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# EXPERIMENTAL STUDY OF CHLORIDE DIFFUSIVITY IN UNSATURATED ORDINARY PORTLAND CEMENT MORTAR

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**Keywords:** Chloride diffusivity; Mortar; Pore structure; Water saturation

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# EXPERIMENTAL STUDY OF CHLORIDE DIFFUSIVITY IN UNSATURATED ORDINARY PORTLAND CEMENT MORTAR

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## Abstract

Experiments are carried out to investigate the chloride diffusivity in partially saturated ordinary Portland cement mortars with water-to-cement (w/c) ratios of 0.4, 0.5 and 0.6. Based on resistivity measurement and Nernst-Einstein equation, the chloride diffusivities of cement mortars at various water saturations are estimated. The pore structures of cement pastes obtained from mercury intrusion porosimetry tests are analysed, which provide basic insight into the moisture distribution of non-saturated cement mortars. It is found that the chloride diffusivity is highly dependent on water saturation. The dependency is closely related to the pore size distribution and pore connectivity of the material. There exists a critical saturation level at which the pore solution becomes discontinuous and ionic diffusion is impossible. An increase of the w/c ratio results in a decrease of the critical saturation level.

**Keywords:** Chloride diffusivity; Mortar; Pore structure; Water saturation

## 1. INTRODUCTION

Chloride-induced corrosion is the main durability concern for reinforced concrete structures in marine environment. Current durability design, e.g. DuraCrete [1], often relies on chloride diffusivity of saturated concrete. In reality, however, concrete is rarely saturated due to either self-desiccation or wetting-drying cycles [2]. It is necessary to study the chloride diffusivity at non-saturated conditions as far as an accurate service life prediction is concerned.

Diffusion test is a basic method to measure the chloride diffusivity of concrete. Chloride source can be imposed into the non-saturated concrete through gaseous source (hydrogen chloride) [3] or chloride-contained solution [4] or solid crystal (sodium chloride) [5]. After a certain period of test, the chloride diffusivity is obtained by applying the Fick's 2<sup>nd</sup> law to fit the chloride profiles [4]. The electrical resistivity test is an alternative approach to determine the chloride diffusivity in non-saturated concrete [6]. The conductivity is the inverse of resistivity. In combination with the Nernst-Einstein equation, the chloride diffusivity is estimated. Compared to diffusion test, resistivity test is fast and easy to perform [2].

The scope of previous studies mainly focused on the measurement of chloride diffusivity in non-saturated cementitious materials. To what extent the non-saturated conditions do influence the chloride diffusivity is still a pending issue. Published results show a great deviation [2]. In particular, the influence of pore structure (resultant from different w/c ratios) on non-saturated chloride diffusivity is rarely studied or remains no consensus [6,7].

The purpose of this paper is to experimentally study the chloride diffusivity in partially saturated ordinary Portland cement mortars with water-to-cement (w/c) ratios of 0.4, 0.5 and 0.6. The resistivity tests are carried out. By using the Nernst-Einstein equation, the chloride diffusivities of cement mortars at various water saturations, i.e. relative chloride diffusivities,

are estimated. The pore structures of cement pastes obtained from mercury intrusion porosimetry provide basic insight into the chloride diffusivity under non-saturated conditions.

## 2. EXPERIMENTAL PROGRAM

### 2.1 Materials and samples preparation

Ordinary Portland cement CEM I 42.5N (OPC) was used to cast cement pastes and mortars with w/c ratios of 0.4, 0.5 and 0.6. The curing age was one year. Paste samples were prepared for pore structure measurements. Mortar samples (50 mm thick) were firstly preconditioned to uniform water saturations ranging from 18% to 100%, and then conducted with resistivity measurements. Details about sample preparations and sample preconditioning procedures can be found in the previous work [8,9]. For the sake of description, paste samples with w/c ratios of 0.4, 0.5 and 0.6 are noted as P4, P5, P6, and mortar samples with w/c ratios of 0.4, 0.5 and 0.6 are noted as M4, M5, M6, respectively.

### 2.2 Pore structure of cement paste

Mercury intrusion porosimetry (MIP) was applied to measure the pore structure of cement paste. Due to ink-bottle effect, the 1<sup>st</sup> intrusion of MIP is considered inappropriate to identify the real pore size distribution (PSD) [10]. The 2<sup>nd</sup> intrusion has no ink-bottle effect. The PSD of cement paste obtained from the 2<sup>nd</sup> intrusion agrees well with that derived from nitrogen sorption measurement [11]. In the present work, the 2<sup>nd</sup> intrusion of MIP was utilized.

The test consisted of five stages: (i) a low pressure intrusion run from 0 to 0.17 MPa; (ii) the 1<sup>st</sup> high pressure intrusion run from 0.17 to 210 MPa; (iii) an extrusion run from 210 to 0.03 MPa; (iv) the 2<sup>nd</sup> intrusion run from 0.03 to 210 MPa; (v) the 2<sup>nd</sup> extrusion run from 210 to 0.03 MPa. The applied pressure  $p$  and pore diameter  $d$  is correlated by the Washburn equation (1a). The pore connectivity  $\eta_p$  of cement paste is estimated by the equation (1b).

$$d = -\frac{4\gamma_{Hg} \cos \theta}{p} \quad (1a)$$

$$\eta_p = \frac{\phi_e}{\phi_t} \times 100\% \quad (1b)$$

where  $\gamma_{Hg}$  is the surface tension of mercury (0.48 N/m);  $\theta$  is the intrusion contact angle (138°);  $\phi_e$  and  $\phi_t$  are total porosity (from stage ii) and effective porosity (from stage iii), respectively.

### 2.3 Conductivity of cement mortar

According to Nernst-Einstein equation, the ratio of the bulk conductivity of pore solution  $\sigma_0$  to the conductivity of cementitious material  $\sigma$  equals to the ratio of chloride diffusivity in the pore solution  $D_0$  to chloride diffusivity in the cementitious material  $D$ , as:

$$\frac{\sigma_0}{\sigma} = \frac{D_0}{D} \quad (2)$$

The coefficient  $D_0$  equals to  $1.5 \times 10^{-9}$  m<sup>2</sup>/s at room temperature when the chloride concentration is within 0.1~1.0 mol/l [6]. Based on equation (2) the conductivity of cement mortar can be converted into its diffusivity. Relative chloride diffusivity ( $D_{rc}$ ) is defined as the ratio of chloride diffusivity at a particular  $S_w$  level ( $D_{S_w}$ ) over that at saturated state ( $D_{Sat}$ ), as:

$$D_{rc} = \frac{D_{S_w}}{D_{Sat}} = \frac{\sigma_{S_w}}{\sigma_{Sat}} \cdot \frac{\sigma_{0,Sat}}{\sigma_{0,S_w}} \quad (3)$$

where  $\sigma_{S_w}$  and  $\sigma_{Sat}$  are conductivities of the cement mortar at a particular  $S_w$  and at saturated state, respectively.  $\sigma_{0,S_w}$  and  $\sigma_{0,Sat}$  are conductivities of pore solution when the cement mortar is at a particular  $S_w$  and at saturated state, respectively. In this work,  $\sigma_{S_w}$  and  $\sigma_{Sat}$  were obtained from resistivity measurements, whose details were presented in a previous work [8]. The details for determining  $\sigma_{0,S_w}$  and  $\sigma_{0,Sat}$  can be found elsewhere in [12].

### 3. EXPERIMENTAL RESULTS

#### 3.1 Pore size distribution of cement paste

Figure 1 shows the pore size distributions of one year old cement pastes. Each pore size distribution curve exhibits a main peak. The pore diameters corresponding to such main peaks are 26.1 nm, 34.6 nm and 34.6 nm for pastes P4, P5 and P6, respectively. The curves between P5 and P6 are approaching, especially for the pores smaller than 20 nm, but the both are very different from the curve of P4 in both size and shape.

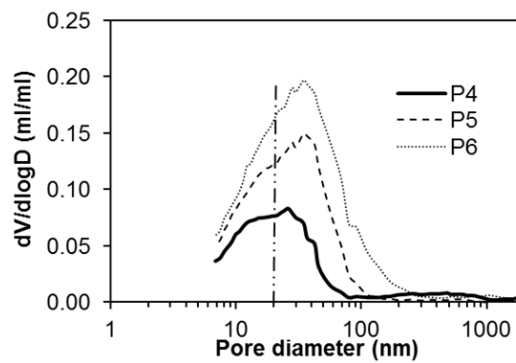


Figure 1 Pore size distributions of cement pastes (one year old, w/c=0.4, 0.5 and 0.6) obtained from the 2<sup>nd</sup> intrusion of MIP test

#### 3.2 Relative chloride diffusivity of cement mortar

Based on equation (3), the relative chloride diffusivities ( $D_{rc}$ ) in cement mortars at various water saturations ( $S_w$ ) were derived. It should be noted that some mortar specimens at very low  $S_w$  levels failed to be measured, possibly because their resistances were too high to be tested. In these cases, the pore solutions are assumed as discontinuous. The water saturation at which the pore solution starts to be discontinuous is defined as “critical saturation”.

Figure 2 shows the relationship between  $D_{rc}$  and  $S_w$  in cement mortars with various w/c ratios. A general trend is observed that the  $D_{rc}$  is reduced as the decrease of  $S_w$ . The  $D_{rc}$ - $S_w$  relation can be divided into three stages. Take mortar M6 as an example, when  $S_w$  starts to decrease the  $D_{rc}$ -value shows a slight decrease (stage I). There is rapid drop in the  $D_{rc}$ -value when the  $S_w$  reduces from 90% to 60% (stage II), followed by a slow decline (stage III). A detailed illustration of the three-stage  $D_{rc}$ - $S_w$  relation will be given in Section 4.1. Once the  $S_w$  is lower than the critical saturation,  $D_{rc}$ -value tends toward infinitely small since there is no continuous pore solution available for chloride diffusion. The critical saturations are found to

be approximately 37%, 28% and 22% for cement mortars with w/c ratios of 0.4, 0.5 and 0.6, respectively.

The  $D_{rc}$ - $S_w$  relation varies for cement mortars with different w/c ratios. An increase of w/c ratio results in an increase of  $D_{rc}$ -value. For example, at  $S_w=80\%$ , the  $D_{rc}$ -value is 0.34 for mortar M4, compared to  $D_{rc}=58\%$  and  $D_{rc}=67\%$  for mortars M5 and M6, respectively. It appears that the curves  $D_{rc}$ - $S_w$  for mortars M5 and M6 are closer. This can be explained by the similar pore size distributions between pastes P5 and P6 (see Figure 1). The role of the w/c ratio in the  $D_{rc}$ - $S_w$  relation is a result of its effect on the continuity of pore solution. More details will be discussed in Section 4.2 in this respect.

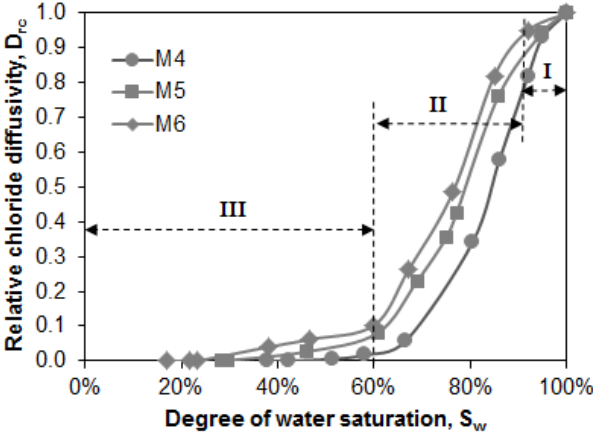


Figure 2  $D_{rc}$ - $S_w$  relations in the cement mortars at one year old, w/c=0.4, 0.5 and 0.6

Some available models in literature are used for quantitative analysis. Figure 3 compares the curves of three different models by fitting the  $D_{rc}$ - $S_w$  plots of mortar M5. It is found that the Gaussian model apparently exhibits the best fit for the  $D_{rc}$ - $S_w$  plots.

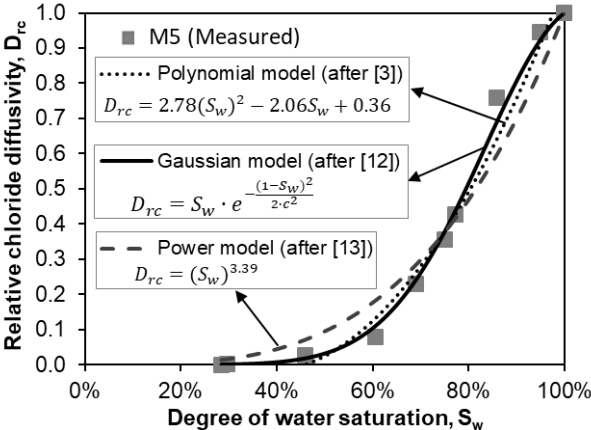


Figure 3 Comparison of different models by fitting the  $D_{rc}$ - $S_w$  plots of mortar M5

## 4. DISCUSSIONS

### 4.1 Three-stage $D_{rc}$ - $S_w$ relation

The  $D_{rc}$  decreases with the decrease of  $S_w$ . There are three main reasons: (i) the amount of water available for ionic diffusion is less; (ii) the number of transport porous channels, in which the pore solution is continuous allowing ionic diffusion, becomes less; (iii) the interaction forces between chloride ions and cement paste are increased due to the decreased thickness of water layers adsorbed on the pore walls. All the three reasons are closely related to the moisture state in the pores. With declining  $S_w$  the moisture state in a pore may remain saturated, or become partially saturated or drained (only adsorbed with water film).

To better understand the moisture state in the entire capillary pores, two pore parameters are introduced: threshold pore diameter ( $d_{th}$ ) and critical pore diameter ( $d_{cr}$ ). Figure 4 shows three different pore categories based on their pore size distributions: (i) macro pores, with pore diameter  $d > d_{th}$ ; (ii) meso pores,  $d_{th} \geq d \geq d_{cr}$ ; (iii) micro pores,  $d < d_{cr}$ . The details for obtaining  $d_{th}$  and  $d_{cr}$  can be found in [14].

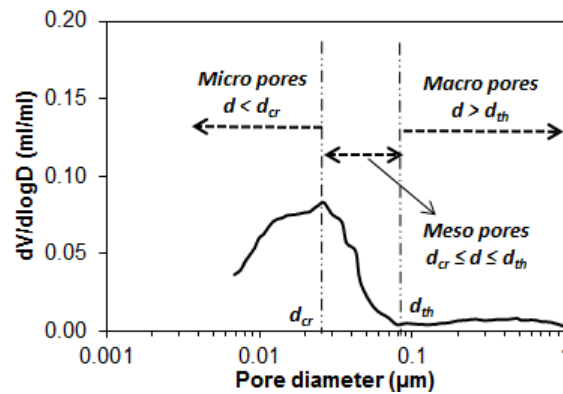


Figure 4 Three pore categories in the cement paste ( $w/c=0.4$ ) based on pore size distribution;  $d_{th}$  and  $d_{cr}$  are threshold and critical pore diameter, respectively.

The meso pores provide the main pathways for moisture transfer as well as for ionic transport [9]. The three-stage  $D_{rc}$ - $S_w$  relation can, therefore, be explained by the three-stage moisture state in the meso pores, as illustrated in Figure 5:

At stage I: All the meso pores are saturated. As  $S_w$  starts to decrease, the macro pores firstly lose water. The main pathways (i.e. meso pores) for ionic diffusion remain filled with pore solution. The  $D_{rc}$ -value is not influenced much and quite close to that in saturated condition.

At stage II: With further decrease of water saturation ( $S_w < S_{w1}$ ), the meso pores become partially saturated. In the meantime the meso pores are gradually filled with water vapour that can hinder the ionic diffusion to a great extent resulting in a sharp drop of  $D_{rc}$ -value.

At stage III: Once the water content is lower than a certain saturation level ( $S_w < S_{w2}$ ), all the meso pores are drained but only adsorbed with nano-scale layers, which are composed of water molecules and chemical compounds, e.g.  $\text{Ca}(\text{OH})_2$ . In this stage, water loss commences in the micro pores. The ionic diffusion is quite slow and  $D_{rc}$ -value decreases less obviously.

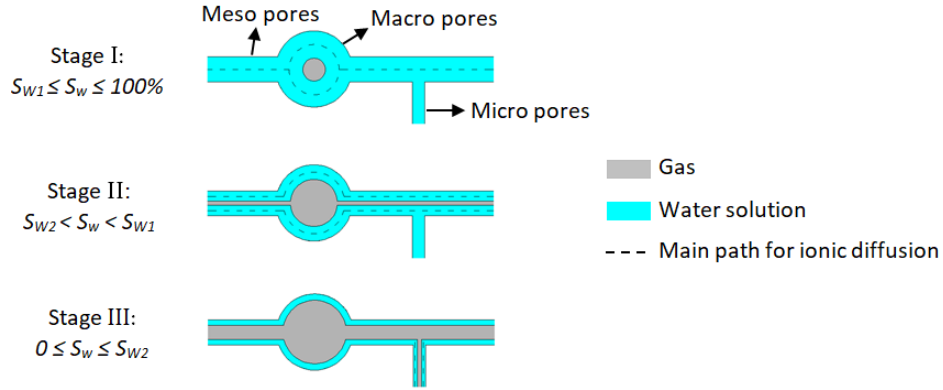


Figure 5 Moisture state and ionic diffusion with the decrease of water saturation  $S_w$

#### 4.2 Role of w/c ratio in the $D_{rc}$ - $S_w$ relation

The different  $D_{rc}$ - $S_w$  relations with varying w/c ratios can be evaluated from pore connectivity point of view. For a material with higher pore connectivity, the continuity of pore solution will be less severely influenced with the decrease of  $S_w$  [7]. As a result, the material has a larger  $D_{rc}$ -value [12].

The hysteresis in the 1<sup>st</sup> intrusion-extrusion cycle of an MIP test was used to determine the pore connectivity  $\eta_p$ , which was expressed as the ratio of effective porosity over total porosity. The  $\eta_p$ -value was determined as 44.2% for paste P4, compared to 56.5% for paste P5 and 62.5% for paste P6. Obviously, the pore connectivities for pastes P5 and P6 are close but both are much higher than that for paste P4. This finding gives a good explanation to the role of the w/c ratio in the  $D_{rc}$ - $S_w$  relation as presented in Figure 2.

### 5. CONCLUSIONS

From the findings of this study, the main conclusions are summarized as follows:

- 1) For OPC mortars the relative chloride diffusivity ( $D_{rc}$ ) highly depends on the water saturation  $S_w$ . The dependency is intimately related to the pore size distribution and pore connectivity of the material. With decrease of  $S_w$  the  $D_{rc}$  shows three-stage change: a slight decrease (stage I), a sharp drop (stage II) and another slight decline (stage III). The  $D_{rc}$ - $S_w$  relation can be well described with the Gaussian model.
- 2) The  $D_{rc}$ - $S_w$  relation is different for OPC mortars with varying w/c ratios. However, the role of the w/c ratio in the  $D_{rc}$ - $S_w$  relation becomes less obvious with increasing w/c ratio.
- 3) There exists a critical saturation level at which the pore solution becomes discontinuous and ionic diffusion is impossible. An increase of the w/c ratio results in a decrease of the critical saturation. The critical saturations are found to be 37%, 28% and 22% for the cement mortars with w/c ratios of 0.4, 0.5 and 0.6, respectively.

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