MODELING OF INTERNAL RELATIVE HUMIDITY EVOLUTION IN CEMENT PASTES AT EARLY-AGES

Hui Chen (1), Mateusz Wyrzykowski (2), Karen Scrivener (1), and Pietro Lura (2,3)

(1) Laboratory of construction material, École Polytechnique Fédérale de Lausanne, Switzerland
(2) Empa - Swiss Federal Laboratories for Materials Science and Technology, Switzerland
(3) Institute for Building Materials, ETH-Zurich, Switzerland

Abstract

High-performance concrete has shown to be more sensitive to early-age cracking than traditional concrete. Such cracks constitute a serious problem with regard to strength and especially to durability. Autogenous deformation is one of the main factors to cause early age cracking in high-performance concrete and needs therefore to be predicted and controlled.

As cement hydration proceeds in low water-to-binder ratio concrete, the water becomes bound into hydration products and adsorbed on their surfaces. The capillary pores are emptied and the air-water menisci become progressively smaller. As a consequence, the internal relative humidity drops (self-desiccation) and an increasing capillary tension is produced in the pore fluid, which may reach several tens of MPa. The capillary stress exerts a compressive stress on the whole porous body, resulting in bulk shrinkage (self-desiccation shrinkage).

In this paper, the chemical shrinkage and the pore size distribution of cement paste (measured by mercury intrusion porosity) are used as input data for the calculation of relative humidity (RH) of Portland cement paste with different water to cement ratio (0.30, 0.35, 0.40). These calculated RH curves are then compared to measured curves, finding satisfactory agreement at early ages but a growing divergence at later ages.

1. INTRODUCTION

In high-performance concrete, the low water-to-binder ratio (w/b) causes a significant drop in the internal relative humidity (RH) of the cement paste during sealed hydration. Closely related to this autogenous RH change, the cement paste undergoes autogenous shrinkage. Autogenous shrinkage should be limited because it may induce microcracking or macrocracking and impair the concrete quality [1].

In particular, as cement hydration proceeds in low w/b cement paste, the water becomes bound into hydration products and adsorbed on their surfaces. As long as the cement paste is in a fluid state, it is not able to sustain the internal voids created by chemical shrinkage. When
a solid skeleton forms in the hardening paste, the stiffness increases and gas bubbles start to nucleate and grow in the larger pores [2]. After setting, the capillary pores are emptied by chemical shrinkage and the air-water menisci become progressively smaller. The presence of menisci simultaneously causes tensile menisci become progressively smaller. The presence of menisci simultaneously causes tensile stresses in the pore fluid and a decrease in the internal RH. The RH drop results also in a change in the thickness of the water layer adsorbed on the solid surfaces [3]. This is accompanied by changes both in the surface tension of the solids and in the disjoining pressure of adsorbed water between solid surfaces. At this early stage of hydration, the stiffness of the paste is so low and the viscous behaviour so pronounced that the slightest stress acting on the system results in a large deformation of the cement paste [4].

Hua et al. [5] assumed that the main cause of autogenous shrinkage of a cement paste is capillary tension in the pore fluid. They used mercury intrusion porosimetry (MIP) to determine the Kelvin radius and as a consequence the capillary tension in the pore water at different ages. Some difficulties are connected with this technique. For example, drying of the paste before mercury intrusion may damage its pore structure, especially at early ages. Also, large internal pores that are accessible only through small entries are identified as smaller ones (the so-called inkbottle effect [6]). A more direct approach is to calculate the capillary depression from an internal state parameter of the hardening cement paste, such as the internal RH. Lura et al. [4] calculated the autogenous shrinkage of a cement paste in the first week of hydration with the capillary tension approach, using RH measurements to calculate the capillary depression. Since part of the RH drop in the cement paste is due to dissolved salts in the pore solution, a method was suggested to separate this effect from self-desiccation and to calculate the actual stress in the pore fluid associated with menisci formation [4].

In this paper, the chemical shrinkage and the pore size distribution of cement paste (measured by MIP) are used as input data for the calculation of relative humidity (RH) of Portland cement paste with different water to cement ratio (0.30, 0.35, 0.40). These calculated RH curves are then compared to the measured RH developments.

2. MATERIALS

In this research, rapid-hardening Portland cement (CEM I 52.5R) with Blaine fineness 4025 cm²/g was used. The XRD-Rietveld phase composition by mass is: alite 68.1%, belite 9.2%, ferrite 8.7%, aluminate 4.9% periclase 0.5%, gypsum 3.6%, hemihydrate 1.8%, anhydrite 0.7%, calcite 1%, quartz 0.4%, arcanite 1.2%. 300 grams of cement were mixed in an epicyclic Perrier mixer; demineralised water was added according to different w/c. The pastes were mixed at 60 r/min for 1 min. After stopping for 20 s to scrape the bowl, another minute of mixing followed at 120 r/min. Samples were cured at 20°C under sealed condition.

3. METHODS

3.1 Chemical shrinkage

Chemical shrinkage measures the absolute volume reduction in a cement paste, due to the fact that the volume occupied by the hydration products is lower than that of the reactants. According to ASTM C 1608-07, after inserting the fresh cement paste into a transparent polystyrene vial (diameter 2.3 mm, height 59 mm), the vial was gently filled distilled water. The vial was then sealed by a rubber stopper with a capillary pipe in its centre. A syringe was used to inject red-coloured oil on the top of the water in the capillary to visually detect the water level change derived from chemical shrinkage. The water level was monitored by a
webcam connected to a desktop computer, which took an image every 20 minutes until 7 days of hydration. For each w/c, 2 to 3 samples were tested and the result shows their average [7].

3.2 Mercury intrusion porosimetry

Mercury intrusion porosity was used to investigate the cumulative volume of cement paste samples with the age of 8 hours, 24 hours, 72 hours and 168 hours. The porosimeter used was Porotec equipped with two devices. The first applies low pressure of Hg up to 400 kPa to measure macroporosity. The second applies a maximum pressure of 400 MPa for the measurement of microporosity. For each analysis, around 1 gram (6-7 pieces) of cubic cement paste samples was placed in the cell of the dilatometer. The contact angle was given at 145° and a model of cylindrical pore was chosen.

3.3 Internal relative humidity

The internal RH development of the cement pastes was measured with two AW-DIO water-activity probes by Rotronic, equipped with high-precision RH sensors with the global nominal accuracy determined by the producer as ±1% RH. The RH stations were connected with a thermal bath with the temperature of 20±1°C. At 20 hours from mixing, the cement paste samples were crushed and then inserted into the sealed measuring chambers of the Rotronic stations, where the internal RH was measured up to 168 hours. The calibration of the stations was conducted using saturated salt solutions in the range 75 to 100%. Duplicate measurements were performed for each mixture.

![Graphs showing chemical shrinkage](image)

Figure 1: Chemical shrinkage of cement paste with different thickness with w/c 0.30 (left) and chemical shrinkage of cement paste of different w/c with the thickness of 5 mm (right).

4. RESULTS

4.1 Chemical shrinkage

It is well-known that in low water to cement pastes, the pore structure depercolates at early ages. As a consequence, extremely thin cement paste samples should be used to measure chemical shrinkage, to ensure that their pores remain saturated [8]. In order to investigate the impact of thickness on the measured chemical shrinkage of cement paste, samples of w/c 0.3 with thickness 2.5, 5, 10, and 20 mm were tested. Figure 1, left, shows chemical shrinkage plotted as mm³ per gram of cement in the mixture. All the curves show about the same
chemical shrinkage up to 20 hours hydration. After about 20 hours, the curves diverge, with the thinnest samples reaching the highest chemical shrinkage at seven days, about 60 mm$^3$/g. On the other hand, after 7 days the value for the thickest sample of 20 mm was 0.04 mm$^3$/g, only 66% of the thinnest. It is noticed that the differences between 2.5 and 5 mm thickness are minor, so that no higher chemical shrinkage is expected by measuring on even thinner samples. For this reason, the chemical shrinkage curves for cement pastes of different w/c shown in Figure 1, right, were measured on 5 mm-thick samples. Notice the higher chemical shrinkage for the higher w/c. It is important to remark here that as chemical shrinkage measurements are based on water imbibition by the cement paste, these pastes hydrate as open systems under saturated conditions. Therefore, both their degree of hydration and their chemical shrinkage are higher than for the same pastes hydrating under sealed conditions.

4.2 Mercury intrusion porosimetry

The evolution of the pore size distribution measured by MIP as a function of age for cement pastes with different w/c is shown in Figure 2. Both the total porosity is decreasing and the pore structure becomes finer when the w/c of the pastes is decreased. For all the cement pastes, the most significant changes of the pore structure are observed in the first 3 days, while the difference between 3 and 7 days is minor. This is due to the fast hydration rate in the first 3 days, as can be also observed in the chemical shrinkage results (Figure 1, right).

![Figure 2: MIP cumulative volume as a function of pore radius for different hydration times. Data for w/c=0.30 (above, left), w/c 0.35 (above, right) and w/c 0.40 (below, left).](image)

4.1 Internal relative humidity

The internal relative humidity development of the cement pastes with different w/c is shown in Figure 3. For each w/c, two separate measurements are shown, to allow an
appreciation of the experimental uncertainty. As expected, the RH drop is highest for w/c 0.30, whereas the differences between the other pastes are minor in the first week.

![Figure 3: Internal relative humidity development as a function of hydration time for curing at 20ºC. Data for w/c=0.30, w/c 0.35 and w/c 0.40 (2 measurements for each paste).](image)

5. DISCUSSION

Due to the chemical shrinkage occurring during cement hydration, empty pores are created within the cement paste. The menisci between the vapour and the liquid become progressively smaller as more porosity is emptied. Due to the creation of the menisci, the internal RH decreases and tensile stresses in the pore fluid arise. The emptying of the capillary pores both induces shrinkage and influences the kinetics of cement hydration, decreasing the hydration speed and limiting the final degree of hydration. The relationship between the radius of the menisci and the internal RH can be expressed by the Kelvin equation [9]:

\[ RH = \exp \left( -\frac{2\gamma \cdot \cos \theta \cdot M_W}{r \cdot RT \cdot \rho} \right) \]  

where \( R \) is the universal gas constant (8.314 J/mol/K), \( T \) is the temperature (293.15 K), \( RH \) is the internal relative humidity, and \( M_W \) (0.01802 kg/mol) is the molar weight of pore solution. \( \rho \) is the density of water (1000 kg/m\(^3\)), \( \theta \) is the contact angle (assumed as 0°), \( \gamma \) is the surface tension of the pore fluid (0.073 N/m, value for pure water) and \( r \) is the radius of the menisci, also known as Kelvin radius.

To calculate the largest capillary pore radius filled with water, the chemical shrinkage and MIP results can be combined [5]. As suggested by Hua et al. [5], the radius of the pores entrained by the mercury according to the Washburn equation is equivalent to the Kelvin radius. With this assumption, by combining the volume of the empty pores at a certain age (i.e., the chemical shrinkage) with a MIP pore size distribution measured at the same age, an approximated value for the the Kelvin radius, \( r_0 \), is obtained (Figure 4, left).

A refinement of this approach was proposed by Bentz et al. [10], who suggested that the actual Kelvin radius, \( r \), is smaller than \( r_0 \), due to the presence on the surface of the pores of adsorbed water layers of thickness \( t \) (Figure 4, right):

\[ r = r_0 - t \]  

This thickness is dependent on the RH and can be calculated with an empirical fit of the experimental data by Badmann et al. [3]:
\[ t = 0.385 - 0.189 \cdot \ln(-\ln(RH)) \]  

(3)

As the thickness \( t \) is dependent on RH (which is unknown at this point in the calculation), \( r \) cannot be found directly and an iterative procedure is needed. This involves calculating a first RH\(_0\) with eq. (1) based on \( r_0 \), which is then used for calculating a value \( t_0 \) with eq. (3). Using \( t_0 \) and \( r_0 \) in eq. (2) yields a better approximation of the Kelvin radius, \( r_1 \). Based on \( r_1 \), RH\(_1\) is calculated with Eq.1 and \( t_1 \) with eq. (3) based on RH\(_1\). At this point, \( r_2 \) is found as \( r_2 = r_0 - t_1 \). The whole procedure is repeated until the thickness \( t \) converges. In practice, only a couple of iterations are needed. All results are shown in Table 1 and the calculated RH developments are compared to the measured ones in Figure 5.

Figure 4: Procedure for the determination of \( r_0 \) from chemical shrinkage and MIP curves (left). Schematic representation of menisci and adsorbed water layer in capillary pores (right).

As seen from Table 1 and Figure 5, the correction to the calculated internal RH taking into account the presence of the adsorbed water layers is almost negligible at high RH and remains small, at most 1%, within the considered RH range. This is due to the small thickness of the adsorbed layers relative to the radius of the menisci (at most 10% for our data). However, the influence of \( t \) would become more important for smaller sizes of the menisci; for instance, starting from \( r_0 = 4 \) nm and RH\(_0\)=76.4%, \( t = 0.6 \) nm and an actual RH=72.8 % are calculated.

Table 1: Calculated radii of menisci, thickness of adsorbed water layer and internal RH

| w/c | 8h   | 156.4 | 99.3 | 1.32 | 155.1 | 99.3 |
|     |      |       |      |      |       |      |
| 0.30 | 0.30  | 18.8  | 94.4 | 0.92 | 17.9  | 94.2 |
| 0.30  | 0.30  | 15.8  | 93.4 | 0.88 | 14.9  | 93.0 |
| 0.30  | 0.30  | 8.8   | 88.5 | 0.77 | 8.1   | 87.5 |
| 0.35  | 0.35  | 340.2 | 99.7 | 1.47 | 338.7 | 99.7 |
| 0.35  | 0.35  | 23.0  | 95.4 | 0.95 | 22.0  | 95.2 |
| 0.35  | 0.35  | 13.8  | 92.5 | 0.85 | 13.0  | 92.0 |
| 0.35  | 0.35  | 13.1  | 92.1 | 0.84 | 12.3  | 91.6 |
| 0.40  | 0.40  | 520.4 | 99.8 | 1.55 | 518.4 | 99.8 |
| 0.30  | 1d   | 44.6  | 97.6 | 1.08 | 43.5  | 97.6 |
| 0.30  | 3d   | 19.3  | 94.6 | 0.92 | 18.4  | 94.3 |
| 0.30  | 7d   | 18.4  | 94.3 | 0.91 | 17.5  | 94.0 |
Figure 5: Measured internal RH (black lines) against RH calculated either using directly $r_0$ obtained from chemical shrinkage and MIP curves (“Calculated (Kelvin)” curve, in red) or taking into account the thickness of the adsorbed layer (“Calculated (Kelvin + t)”, blue line). Data for w/c=0.30 (above, left), w/c 0.35 (above, right) and w/c 0.40 (below, left).

The calculated and measured RH developments are quite close in the first 3 days and diverge sensibly (about 5%) at 7 days. A number of factors could be responsible for this. The ions dissolved in the pore fluid, especially the alkali, sulphate and hydroxyl ions, contribute to reduce the activity of the water and with it the internal RH [4]. This effect can be calculated as a first approximation with Raoult’s law. Based on expressed pore fluid compositions found in literature, the RH drop in a cement paste due to dissolved salts was estimated as several percents [4]. In a later paper, the pore solution composition of a w/c 0.35 cement paste with 5% silica fume was measured during hydration, yielding a RH drop at 2 days of 5-6% only due to dissolved salts [11]. As the pore solution becomes more concentrated with the progress of hydration and self-desiccation, the RH drop due to salts could explain the progressive divergence between calculated and measured values at lower RH.

Other factors that might explain the difference between the calculated and measured RH are the experimental uncertainties in the measured MIP and chemical shrinkage curves. However, a sensitivity analysis using extreme values for MIP and chemical shrinkage (not shown in this paper) yielded minimal differences in the calculated values. The ink-bottle effect, which is known to bias the pore size distribution measured by MIP towards smaller pore radii, would actually be expected to influence the calculated RH towards lower values.
About the chemical shrinkage value used in the calculations, two observations should be made. The chemical shrinkage taken from experiments is necessarily measured on saturated samples, while the calculated RH is for sealed, self-desiccating samples. Part of the chemical shrinkage, that occurring before setting, induces an external volume change of the pastes and does not contribute towards emptying the porosity [2]. However, to take into account both these effects, a lower chemical shrinkage would need to be used, which would increase the differences with the measured RH. Finally, the parameters assumed when using the Kelvin equation, in particular the molar weight of pore solution, its density, surface tension and contact angle, could be better determined for specific pore solution compositions.

6. CONCLUSIONS

In this paper, the chemical shrinkage and the pore size distribution of cement paste (measured by mercury intrusion porosity) are used as input data for the calculation of relative humidity (RH) of Portland cement paste with different water to cement ratio (0.30, 0.35, 0.40). These calculated RH curves are then compared to measured curves, finding satisfactory agreement at early ages but a growing divergence at later ages. A possible explanation of this divergence is the reduction of water activity due to ions dissolved in the pore solution. However, other errors including experimental uncertainties and incorrect assumption for the parameters in the Kelvin equation cannot be excluded.

REFERENCES