

# Chloride Diffusivity through Partially Saturated, Binary-Blended Concrete

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*The surface of concrete at the tidal, splash, and atmospheric regions of partially immersed marine structures experiences different degrees of water saturation. Hence, the concrete pore structure is partially filled with water at some of these regions. The present work experimentally investigates chloride transport into partially saturated concrete with 20% fly ash replacement, and the effect of the mortar layer/concrete surface condition on chloride diffusivity at four degrees of water saturation relevant to the Florida marine environments. The results indicate that the mortar layer of concrete provides protection against chloride penetration, leading to lower chloride diffusivity values. Moreover, chloride diffusivity as a function of the degree of water saturation for concrete with and without mortar layers is found to be different. The diffusivity of the former hardly changes when the degree of water saturation increases from 70 to 80%.*

**Keywords:** chloride; diffusivity; fly ash; mortar layer; partially saturated concrete; water saturation degree.

## INTRODUCTION

Reinforced concrete structures have been widely employed for transportation infrastructure exposed to marine environments.<sup>1</sup> The permanently immersed portion of a marine reinforced concrete substructure can be considered water saturated and exposed to a constant chloride concentration, but concrete at elevations above water (that is, tidal, splash, and atmospheric regions) experience different degrees of water saturation and the chloride concentration at the surface is not constant with time or elevation.<sup>1</sup> Hence, the concrete pore structure is only partially filled with water, and chloride transport takes place through a partially filled interconnected pore structure.

The transport properties of concrete can be affected by the amount of pore water in the concrete.<sup>2,3</sup> Past studies have demonstrated that the degree of water saturation is a very important factor in the transport of ions in porous media<sup>4</sup> and in the transport of chloride ions into partially saturated concrete.<sup>5</sup> Moreover, chloride diffusivity is strongly dependent on the degree of water saturation,<sup>6-12</sup> which is significantly related to the material microstructure such as pore size distribution, tortuosity, and connectivity. Such microstructure is influenced by various factors, including the water-cementitious materials ratio ( $w/cm$ ), the material type, the degree of hydration, the age of the concrete, and the curing temperature.<sup>13-19</sup>

Mathematical models describing the diffusion of chloride and its dependence on the moisture content and relative humidity have been proposed,<sup>20-22</sup> while modeling work has been also conducted<sup>13,23-25</sup> since the early 1990s. Innovative test methods were not reported until Climent et al.<sup>6</sup> developed an

experimental procedure by exposing the surface of non-saturated concrete samples with controlled water content to interact with a gaseous hydrogen chloride (HCl) atmosphere produced from the combustion of polyvinyl chloride (PVC), and then returning the specimens to a controlled moisture condition for the transport of chloride ions. The chloride profiles obtained were fitted to Fick's Second Law of Diffusion with an instantaneous plane source. Vera et al.<sup>7</sup> further developed this method and included the effects of chloride binding. Nielsen and Geiker<sup>2</sup> employed a different method where portland cement mortar specimens were conditioned to reach the targeted relative humidity and contaminated by immersion in a high concentration of sodium chloride (NaCl) solution for a limited exposure time, followed by a drying process until the initial weight (prior to immersion) of each specimen was obtained. Subsequently, the specimens were returned to a moisture-controlled room for additional chloride transport. Nielsen and Geiker<sup>2</sup> obtained the chloride profiles that included the effects of binding of chlorides, then used a composite theory and Powers' model for estimating the diffusion coefficient as a function of the specimen moisture content. In parallel with the aforementioned work, Guimaraes et al.<sup>10</sup> investigated chloride diffusion through partially saturated portland cement paste and mortar specimens by employing an alternative method, where the test samples with relevant water saturation degrees were first conditioned. After some time, finely ground solid NaCl was placed on the exposed surface and then covered with plastic wrap. Finally, each sample was exposed in a vacuum for the duration of the diffusion experiment. The chloride profiles obtained after exposure were fitted to Fick's Second Law of Diffusion. Additionally, other methods and procedures have been also developed by Olsson et al.,<sup>11</sup> Mercado-Mendoza et al.,<sup>12</sup> Vedalakshmi et al.,<sup>26</sup> and Dridi and Lacour.<sup>27</sup>

These previous studies have proven that the degree of water saturation significantly influences the chloride diffusivity in partially saturated concrete. It should be pointed out that most of these studies were generally focused on cement pastes and mortars with different binders (ordinary portland cement [OPC], OPC with fly ash, slag, silica fume, slag plus fly ash, and so on), and OPC concrete. However, experimental studies and results on the chloride transport

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**Table 1—Details of concrete mixtures**

Mixture name	Cementitious, lb/yd <sup>3</sup> (kg/m <sup>3</sup> )	Cement, lb/yd <sup>3</sup> (kg/m <sup>3</sup> )	20% FA, lb/yd <sup>3</sup> (kg/m <sup>3</sup> )	Fine aggregate, lb/yd <sup>3</sup> (kg/m <sup>3</sup> )	Coarse aggregate, lb/yd <sup>3</sup> (kg/m <sup>3</sup> )	FA, %	w/cm
DCL1	659 (390)	527 (312)	132 (78)	1795 (1062)	1104 (653)	20	0.35
DCL2	659 (390)	527 (312)	132 (78)	1604 (949)	1218 (721)	20	0.41
DCL3	659 (390)	527 (312)	132 (78)	1551 (918)	1178 (697)	20	0.47
DCL10b	566 (335)	453 (268)	113 (67)	1293 (765)	1702 (1007)	20	0.41
DCL11	472 (279)	377 (223)	95 (56)	1293 (765)	1705 (1009)	20	0.41

**Table 2—Chemical composition of cement**

Component	Aluminum oxide	Ferric oxide	Magnesium oxide	Sulfur trioxide	Tricalcium aluminate	Tricalcium silicate	Total alkali as Na <sub>2</sub> O
Content, %	5.1	3.8	1.0	2.8	7	68	0.36

in partially saturated binary blended concrete have not been reported.

Additionally, the surface concrete, where a thin layer of mortar covers the bulk concrete and is usually called “concrete skin,” can influence the chloride penetration into concrete.<sup>28</sup> Kreijer’s study<sup>29</sup> demonstrated that the “concrete skin” composition is different from concrete bulk and the formation of a gradient in composition from the concrete surface is due to the formwork/mold effect during casting. The concrete skin effect on the chloride transport has been verified by past experiences in the Florida marine environment, where cored concrete specimens with concrete cover from the field had significantly lower apparent chloride diffusion coefficients than those of the bulk diffusion tested specimens without concrete cover in the laboratory at comparable ages.<sup>30</sup> Furthermore, a previous laboratory study<sup>31</sup> confirmed that mortar rendering can act positively in relation to chloride penetration into concrete structures under high cement content and mortar thickness. However, there is not sufficient knowledge about the effect of mortar layers on the chloride diffusion in unsaturated concrete exposed to marine environments. It is therefore apparent that more work is beneficial to gain additional knowledge in this area.

## RESEARCH SIGNIFICANCE

Experimental studies and results on the chloride transport in partially saturated binary blended concrete exposed to marine environments have been rarely reported. Also, there is insufficient knowledge about the effect of mortar layers on the chloride diffusion in such unsaturated concrete. This paper presents experimental studies on the chloride diffusion into partially saturated concrete with 20% fly ash replacement under four degrees of water saturation relevant to Florida marine environments. The effect of mortar layers/concrete surface condition on the chloride diffusion was also investigated. The outcome provides insight into the chloride diffusion properties in partially saturated, binary-blended concrete in marine environments.

## EXPERIMENTS

### Materials

Five concrete mixtures were prepared as part of this research effort, and all mixtures had 20% fly ash (FA) Type F

as a cementitious replacement by the mass of cement. DCL1, DCL2, and DCL3 mixtures had a w/cm of 0.35, 0.41, and 0.47, respectively (refer to Table 1). DCL10b and DCL11 mixtures had a w/cm of 0.41, but were prepared with a lower cementitious content (refer to Table 1). Type I/II cement was used for all mixtures (refer to Table 2). The coarse aggregate and fine aggregate were crushed Florida limestone No. 57 and Florida river sand, respectively. Water-reducing and high-range water-reducing chemical admixtures were used to allow the design of low w/cm concrete and to control the plastic properties of the concrete. Table 1 shows the details of the concrete mixtures prepared for the present study.

Concrete cylinder specimens with a diameter of 3.94 in. (100 mm) and a height of 7.87 in. (200 mm) were prepared. Thirty-six concrete cylinders were cast per each mixture, but not all were used for the study described herein. The specimens were demolded 24 hours after casting and then exposed to different curing regimes. Four curing regimes were used, but only two correspond to the specimens described herein. Fifteen cylinders from each mixture were exposed to high humidity with a relative humidity (RH) in the range of 90 to 95% at room temperature (RT) at 70 ± 2°F (21 ± 1°C) for at least 150 days. Nine cylinders from each mixture were cured in high humidity at room temperature for 14 days (14RT), followed by immersing the specimens in calcium hydroxide solution and then storing them in an elevated temperature room at 97 ± 2°F (36 ± 1°C) for 28 days (28ET), after which they were transferred back to high humidity at RT exposure for additional curing to an age of at least 150 days. This process is represented with 14RT/28ET/RT. Details for the other curing regimes and other testing can be found in Reference 32.

Three cylinders from each mixture DCL1, DCL3, DCL10b, and DCL11 RT-cured were used for studying chloride diffusion under non-saturated and saturated conditions. Furthermore, four cylinders from Mixture DCL2 that were cured in RT and three cylinders cured in 14RT/28ET/RT from the same mixture were used for investigating the effect of curing regimes on the chloride transport under non-saturated and saturated conditions. Moreover, one cylinder per mixture corresponding to each set described previously was tested for measuring bulk density, water absorption, and porosity.

## Bulk density, water absorption, and porosity testing of specimens

As described previously, one cylinder from each mixture DCL1, DCL2, DCL3, DCL10b, and DCL11 cured in RT and one cylinder from DCL2 cured in 14RT/28ET/RT were used to determine their bulk densities, water absorption, and porosity.

Before testing, and after 150 days of curing, these cylinders were immersed in lime water for 30 days to increase the moisture content. Then each cylinder was cut into three pieces, identified as Slices A, B, and C, which were: the bottom (mold) slice, middle slice, and the top slice of each cylinder, respectively. Each section had the same length with cuts perpendicular to the cylinder axis. All specimens were then re-immersed into saturated  $\text{Ca}(\text{OH})_2$  solution at room temperature  $70 \pm 2^\circ\text{F}$  ( $21 \pm 1^\circ\text{C}$ ) until all the specimen mass stabilized. At this point, the bulk density, water absorption, and porosity of these specimens were performed in accordance with ASTM C642-06.<sup>33</sup> The maximum temperature used to dry the specimens was  $140^\circ\text{F}$  ( $60^\circ\text{C}$ ) so as to minimize the microstructure changes. The absorption results were later used to calculate the target mass for the desired degree of water saturation.

## Preparation and conditioning of specimens

**Saturated specimens**—For the saturated concrete diffusion test, one concrete cylinder was selected from each mixture DCL1, DCL2, DCL3, DCL10b, and DCL11 cured in high humidity at RT and immersed in calcium hydroxide solution at the age of 420, 496, 469, 441, and 448 days from casting, respectively. These concrete cylinders remained immersed in calcium hydroxide solution for at least 100 days until a stable mass was reached. Each cylinder was cut into four pieces (identified as Slices A, B, C, and D), which were Slice A, the bottom mold surface section; B and C, the two middle



Fig. 1—Specimen for 100% SD with and without mortar layer.

sections; and D, the top section of each concrete cylinder, respectively. Each section had the same length with the cuts perpendicular to the cylinder axis (approximately 1.97 in. [5 cm] thick). The exposed surface for Sections A and D was the mortar surface (A, mold surface and D, trowel surface). Half of the mortar layer was then removed with a wet saw on Sections A and D. The thickness removed was less than 0.039 in. (1 mm); refer to Fig. 1. This was done to investigate the effect of the mortar layer presence and absence on the chloride diffusion. An epoxy paint was applied at the interface to avoid transport at the step region (refer to Fig. 1). Section C was also used for saturated exposure. All specimens were then re-immersed in saturated  $\text{Ca}(\text{OH})_2$  solution at room temperature  $70^\circ\text{F}$  ( $21^\circ\text{C}$ ) until a stable mass was achieved on consecutive days. B slices were not used for this study (refer to Table 2).

**Non-saturated specimens**—For the non-saturated concrete diffusion test, the concrete cylinders selected from each mixture DCL1, DCL2, DCL3, DCL10b, and DCL11 cured in high humidity at RT and the DCL2 cured in 14RT/28ET/RT were immersed in calcium hydroxide solution at the age of 150 days from casting. These cylinders remained immersed until an age of 220 days and then were cut into three sections. The procedure for cutting cylinders was the same as previously described for the water absorption specimens. All concrete sections after cutting were re-immersed in a saturated  $\text{Ca}(\text{OH})_2$  solution until the mass of the sections stabilized, which usually took approximately 2 to 3 additional days. Three water saturation degrees were investigated: 70, 80, and 90%. There were 24 concrete sections obtained by cutting the two cylinders per each mixture, which means there were six sections per mixture from DCL1, DCL3, DCL10b, and DCL11. The specimens were randomly/arbitrary assigned to reach one of the three degrees of water saturation (refer to Table 3). There were 18 concrete sections, A, B, and C, obtained from mixture DCL2 cylinders: nine slices were obtained from three RT cured cylinders and the other nine slices from three cylinders cured in 14RT/28ET/RT. Six DCL2 sections were stabilized within each of the three water saturation degrees. For the other mixtures, only two sections were exposed to each degree of water saturation. Table 3 lists the targeted degree of water saturation and their corresponding concrete sections. The targeted degree of water saturation was obtained by drying the specimens in an oven at a temperature range from  $104$  to  $116.6^\circ\text{F}$  ( $40$  to  $47^\circ\text{C}$ ) until they achieved the target mass  $m_{SD}$ . The target  $m_{SD}$  for each slice was determined by the following equation<sup>8-10</sup>

Table 3—Degree of water saturation (SD) and concrete sections

Targeted SD, %	DCL1 (RT)	DCL2 (RT)	DCL2 (14RT/28ET/RT)	DCL3 (RT)	DCL10b (RT)	DCL11 (RT)
70	C,C	A,B,C	A,B,C	A,A	B,B	A,C
80	B,B	A,B,C	A,B,C	C,C	A,A	B,C
90	A,A	A,B,C	A,B,C	B,B	C,C	A,B
100*	A,C,D	A,D	A,C,D	A,C,D	A,C,D	A,C,D

Note: Concrete sections with 100% SD were 1.97 in. (5 cm) thick slices.



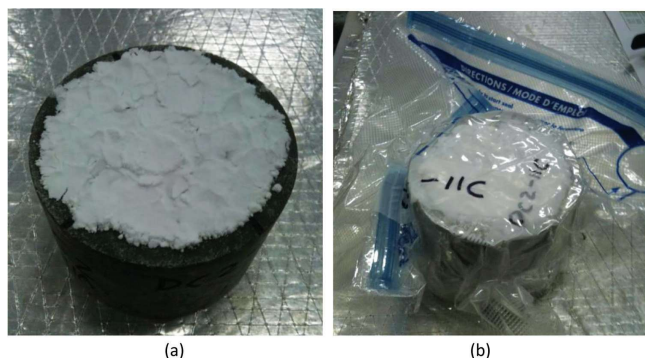


Fig. 2—Diffusion experiment setup for unsaturated specimens.

$$SD = \left( \frac{m_{SD} - m_{dry}}{m_{dry}} \right) * \frac{10,000}{A} \quad (1)$$

where  $SD$  is the targeted degree of water saturation, %;  $m_{SD}$  is the mass of the specimen for the targeted water saturation degree, in grams;  $m_{dry}$  is the dry mass of the specimen, in grams; and  $A$  is the water absorption, %. Once the targeted degree of water saturation was obtained, the specimens were allowed to homogenize their moisture content. Each specimen was isolated by wrapping it with three layers of plastic wrap and then housing it in a plastic vacuum bag for 35 to 42 days. A manual vacuum pump was used to remove the air. During the stabilization period, the mass of the specimens was monitored, and a re-vacuum was performed once per week to ensure that the  $m_{SD}$  of each specimen remained the same.

### Diffusion experiment setup

**Saturated specimens**—Slices A, C, and D were used. A 1 in. (25.4 mm) tall plastic pipe (with internal diameter identical to the concrete cylinder diameter) slice was attached to the test surface of each specimen with marine-grade epoxy. After the epoxy dried (approximately 12 hours), these specimens were re-immersed into the calcium hydroxide solution until saturated again. Thereafter, the test surfaces were dried with paper towels. Immediately, finely ground solid sodium chloride (passing No. 100 sieve) was used as the chloride source and placed on the tested surface of each specimen. For Slice A, the tested surface was the bottom mold surface. For Slice C, the exposed surface was the surface produced by the cut between Slice B and Slice C (that is, the surface at the center of the concrete cylinder). For Slice D, the exposed surface was the top (trowel) surface. After placing the finely ground solid NaCl, the specimens were partly immersed (approximately 2/3 of their height) in saturated  $\text{Ca}(\text{OH})_2$  solution. The specimens were placed in purposely made storage boxes, which were sealed and vacuumed twice a week to remove air. The diffusion period ranged between 10 and 28 days. This exposure duration was longer than that used by Guimaraes and Helene<sup>8,9</sup> and Guimaraes et al.<sup>10</sup>

**Non-saturated specimens**—After the moisture homogenization was achieved, all vacuum bags and plastic layers were removed and the mass of the specimens was recorded.

Immediately, finely ground solid sodium chloride (passing No. 100 sieve) was used as the chloride source and placed on the tested surface of each specimen as shown in Fig. 2(a). For Section A (bottom), the tested surface was on the bottom mold surface (that is, smooth face with mortar layer). For the middle Slice B, the exposed surface was the cut surface between Slice A and Slice B. Finally, for Section C, the exposed surface was the cut surface between Slice B and Slice C. Thus, the surface with coarse aggregate and mortar were exposed to NaCl for Slice B and Slice C. After placing the finely ground solid NaCl, each specimen was isolated by wrapping with four layers of plastic wrap and placing this arrangement into vacuum bags as shown in Fig. 2(b). A manual vacuum pump was used to remove the air. During the diffusion exposure period, the mass of each specimen was monitored, and re-vacuuming was performed periodically. The diffusion times for 70, 80, and 90% of the degree of water saturation were 103 to 130 days, 74 to 102 days, and 46 to 69 days, respectively. These exposure durations were at least twice longer than those used by Guimaraes and Helene<sup>8,9</sup> and Guimaraes et al.<sup>10</sup> After the diffusion exposure periods, all vacuum bags and plastic layers were removed, and the NaCl footprint on the top of the specimen was marked. Any remaining NaCl was removed as much as possible without scraping the concrete, and the tested surface of the specimen was then carefully cleaned with compressed air. An octagon shape was marked on the top surface, and vertical cuts were made to minimize edge effects, similar to what is done for bulk diffusion test specimens.

### Concrete powder collection and chloride analysis

For all specimens, the concrete powder was obtained by milling the material in layers parallel to the exposed surface. The first layer thickness was typically 0.039 in. (1 mm). The target thickness of the second, third, fourth, fifth, and sixth layers was 0.07874 in. (2 mm). In some cases, a seventh layer was obtained, depending on the chloride concentration of the sixth layer. Chloride concentrations were obtained via a total chloride method in accordance with a slightly modified FDOT method.<sup>34</sup> Assuming that the chloride diffusion coefficients and chloride surface concentration are constant with time, the chloride concentration profiles obtained from the chloride analyses can then be used to fit Fick's Second Law of Diffusion, expressed as follows<sup>35</sup>

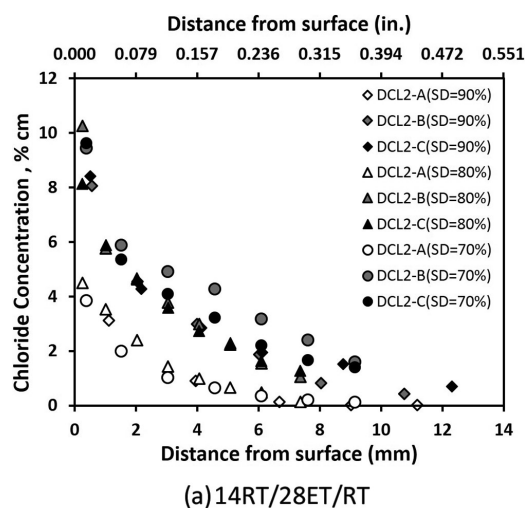
$$C(x, t) = C_s \left[ 1 - \operatorname{erf} \left( \frac{x}{2\sqrt{D_{app}t}} \right) \right] \quad (2)$$

where  $C(x, t)$  is the chloride concentration at depth  $x$  at time  $t$ ;  $C_s$  is the chloride content at the concrete surface;  $x$  is depth;  $t$  is time; and  $D_{app}$  is the apparent diffusion coefficient. The fit to each profile produces  $D_{app}$  and  $C_s$  values.  $D_{app}$  is the average apparent diffusion coefficient value over the exposure period.<sup>36</sup> A better fit was obtained (that is, better R2) for most profiles by removing the chloride concentration measured for the first layer (depth).

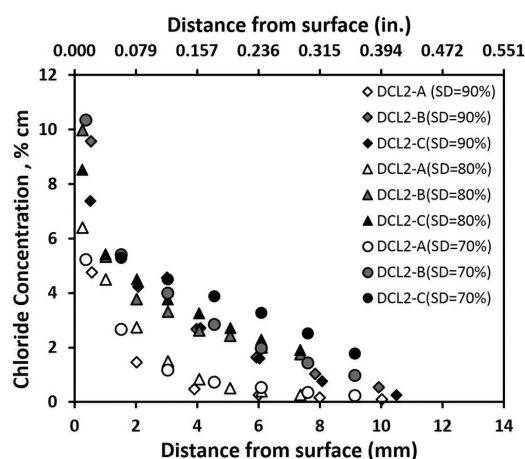


**Table 4—Absorption and porosity of specimens, %**

Specimens	A		B		C	
	Absorption	Porosity	Absorption	Porosity	Absorption	Porosity
DCL1 (RT)	2.44	5.44	2.86	6.30	2.52	5.54
DCL2 (RT)	3.58	7.88	3.59	7.91	3.55	7.82
DCL2 (14RT/28ET/RT)	2.97	6.61	3.51	7.73	3.48	7.71
DCL3 (RT)	4.45	9.81	4.98	10.78	5.04	10.93
DCL10b (RT)	4.44	9.56	4.98	10.48	4.53	9.54
DCL11 (RT)	3.33	7.48	4.17	9.11	3.89	8.52



(a) 14RT/28ET/RT



(b) RT

*Fig. 3—Measured chloride profiles for DCL2. (Note: chloride concentration % by weight of cementitious.)*

## RESULTS AND DISCUSSIONS

### Absorption and porosity of specimens

Table 4 shows the absorption and porosity measured. These results were used to calculate and control the degree of water saturation weights for the non-saturated diffusion test samples.

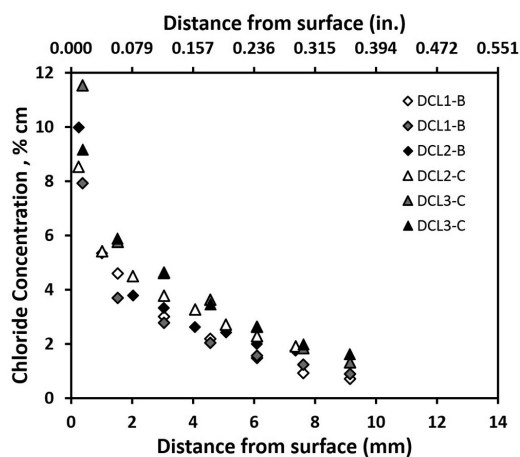
### Chloride concentration profiles

Figure 3 shows the chloride profiles obtained from DCL2 specimens after non-saturated exposure to 70, 80, and 90% degree of water saturation. The selected specimens were

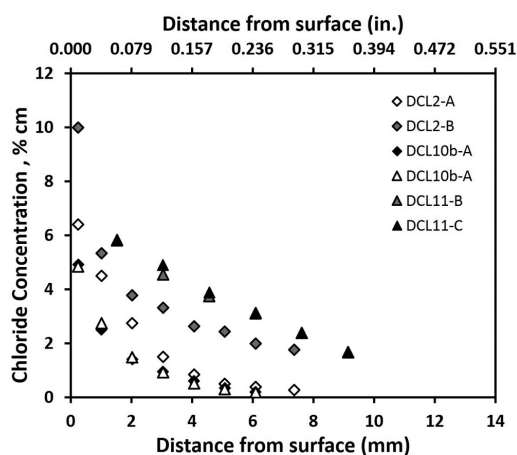
cured in 14RT/28ET/RT and in RT. The diffusion time for specimens with 70, 80, and 90% degree of water saturation is 105, 74, and 46 days, respectively. Figure 3(a) shows concentration profiles for DCL2 specimens initially cured in 14RT/28ET/RT and Fig. 3(b) shows concentration profiles for RT cured specimens.

It can be observed in Fig. 3 that the chloride concentrations profiles obtained on the three Slices A are significantly lower than the concentrations profiles obtained from Slices B and C, regardless of curing type and degree of water saturation during the diffusion period. These results are in agreement with past experience in which cored specimens with concrete cover from the field in the Florida marine environment had significantly lower apparent chloride diffusion coefficients than those of the bulk diffusion tested specimens without concrete cover in the laboratory at comparable ages.<sup>30</sup> This difference in chloride profiles has been attributed to the “skin effect”.<sup>28,29</sup> In Reference 37, the authors verified that chloride profiles through concrete cover are lower than that on profiles from the cored inner portion; and this was explained by the carbonation of concrete cover, which reduces the porosity of concrete cover and makes the passage of chlorides more difficult, leading to lower chloride diffusion coefficients. In the present study such carbonation was not present; however, the presence of FA and its corresponding pozzolanic reaction likely reduced the porosity of the cover mortar in Slice A when compared to the exposed cut surface on Slices B and C. The thin mortar layer where the salt was deposited on Slice A, which is the cylinder bottom part, has resulted in slower chloride transport than portions B and C without the mortar layer. In addition, the thin mortar layer on Slice A might behave to some extent as a mortar rendering to protect concrete against chloride penetration.<sup>31</sup> It is therefore clear that the chloride concentration is influenced by the surface condition (mortar layer/mortar content) regardless of curing type (14RT/28ET/RT or RT) and the degree of water saturation during the diffusion period.

Figure 3(a) also shows that the chloride concentrations profiles from Sections A cured in 14RT/28ET/RT are almost identical for profiles corresponding to 80 and 90% degree of water saturation and slightly lower concentrations are observed for the profile obtained after exposure to 70% degree of water saturation. It should be noted that the diffusion time for specimens with 70%, 80%, and 90% degree of water saturation is 105, 74, and 46 days, respectively. Although the exposure time is different, the concentration profiles are similar, which suggests that the degree



(a)



(b)

Fig. 4—Chloride profiles for DCL1, DC2, DC3, and DC10b and DCL11 with SD = 80%. (Note: chloride concentration % by weight of cementitious.)

of water saturation plays a key role in the chloride transport. For concrete sections B cured in 14RT/28ET/RT with 80 and 90% degree of water saturation, the chloride concentrations are similar, but higher chloride content is observed in concrete section B with a 70% SD, which may be attributed to the longer exposure time. Similar observation could be made from profiles of Section C. For the concrete cured in RT as shown in Fig. 3(b), the chloride profiles from Section A with mortar layers and regardless of the degree of water saturation are lower than those obtained from Slices B and C. The difference in concentration might be attributed to the effect of mortar layer presence and shorter exposure. Incidentally, no significant difference was observed when comparing other corresponding profiles of specimens RT cured and 14RT/28ET/RT cured. This might be due to the mature age at which the diffusion test exposure began (>220 days of age). It should be noticed that the chloride profile of DCL2 Slice C with 70% degree of water saturation in Fig. 3(b) is generally higher than the profiles for the other DC2 specimens in Fig. 3(b). A reason for this might be associated with the exposed surface (cut surface) and longer exposure time. Moreover, it can be seen that the chloride

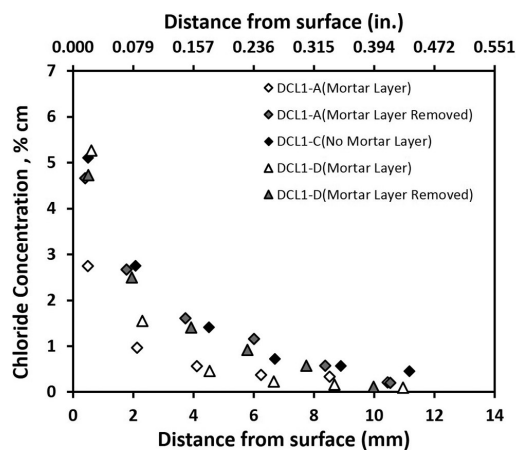
concentration of the first layer was significantly higher than the second layer on Slices B and C, while a more modest difference was observed when comparing the concentration of the first two layers on Slices A. Because of this, the diffusion coefficient was computed both with the concentration of all layers and with the first layer omitted. The latter is a common practice when a skin effect is observed in experimentally obtained chloride profiles. Therefore, it is apparent that the chloride concentrations are affected by the surface condition (mortar layer/mortar content), the degree of water saturation, and exposure time for specimens of a given concrete mixture.

Figure 4 shows the chloride profiles that correspond to the specimens cured in RT exposed to 80% degree of water saturation. Recall that the  $w/cm$  for DCL1, DCL2, and DCL3 are 0.37, 0.41, and 0.47, respectively. It can be observed in Fig. 4 (a) that chloride profiles that correspond to DCL3 have the highest chloride concentrations while the profiles for DCL1 have the lowest chloride concentrations under the same exposure time (90 days). The exposure time of DCL2 specimen is 74 days, and its chloride concentration profile of DCL2 is between the former two profiles. The cause for this trend is in part associated with the different  $w/cm$ . Figure 4(b) shows that for DCL11, the chloride profile concentrations of Sections B and C, which are both without mortar layers, are higher than those in Section A with the mortar layer. The cause for this difference might be attributed to the mortar layer presence and its behavior as a mortar rendering to protect concrete against chloride penetration into Section A, as discussed previously. The exposure times for DCL2, DCL10b, and DCL11 are 74, 92, and 102 days, respectively. It is also observed that the chloride profiles of DCL2-A and DCL10b-A are comparable; while the chloride profiles of DCL2-B and DCL11-B are almost identical, which suggests that the cementitious content does not appear to have a significant effect on chloride penetration under the same  $w/cm$  in the present study. Also, the chloride profiles obtained from the concrete specimens cured in RT respectively exposed to 90% and 70% degrees of water saturation have similar trends, which are not shown herein. On the basis of these results, it is apparent that the chloride profiles of the specimens with lower  $w/cm$  values are less than those of the specimen with high  $w/cm$  values for a given degree of water saturation and curing type. Furthermore, the cementitious content does not appear to significantly influence the chloride penetration for a given degree of water saturation under the same  $w/cm$ .

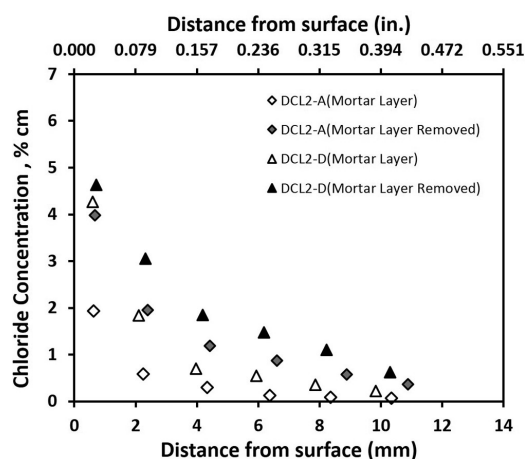
### Further analysis of effect of mortar layer on chloride concentration

The results shown in the previous section have indicated that the chloride concentration profiles obtained from Slice A are significantly lower than the concentrations obtained from Slices B and C, and it might be attributed to the effect of the mortar layer. This topic was further investigated and the findings are presented herein.

Figure 5 shows the chloride concentration profiles of DCL1 and DCL2 cured in RT up to day 560 and then exposed to finely ground salt at 100% degree of water satu-



(a) DCL1



(b) DCL2

Fig. 5—Chloride profiles from DCL1 and DC2 cured in RT with SD = 100% under conditions of exposed surface with and without mortar layers. (Note: Chloride concentration % by weight of cementitious.)

ration. Due to the space limitation, the results obtained from DCL3, DCL10b, and DCL11 are not listed and discussed herein. Recall that Slices A and D were exposed with a half-mortar layer and the other half-mortar layer removed (half and half), as shown in the pictures of Fig. 1. It was observed in Fig. 5(a) that the chloride concentrations profiles obtained from the concrete portion DCL1-A with half-mortar layer, and DCL1-D with half-mortar layer were generally lower than those obtained from the concrete slices DCL1-A with the mortar layer removed, DCL1-C without the mortar layer and DCL1-D with the mortar layer removed. Similarly, this trend was also observed for the chloride profiles obtained on concrete sections for Mixture DCL2 shown in Fig. 5(b). On the basis of the results in the previous section and in this section, it has been confirmed that the surface conditions of concrete/mortar contents have affected the chloride diffusion in both unsaturated and saturated concrete. The chloride concentrations obtained from a given concrete mixture with mortar layer/high-mortar content are generally lower than those obtained from the same concrete sample without

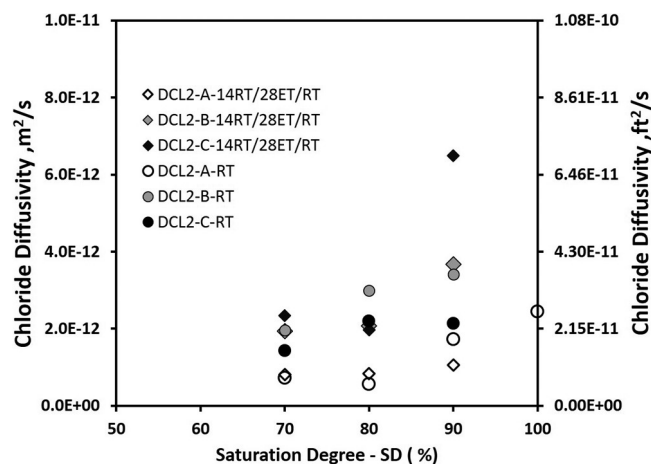


Fig. 6—Chloride diffusivity of DCL2 specimens versus SD.

a mortar layer/low-mortar content for the 70, 80, 90, and 100% degree of water saturation under the given  $w/cm$  and curing type. It is therefore evident that the mortar layer can reduce the chloride transport in concrete with a certain  $w/cm$  against chloride penetration.

### Effect of degrees of water saturation on chloride diffusivity under different curing regimes

Figure 6 shows  $D_{app}$  chloride coefficients of DCL2 as a function of the degrees of water saturation for specimens cured in two different curing regimes. The shown fitted  $D_{app}$  values were obtained after removing the first layer. Recall that the exposed surface in Sections A are the surface with mortar layers. It was observed that the chloride diffusivities of concrete Section A are generally lower than the  $D_{app}$  for concrete Sections B and C at a given degree of water saturation and for a given curing regime. As discussed previously, this is attributed to the better compacted concrete of Section A. It is also associated with the concrete skin effect<sup>28,29</sup> and the mortar layer present on Section A that appears to slow the chloride penetration.<sup>31</sup> These factors contributed to the lower chloride diffusivities observed on Section A compared to the diffusivities observed on concrete Sections B and C. The present study has demonstrated that the surface condition (mortar layer/mortar content) plays a key role in chloride diffusion in partially saturated high-performance concrete.

For the chloride diffusivities of the DCL2 cured at 14RT/28ET/RT as a function of the degree of saturation (SD), it was observed that the  $D_{app}$  values of Section A hardly changed when the SD varied from 70 to 80%. However, a gradual increase in the  $D_{app}$  value was observed when the SD increased from 80 to 90%. It should be pointed out that the concrete age and exposure duration might have affected the measured  $D_{app}$  values. A similar trend was also observed on Sections B and C, but a greater increase in  $D_{app}$  values was observed when SD changed from 80% SD to 90% SD. Thus, the present results demonstrate that the chloride diffusivity value of the DCL2 (concrete mixture with 20% fly ash replacement and 0.41 of  $w/cm$ ) cured at 14RT/28ET/RT is generally not sensitive to the SD change when SD is in the range of 70 to 80%, compared with that from 80% SD to 90% SD.



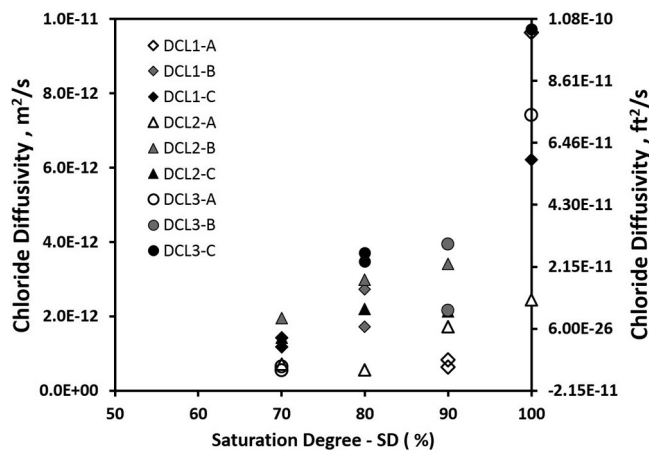


Fig. 7—Chloride diffusivity of DCL1, DCL2, and DCL3 specimens cured in RT versus SD.

For the chloride diffusivities of the DCL2 cured at RT as a function of SD, comparable  $D_{app}$  values of Section A were observed for both 70% SD and 80% SD, but the  $D_{app}$  values of Section A gradually increased as the SD went from 80 to 100%. The  $D_{app}$  value measured on Section B increased when the SD changed from 70 to 80%, which was followed by a relatively lower increase rate when the SD was varied from 80 to 90%. The  $D_{app}$  value of Section C increased when the SD went from 70 to 80% and showed a  $D_{app}$  value plateau when the SD ranged from 80 to 90%.

Comparing the chloride diffusivity value as a function of SD for the DCL2 Sections A, B, and C cured at 14RT/28ET/RT with those of the DL2 counterparts cured at RT, it can be seen that the  $D_{app}$  values of Sections A cured at 14RT/28ET/RT and at RT are comparable in the range of 70% SD—80% SD and then the former increased at a lower ratio than the latter when the SD went from 80 to 90%. The trends of the chloride diffusivity value as a function of SD for the DCL2 Sections B and C cured at 14RT/28ET/RT is different from that for the DCL2 Sections B and C cured at RT, suggesting that the chloride diffusivity value as a function of SD for concrete (Sections B and C) with 20% fly ash replacement and 0.41 of  $w/cm$  is somewhat affected by the curing regimes which has not been reported in literature. A possible explanation is associated with differences in the concrete microstructure due to the differences in curing regimes<sup>38</sup> at early age. The 4-week elevated temperature curing likely accelerated the pozzolanic reaction on samples cured in 14RT/28ET/RT.

### Effect of degrees of water saturation on chloride diffusivity for samples with different $w/cm$

Figure 7 shows the  $D_{app}$  value as a SD function of DCL1, DCL2, and DCL3 cured in RT. Their  $w/cm$  is 0.35, 0.41, and 0.47, respectively. All Sections A are with mortar layers.

Having an insight into the general trend of all these concrete specimens, it was interesting to find out that the  $D_{app}$  value at SD = 70% for all DCL1, DCL2, and DCL3 Sections A cured in RT were comparable, regardless of the  $w/cm$ . It was also observed that the  $D_{app}$  value of DCL1 Section A at SD = 90% was comparable to the  $D_{app}$  measured on DCL2 Section A at SD = 80%. Furthermore, the  $D_{app}$  value of DCL2 Section A increased when SD went from 80 to 90%. However, the

general trend of the  $D_{app}$  value as a function of SD for all DCL1, DCL2, and DCL3 Sections B and C was different. It is apparent that there is a difference between the general trend of the  $D_{app}$  value of concrete Sections A as function of SD and the  $D_{app}$  value of concrete Sections B and C as a function of SD.

Guimaraes et al.<sup>10</sup> reported that the  $D_{app}$  values of Mortars H1, H2, and H5 with a content of 12% fly ash and 0.55, 0.48, and 0.57 of  $w/cm$  increased in various rates when the SD was increased from 50 to 100%, but the  $D_{app}$  values of some mixtures H3 and H4 with a content of 12% fly ash and 0.66 and 0.55 of  $w/cm$  increased in a range of 50% SD—75% SD (approximately) and then only slightly or actually reached a plateau in a range of SD between 75 and 100% on mortars. Comparing Guimaraes et al.<sup>10</sup> results with the present study, it is apparent that the trend of the  $D_{app}$  values as function of SD obtained from both studies is quite different. Additionally, the  $D_{app}$  values obtained from the Guimaraes et al.<sup>10</sup> study were generally higher than the results obtained from the present study for a given SD due to the  $w/cm$ , materials type, and concrete surface conditions.<sup>13-19,28,29</sup>

Mercado-Mendoza et al.<sup>12</sup> developed an approach (based on the electrochemical impedance spectroscopy) to investigate the  $D_{app}$  evolution with the SD level of OPC cement paste, OPC cement concrete, blended cement (55%OPC+22%BFS+23%FA) paste, and blended cement (55%OPC+22%BFS+23%FA) concrete. A  $w/cm$  of 0.43 and 0.41 was used, respectively. The results obtained from concrete indicated that the  $D_{app}$  values of the OPC cement concrete increased in a more pronounced way from 68% SD to 76% SD than those in a range of SD between 76 and 100% with the latter only slightly or actually reached a plateau. But the trend of the  $D_{app}$  as a function of SD for the blended cement concrete is different, where it increased in a drastic way when SD increased from 68 to 74% and then the  $D_{app}$  had a lower increase rate in the range of 74% SD to 100% SD. Clearly, the  $D_{app}$  evolution with the SD level between OPC cement concrete and blended cement concrete is different. Mercado-Mendoza et al.<sup>12</sup> suggested that the  $D_{app}$  values of both OPC cement concrete and blended cement concrete increased in a more pronounced or uniform way in the corresponding SD could be ascribed to the progressive loss of the liquid phase contained in a pore mode (capillary porosity), which is associated with many factors, including materials type, tortuosity, age, and so on. As observed in Fig. 7, the present study demonstrates that the  $D_{app}$  value as a function of SD for all DCL1, DCL2, and DCL3 Sections A cured in RT rarely changes in the range of 70% SD—80% SD, which is followed by an increase of the  $D_{app}$  values of these specimens Sections A in different increase rate when the SD varied from 80% SD to 90% SD. The findings from the current study also verifies that the general trend of the  $D_{app}$  value as a function of SD for all DCL1, DCL2, and DCL3 Sections B and C increases from 70 to 80% at a higher rate than that from 80 to 90%. And then it increases at an even higher rate again in the range of 90 to 100% (no DCL2-C at SD = 100%). Comparing the results obtained from Mercado-Mendoza et al.<sup>12</sup> work with obtained in the present study, there is an obvious difference between

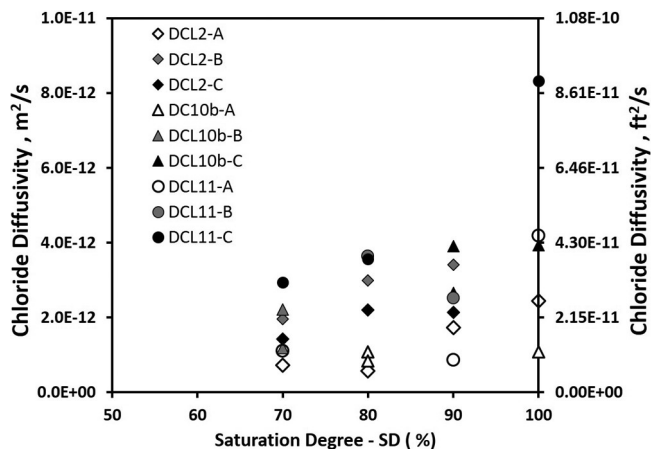


Fig. 8—Chloride diffusivity of DCL2, DCL10b, and DCL11 cured in RT versus SD.

the two studies, even though the  $w/cm$  is the same (DCL2  $w/cm = 0.41$ ). The observed difference might have resulted due to the difference in materials used, concrete preparation, concrete surface conditions and experimental methods,<sup>19</sup> aggregate size,<sup>10</sup> and so on.

### Effect of degrees of water saturation on chloride diffusivity under different cementitious content

Figure 8 shows the calculated  $D_{app}$  value as a function of SD obtained on DCL2, DCL10b, and DCL11 RT cured specimens. Recall that Sections A are with mortar layers. These specimens have the same  $w/cm$  ( $w/cm = 0.41$ ), but different cementitious content. Once again, the  $D_{app}$  values of concrete Sections A are generally lower than the  $D_{app}$  values observed in concrete Sections B and C at a given SD. At 80% SD, DCL10b two Sections A  $D_{app}$  had values of  $14.42 \times 10^{-12} \text{ ft}^2/\text{s}$  ( $1.34 \times 10^{-12} \text{ m}^2/\text{s}$ ) and  $11.94 \times 10^{-12} \text{ ft}^2/\text{s}$  ( $1.11 \times 10^{-12} \text{ m}^2/\text{s}$ ), which are slightly higher than the  $D_{app}$  value ( $6.03 \times 10^{-12} \text{ ft}^2/\text{s}$  [ $0.56 \times 10^{-12} \text{ m}^2/\text{s}$ ]) of DCL2 Section A. It can be also seen that at 70% SD, the  $D_{app}$  value ( $31.63 \times 10^{-12} \text{ ft}^2/\text{s}$  [ $2.94 \times 10^{-12} \text{ m}^2/\text{s}$ ]) of DCL11 Section C is higher than the  $D_{app}$  value ( $15.39 \times 10^{-12} \text{ ft}^2/\text{s}$  [ $1.43 \times 10^{-12} \text{ m}^2/\text{s}$ ]) for DCL2-C. Somewhat similar results can also be inferred by comparing the  $D_{app}$  value of DCL2-C with that of DCL11-C at 70% degrees of water saturation. However, when comparing the  $D_{app}$  value of DCL11 Section A ( $9.23 \times 10^{-12} \text{ ft}^2/\text{s}$  [ $8.58 \times 10^{-13} \text{ m}^2/\text{s}$ ]) with the  $D_{app}$  value for DCL2 Section A ( $18.51 \times 10^{-12} \text{ ft}^2/\text{s}$  [ $1.72 \times 10^{-12} \text{ m}^2/\text{s}$ ]) at 90% SD, the latter is higher than the former, which is different from that described previously. It was also observed that the  $D_{app}$  value of both DCL11 Section A and DCL10b Section A are greater than the  $D_{app}$  of DCL2 Section A at 100% SD. A similar trend was observed when comparing the  $D_{app}$  for Sections C and 100% SD (no DCL2-C herein), but the values were higher. Therefore, the effect of cementitious content on the chloride diffusivity is complicated for a given degree of water saturation and it should be further investigated.

### Further discussion on effect of mortar layer on chloride diffusivity

Figure 9 shows the  $D_{app}$  values of Sections A, C, and D of DCL1, DCL2, DCL3, DCL10b, and DCL11 cured in

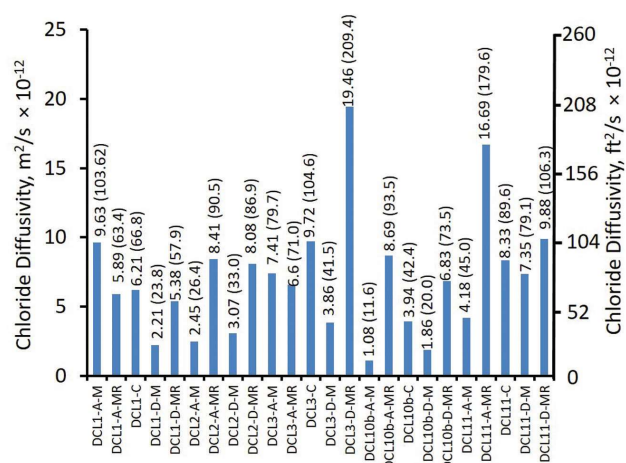


Fig. 9—Chloride diffusivity values of Sections A, C, and D of DCL1, DCL2, DCL3, DCL10b, and DCL11 at SD = 100% in RT. (Note: M = with mortar layer; MR = mortar layer removed.)

RT and exposed to chlorides at SD = 100%. Recall that the exposed surface for Layers A was the mold surface and for D was the trowel surface—that is, the mortar surface but with half of it removed. In Fig. 9, the samples are keyed mix-section. For A and D slices, the key is followed with “-M” (surface with mortar layers) or “-MR” (mortar layer removed). Section C is one of the center sections (cut surface without mortar layer). It was observed that the  $D_{app}$  values of DCL1-A-M were higher than those of DCL1-A-MR, but the chloride concentration profile was higher on the latter (refer to Fig. 5(a)). The  $D_{app}$  values of DCL3-A-M (with mortar layer) and DCL3-A-MR (mortar layer removed) were almost identical. However, the  $D_{app}$  values of the other concrete sections (A and D) with the mortar layer were lower than those of concrete sections (A and D) with the mortar layer removed and concrete sections (C) without mortar layers. In term of the results obtained from the concrete at SD = 100% and from the concrete cured in RT and 14RT/28ET/RT at SD = 70, 80, and 90%, it is evident that the  $D_{app}$  values of concrete sections with mortar layers (concrete mold surface and trowel surface) are generally lower than those of concrete sections with mortar layers removed and concrete sections without mortar layers for a given  $w/cm$ , such that the  $D_{app}$  value of DC1-D-M is less than that of DC1-D-MR and DC1-C by 58.91% and by 64.41%, respectively, when cured in RT and SD = 100%; the  $D_{app}$  value of DC2-A-M is less than that of DC2-A-MR by 70.86% while the  $D_{app}$  value of DC2-D-M is less than that of DC2-D-MR by 60.0% when cured in RT and SD = 100%. Similarly, this was observed in other specimens. As previously discussed, this is attributed to the microstructure of concrete Sections A with mortar layer (except for DCL1-A and DCL3-A) and D with mortar layer—for example, due to its lower porosity, tortuosity, pore connectivity, and so on. It is also related to the concrete skin effect<sup>28,29</sup> and the mortar layer on Sections A and D (with mortar layers) that can protect concrete against chloride penetration.<sup>31</sup> These factors have improved the resistance to chloride transport into concrete, leading to the chloride diffusivities of concrete Section A with mortar layers



(except for DCL1 and DCL3) and D with mortar layers to be generally lower than those of concrete Sections A and D (mortar layer removed) and C (without mortar layers), respectively. The study has therefore demonstrated that the surface condition (mortar layer/mortar content) plays a key role in chloride diffusion in partially saturated and saturated binary blended concrete.

## CONCLUSIONS

The present work has experimentally investigated the chloride diffusion into partially saturated concrete with 20% fly ash replacement and the effect of mortar layers/concrete surface conditions on the chloride diffusion at four SD related to the Florida marine environments under various curing regimes,  $w/cm$ , and cement contents. The study leads to the following conclusions:

1. The surface condition (mortar layer/mortar content) of concrete plays a key role in chloride diffusion in partially saturated concrete with 20% fly ash. It can reduce the chloride transport in concrete, leading to lower chloride concentration profiles and lower  $D_{app}$  values of concrete specimens with mortar layers when compared to concrete without the mortar layer or with the mortar layer removed at a given SD under a given  $w/cm$  and curing regime.

2. The  $D_{app}$  value of all concrete specimens with mortar layers hardly changes when SD increases from 70 to 80% and then it is increased at various rates from 80% SD to 100% SD.

3. The effect of the curing regimes on the  $D_{app}$  trend is not significant after the concrete has matured for a given concrete without mortar layer (B and C slices). A modest difference in the trend of the  $D_{app}$  is observed with no change between SD = 70% and SD = 80% for the concrete without mortar layer cured in 14RT/28ET/RT, but a larger increase in  $D_{app}$  when SD went from 80 to 90%, whereas  $D_{app}$  values for those samples RT cured (B and C slices) tend to monotonically increase when SD increases from 70 to 80% with plateau at SD = 90%. However, the range of the  $D_{app}$  values for the latter is not large.

4. The  $D_{app}$  value as an SD function of concrete without mortar layer (B and C slices) is clearly affected by  $w/cm$ , resulting in different trends of evolution.

5. The influence of cementitious content on  $D_{app}$  is complicated and should be further investigated.

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## REFERENCES

- Gjorv, O. E., *Durability Design of Concrete Structures in Severe Environments*, second edition, CRC Press, Boca Raton, FL, Feb. 7, 2014, 270 pp.
- Neilson, E. P., and Geiker, M. R., "Chloride Diffusion in Partially Saturated Cementitious Materials," *Cement and Concrete Research*, V. 33, No. 1, 2003, pp. 133-138. doi: 10.1016/S0008-8846(02)00939-0
- Parrot, L. J., "Moisture Conditioning and Transport Properties of Concrete Test Specimens," *Materials and Structures*, V. 27, Oct. 1994, pp. 460-468. doi: 10.1007/BF02473450
- Martys, N. S., "Diffusion in Partially-Saturated Porous Materials," *Materials and Structures*, V. 32, Oct. 1999, pp. 555-562. doi: 10.1007/BF02480489
- Chatterji, S., "On the Non-Applicability of Unmodified Fick's Law to Ion Transport through Cement Based Materials," *Proceedings of the 1st International Workshop on Chloride Penetration into Concrete*, RILEM Publication, Saint-Rémy-lès-Chevreuse, France, 1997, pp. 64-73.
- Climent, M. A.; de Vera, G.; Lopez, J. F.; Viqueira, E.; and Andrade, C., "A Test Method for Measuring Chloride Diffusion Coefficients through Nonsaturated Concrete. Part I: The Instantaneous Plane Source Diffusion Case," *Cement and Concrete Research*, V. 32, No. 7, 2002, pp. 1113-1123. doi: 10.1016/S0008-8846(02)00750-0
- Vera, G.; Climent, M. A.; Viqueira, E.; Anton, C.; and Andrade, C., "A Test Method for Measuring Chloride Diffusion Coefficients through Nonsaturated Concrete. Part II: The Instantaneous Plane Source Diffusion Case with Chloride Binding Consideration," *Cement and Concrete Research*, V. 37, No. 5, 2007, pp. 714-724. doi: 10.1016/j.cemconres.2007.01.008
- Guimaraes, A. T. C., and Helene, P. R. L., "The Moisture Effect on the Diffusion of Chloride Ions in Hydrated Cement Paste," *Proceedings of the International Symposium on Marine Corrosion in Tropical Environments*, C.S.W. Dean, G. H. Degadillo, and J. B. Bushman, eds., ASTM STP 1399, Philadelphia, PA, 2000, pp. 135-149.
- Guimaraes, A. T. C., and Helene, P. R. L., "Models of Variation of Chloride Ion Diffusion as a Function of Changes in the Saturation Degree of Concrete Mixes Prepared with Pozzolanic Cement," R. M. Ferreira, J. Gulikers, and C. Andrade, eds., *Proceedings of the International RILEM Workshop on Integral Service Life Modelling of Concrete Structures*, RILEM Publications, Cachan, France, 2007, pp. 63-70.
- Guimaraes, A. T. C.; Climent, M. A.; de Vera, G.; Vicente, F. J.; Rodrigues, F. T.; and Andrade, C., "Determination of Chloride Diffusivity through Partially Saturated Portland Concrete by a Simplified Procedure," *Construction and Building Materials*, V. 25, No. 2, 2011, pp. 785-790. doi: 10.1016/j.conbuildmat.2010.07.005
- Olsson, N.; Baroghel-Bouny, V.; Nilsson, L. O.; and Thiery, M., "Non-Saturated Ion Diffusion in Concrete—A New Approach to Evaluate Conductivity Measurements," *Cement and Concrete Composites*, V. 40, July 2013, pp. 40-47. doi: 10.1016/j.cemconcomp.2013.04.001
- Mercado-Mendoza, H.; Lorente, S.; and Bourbon, X., "Ionic Aqueous Diffusion through Unsaturated Cementitious Materials—A Comparative Study," *Construction and Building Materials*, V. 51, No. 31, 2014, pp. 1-8. doi: 10.1016/j.conbuildmat.2013.10.026
- Zhang, M.; Ye, G.; and van Breugel, K., "Modelling of Ionic Diffusivity in Non-Saturated Cement-Based Materials Using Lattice Boltzmann Method," *Cement and Concrete Research*, V. 42, No. 11, 2012, pp. 1524-1533. doi: 10.1016/j.cemconres.2012.08.005
- Mangat, P. S.; Khatib, J. M.; and Molloy, B. T., "Microstructure, Chloride Diffusion and Reinforcement Corrosion in Blended Cement Paste and Concrete," *Cement and Concrete Composites*, V. 16, No. 2, 1994, pp. 73-81. doi: 10.1016/0958-9465(94)90002-7
- Gjorv, O. E., "Effect of Condensed Silica Fume on Steel Corrosion in Concrete," *ACI Materials Journal*, V. 92, No. 6, Nov.-Dec. 1995, pp. 591-598.
- Saraswathy, V., and Song, H. W., "Corrosion Performance of Fly Ash Blended Cement Concrete: A State-of-the-Art Review," *Corrosion Review*, V. 24, Apr. 2006, pp. 87-122.
- Yu, Z., and Ye, G., "The Pore Structure of Cement Paste Blended with Fly Ash," *Construction and Building Materials*, V. 45, Aug. 2013, pp. 30-35. doi: 10.1016/j.conbuildmat.2013.04.012
- Leng, F. G.; Feng, N. Q.; and Lu, X. Y., "An Experimental Study on the Properties of Resistance to Diffusion of Chloride Ions of Fly Ash and Blast Furnace Slag Concrete," *Cement and Concrete Research*, V. 30, No. 6, 2000, pp. 989-992. doi: 10.1016/S0008-8846(00)00250-7
- Zhang, Y., and Zhang, M., "Transport Properties in Unsaturated Cement-Based Materials—A Review," *Construction and Building*



Materials, V. 72, Dec. 2014, pp. 367-379. doi: 10.1016/j.conbuildmat.2014.09.037

20. Saetta, A. V.; Scotta, R. V.; and Vitaliani, R. V., "Analysis of Chloride Diffusion Into Partially Saturated Concrete," *ACI Materials Journal*, V. 90, No. 5, Sept.-Oct. 1993, pp. 441-451.

21. Swaddiwudhipong, S.; Wong, S. F.; Wee, T. H.; and Lee, S. L., "Chloride Ingress In Partially And Fully Saturated Concretes," *Concrete Science and Engineering*, V. 2, No. 5, 2000, pp. 17-31.

22. Oh, B. H., and Jang, S. Y., "Effects of Material and Environmental Parameters on Chloride Penetration Profiles in Concrete Structures," *Cement and Concrete Research*, V. 37, No. 1, 2007, pp. 47-53. doi: 10.1016/j.cemconres.2006.09.005

23. Samson, E.; Marchand, J.; Snyder, K. A.; and Beaudoin, J. J., "Modelling Ion and Fluid Transport in Unsaturated Cement Systems in Isothermal Conditions," *Cement and Concrete Research*, V. 35, No. 1, 2005, pp. 141-153. doi: 10.1016/j.cemconres.2004.07.016

24. Nguyen, T. Q.; Petkovic', J.; Dangla, P.; and Baroghel-Bouny, V., "Modelling of Coupled Ion and Moisture Transport in Porous Building Materials," *Construction and Building Materials*, V. 22, No. 11, 2008, pp. 2185-2195. doi: 10.1016/j.conbuildmat.2007.08.013

25. Baroghel-Bouny, V.; Thiéry, M.; and Wang, X., "Modelling of Isothermal Coupled Moisture-Ion Transport in Cementitious Materials," *Cement and Concrete Research*, V. 41, No. 8, 2011, pp. 828-841. doi: 10.1016/j.cemconres.2011.04.001

26. Vedalakshmi, R.; Devi, R. R.; Emmanuel, B.; and Palaniswamy, N., "Determination of Diffusion Coefficient of Chloride in Concrete: An Electrochemical Impedance Spectroscopic Approach," *Materials and Structures*, V. 41, No. 7, 2008, pp. 1315-1326. doi: 10.1617/s11527-007-9330-1

27. Dridi, W., and Lacour, J.-L., "Experimental Investigation of Solute Transport in Unsaturated Cement Pastes," *Cement and Concrete Research*, V. 63, Sept. 2014, pp. 46-53. doi: 10.1016/j.cemconres.2014.05.002

28. Andrade, C.; Diez, J. M.; and Alonso, C., "Mathematical Modeling of a Concrete Surface 'Skin Effect' on Diffusion in Chloride Contaminated Media," *Advanced Cement Based Materials*, V. 6, No. 2, 1997, pp. 39-44. doi: 10.1016/S1065-7355(97)00002-3

29. Kreijer, P. C., "The Skin of Concrete: Composition and Properties," *Matériaux et Constructions*, V. 17, No. 4, 1984, pp. 275-283. doi: 10.1007/BF02479083

30. Presuel-Moreno, F. J.; Liu, Y.; Wu, Y.-Y.; and Arias, W., "Analysis and Estimation of Service Life Corrosion Prevention Materials Using Diffusion, Resistivity and Accelerated Curing for New Bridge Structures – Volume 1: Corrosion Prevention Materials," Chapter 3, BDK79-977-02, Final Report Submitted to Florida Department of Transportation, Gainesville, FL, 2013.

31. Malheiro, R.; Meira, G.; Lima, M.; and Perazzo, N., "Influence of Mortar Rendering on Chloride Penetration into Concrete Structures," *Cement and Concrete Composites*, V. 33, No. 2, 2011, pp. 233-239. doi: 10.1016/j.cemconcomp.2010.11.003

32. Echevarria, V., "Chloride Diffusivity and Its Correlation with Chloride Deposition Rate on Concrete Exposed to Marine Environments," master's thesis, Florida Atlantic University, Boca Raton, FL, Dec. 2012, 118 pp.

33. ASTM C642-06, "Standard Test Method for Density, Absorption, and Voids in Hardened Concrete, ASTM International, West Conshohocken, PA, 2006, 3 pp.

34. FM5-516, "Florida Method of Test For Determining Low-Level of Chloride in Concrete and Raw Materials," Florida Department of Transportation, Gainesville, FL, May 13, 2009, 9 pp.

35. Crank, J., *The Mathematics of Diffusion*, second edition, Clarendon Press, Oxford, UK, 1975, 414 pp.

36. Thomas, M. D. A., and Bamforth, P. B., "Modelling Chloride Diffusion in Concrete: Effect of Fly Ash and Slag," *Cement and Concrete Research*, V. 29, No. 4, 1999, pp. 487-495. doi: 10.1016/S0008-8846(98)00192-6

37. Cascudo, O.; Carasek, H.; Yssorche-Cubaynes, M.-P.; and Lopes, A. N.; and Oliver, J.-P., "Evaluation of Cover Concrete by Analysis of Chloride Diffusion Coefficients," *Quality of Concrete Structures and Recent Advances in Concrete Materials and Testing 2005: An International Conference Honoring V. Mohan Malhotra*, SP-229, P. Helene, E. P. Figueiredo, T. C. Holland, and R. Bittencourt, eds., American Concrete Institute, Farmington Hills, MI, Sept. 2005, pp. 135-150.

38. Ramezaniapour, A. A., and Malhotra, V. M., "Effect of Curing on the Compressive Strength, Resistance to Chloride-Ion Penetration and Porosity of Concretes Incorporating Slag, Fly Ash or Silica Fume," *Cement and Concrete Composites*, V. 17, No. 2, 1995, pp. 125-133. doi: 10.1016/0958-9465(95)00005-W

## NOTES:

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