two for each of the following thicknesses: 4, 8, 12, 16 and 20 mm. Each of them were sealed on the lateral sides with the top and bottom surfaces left exposed to drying. Those were intended to be representative of 2-, 4-, 6-, 8- and 10-mm slabs that would have been exposed to on the top surface only (figure 2).

The test specimens have been placed in chambers similar to those used for the sorption and shrinkage tests. They were exposed during 6 months at a temperature of 21°C and a relative humidity of 53% obtained with a saturated salt solution of Mg(NO3)2. Nitrogen was frequently used to expel carbon dioxide from the boxes and prevent carbonation of the specimens. Weight measurements were performed on a daily basis during the first week, and once every two weeks afterwards.

2.8 Diffusion coefficient

The diffusion coefficient has been calculated from a method used to determine the effective water conductivity of wood [11]. In accordance with this method, the liquid water, the water vapor and the chemically bound water are assumed to be in equilibrium in the porous media during drying. The equation of water movement in one dimension is given by the following expression:

\[
\frac{\partial C}{\partial t} = \frac{\partial}{\partial x} \left( K \frac{\partial \psi}{\partial x} \right) \quad (9)
\]

In the latter expression, the \( \psi \) gradient is considered as being the driving force of the three phases of water during drying. The effective water conductivity \( K \) (kg/m·s·J) can then be defined in the following way:

\[
[K_x]_{x=0} = \frac{\int C \frac{\partial C}{\partial x} }{\int \frac{\partial \psi}{\partial x}} \quad (10)
\]

with

\[ I_x = \int_{x=0}^{x} C \, dx \quad \text{and} \quad \frac{\partial \psi}{\partial x} = \frac{\partial C}{\partial x} \frac{\partial \psi}{\partial C} \]

From the curves of moisture concentration (C) as a function of position \( x \) (m) from the drying surface, the integral \( I \) can be calculated at each time \( t \) and at each position \( x \). This integral is then expressed as a function of time and the slope of the resulting curve represents \( \partial I/\partial t \) at time \( t \) and position \( x \). The gradient in water potential is inferred from the moisture concentration profiles and from the moisture content – water potential relationship.
3. Results and analysis

3.1 Degree of hydration
The degree of hydration of the 0.40 mortar was determined for each water curing duration (1, 3, 7 and 28 days) using three samples. The results are presented on figure 4, together with the corresponding compressive strength measured in accordance with ASTM C109. As can be seen, the evolution of hydration is very similar to that of compressive strength. This explains why mechanical strength, most often compressive strength, is sometimes used to evaluate the degree of hydration of concrete.

![Figure 4: Mortar degree of hydration and compressive strength as a function of time](image)

3.2 Sorption isotherms
The results of the desorption and adsorption tests performed on thin mortar samples over saturated salt solutions after 475 days and 130 days respectively are presented hereafter. Figure 5 presents the dynamic weight loss curves for the 4 maturities and the 4 relative humidities investigated (one shall notice that the Y-scale is different in the four graphs). The specimens exposed to 97% R.H. show an increase in weight from the first days of drying. The increase is such that the 1-day and 3-day specimens weighed more after 200 days than they did at the beginning of the experiments. The same phenomenon is observed after 300 days for the 7-day and 28-day specimens. This is due to the additional hydration that has been taking place, given the high relative humidity inside the
The observed trend clearly supports the fact that the lower the degree of hydration is, the more rapid the rate of hydration is [12].

Figure 5: Dynamic weight loss curves in desorption, a) 53%, b) 75%, c) 84%, d) 97%

The adsorption-desorption isotherm has been plotted in figure 6 for the 50% to 100% R.H. range. The hysteresis that can be observed is explained by the different angles of contact characterizing the wetting and the drying processes (air-water system), and by the "ink bottle" effect associated with the capillary condensation phenomenon [3]. At low relative humidities, it can be seen that the moisture content decreases with the initial curing duration. This can be explained by the Kelvin's law (11), according to which the lower the relative humidity, the lower the pore size that is emptied. Hence, materials cured for 28 days, containing more small pores than those cured for only one day, will retain more water at low relative humidity. Conversely, at high R.H., the moisture content increases with a diminution in curing duration because there are more large pores.
Figure 7 presents the desorption isotherm for relative humidities ranging between 95% and 100%. On this figure, the moisture content data expressed as a function of relative humidity are those obtained with the porous membrane test. For sake of comparison, the values obtained over a 97% R.H. saturated salt solution after almost 500 days are posted on the same graph. Yet, one can notice that the younger the specimens at the beginning of experiments, the more significant the extraneous hydration was. Thus, the sorption results obtained in desiccators cannot be used to plot the desorption in this very high R.H. range provided that hydration of the material has occurred all throughout the experiments and that, as a result, the material has an effective maturity much higher than that corresponding to the nominal 1-day, 3-day, 7-day or 28-day period.

The equilibrium being much faster to achieve in the porous membrane test, more especially at high relative humidities (table 3), the specimens barely have time to undergo further hydration during the test. The maturity (1, 3, 7 and 28 days) of the specimens is therefore much less affected than that of the specimens exposed over high R.H. saturated salt solution.
Figure 7: Desorption isotherm at high relative humidity

Figure 8: Moisture content as a function of the water potential

Figure 8 presents the water potential - moisture content relationship. It is the same graph than in figure 7, but the R.H. is now expressed in terms of water potential. The latter relationship is usually presented using semi-logarithmic graphs and, as can be seen when
comparing figures 7 and 8, the effect of the maturity on the first desorption curve becomes more evident.

Figure 5 shows a weight gain for the specimens exposed to 84% R.H. after about 200 days, respective to the curing duration. However, this weight gain is much less considerable than for specimens exposed to 97% R.H. So, additional hydration took place too, but to a much more lesser extend. With the test still going on, it will be interesting to observe how long it will take to stabilize.

Figure 9: Pore size distribution measured with mercury

Figure 9 shows the pore size distribution of the mortar for the various curing durations. Curves corresponding to 1-day and 3-day specimens almost superimpose, though the 1-day curve is slightly above, indicating the presence of more large pores. Samples water-cured for 7 and 28 days are characterized by a finer porosity. The percolation radius decreases significantly as the maturity at the time of testing increases. According to the Kelvin’s law (11), it means that as hydration proceeds, the R.H. that must be achieved within the material in order to empty all pores (through the entire porous body) of a given entry size decreases.

\[ r_p = \frac{2\sigma_{lv} \cdot v_l}{RT \ln(R.H.)} (R.H. \downarrow \Rightarrow r_p \downarrow) \]  \hspace{1cm} (11)

3.3 Diffusion coefficient

Figures 10 and 11 show the relationship between the diffusion coefficient and water content for the 3-day and 28-day cured specimens respectively, evaluated at 5 different
depths in the specimen, namely 1, 3, 5, 7 and 9 mm from the drying surface. For each depth, experimental data follow an S-shape trend (on a semi-log graph). The observed tendency is consistent with the results of previous studies on both concrete [3, 10] and wood [9].

Results obtained clearly show a dependence of the coefficient of diffusion on moisture content of the material. On figures 10 and 11, one can observe that for mid-range water contents, the curve slope is moderate, while for high water contents it generally tends to increase significantly.
The comparison of 1-, 3- and 5-mm depth curves on both graphs indicate that the diffusion coefficient in the upper layers of the specimens decreases as the curing duration is extended. This observation is consistent with the corresponding refinement of the porosity shown in figure 9 and tends to indicate a strong dependence of the coefficient of diffusion on the maturity of the material. However, in deeper layers, the effect of initial curing vanishes, and it even appears to be reversed to some degree (9-mm depth). On the one hand, this surprising behavior might be due to the lack of experimental values. In fact, the $\partial C/\partial x$ derivative term on which relies the calculation of the diffusion coefficient is very dependent of the accuracy of the curve fitting. On the second hand, it may directly come from the assumption made to evaluate the profile of water concentration. As explained previously, the assumption has been made that the distribution of moisture at a given drying time and a given distance from the drying surface is the same without regard to the thickness of the specimen. This is not necessarily true since in a specimen having a thickness two times ($2l_1$) that of a reference sample ($l_1$) for instance, the water flux that comes from the underneath layer ($l_2$) in the thicker sample has to go through the upper layer ($l_1$) to get to the drying surface. Though it will have to be verified experimentally with further tests and comparisons with a reliable method, limits of this assumption may be accountable for the unexpected observation made when comparing coefficient of diffusion calculated at deeper locations from the drying surface.

Nevertheless, it has to be stressed that deeper locations are kept longer at a high R.H. and are thus likely to hydrate significantly more, as demonstrated in the graphs of figures 10 and 11. Conversely, the coefficient of diffusion increases near the surface as the upper layers dry out earlier, which leads to an earlier ending or at least a deceleration of the hydration process. Then, the validity of these results could be questioned, since a single set of diffusion coefficients for a given initial maturity in fact integrates some potential microstructural modification as a function of the distance to the drying surface and hence, what could be referred to as a spatial maturity gradient. It is in fact impossible, even with samples as thin as those used in this study, to stop the system and determine the actual single diffusion coefficient curve for a given maturity. The results obtained in the surface layers after, however, can be assumed to fairly represent the upper boundary of the spectrum within which the coefficient is varying from a given initial maturity. It at least allows to appreciate to what extent it might evolve during the drying process and then, with the use of a model, to evaluate to what extent the predictions can be affected by taking it into account or not.

Values of the diffusion coefficient have also been calculated for 1- and 7-day curing. The calculated values lie in the following ranges:

1-day: $1.1 \times 10^{-13}$ to $4.2 \times 10^{-10}$ m²/s
3-day: $1.1 \times 10^{-13}$ to $2.4 \times 10^{-10}$ m²/s
7-day: $1.8 \times 10^{-13}$ to $1.4 \times 10^{-10}$ m²/s
28-day: $4.4 \times 10^{-13}$ to $1.5 \times 10^{-10}$ m²/s
3.4 Drying shrinkage
Figure 12 presents results of shrinkage tests carried out on very thin mortar samples after more than 16 months of exposure to the various relative humidities. It is obvious that drying shrinkage is closely linked to desorption. The desorption curves of the shrinkage prisms, shown on figure 13, correspond to the curves presented previously in figure 8, provided that the data from the pressure membrane tests at high R.H. are neglected and that the weight loss is used in lieu of the water content. Between 100% and 75% R.H., both the drying shrinkage curves show an approximately linear behavior. From 75% R.H. to 50% R.H. however, while the weight loss curves do not change drastically, there is a rather sharp reduction in the slope of the shrinkage curves, irrespective to the water curing duration. This change in the shrinkage R.H. relationship probably reflects a change in terms of shrinkage driving mechanisms [13]. It is known that below a certain R.H. level, which would be around 50% R.H. according to basic calculations [14] menisci can no longer form and capillary stresses vanish. Besides, although the capillary stress increase with the diminution of the percolation pore radius, the total volume of water is decreasing at the same time, such that the global effect is most likely non linear.

As for sorption and diffusion coefficient, drying shrinkage is significantly influenced by the maturity. The influence appears to become more pronounced as the relative humidity decreases, the ratio between long-term shrinkage values of 1-day and 28-day cured specimens at 53% R.H. being of the order of 1.5. This can have very significant practical consequences as far as cracking of concrete is concerned. Though other important aspects involved in the cracking issue such as creep are not taken into account here, it stresses the importance of water curing, especially in view of skin cracking problems.
Given the relative rapidity and ease with which the first few millimeters can prematurely be dried out, these results are not only going to be useful as input parameters in a model, but they certainly call for attention from a practical point perspective. Though it may sound strange, very few reliable data are reported in the literature regarding the actual effect of water curing duration over drying shrinkage.

Finally, the attention of the reader is brought to the fact that at 97% R.H., all except the 1-day specimens ultimately undergo some swelling rather than shrinkage. Correspondingly, on figure 13, a small mass increase of these specimens in the 97% R.H. environment is observed. Both the swelling and the weight gain is attributed to the continuation of hydration under favorable conditions. At the present time however, no rational explanation is available to account for the peculiar 1-day specimens behavior. Analyzing such a result is complicated by the extremely low degree of hydration at the time the experiment was undertaken.

![Figure 13: Shrinkage prisms weight loss as a function of relative humidity](image)

**4. Conclusion**

The results reported in the present study clearly show the influence of maturity on the mass transfer properties of a 0.40 W/C Portland cement mortar, more specifically the sorption isotherms and the relationship between the diffusion coefficient and R.H. Such a conclusion is certainly not a tremendous surprise, since the porous network of mortar, which basically controls these properties, is a function of that paramount maturity parameter and, thus, of the water curing regimen duration. Nevertheless, it provides
some useful and rather complete data in a segment of the experimental field that was barely virgin. In particular, they will soon be used as input data in a model designed to predict the behavior of concrete repairs submitted to hygro-thermal loading. It is anticipated that the simulations will help for instance evaluating the sensitivity of the predictions to the actual transfer properties changes undergone by an hydrating material and the necessity of characterizing precisely those variations.

In addition to its sensitivity to maturity, the dependence of the mortar diffusion coefficient on the water content has clearly been demonstrated. As previously reported by different authors, it has been found that the coefficient of diffusion decreases along with the water content, the relationship being characterized by an S-shape [10,15]. The diffusion coefficient results as such are not to be taken as a pure material property since they integrate significant and unavoidable changes in maturity that occur during the experiment. Nevertheless, for a given material and a given maturity, it provides a realistic range between which the actual relationship evolves right from the outset of drying. Still, additional research is necessary to soundly assess the validity of this test procedure based on the assumption that the water distribution from the drying surface is the same, irrespective to the sample thickness.

Finally, the drying shrinkage results clearly demonstrate a significant dependency of the material behavior on the degree of hydration. When extending the water curing duration from 1 day to 28 days, the ultimate shrinkage value at 53% R.H. was approximately cut by one third. Such a finding, though again it is not much surprising, certainly has some practical interest in view of better controlling shrinkage cracking, especially considering the lack of reliable data on this particular issue. Besides, as the mortar is exposed to lower relative humidity, shrinkage increases almost linearly from 100% R.H. to approximately 75% R.H., after which the rate becomes lower, owing presumably to some changes in terms of physical mechanisms.

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6. References


