CHLORIDE DIFFUSIVITY IN PARTIALLY SATURATED CEMENT-BASED MATERIALS ASSESSED BY RESISTIVITY MEASUREMENTS

Yong Zhang[1] and Guang Ye[2]

[1]Microlab, Civil Engineering and Geoscience, Delft University of Technology, 2628 CN Delft, The Netherlands;

[2]Microlab, Civil Engineering and Geoscience, Delft University of Technology, 2628 CN Delft, The Netherlands

[a]email: y.zhang-1@tudelft.nl, [b]email: g.ye@tudelft.nl

Abstract: Concrete is seldom saturated due to its self-desiccation. Even the submerged concrete structures may remain unsaturated for quite a long time. It has been reported the saturation level of pore solution has significant effect on species penetration. However, very little work was proposed regarding the transport properties and serviceability of concrete structures made of blended cementitious materials. This paper initiated the study of chloride ion diffusion in various blended cement-based system under non-saturated condition by resistivity measurements. Experiments have been performed on mortars made of different cement-based materials (Portland cement, fly ash, blast furnace slag, limestone powder) with different water to binding ratio (w/b=0.4, 0.5, 0.6). The mortar specimens have been curing for 200 days conditioning with 98% RH and 20°C, followed by oven drying at 50°C until the specimens reach different saturation levels from 95% down to 18%. The resistivity measurements for different cement-based systems are performed.

The results showed that saturation level has significant effect on the chloride diffusion coefficient. As to the relation between relative diffusivity and water saturation, the effect of w/b is less obvious in system with higher w/b. Compared with FA and LP system, the deepest decrease in relative diffusivity was found in BFS-blended system with the decrease of water saturation level.

Key words: blended materials, relative diffusivity, non-saturated, chloride, resistivity

1. INTRODUCTION

Increasing awareness has been directed to the durability problem of cement-based materials as a result of the premature failure and serviceability issues of reinforced concrete structures. The chloride ingression is the main cause of reinforcement

corrosion [1], and the time to corrosion initiation is usually defined as the service life of concrete materials. The transport property of external chlorides through concrete is a complex phenomenon, and governed by various physical-chemical mechanisms [2], i.e. diffusion of species due to concentration gradient, diffusion of moisture, electrical migration. On the other hand, the buffering effect (i.e. binding capacity) also plays important role during the chloride penetration, especially for the concrete made with blended cement materials [3].

Nowadays the service life design in recommendation, such as DuraCrete, relies on chloride transport properties of concrete in saturated condition. However, concrete is seldom saturated due to its long term self-desiccation, and it is very difficult to become resaturated once the self-desiccated state is achieved [4]. Chatterji [5] illustrated this phenomenon on the basis of hydrodynamics of water flow through concrete, and claimed the propagation of the saturation front is quite slow after contact with water. It was also reported that the thickness of saturated layer is not so much related to the depth of immersion, but determined by the average pore diameter of porous medium. Because in general it is the average capillary water pressure (corresponding to an average pore diameter) rather than water pressure from the external curing water that provides the driving force for water penetration.

Ion transport occurs only when water is present in porous channels. In this respect, the water content might be a key parameter for concrete linked to its transport properties and durability issues. The diffusivity in unsaturated condition relative to saturated condition is defined as the relative diffusivity, which is usually used to indicate the transport properties in non-saturated cement-based materials. The water content relative to that in saturated condition is usually noted as saturation degree (SD). In the past decade, various investigations have been performed to measure the relative diffusivity coefficient. By fitting limited previous experimental results, Saetta [2] was firstly proposed the S-shaped curve relation of diffusivity at a given relative humidity (RH). Francy et al [6] in the first place simulated the relative chloride diffusivity at different saturation level, and further simulated the coupled effect of both moisture and chloride transport. Climent et al [7] developed an novel method to measure chloride diffusivity in non-saturated concrete by interaction with PVC combustion gases, the diffusivity coefficients were estimated under the RH condition of 54%, 75%, 86%, 95% respectively. Guimaraes [8] studied the chloride diffusivity in unsaturated condition based on interaction the surface concrete with solid NaCl. Recently, Olsson [9] proposed a new approach and evaluated the ion diffusion in non-saturated concrete by resistivity measurement. Wissen [10] presented a modified “half-cell” method and analyzed the lithium diffusion profile in unsaturated cement paste by using the Laser Induced Breakdown Spectroscopy technique (LIBS).

The study of relative chloride diffusivity has been initiated since last decade. The water saturation level has proved to significantly influence chloride diffusivity property in cement-based materials. However, the research in this field remains in its infancy. In addition, most of the previous studies focus on the OPC materials. The objective of this paper is to investigate the effect of water saturation degree on chloride diffusivity of partially saturated cementitious system made of blended cement. The materials used in

this study contain CEM I 42.5, ground granulated blast furnace slag (BFS), fly ash (FA), limestone powder (LP). The different water to binder ratios (w/b=0.4, 0.5, 0.6) are taken into account. The samples have been curing for 200 days conditioning with 98% RH and 20°C, followed by oven drying (50°C) until the targeted SD attained (from 95% down to 18%). Resistivity measurements were employed to assess the chloride diffusivity, the results are compared. It concludes with a look to the future.

2. EXPERIMENTS

2.1 Materials

In this experimental work, the mortar samples were cast. Each mortar was made with the same content of siliceous sand, but varies with binders and water to binder ratio (w/b=0.4, 0.5, 0.6). The chemical compositions of cement and SCMs are given in Table 1. The particle size of siliceous sand is range from 0.125 mm to 2 mm. The dosage of binder to sand is 1:3 by weight. For a detailed description of each binder, see Table 2.

Table 1 Composition of cement and SCMs

Chemical composition	XRF analysis (g/100g)			
	OPC	FA	BFS	LP
CaO	64.495	5.537	41.398	-
SiO_2	18.875	50.554	34.015	0.737
Al_2O_3	4.481	30.743	11.117	0.180
Fe_2O_3	4.038	6.301	0.529	0.073
MgO	2.012	1.009	8.284	0.523
K_2O	0.508	1.109	0.398	0.026
Na_2O	0.341	0.284	0.205	-
SO_3	4.038	0.785	2.430	0.082
TiO_2	0.319	2.362	1.027	-
$CaCO_3$	-	-	-	98.316
others	0.893	1.316	0.597	0.063

Table 2 Mix proportions (weight percentage) used for the binders

Mortar	OPC	FA	BFS	LP	W/B
H_1:(P-4)	100%	-	-	-	0.4
H_2:(P-5)	100%	-	-	-	0.5
H_3:(P-6)	100%	-	-	-	0.6
H_4:(PB-5)	30%	-	70%	-	0.5
H_5:(PF-5)	70%	30%	-	-	0.5
H_6:(PFL-5)	65%	30%	-	5%	0.5

Cylindrical mortars 800 mm in height and 100 mm in diameter were cast in the lab, which were demoulded after one day's curing. The mortars were then moved to standard curing condition (98% RH, 20°C) for 200 days. Both the top surface and bottom of the

mortars with the thickness of 15 mm were cut off, followed by the sample preconditioning procedure which is described in section 2.2.

2.2 Sample preconditioning

A well prepared partial water saturation state must be obtained before experimental measurements. In this research, once the mortars were 200 days' old, they were going to be conditioned for obtaining desired water saturation level. The favorite protocol for sample preconditioning should be easy to perform and suitable for different cement-based materials [11]. In addition, the minimum alteration of microstructure and homogeneous moisture are required when equilibrium attained. To this end, these mortars were dried in oven at 50°C in chamber [12,13].

The mass loss curves with each sample were recorded. The sample mass corresponding to a certain SD, m_h, is calculated according to the following equation:

$$m_h = m_s \cdot \frac{1+SD \cdot A}{1+A} \quad (1)$$

where m_s is the mass of the specimen with saturated condition (g), A is the water absorption coefficient (%). Due to its crucial role in sample preconditioning, coefficient A is obtained following recommendation ASTM C642-13 and based on measurements at least 3 specimens [14].

The samples intended for test are required to seal the lateral sides to avoid any multi-side directional moisture transfers. In order to obtain homogeneous moisture, the samples were completely sealed in a bag and maintaining the temperature of 50°C. The time required for this moisture redistribution step should be no less than the days required for the drying process. In this research, one month is long enough for all the samples for redistribution step. Then, the samples are cooling down slowly to the room temperature to avoid any initiation of crack. Finally, the mortars were stabilized inside the bag at their corresponding saturation state before resistivity measurements.

Before sample preconditioning, the water absorption coefficient of each mixture is obtained. Then all the mortar samples will be preconditioning following as Fig. 1.

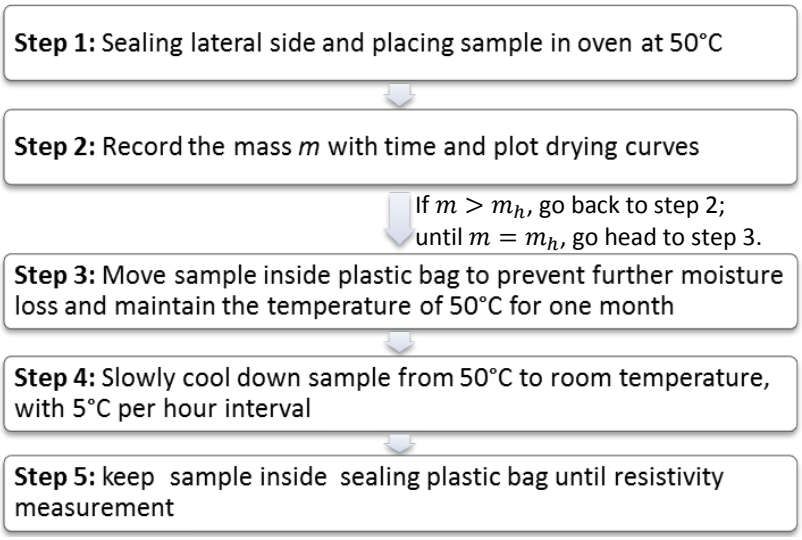

Fig. 1 Sample preconditioning for mortar until targeted saturation degree

2.3 Resistivity measurement

The bulk resistivity is theoretically correlated to the chloride diffusion coefficient [15]. The resistivity (ρ_e) is defined as the inverse of conductivity [σ]. Usually, Nernst-Einstein equation is used to assess the transport properties (e.g. chloride diffusivity *D*) of cement-based materials, which is expressed as following equation (2)

$$\frac{\sigma}{\sigma_0} = \frac{D}{D_0} \tag{2}$$

where σ_0 (S/m) and D_0 (m^2/s) are the conductivity and diffusivity coefficient of chloride ion through liquid phase of cement-based materials. In general, $\sigma_0 \approx 1\sim20\ S/\mathrm{m}$, $D_0 \approx 1.483 \times 10^{-9}$ m^2/s [9].

A portable resistance meter, type ESCORT LCR using alternating current (AC) at 120 Hz was used for resistivity test in this study. For the specimens with each SD, the resistivity was measured with one stainless electrode covering each side of the specimen. Humid sponge was employed in between surface specimen and each electrode to ensure the whole surface of specimen under current flow. The measurements are performed at constant room temperature 20°C. Based on this simple set-up, the measured resistivity was found to decrease with the time duration, which can be ascribed to the moisture absorption due to the contact with sponge. In this respect, only the first measurement was employed for the final analysis. The resistivity can be expressed as equation (3).

$$\rho_e = k_e \cdot \frac{U_x}{I_x} = \frac{1}{\sigma} \tag{3}$$

where, ρ_e is electrolytic resistivity of mortar in [Ωm], k_e denotes the geometrical constant which is calculated as the ratio of mortar cross-section [m^2] over the distance between electrodes in [m], U_x is the potential difference between electrodes in [V], I_x is the current flowing between electrodes in [A].

3. RESULTS AND DISCUSSIONS

In this study, all the specimens were well prepared with targeted SD level and with homogeneous moisture distribution inside the specimens. The resistivity measurements were performed on all the specimens. However, some specimens with low SD failed to be measured with the resistance meter, because the resistivity is too high to be tested out. In these cases, the liquid phase in the porous network was assumed no longer connected. In other words, the depercolation of the liquid phase has been attained, the corresponding saturation is defined as depercolation saturation level (noted as SD_{de}). The main results of resistivity measurements were transferred and directly expressed in terms of diffusivity. All the points shown in the graphs represent the average value of three specimens.

3.1 Relative diffusivity vs. SD

The relative diffusivity as a function of SD is summarized. As shown in Fig. 2, apparently the diffusivity is significantly influenced by SD regardless of cement type. A slight decrease in relative diffusivity occurs when SD starts to drop down from saturated state. When SD decreases to a certain level, a sharp decrease in relative diffusivity was

observed, which is defined in this paper as first critical saturation level (SD_1), Nevertheless, once the relative diffusivity is less than 0.1, the corresponding saturation is defined as the second critical saturation level (SD_2), the curves tend to be flat until the depercolation of the transport medias being attained. Interestingly to note that the value (0.1) of relative diffusivity is true for all the materials tested. Possibly because in this condition, all the pores for main ionic diffusion channels are no longer saturated but absorbed with nano scale water molecules, and the relative diffusivity is less dependent on saturation level.

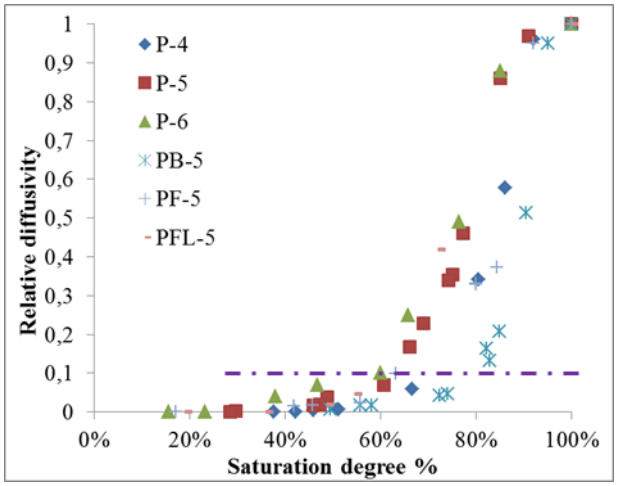

Fig. 2. Relative diffusivity as a function of saturation degree

These curves showed similar pattern, and seem in agreement with the simulated S-shaped relationship proposed by Saetta et al [2]. However, the sensitivity of relativity diffusivity to SD level is different for the cement-based materials used in this study. The critical saturation level SD_1 varies from 86%- 95%, SD_2 is in the range of 60-82%, the SD for depercolation is different from 22% to 45%. Such varieties in these values indicate the relative diffusivity as a functions of SD might be highly related to the microstructure characteristics, especially pore structure, of each materials. At certain SD level, the moisture distribution and connectivity of liquid phase in the pore structure would be completely different from materials [16].

The critical pore diameter has been widely used to describe the pore characteristics of cement-based materials, the pores whose diameter are greater than critical pore size can not form connected path throughout the material [17]. Assuming all the critical pores are interconnected and provide the main transport path for ion diffusion, the relative diffusivity as a function of SD can be illustrated as Fig. 3:

i. When SD starts to drop down from saturated state (SD < 100%), the macro big pores firstly loss water, the main routes for chloride diffusion (interconnected critical pores) are saturated. The chloride diffusivity is not severely influenced and quite closed to that in saturated condition.

ii. If SD continues to reduce, i.e. SD < SD_1, the water in critical pores starts to loss. The main diffusion routes become unsaturated, and part of the critical pores is filled with water vapor and nano-scale water molecule layers, which

depends on the RH inside the material [18]. Subsequently, a sharp decrease in relative diffusivity was observed.

iii. Once the SD < SD_2, all the critical pores are unsaturated, the chloride ion diffuses through nano meters thick liquid phase, which is composed of water molecules and chemical compounds (e.g. $Ca(OH)_2$). In this condition, the diffusion process is quite slow and decreases slightly.

iv. When SD drops down to a certain low level, the RH is too low that only very thin water layers are absorbed on the critical pores. The interaction between various ions and the strong force between pore walls and ions greatly affect the chloride diffusivity. Moreover, the precipitation of hydration products, i.e. $Ca(OH)_2$, hindered the chloride diffusion (diameter of H_2O=0.275 nm, diameter of Cl^-=0.36 nm). In this case, the depercolation saturation level has been attained, and the diffusion becomes impossible.

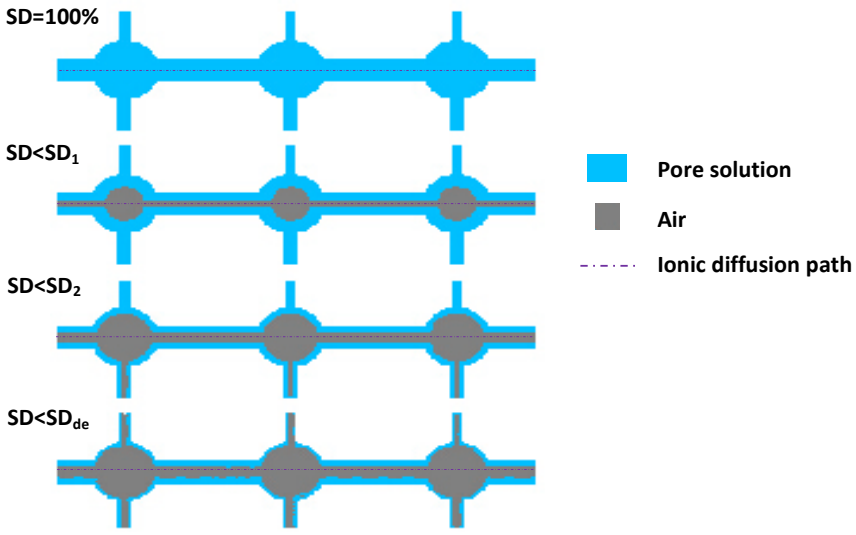

Figure 3. Ionic transport in cement-based materials under different saturation levels

As deduced above, the relative diffusivity as a function of SD is highly variable with different cementitious systems. W/b and SCMs are in general considered as the two main factors governing the constitution of cementitious system, the effect of these two factors on relative diffusivity in non-saturated condition will be discussed in the following sections.

3.2 Effect of w/b

Resistivity measurements were performed on OPC mortars with w/b ratios of 0.4, 0.5, 0.6. As indicated in Fig. 4 (left), the resistance for ionic diffusion is larger in mortar with lower w/b. With the decrease of SD, the effect of w/b on resistance is enhanced. In particular, at low SD level, i.e. 45%, the resistance for each mortar is in ratio of 23:5:1 when increases the w/b from 0.4 to 0.6.

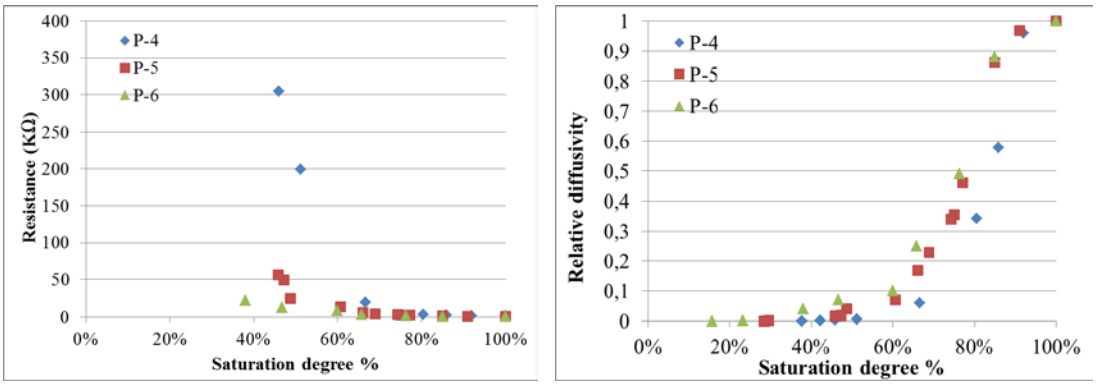

Fig. 4. Resistance (left) and relative diffusivity vs. SD (right) for OPC mortars with w/b of 0.4, 0.5, 0.6

However, as to the relative diffusivity properties, as depicted in Fig. 4 (right), the value tends to be a little larger in higher w/b mortar system throughout the entire SD range. It is also found from the figure that a sharp decrease occurs when the SD is in between 62-90%, followed a slight decrease until depercolation attained. According to the experimental results, the SD for depercolation is 37%, 28.4% and 22% which are related to mortar with w/b ratio of 0.4, 0.5 and 0.6 respectively. In addition, the relative diffusivity as a function of SD is quite closed for mortar system with w/b=0.5 and 0.6. These experimental conclusions are in good agreement with the previous modeling results in [19].

3.3 Effect of SCMs

The addition of SCMs influences the pore structure of cement-based system either by chemical effect (i.e. pozzolanic reaction) or physical effect (i.e. nucleation, dilution, filler etc.). The cement was partially replaced by SCMs in binary or ternary cement-based materials. The effect of SCMs, i.e. FA, BFS, LP, on resistivity measurements was assessed and the results were presented in Fig. 5. As it is shown, compared with pure OPC system, the addition of FA has a little effect on the correlation between relative diffusivity and SD. While the diffusivity of BFS-blended mortar was much more sensitive to the loss of water. To be specific, the diffusivity in BFS-blended system is a half of that in saturated condition when the SD equals to 90%. Furthermore, it is ten times smaller reference to saturated system, even the SD is still in high level of 80%. While the two values are 85% and 60% respectively in OPC mortar system. The drastic decrease might be related to the highly refined pore size distribution with the addition of BFS.

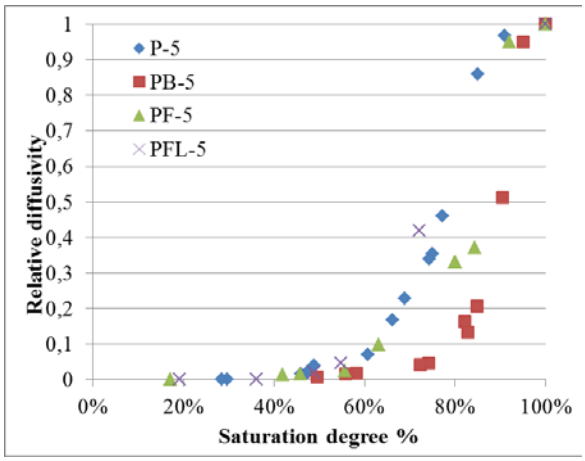

Fig. 5. Relative diffusivity vs. SD in blended cement mortar system

The incorporation of FA was reported to increase the total porosity of cement-based system, and the volume fraction of small pores is increased as well [20, 21]. This explains the relative diffusivity is a little bit lower at the high SD levels. LP is considered to be an inert blended material, the addition of LP was assumed to dilute the hydrating cement-based system. In other words, the presence of LP increases the potential w/b of the cement-based materials. Consequently, compared with PF system, the addition of LP (for PFL system) increases the relative diffusivity coefficient. These results are in consistent with the conclusions from section 3.2. In addition, the depercolation SD level for chloride diffusivity is 45%, 37%, and 36% for PB, PF, PFL mortar systems, which are higher than that of OPC system (28.4%).

4. CONCLUSIONS AND OUTLOOKS

This paper studied the chloride diffusivity in unsaturated cement-based materials by resistivity measurements. The effect of w/b and SCMs were figured out. The results are in good agreement with the previous simulation work. In addition, the results contribute to the available data base and may provide references for modeling the chloride diffusivity of blended cement-based materials under non-saturated condition.

The key findings of this research is summarized as follows:

i. Chloride diffusivity is significantly influenced by the SD level, the correlation is variable with different cement-based materials.

ii. The mortar with lower w/b has lower chloride diffusion through the entire SD range. With the decrease of SD, the effect of w/b on diffusivity is enhanced. However, with related to relative diffusivity, the effect of w/b is less obvious in mortar with higher w/b.

iii. Compared with OPC system, the addition of FA and/or LP have small effect on the relationship between relative diffusivity and SD. However, a much sharper decrease in relative diffusivity was observed with the decrease of SD in BFS-blended system.

A few words should be added regarding the influence of SD on the microstructural changes of cement-based materials. Especially when the water content bellows a certain

level, the mineral crystallization and the extremely low RH inside the porous system may break down the initial thermodynamic constitutions. To which extent the microstructure is changed at such condition, and how does the transport property would be influenced, further investigations needs to be progressed. In addition, an advanced research work on fundamental mechanisms is needed to basically understand the knowledge of transport properties under non-saturated condition.

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