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DEVELOPMENT OF INTERIOR RELATIVE HUMIDITY DUE TO SELF-DESICCATION IN BLENDED CEMENTITIOUS SYSTEM

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Abstract

In engineering practise, interior relative humidity (RH) of concrete significantly affects the transport properties and thus the service life of concrete structures. In this paper, the development of RH due to self-desiccation in blended cement pastes was studied from 1 day to 1.5 years. The pore structure and non-evaporable water content at same ages were determined by mercury intrusion porosimetry and thermogravimetric analysis, respectively. The results revealed that interior RH was significantly reduced at the first 105 days' curing and falls off slightly afterwards, regardless of water to binder ratios and type of blends. Compared to ordinary Portland cement (OPC) paste, the OPC paste blended with slag shows much lower interior RH, whereas the addition of fly ash slightly increases the interior RH. Minor amount of limestone addition i.e., 5% wt. greatly increases the RH in ternary system consisting of OPC, slag and limestone, whilst slightly decreases the RH in OPC paste blended with fly ash. In the presence of blends, high total porosity corresponds to low interior RH. In case of self-desiccation, it is concluded that interior RH is mainly controlled by average pore size in the cement-based materials.

1. Introduction

The interior relative humidity (RH) of cementitious system has been of great interest over the past decade due to its crucial role on cement hydration and potential impact on engineering properties. By tracing the evolution of interior RH, one can reveal the hydration kinetics for a cementitious system. Suspended hydration was found at 90% RH [1]. Through thermodynamic analysis, Flatt et al. [2] figured out that alite stops hydration at RH approximately below 80%, because a negative capillary pressure opposes the chemical reaction. Usually, a good curing condition at early age is very important for the development of concrete microstructure, and hence improving its durability and performance [3]. The interior RH can significantly affect the gas permeation, the rate of water absorption, autogenous shrinkage and ionic transport [4-7].

In many cases, the drop of interior RH in cementitious system can be mainly attributed to continuous cement hydration, also referred to as self-desiccation. As the hydration of cement, the available free water in capillary pores is reacting and transforming into chemically bound water. At the same time, the hydration products are gradually filling the capillary pore space, reducing the porosity and decreasing RH where the pores remain saturated via Kelvin-Laplace effect [1]. On the other hand, the gas bubbles, i.e. air and water vapour, start to nucleate and grow in larger pores [6]. Menisci are formed at the interface between pore solution and water vapour. As the consumption of free capillary water, the capillary pores are progressively smaller whilst the curvatures of the menisci are higher.

In order to better understand the performance of cement-based materials, knowledge of the time-dependent interior RH is essential. However, current cognition is inadequate for this purpose. Especially for the blended cements, the research in this field is seriously insufficient.

The aim of this study is to investigate the time-dependent interior RH due to continuous self-desiccation in blended cementitious system. The influence factors, such as curing age, water to binder ratio and supplementary cementitious materials (SCMs), i.e. fly ash, ground granulated blast furnace slag and limestone powder, were taken into account. The measured RH value was further analyzed in relation to microstructure parameters, i.e. porosity, pore size and free capillary water content.

2. Experimental program

2.1 Raw materials and sample preparation

In this study, cement paste specimens are cast. The binders are binary or ternary mixtures of ordinary Portland cement (OPC) blended with low calcium fly ash (FA), ground granulated blast furnace slag (GGBFS) or limestone powder (LP). The replacement of OPC by SCMs is at dosage levels of 30% for FA, 70% for GGBFS and 5% for LP by mass of cement binder. Water to binder ratio (w/b) varies from 0.35 to 0.6. Paste specimens were curing under sealed condition. Ten series of cement binders were used in this work. The detailed mixture design for all binders was presented in Table 1.

Table 1: Mix proportions (weight percentage) used for the binders.

Mixture	OPC	FA	BFS	LP	W/B
P35	100%	-	-	-	0.35
P40	100%	-	-	-	0.4
P50	100%	-	-	-	0.5
P60	100%	-	-	-	0.6
PF50	70%	30%	-	-	0.5
PFL50	65%	30%	-	5%	0.5
PB40	30%	-	70%	-	0.4

PB50	30%	-	70%	-	0.5
PB60	30%	-	70%	-	0.6
PBL50	25%	-	70%	5%	0.5

2.2 Measurement of relative humidity

The measurement of RH was performed with Rotronic HygroClip2 sensors, which can be used to measure the RH and temperature simultaneously. The nominal accuracy of the sensors is ±0.5% RH/±0.1 °C. Before and after each measurement cycle, the sensors were calibrated with three saturated salt solutions at 65%, 80% and 95% RH, which encompassed all of the measured RH of the paste specimens in this study. This allows gaining better accuracy for the measured value. The temperature during the whole measurement was controlled at 20 ± 0.1 ºC. The set-up for RH measurement is illustrated in Fig. 1.

Fig. 1 Set-up for RH measurement

All RH measurements were performed on paste specimens at curing age of 1 day, 28 days, 105 days, 200 days and 575 days, which aims to understand the moisture loss due to continuous self-desiccation. Prior to test, cement paste with expected curing age was splitted into pieces. These pieces specimens were then placed into a sample holder and sealed thereafter. The pieces specimens used for RH measurement must be as small as possible to easily reach equilibrium of moisture. RH readings were logged at 2 minutes interval using a data logger until stable RH data was derived. The presented RH values in this paper were obtained on the basis of the average of two sensors. In all cases, the absolute differences between the two sensors were approximately unchanged over time, with maximum 1%. The differences can be ascribed to the systematic and random errors during calibration and measurement.

3. Results and discussions

The experimental results are presented in five groups. The first two groups present the development of interior RH due to continuous self-desiccation in OPC paste specimens and blended cement paste specimens, respectively. The subsequent three groups analyzed the microstructure characteristics and their correlations to interior RH in the paste specimens, including total porosity *vs.* RH, average pore size *vs.* RH, free capillary water content *vs.* RH. The total porosity and average pore size were measured by mercury intrusion porosimetry (MIP). The free capillary water content was evaluated by thermogravimetric analysis (TGA).

3.1 Development of relative humidity with curing age in OPC pastes

For hardened cement paste (hcp) with sealed curing, the interior RH presents in a homogeneous distribution due to no ingress of extra water. In this case, the free water in the capillary pores will be gradually consumed with cement hydration and transformed into chemically bound water in hydration products, filling the capillary pore space. As a result, the interior RH is expected to be decreasing with cement hydration, also known as self-desiccation. This finding is proved by the measured results in following paragraphs. Note that RH measurements were performed in duplicate pairs, and the average value was used for the plots. In all cases, the differences between duplicate measurements are within ±1%.

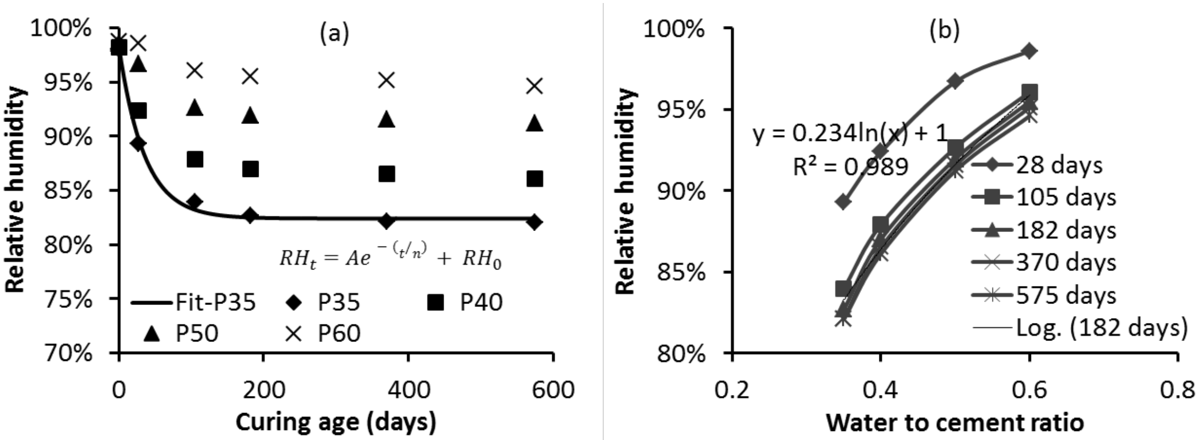


Fig. 2 Development of interior relative humidity with curing age in OPC pastes (a) and effect of water to cement ratio on interior RH in OPC pastes (b)

Fig. 2a plots the development of interior RH due to self-desiccation up to 575 days in OPC pastes with w/c ratios from 0.35 to 0.6. The data clearly show that the interior RH of all OPC pastes is significantly decreased in the first 105 days, followed by a gradual decrease afterwards. In addition, the effect of self-desiccation substantially increases with the decrease of w/c. The similar findings have been also presented in previous studies [8]. Quantitatively, it is found that the interior RH is negatively and exponentially correlated to the curing age (t), which can be expressed as Eq. (1):

$$\mathrm{RH}_t = A \cdot e^{-(\frac{t}{n})} + RH_0 \tag{1}$$

There are three parameters in the above equation, A, n and RH_0, which can be all figured out by curve fittings in this study. Parameter A is related to the material and mainly affected by w/c. n denotes ageing effect due to curing. RH_0 represents the humidity level at infinite curing age. According to curve fittings on data in Fig. 2a, these parameters as well as standard deviations corresponding to different OPC binders are tabulated in table 2.

Table 2: Parameters for Eq. (1) in various OPC binders

Mixtures	**A**	**n**	**RH_0**	**R^2**
P35	0.154	36.87	0.82	0.9925
P40	0.118	42.47	0.86	0.9924
P50	0.075	68.75	0.91	0.9893
P60	0.044	106.76	0.94	0.9657

For further analysis, the effect of w/c on interior RH at various curing ages is illustrated in Fig. 2b. As can be seen, RH is expressed as a function of w/c. For maturated systems, i.e. after 182 days' hydration, the evolution of interior RH is very limited, therefore the curves thereafter appear to be overlapped. According to the curve fitting on the presented results, logarithmic relationships are observed regardless of curing age. Take the RH data at 182 days for an example, RH is logarithmically in relation to w/c, with high correlation coefficient 0.989.

$$\mathrm{RH}_{w/c} = 0.234 \cdot \ln\left(\frac{\mathrm{w}}{\mathrm{c}}\right) + 1 \tag{2}$$

In combination of Eq. (1) and Eq. (2), the interior RH is summarized as Eq. (3). This equation indicates that, in case of sealed curing condition, the interior RH of OPC paste systems due to self-desiccation can be expressed as a function of both curing age and w/c. In this respect, Eq. (3) can be used as a tool to predict the interior RH due to long term self-desiccation in OPC cement pastes. Moreover, it provides a reference for the initial mixture design in case the interior RH is of concern.

$$\mathrm{RH} = \mathrm{RH}_t \cdot \mathrm{RH}_{\frac{w}{c}} = \left[A \cdot e^{-\left(\frac{t}{n}\right)} + RH_0\right] \cdot \left[0.234 \cdot \ln\left(\frac{\mathrm{w}}{\mathrm{c}}\right) + 1\right] \tag{3}$$

3.2 Development of relative humidity with curing age in blended cement pastes

The use of SCMs causes changes in the interior RH. This is due to the changes of initial particle size distribution and chemical constitutions, resulting in changes of hydration process and pore structure formation as well as pore solution chemistry.

Fig. 3a and 3b show the time-related RH in pastes made with various SCMs. For comparison, the data of neat OPC paste P50 is displayed as well. It is observed from Fig. 3a that regardless of w/b, the curves for slag-blended cement pastes are all below the reference specimen P50, which means that slag has a big influence on the reduction of RH in the paste systems. On the contrary, the curves for FA-blended cement pastes are a little higher than reference P50 in the entire curing age (Fig. 3b), which means that the inclusion of FA slightly increases the RH in the paste systems. It is also found that, in comparison with neat OPC binders, the effect w/b plays less important role in the change of interior RH for slag-blended cement pastes. For instance, at 182 days, the interior RH in w/c 0.6 system (P60) is 8.46% higher than that in w/c 0.4 system (P40), nevertheless, the difference is 4.4% when comparing PB60 with PB40.

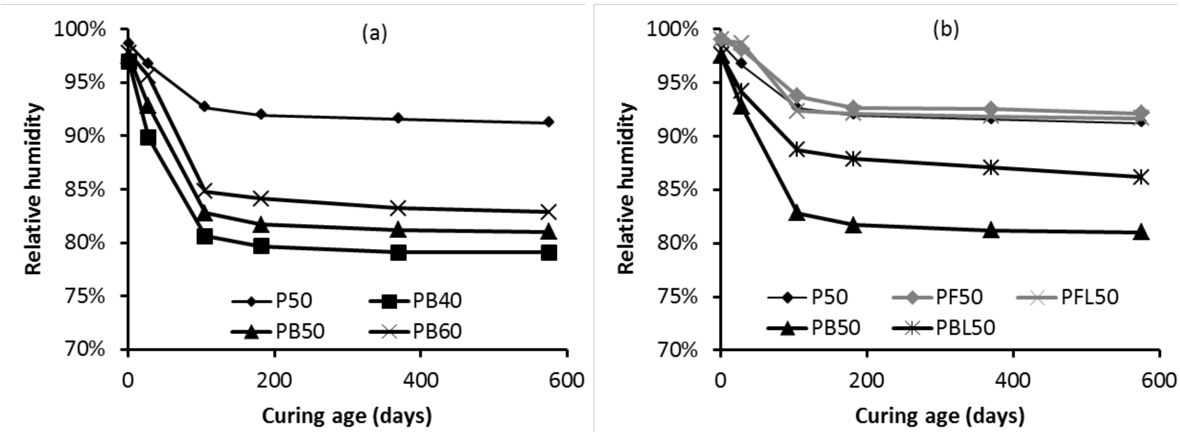


Fig. 3 Development of interior relative humidity with hydration age: (a) effect of w/b in slag-containing pastes; (b) effect of various blended materials

The different influences on interior RH between FA and slag can be attributed to their distinct effects on cement hydration. First of all, partial replacement of OPC by either FA or slag increases the effective w/c ratio, which may potentially increase the interior RH of the paste materials. Secondly, both slag and FA are pozzolana materials, the ingredient SiO_2 reacts with $Ca(OH)_2$ and produces extra C-S-H. Consequently the capillary pores can be refined, which tends to reduce the interior RH. This pozzolanic behaviour could offset the increased RH due to replacement of mineral additives, i.e. FA, slag. Thirdly, the pozzolanic reactivity of slag is much stronger than FA, which consumes more free water and produces finer pore structure. Moreover, due to latent hydraulic reactions [9], slag not only reacts with CH, but also consumes water at later ages, which further reduces the interior RH of paste specimen.

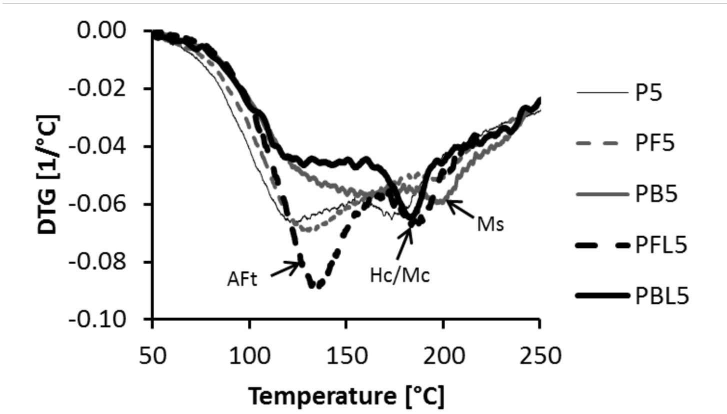


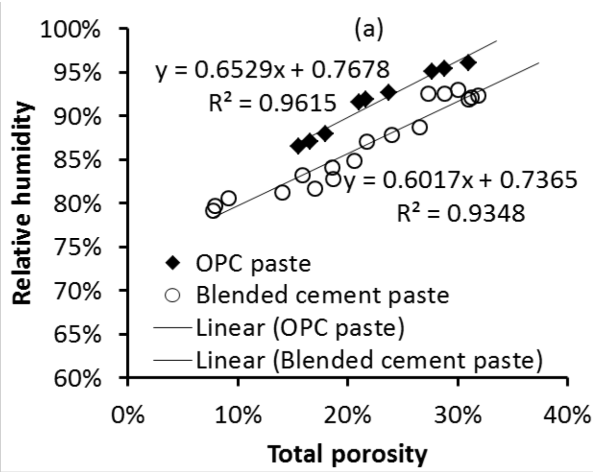
Fig. 4 Thermogravimetric analysis on pozzolana-containing paste specimens with and without LP curing 200 days. Hc: Hemicarboaluminate, Mc: monocarboaluminate, Ms: monosulphate, AFt: ettringite

With further addition of LP into ternary cement, the change of interior RH becomes more complicated. As seen from Fig. 3, the interior RH of paste PFL50 is a little lower than that of paste PF50, while inversely the interior RH of paste PBL50 is much higher than that of paste without LP, i.e. PB50. The variable effect of LP addition on interior RH indicates the distinct combined effects of LP and alumina-contained additives (i.e. FA, slag), which can be further

verified by the results from TGA. Fig. 4 confirms the changes in AFm phases when limestone is present that carboaluminate is formed instead of monosulphate. Even in the neat OPC paste, i.e. P5, much more carboaluminate is formed than monosulphate, which is as a result of $CaCO_3$ inclusion in the raw OPC material. In addition, much more ettringite is formed in specimen PFL5 than PBL5. The formation of considerable amount of ettringite has also been reported in Weerdt et al. [10], where 30% FA and 5% LP is added into cement.
Two aspects can be introduced herein to interpret the observation of large amount of ettringite due to combined addition of FA and LP: (1) The combination of FA and LP promotes the formation of alumina-carbonate compounds, and stabilises alumina-carbonate in favour of monosulphate, whereby the transformation of ettringite to monosulphate at later hydration age is hampered [11]; (2) FA-blended system is much porous and even FA particles tend to be hollow in shape, which can promote the formation of voluminous ettringite.

3.3 Total porosity *vs.* RH

Fig. 5a illustrates the relationship between interior RH and total porosity for binders made with and without SCMs curing from 105 to 370 days. The w/b ratio varies from 0.4 to 0.6. As can be seen, there are two sets of data corresponding to OPC paste specimens and blended cement paste specimens. It is found that both neat OPC pastes and blended cement pastes present nearly linear relationships between interior RH and total porosity. However, the fitted linear curve of blended cement pastes is underneath that of neat OPC pastes. This observation manifests that with equal total porosity, the blended cement pastes show lower interior RH in comparison to neat OPC pastes. The lower interior RH in blended cement pastes might be either due to their finer pore size distributions via Kelvin effect or to more water consumption during hydration. These two aspects will be discussed in following sections 3.4 and 3.5.



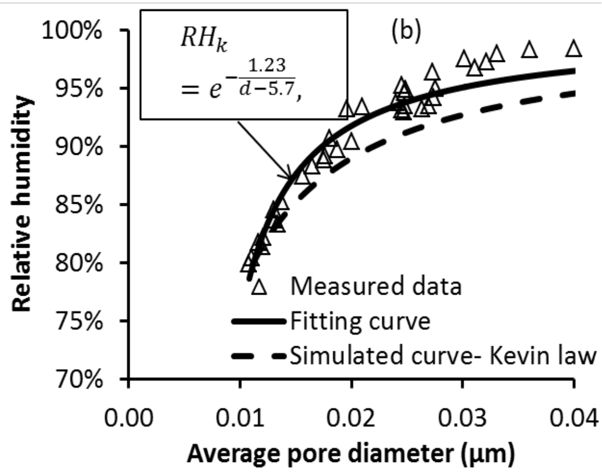


Fig. 5 Relative humidity vs. total porosity (a) and Relative humidity vs. average pore diameter (b) in neat OPC pastes and blended cement pastes

3.4 Average pore diameter *vs.* RH

The abovementioned analysis deduces that the effect of pore size might play more important role than total porosity in determining the interior RH of cementitious system. Representing the pore size characteristic of hydrated cement-based materials, the average pore diameter D_a can be expressed by Eq. (4).

$$D_a = \frac{4 \cdot V_t}{S_t} \quad (4)$$

where, V_t and S_t are the total volume and total surface area of capillary pores, respectively.
Fig. 5b shows the relationship between interior RH and average pore diameter for all the binders at curing age from 28 days to 370 days. The average pore diameter is calculated based on the cumulative intrusion volume derived from MIP. The data set in Fig. 5b shows that there appears an inherent correlation between interior RH and average pore diameter in cementitious systems. The best fit with the experimental results can be obtained using an exponential relationship, by Eq. (5)

$$RH_c = e^{-\frac{1.23}{d-5.7}},\ R^2 = 0.953 \quad (5)$$

where, RH_c indicates the moisture condition controlled by curvature effect, d denotes the average pore diameter in nm.
The fitting curve apparently shows a closely relationship between interior RH and average pore diameter of paste systems under sealed curing condition. In comparison to the simulated curve via Kelvin law, it is found that the derived fitting curve tends to overestimate the interior RH or underestimate the average pore diameter. The main reason can be ascribed to the inherent error of MIP measurement, namely ink-bottle effect. This often leads to an underestimation of large pores and an overestimation of small pores. As a result, the average pore diameter derived from MIP tends to be smaller than that in realistic condition. However, the high correlation coefficient, i.e. 0.953, do impose the fact that, in case of self-desiccation, the interior RH is significantly associated with the average pore diameter in cementitious system, regardless of curing age, cement type and w/b ratios.

3.5 Free capillary water content *vs.* RH

Figs. 6a and 6b respectively show the non-evaporable water content W_n *vs.* curing age and RH *vs.* free capillary water content in five paste systems. The free capillary water content is derived by subtracting the non-evaporable water from the initial water content, and expressed as the mass of free capillary water in 1 gram cement paste. The mass of free capillary water equals to the differences between initial total water content before casting and non-evaporable water content after hydration, with both parameters normalized to the mass of cement paste. For 1 gram hydrated cement paste with w/b of 0.5, the mass of free capillary water m_w can be expressed as

$$m_w = \frac{0.5}{1+0.5} - \frac{1}{1+0.5} \cdot (1 - I_{bc}) \cdot W_n \quad (6)$$

where, I_{bc} is loss on ignition of blended cement. W_n is non-evaporable water derived by TGA. As indicated in Figs. 6a and 6b, the plain OPC paste (P50) shows the highest W_n and the lowest free capillary water content than the rest blended cement pastes. However, it appears that with equal content of free capillary water, the interior RH in P50 tends to be higher than that in blended cement pastes. This further verifies that the interior RH of cementitious system, in case of self-desiccation, is more related to its pore size distribution via Kelvin effect rather than to free capillary water content. This finding is in good agreement with conclusion presented in section 3.4. For quantitative analysis, there seems no inherent expression between the interior RH and free capillary water content, since the two parameters cannot be fixedly correlated in view of different binders.

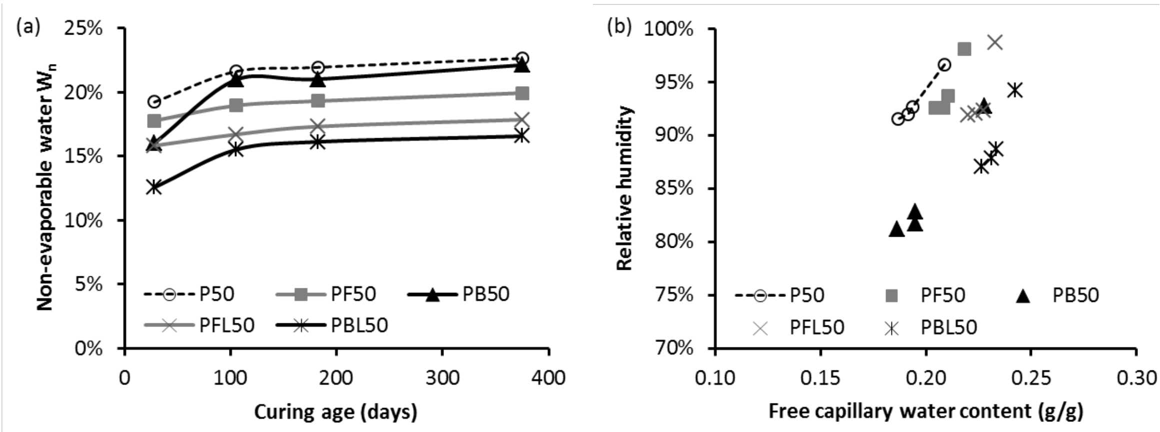


Fig. 6 Non-evaporable water vs. curing age (a) and RH vs. free capillary water content (b)

4. Conclusion remarks

The development of interior RH under sealed curing condition for various cement-based materials was investigated. The effects of different types of cement on interior RH due to self-desiccation are compared by examining the total porosity, average pore size and free capillary water content. The main findings can be summarized as follows:

- For all binders, the interior RH due to continuous cement hydration is declining with curing age. In particular, significant decrease occurs in the first 105 days, followed by a gradual decrease.
- The inclusion of slag in cement paste significantly decreases interior RH, whilst FA addition slightly increases interior RH. It is mainly because slag shows much stronger pozzolanic reactions and latent hydraulic reactions than FA.
- The effect of LP addition on interior RH is complicated. In FA-OPC system, further addition of LP 5% wt. slightly decreases interior RH. Whereas in Slag-OPC system, further addition of LP 5% wt. greatly increases interior RH. There appears a synergistic effect between alumina-rich FA and LP, which can be attributed to the formation of carboaluminate and the stabilisation of water-rich, voluminous ettringite instead of less voluminous monosulphate.
- In view of different binders, the plots regarding the relationships between interior RH and total porosity cannot be linearly fitted, but are separated into two groups: OPC pastes and pozzolana-contained cement pastes. The blended cement pastes tend to present higher total porosity corresponding to lower interior RH.
- In case of self-desiccation, no apparent relationship is observed between interior RH and free capillary water content. However, there appears an inherent correlation between interior RH and the average pore diameter in cementitious system, regardless of curing age, cement type and w/b ratios.

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Reference

[1] Snyder K. A. and Bentz D. P., Suspended hydration and loss of freezable water in cement pastes exposed to 90% relative humidity, Cem Concr Res 34 (2004) 2045–2056
[2] Flatt R. J., Scherer G. W. and Bullard J. W., Why alite stops hydrating below 80% relative humidity, Cem Concr Res 41 (2011) 987–992
[3] El-Dieb A. S., Self-curing concrete: Water retention, hydration and moisture transport, Constr Build Mater 21 (2007) 1282–1287.
[4] Parrott L. J. and Hong C. Z., Some factors influencing air permeation measurements in cover concrete, Mater Struct 24 (1991) 403-408.
[5] Parrott L. J., Water absorption in cover concrete, Mater Struct 25 (1992) 284-292.
[6] Lura P., Jensen O. M. and K. van Breugel, Autogenous shrinkage in high-performance cement paste: An evaluation of basic mechanisms, Cem Concr Res 33 (2003) 223–232.
[7] Zhang Y. and Zhang M. Z., Transport properties in unsaturated cement-based materials – A review, Constr Build Mater 72 (2014) 367–379.
[8] Persson B., Self-desiccation and its importance in concrete technology, Mater Struct 30 (1997) 293.
[9] Robins P. J., Austin S. A. and Issaad A., Suitability of GGBFS as a cement replacement for concrete in hot arid climates, Mater Struct 1992;25(10):598–612.
[10] De Weerdt K., Haha M. B., Le Saout G., Kjellsen K. O., Justnes H., Lothenbach B., Hydration mechanisms of ternary Portland cements containing limestone powder and fly ash, Cem Concr Res 41 (2011) 279–291
[11] Lothenbach B., Le Saout G., Gallucci E. and Scrivener K., Influence of limestone on the hydration of Portland cements, Cem Concr Res 38 (2008) 848–860.