Penetration of chloride in cement concrete structure exposed to drying wetting cycle

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Abstract: Penetration of chlorides in cement concrete structures in marine environmental conditions is becoming a serious issue especially when structures experience dry-wet cycles. To determine the depth of convection-zone formed by capillary-suction, three types of cement concrete, ordinary, high performance and fly ash (FA) were used in the experiment. Samples were test in sodium chloride (NaCl) solution in dry-wet cyclic immersion conditions. Exposure time was 30 and 60 weeks. By the experimental profiles of chlorides concentration, the depth of convection-zone was found between of 7-13.5mm. Depth of convection-zone has shown the increasing trend when the drying-period was increased in on cycle and also when the exposure-time was increased. The effects of capillary-absorption on the depth of convection-zone were discussed. Fly ash cement concrete has shown better resistance against the chlorides.

I. Introduction

Reinforced cement concrete (RCC) structures are usually durable. Though, chloride ingress has turned out to be a major problem that affects the durability of RCC structures, this case will become severe if the RCC structure is exposed to marine environment. Therefore, the durability of RCC structures present in marine environmental conditions has attained growing attention in past few years (Da Costa et al., 2013); (Lindvall, 2007). Usually, chloride ions after entering in the concrete do not cause a direct damage; rather induce or try to induce the corrosion in the steel bars embedded in concrete (Ababneh et al., 2003). Corrosion induction period (Conciatori, 2005) based upon the time through which constituents such as chlorides ions, CO₂ and water penetrate through concrete cover (that is the concrete provided in form of cover to protect the reinforcement), and extent to a definite concentration essential to initiate the corrosion in reinforcement. This period is characterized as the chemically reaction among the different constituents and the motion of the different constituents in the RCC. Once the reinforcement starts to corrode, serviceability of RCC structure might decline considerably (Riding et al., 2013).

In marine environmental conditions the corrosion of steel induced by chlorides is considered a major reason of structural degradation that could be in the shape of spalling, cracking and the concrete cover delamination. Furthermore, a corroded RCC member can have the tendency of further damage because of the loss in bond between cement concrete and steel also reduction in cross sectional area of steel. For better understanding of chloride ingress into cement concrete is required to calculate the serviceable life of RCC structures open to marine environment. Consequently, it’s required to calculate the chlorides ingress in cement concrete to estimate serviceable life of these structures precisely. Generally, the properties of chloride ingress in concrete (particularly, diffusion and permeability) is affected by some factors, for example, quality of concrete, existence of cracks and exposure conditions (Gowripalan et al., 2000); (Win et al., 2004); (Wang et al., 2011). In sound saturated cement concrete the diffusion is generally regarded as the basic mode of chlorides transportation in to concrete and it has been demonstrated or modeled by several scholars by applying the second law of Fick (Xi and Bažant, 1999); (Martín-Pérez et al., 2000); (Thomas and Bentz, 2001); (Luping and Gulikers, 2007).

The penetration of chlorides into cement concrete is a very complex phenomenon for quite a few reasons (Bazant, 1979, Saetta et al., 1993, Balabanić et al., 1996); 1) the coefficient of diffusion cannot be taken as a constant parameter, it varies with temperature, relative humidity (Rh) and age. 2) The binding of chlorides has an important effect on penetration of chlorides since only the free chlorides can penetrate in to bulk cement concrete. 3) Not only the diffusion of chlorides but also the convection flow of chloride particles plays an important part in penetration of the chloride particles in cement concrete, particularly when subjected to drying-wetting situation.
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In an actual environment, though, cement concrete is generally found in an unsaturated condition instead of saturated one, particularly when it has exposed to drying–wetting cyclic conditions. By the results made by some field surveys, it is generally believed that the splash and tidal zones experience drying-wetting cycles of seawater and these zones are considered most vulnerable zones in case of corrosion of steel. This can be considered as the main attention in durability design. Several researchers have studied chloride ingress in unsaturated cement concrete. For cement concrete structures which are open to marine environment, drying-wetting cycles can increase the speed of deterioration of cement concrete as two actions happen at the same time, i.e. diffusion and capillary suction (Gao et al., 2013). Through a wetting-period, seawater having chlorides enters the cement concrete through the help of capillary-suction, up-to a significant depth, while during in the drying-period water evaporates from cement concrete, that water leaves the ions containing chlorides in the cement concrete, which can spread in cement concrete by diffusion action. For the RCC present in marine environmental conditions it is possible to replace some part of cement with a pozzolanic material for example fly ash (FA), to increase the performance of cement concrete. By the researches it is known that reaction of fly ash (FA) decreases the chloride ingress in cement concrete and improves binding of chlorides in contrast with simple cement concrete prepared by using the ordinary Portland cement (OPC). (Andrade and Bercke, 2011, Chalee and Jaturapitakkul, 2009, Yuan et al., 2009).

The main purpose of this paper is to study the convection action effect on the penetration of chlorides in cement concrete under the drying–wetting cyclic conditions. The depth of convection-zone in the Surface-layer of cement concrete is determined and compared based on experimental results. Also, effects of mix-proportion of cement concrete, period-ratio of wetting to drying and different exposure times are studied.

II. Material and Methods

Experimental Investigation
Preparation of samples

In this experiment 4 types of cement concrete specimens “OC1, OC2, Fas1, and Fas2” were casted for the experiment. Ordinary Portland cement (OPC) of Grade 42.5 was used to prepare all the specimens. Table 1 contains the composition of cement.

<table>
<thead>
<tr>
<th>Table no. 1: Mineral and chemical composition of cement.</th>
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<tbody>
<tr>
<td><strong>Composition</strong></td>
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<td>Mineral composition</td>
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</table>

This Ordinary Portland cement can be classified as “ASTM C-150 Type I” it’s approximately conforms to the Chinese national standard GB-175-2007 cement stated in National Standard of the People’s Republic of China 2007.

Grade II fly ash (FA) was used for fly ash (FA) specimens and the main substances of its composition, Al₂O₃ and SiO₂ and, is nearly 24% and 60%, respectively. Grade II fly ash can approximately be categorized as the Class F fly ash (FA) established by ASTM C-618 standards “ASTM 2005a”. For coarse aggregate crushed-gravels and for fine aggregate sand from river was used. The size of gravels was 24 mm (maximum), and the sand of 1.60 fineness modulus was used. Water reducing agent used in fly ash sample named TMS-F1. Samples were designed to get the strength grades between 30 to 35 MPa according to the mix proportion and the Design Specification for ordinary Portland cement concrete (Standard of the People’s Republic of China 2011) in People Republic of China. Both OC1 and OC2 samples were designed as ordinary cement concrete with the water-cement (w/c) ratio of 0.44 and 0.390 respectively, while fly ash samples were prepared as high-performance cement concrete with the 0.390 water-cement (w/c) ratio.

For every sample, three prisms of 150 × 150 × 400 mm dimensions were prepared. The mixing of materials and casting of cement concrete was carried-out in the laboratory of Jiangsu University at 19±3°C temperature and 50±5% relative humidity (RH). After removing the molds, moist-curing with hessian 7 days were done and then all
the samples were placed in the structural laboratory of Jiangsu University with curing for 28-days. Throughout this period laboratory’s temperature and relative humidity (Rh), were approximately 20 to 26°C and 58 to 65%, respectively which were recorded at noon. The details of mixing parameters and compressive strength of 28 days are listed in Table 2. For OC2 and fly ash (Fas1, Fas2) samples a comparison is presented in (Table 2) which presents the total quantity of cementitious material was same for each sample. Though, the replacement of cementitious material with fly ash is 0, 15, and 30%, respectively.

### Table no. 2: Mixture proportion and 28-days strength of concrete.

<table>
<thead>
<tr>
<th>Sample name</th>
<th>Water-cement ratio</th>
<th>OPC Kgm⁻³</th>
<th>Binders</th>
<th>Water Kgm⁻³</th>
<th>Fine-aggregate Kgm⁻³</th>
<th>Coarse-aggregate Kgm⁻³</th>
<th>Water-reducing agent (%)</th>
<th>28-days compressive strength (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>OC1</td>
<td>0.44</td>
<td>440</td>
<td>0</td>
<td>190</td>
<td>570</td>
<td>1270</td>
<td>0</td>
<td>32.1</td>
</tr>
<tr>
<td>OC2</td>
<td>0.390</td>
<td>490</td>
<td>0</td>
<td>190</td>
<td>640</td>
<td>1105</td>
<td>0</td>
<td>36.6</td>
</tr>
<tr>
<td>Fas1</td>
<td>0.390</td>
<td>417</td>
<td>74</td>
<td>190</td>
<td>640</td>
<td>1105</td>
<td>0.4</td>
<td>30.4</td>
</tr>
<tr>
<td>Fas2</td>
<td>0.390</td>
<td>343</td>
<td>147</td>
<td>190</td>
<td>640</td>
<td>1105</td>
<td>0.4</td>
<td>29.8</td>
</tr>
</tbody>
</table>

Note: The content of water reducing agent is the mass percentage of cementitious material.

### Cyclic immersion Experiment

After 28 days of curing, before drying–wetting cyclic experiment, one side of the sample, 150×400mm, which has not used to cast the sample was chosen as the open surface to aggressive environment to ensure that penetration of the chlorides should be from one side. All other sides were sealed with a good epoxy resin. After this all the samples were put in water pond containing 5% by weight Sodium chloride (NaCl) solution. Here they were open to drying– wetting cyclic conditions. Due to the nature of ocean ebb and flow, the ratio of the ebb-tide (drying period) to flood-tide (wetting period) is almost 1:1. Thus, the same period ratio of drying-time to wetting-time is selected for this experiment.

In this experiment 2 types of drying wetting cycles were used

1. 7 drying days and 7 wetting days, 2 weeks for a complete cycle
2. 7 wetting days and 14drying days, 3 weeks for one complete cycle

The total duration was 60 weeks for this experiment. Experiment was done in an in-door water pool in the structural laboratory, located in the Jiangsu University, Zhenjiang, Jiangsu, Peoples Republic of China. Throughout the whole period of 60 weeks with drying–wetting cycles, the temperature and relative humidity (Rh) in the laboratory were not controlled intentionally. Hence, temperature and relative humidity (Rh) can be supposed approximately as the yearly average-temperature and relative humidity (Rh) in Zhenjiang Jiangsu China, which are 16.5°C and 74 %, correspondingly.

### Determination of Chloride Content

Chloride contents were twice determined in this experiment. Firstly, after the period of 30-weeks and secondly after the period of 60-weeks. Before taking samples from cement concrete beams, the tested cement concrete beams were taken out from the NaCl (Sodium Chloride) solution’s pool and all the samples placed in a dry and ventilated room for one week to decrease the free evaporable-water present in cement concrete. Now, for each tested sample, three locations were selected for testing; first location was 50 mm from the edge of sample, second and third location was at about 150 mm after first location, as shown in Figure 1. From each testing location, sample in shape of powder was obtained by the help of an electric-drill with auger head 16 mm. Drilling was exactly perpendicular to the testing surface. The powder-samples were acquired at the different depth-intervals: for the first 20 mm at 5 mm intervals and after that increment of 10 mm from distances of 20mm to 60mm (Figure 2). Then, the powder-samples were crushed and ground carefully then pass by a sieve of 0.63 mm and then those samples were dried in oven for 1.5 hours at 120°C. Now the samples were taken out from oven and left for few hours to cool down at laboratory temperature. Every sample was distributed into 3 groups. From all the sample only 1.5 g powder-sample was weighed and used to determine the chloride content this practice has been done with every group. Free chloride contents were determined by the distilled water extraction. Values of chloride-contents indicated as the mass percentage of cement concrete. Rapid-Chloride Test RCT-500 system was used, this equipment was manufactured by Germann Instruments Co. (Copenhagen, Denmark), a good correlation exists among this RCT method and some other methods stated in “AASHTO T-260” (AASHTO 2009) and “ASTM C-1202” (ASTM 2012). the mean values of the three groups were considered as the test values.
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Figure 1: Diagram of drilling the specimen and powder obtained.

Figure 2: Drilling locations for cement concrete sample powder.

Statistical analysis
All data was analyzed by analysis of variance (ANOVA) for significant differences \((P \leq 0.05)\). Measurements are presented as the mean \pm standard error (SE) \((n = 5)\). The mean values of data were analyzed statistically by using SPSS software (version 13.0, SPSS Inc.) at the level of 5% significance \((P < 0.05)\).

III. Result

Profiles of Free Chloride Ion Concentration
30 weeks Samples with 15 cycles
Four sample beams were subjected to 7-days wet and 7-days dry cycle for 30 weeks. These specific samples had experienced 15 drying-wetting cycles. Profiles of the free chlorides concentration which is percentage of mass of cement concrete are shown in Figure 3. There is an ascending stage of chlorides in the surface layer of cement concrete in all 4 types of samples where the value of chlorides is increasing. Chloride profiles of all samples are showing that the content of chlorides in the convection-zone of cement concrete are very close to each other, they are ranging from 0.32-0.49\% by the mass of cement concrete. And the depth is ranging between 7.5-13 mm for the same exposure time. In OC1 samples the value of free chlorides is started from 0.35\% and it goes to peak concentration of around 0.49\% by the mass of cement concrete while the depth of the peak concentration is around 12.5 mm. In OC2 samples the value of free chlorides is started from around 0.36\% and it goes to peak concentration of around 0.44\% by the mass of cement concrete while the depth of the peak concentration is around 7.5 mm. In Fas1 samples the value of free chlorides is started from 0.39\% and it goes to peak concentration of around 0.43\% by the mass of cement concrete while the depth of the peak concentration is around 8.5-9 mm. In Fas2 samples the value of
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free chlorides is started from 0.39% and it goes to peak concentration of around 0.48% by the mass of cement concrete while the depth of the peak concentration is around 9mm.

So, it can observe that the strength of cement concrete and mixture properties has an obvious effect on chloride penetration. By comparing the chloride profiles of OC1 and OC2 samples it is clearly evident that the high strength of cement concrete can resist the penetration of chlorides into cement concrete. Moreover, the OC1, Fas1, and Fas2 samples are having compressive-strength around 30 MPa, but concentration of chlorides at some depths in fly ash samples are less than OC1 samples, that shows the fly ash replacement in cement concrete can enhance the resistance against chlorides.

In the OC1 sample the value of chlorides is increasing to the depth of approximately 12.5mm while in all other samples this value is ranging until 8-9.5mm. That is showing the greater resistance of high performance and fly ash cement concrete.

30 weeks samples with 10 cycles

The chloride profiles of samples which had experienced for 7-days wet and 14-days dry are shown in Figure 4. The peak concentration of chlorides in this cyclic condition in ranging between 0.35-0.53% by the mass of the cement concrete. Depth of convection zone is ranging between 11-15mm. Chloride contents of OC1 and OC2 samples are showing the less resistance of OC1 sample against chloride-ions in convection zone as well as in the depth of 15-60mm.

![Figure 3: Chloride concentration profiles of the sample experienced 15 dry-wet cycles in 30 weeks.](image-url)

It can be observed that in OC1 samples the value of free chlorides is started from 0.35% and it goes to peak concentration of around 0.52% by the mass of cement concrete while the depth of the peak concentration is around 12.5-13.5mm. In OC2 samples the value of free chlorides is started from around 0.34% and it goes to peak concentration of around 0.50% by the mass of cement concrete while the depth of the peak concentration is around 12.5-13.5mm.
concentration of around 0.46% by the mass of cement concrete while the depth of the peak concentration is around 12.5mm. In Fas1 samples the value of free chlorides is started from around 0.40% and it goes to peak concentration of around 0.49% by the mass of cement concrete while the depth of the peak concentration is around 12.5mm. in Fas2 samples the value of free chlorides is started from 0.36% and it goes to peak concentration of around 0.46% by the mass of cement concrete while the depth of the peak concentration is around 11-12.5mm. Fly ash cement concrete samples are showing better resistance against chloride ions in comparison of OC1 but the results are not good enough as compared to OC2 samples. This is the effect of the specific drying-wetting cyclic condition.

60 weeks with 30 cycles

Remaining samples which in total had experienced 30 complete cycles. The chlorides profiles for the samples experienced 7-days wet and 7-days dry cycles for 60 weeks are shown in Figure 5. It is found that the concentration of chlorides in the convection-zone under same wetting-drying cyclic conditions is evidently decreasing by increasing the time and cycles. Values of OC2 sample and Fas1 sample are relatively close to each other. The chloride concentration values of all samples are ranging between 0.25-0.35% by the mass of cement concrete in convection-zone and the depth is ranging between 7.5-14mm. The concentration of chlorides in the inner part of cement concrete from 15-60 mm is increasing with increasing the time of exposure.

![Figure 4](image_url)

Figure 4: Chloride concentration profiles of the sample experienced 10 dry-wet cycles in 30 weeks.

In OC1 samples the value of free chlorides is started from 0.22% and it goes to peak concentration of around 0.37% by the mass of cement concrete while the depth of the peak concentration is around 13.5mm. In OC2 samples the value of free chlorides is started from around 0.28% and it goes to peak concentration of around 0.37% by the mass of cement concrete while the depth of the peak concentration is around 12mm.
In Fas1 samples the value of free chlorides is started from around 0.31% and it goes to peak concentration of around 0.37% by the mass of cement concrete while the depth of the peak concentration is around 7-9mm. In Fas2 samples the value of free chlorides is started from 0.26% and it goes to peak concentration of around 0.39% by the mass of cement concrete while the depth of the peak concentration is around 10-13mm.

**Figure 5:** Chloride concentration profiles of the sample experienced 30 dry-wet cycles in 60 weeks.

**IV. Discussion**

The general aim of this study was proper understanding of the importance of capillary-absorption to penetration of chloride in cement concrete exposed to a salt solution and wetting and drying conditions. The results show that capillary absorption is strongly influenced by the moisture state of the concrete: the drier the concrete, the greater the volume of chloride solution absorbed (Arya et al., 2014).

By comparing the chloride concentration profiles given in Figure 4 with the profiles given in Figure 3, it is observed that content of chlorides in the convection-zone of cement concrete are marginally larger, around 0.35-0.53% by the mass of cement concrete. Furthermore, the peak value of chloride concentration in Figure 4 is obviously larger than the peak-concentration in Fig. 3. This specific phenomenon is ascribed as the effect of period ratio of wetting to drying. It is because of the capillary-absorption in the surface layer of cement concrete is greater by the sea-water when the air-drying period will be longer. (Corvo et al., 2008, Hong and Hooton, 2000, Sadati et al., 2015) also explained the same phenomena, Capillary adsorption is the cause of penetration of chlorides in surface layer of cement concrete, which happened due to dry-wet cycles. The results presented in Figure 5 and Figure 3 had faced 30 and 15 dry-wet cycles respectively. By comparison of the results given in Figure 5 with the results given in Fig. 3, it can clearly observe that under the same cyclic-condition the concentration of chlorides in the convection zone decreasing with increasing the dry-wet cycles (Hong and Hooton, 1999). Because the chlorides gathered in convection-zone resulted by capillary-absorption start moving into deeper zone (Zhang et al., 2010).
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This phenomenon is known as diffusion (Thomas and Bamforth, 1999, Petcherdchoo, 2013). In the deeper zone 15-60 mm, the concentration of chlorides at some depths increases with the exposure time.

Consequently, the depth of convection-zone is an interval that covers the area around the value of peak-concentration presented in Figure 3, 4 and 5. Table 3 contains the value of depth of convection-zone for all samples. It can be confirmed by the values of the depth of convection-zone is directly associated to the material and mixture properties, exposure conditions of the marine environment and time of exposure (Bastidas-Arteaga et al., 2011, Ye et al., 2012). For 30-weeks times, convection-zone depth propagates higher when the period of air-drying is increasing. In exposure conditions of 7-days drying and 7-days wetting cycle, depth of convection zone increasing with increase in time of exposure. The depth of convection zone is definitely affected by strength of the cement concrete (Thomas and Bamforth, 1999). Comparison of experimental results of OC1 samples with other samples explains that increase in the strength of the cement concrete (OC2 samples) or mineral addition in the cement concrete (Fly ash samples) can decrease the action of capillary-absorption. This may further explain the point that the convection zone’s depth is associated with the micro-pore structure and the chlorides binding ability of the cement concrete (Liu et al., 2016).

<table>
<thead>
<tr>
<th>Duration</th>
<th>Cyclic exposure arrangement</th>
<th>Depth of convection zone (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>30 weeks</td>
<td>7-days dry 7-days wet</td>
<td>OC1  12.5, OC2  7.5, Fas1  8.5-9, Fas2  9</td>
</tr>
<tr>
<td>30 weeks</td>
<td>7-days wet, 14-days dry</td>
<td>OC1  12.5-13.5, OC2  12.5, Fas1  12.5, Fas2  11-12.5</td>
</tr>
<tr>
<td>60 weeks</td>
<td>7-days dry 7-days wet</td>
<td>OC1  13.5, OC2  12, Fas1  7-9, Fas2  10-13</td>
</tr>
</tbody>
</table>

By the results we can see that the Fly ash (FA) samples (Fas1, Fas2) has shown better resistance against the penetration of chlorides. Fly ash can significantly increase the capacity of chloride binding. It is well known fact that the high ratio of chloride binding gives the high resistance against penetration of chlorides (Liu et al., 2016). The chloride-binding ratio has an abundant influence on the penetration of chlorides (Luo et al., 2003). Chloride binding ration is inversely proportional to the chloride-content in cement concrete, means the high ration of chloride-binding give the less chlorides value in cement concrete (Sandberg, 1999). The chloride-binding ratio affects directly not just the chloride-concentration, but also affects the chloride-contents near the surface of cement concrete surface.

V. Conclusion

The general aim of this research was to develop/explain a proper knowledge of the importance of capillary-absorption to the penetration of chlorides in cement concrete open to marine environment under drying-wetting cyclic conditions. Experimental result shows that the capillary-absorption is mainly affected by the moisture-state of the cement concrete. The drier cement concrete will absorb the bigger volume of contaminated solutions (chlorides). By the results the depth of convection-zone lies between 7-15mm which mainly depends on the marine environmental conditions, materials and mixture properties and dry-wet cyclic conditions. FA is a good admixture for chloride-binding and has shown good results against chlorides even for longer period. It can be used widely because it’s cost effective and available easily.

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