Chloride Distribution Feature in Surface Layer of Cementitious-based Materials under Mere Cyclic Wetting and Drying Action

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Abstract: Chloride transport under wetting and drying environment is very complicated. A lot of research has reported maximum phenomena in chloride profiles under such environment. Considering the fact that most specimens in which chloride maximum was detected before either had inhomogeneous surface (might be influenced by skin effect) or were exposed to natural environment (might be influenced by rain washing), this study aims to reveal chloride distribution under mere wetting and drying condition in cement-based materials. The chloride distribution results in the surface layer of specimens with different water to binder ratio (W/B) detected by silver nitrate titration method (SNT), ion chromatography method (IC) and electric probe micro analysis (EPMA) present a fact that: maximum phenomena occur in all specimens under four wetting-drying regimes, no matter in paste or mortar, in free or total chloride, and whether with slag (SL) and fly ash (FA) or not. It suggests that mere wetting and drying action can incur chloride maximum phenomenon without the attendance of skin effect and rain washing, though sometimes confined by the accuracy of testing method, the position of maximum phenomenon can not be presented.

1. Introduction

Steel corrosion initiated by chloride ingress is an important cause of concrete deterioration. And wetting and drying environment is one of the most aggressive conditions for reinforced concrete structures due to the fast penetration of chloride ions. Therefore, chloride distribution under such condition is vital to the durability and service life of concrete structures.

Normally, chloride content decreases monotonically with depth from the exposed surface increasing. However, under cyclic wetting and drying conditions (no matter in outdoor wet-dry environments like tide zone, splash zone, and deicing environment, or in indoor laboratorial wet-dry condition), a phenomenon that chloride content first climbs to a local maximum then decreases with depth has been reported by several studies [1-7], as shown in Fig. 1. It is often called the “chloride maximum phenomenon” [7-9].

The maximum phenomenon is receiving more attention recently because it greatly complicates the concrete service life prediction models that rely on fitting standard error function of Fick’s second law [9,11-13]. Yet, the fundamental mechanism driving the formation of maximum phenomenon is still in discussion so far. And four causations may be accountable for it: skin effect, rain washing, capillary
adsorption/moisture evaporation, and carbonation. Skin effect was first proposed by Andrade [14]. Due to contacting with molds or separation between paste and aggregate, the surface layer of concrete will diff

![Figure 1. Chloride profile with appearance of maximum phenomenon in the surface layer](https://example.com/figure1.png)

-er from the inner part. Consequently, the chloride penetration resistance of the two parts is different, and chloride might accumulate in the interface between them, gradually forming a chloride content peak there. The depth of the chloride concentration peak caused by this effect depends on the size of the stones in concrete, and some of the research findings can be explained by this effect [15]. In outdoor wetting and drying environment, rain will scour concrete surface and dissolve and wash away chlorides there. As a result, chloride content in surface decreases and becomes lower than that in the inner part gradually, presenting a trend of chloride content first increasing then decreasing in a certain depth range. Research has verified that chloride concentration in surface layer of concrete can be lowered by being washed with or immersed in deionized water [16], and the maximum phenomena in concrete exposed to outdoor environments are probably caused by this effect [4,5,17]. Capillary adsorption/moisture evaporation refers to a process that at the beginning of wetting, concrete surface, originally in non-saturation state, will produce capillary suction force when contacting with salt solution, which drives salt solution to enter a certain depth of surface layer rapidly; and then in the drying process, during water evaporation from surface layer, chloride ions accumulate in pores of matrix in the form of crystals [1]. The chloride maximum phenomenon is probably formed by the rapid chloride accumulation at a certain depth of surface driven by capillary adsorption/moisture evaporation [18,19], and that conclusion has been confirmed by many researchers [4-6,20,21]. Carbonation also plays an important role in affecting chloride distribution [22,23]. On the one hand, carbonation reaction produces new materials like calcium carbonate which impedes chloride diffusion with its deposition in pore structures. On the other hand, carbonation decomposes chloroaluminium compounds like Friedel’s salt, and transforms bound chloride into free chloride [24,25]. Those free chloride ions dissolve in pore solution, migrate and deposit in deeper positions, probably leading to the chloride maximum phenomenon at a certain depth.

Among the above four causations, capillary adsorption/moisture evaporation and carbonation are initiated by cyclic wetting and drying and exist throughout the whole exposure period. In contrary, skin effect and rain washing depend on the different composition at different positions of specimens and external environment separately, rather than wetting and drying action itself. Considering the fact that most specimens in which chloride maximum were detected in previous research either had inhomogeneous surface layer [6,15,17,20,26,27] (could by influenced by skin effect) or were exposed to outdoor environment [4,28-30] (could be influenced by rain washing), whether the mere function of cyclic wetting and drying, excluding skin effect and rain washing, can lead to maximum phenomenon
or not in cement-based materials needs to be further investigated. Therefore, paste and mortar specimens with different mix proportions were cut away the inhomogeneous surface and exposed to four indoor dry-wet regimes, and the free and total chloride distribution in surface layer of them was portrayed by varying methods.

2. Material and Methods

2.1 Raw materials and mix proportions

The cement used in this study is P.II. 52.5 Portland Cement produced by Nanjing Xiaoyetian company. Two kinds of mineral admixtures, slag (SL) of 423m²/kg fineness and fly ash (FL) of 625m²/kg fineness, are employed. The fine aggregate is river sand and its fineness modulus is 2.20. The chemical composition of cement, SL and FA is presented in Table 1.

| Table 1. Chemical composition (%) of cement P.II.52.5, SL and FA |
|---------------------------------------------------------------|
| SiO₂ | Al₂O₃ | CaO | Fe₂O₃ | K₂O | MgO | Na₂O | TiO₂ |
| P.II.52.5 | 20.0 | 4.46 | 63.9 | 2.99 | 0.660 | 0.510 | 0.110 | 0.262 |
| SL | 32.1 | 16.7 | 39.3 | 0.746 | 0.348 | 6.41 | 0.151 | 0.895 |
| FA | 45.4 | 36.3 | 6.97 | 5.30 | 0.864 | 0.599 | 0.314 | 1.65 |

Five different mixing proportions of cement paste and mortar were designed, and the water to blinder ratio (W/B) and mineral admixture dosage of each proportion are shown in Table 2.

| Table 2. Mixing proportions of pastes and mortars |
|-----------------------------------------------|
| Corresponding No. | W30 | W40 | W50 | SL20 | FA20 |
| Cement (%) | 100 | 100 | 100 | 80 | 80 |
| SL substitution (%) | 0 | 0 | 0 | 20 | 0 |
| FA substitution (%) | 0 | 0 | 0 | 0 | 20 |
| Paste W/B | 0.30 | 0.40 | 0.50 | 0.50 | 0.50 |
| Mortar Sand/binder | / | / | 0.50 | 0.50 | 0.50 |

2.2 Samples preparation

The molding size of paste specimen is 100mm×100mm ×100mm, and that of mortar is 70mm×70mm×70mm. To prevent moisture evaporation, the mold surface was sealed with tape and thin film after casting. After hardening for 24h, paste and mortar specimens were demolded and then cured in saturated calcium hydroxide solution at
temperature 20±1℃. After curing, paste specimens of 100mm×100mm×100mm were cutting into size of 40mm ×40mm×40mm with a precision cutting machine, and one cutting surface was used as the exposed surface in the following wetting and drying process. Meanwhile, mortar specimens were cut away 20mm from the molding free surface, and the cutting surface was also used as the exposed surface. The treatment and size chosen for paste and mortar specimens guaranteed the homogeneity of matrix (to exclude the skin effect). Moreover, five other surfaces except the exposed surface of specimens were sealed with epoxy resin before being exposed to corresponding wetting and drying conditions.

2.3 Exposure conditions

Four different wetting and drying regimes and one immersion regime (used as reference) were employed, shown in Table 3. Note that not all mixing proportions in Table 2 were exposed to every regime, and the corresponding specimens under each regime were also presented in Table 3. Besides, all wetting and drying processes were conducted indoor, and thus the rain washing effect is eliminated.

2.4 Chloride testing methods

2.4.1 Grinding power method

Powder samples at different depths are needed here, and through detecting chloride content in them, chloride distribution at different depths can be obtained. From literature [31], it can be learned that if the testing depth intervals are too big, even though chloride maximum phenomena were formed, it cannot be presented in chloride profile. Therefore, to obtain a more accurate chloride profile, the depth intervals for testing chloride content should be minimized. This study employed a high precision auto milling machine [7,31] to grind powder. The grinding thickness is 0.5mm with error being controlled to less than 0.02mm, which highly improve the accuracy of chloride distribution along with depth.

1) Silver nitrate titration method (SNT)

The procedures for testing free (water-soluble) chloride content are described in details below:

— Sift power samples through a 160µm sieve and then put them in a vacuum oven at 65℃ till constant weight is reached;
— Weigh a 2.0g sample in a plastic bottle and mix with 50mL deionized water;
— Place plastic bottles on an oscillator and shake for 24h;
— Filtrate 20mL solution and titrate with silver nitration of 0.1M concentration. Record the consumed volume of silver nitration.

The content of free chloride can be calculated by Eq.1:

\[
C_f = \frac{V \times 0.01 \times 35.45 \times 50}{1000 \times 2.0 \times 20} \times 100\%
\]
Where, \( C_f \) is the free chloride content, % wgt sample; \( V \) is the volume of silver nitrate solution consumed by 20mL filtrated solution, mL.

The procedures for testing total (acid-soluble) chloride content are described in details below:

- Sift powder samples through an 80µm sieve and then put them a vacuum oven at 65℃ till constant weight is reached;
- Weigh a 2.0g sample in plastic bottles and mix with 50mL nitric acid of 6mol/l concentration;
- Place plastic bottles on an oscillator, shake for 2h, and then stand for 22h;
- Filtrate 20mL solution and mix with excessive silver nitrate solution of 0.1M concentration to precipitate all chloride ions.
- Titrate the above solution with potassium chromate solution of 0.1M concentration. Record the consumed volume of potassium chromate solution.

The content of total chloride can be calculated by Eq.2:

\[
C_t = \frac{35.45 \times (V1 \times 0.01 - V2 \times 0.01)}{1000 \times 2.0} \times 100\%
\]  

(2)

Where, \( C_t \) is the total chloride content, %wgt sample; \( V1 \) is the volume of silver nitrate solution added in filtrated solution. mL; \( V2 \) is the consumed volume of potassium chromate solution, mL.

| Condition ID | Corresponding specimens | Experimental procedure for one cycle | Exposure time |
|--------------|--------------------------|-------------------------------------|---------------|
| A            | W30 W40 W50 W50-M SL20-M FA20-M | Immersion in 3.5% NaCl solution | 36days/84days |
| B            | W30 W40 W50              | Wetting in 3.5% NaCl solution for 8h | Drying in a room for 16h: 20±1℃, 65%~70% RH | 30 cycles/30days |
| C            | W30 W40 W50              | Wetting in 3.5%NaCl solution for 16h | Drying in a oven for 8h at65℃ | 30 cycles/30days |
| D            | W30 W40 W50              | Wetting in 3.5%NaCl solution for 12h | Drying in a oven for 36h at 45℃ | 18 cycles/36days |
| E            | W50 SL20 FA20 W50-M SL20-M FA20-M | Wetting in 3.5% NaCl solution for 1 day | Drying in a room for 6 days: 20±1℃, 65%~70% RH | 12 cycles/84days |

Note: The names of specimens with –M mean mortar specimens, the others mean paste specimens; RH means relative humidity.

2) Ion chromatography method (IC)

IC is commonly used in detecting chloride content in cement or admixtures. For its small testing scope, usually within 1~500ppm, IC was not supposed to be used for determining chloride content in cement-based materials under chloride attack. However, it becomes feasible through diluting the target chloride solution, and 5~100 times dilution can be processed through ion chromatography automatically. Therefore, in view of the high efficiency and automaticity of IC, it was also employed in this study to detect free and total chloride content. The detailed procedure of IC is as follows:

- Obtain filtration of free and total chloride solution separately using method mentioned in silver nitrate titration;
- Inject filtration into the special vessels in graph 3(a) and (b);
- Embed all those vessels in IC (TOSOH IC-2012), and IC will detect and report chloride content
automatically.

Note that before the above steps, NaCl solution of four standard concentrations (1ppm, 5ppm, 10ppm, 50ppm, presenting a linear distribution) should be used to set up a standard curve. The higher the linear correlation of the standard curve is, the more accurate the calculated chloride content is based on the standard curve. The correlation index of the standard curve in this study is 0.999. Besides, the chloride content reported by IC is measured in ppm, and it need to be transformed into percentage of sample mass using Eq. 3.

\[ C = \frac{C_{IC} \times V}{m \times 1000} \]  

Where, \( C \) is the chloride content per unit sample mass, \( \% \) wgt sample; \( C_{IC} \) is the chloride content detected by IC, ppm; \( V \) is the volume of deionized water or nitrate in sample solution, mL; \( m \) is the mass of sample, g.

2.4.2 Electric Probe Micro Analysis (EPMA)

EPMA has already been applied in presenting chloride distribution in cement-based materials, especially for that in crack concrete [32,33]. This method can characterize chloride distribution without intervals through the shading of color that signifies chloride content [34]. The report of EPMA is clear and direct, and can be used as an auxiliary tool for analyzing chloride distribution.

The sampling method of EPMA is as following:

— Sample specimens along chloride penetration direction into ones with cross section of 10mm×10mm using a high precision cutting machine;
— Soak samples in epoxy resin and wait for the hardening of epoxy resin;
— Polish the target surface for testing chloride distribution, and dry samples in a vacuum oven.

Note that samples should be avoided contacting with water during the cutting and polishing process, and absolute ethanol is used for cooling. The sample and EPMA are shown in Fig. 4.

Figure 4. Method of EPMA: (a) the sample (b) Electric Probe Micro Analyzer

3 Results

3.1 Immersion regime A
Fig. 5 presents chloride distribution in specimens under total immersion condition using SNT. It can be observed that chloride content in all specimens decreases monotonously with distance from the exposed surface increasing without appearance of maximum phenomena, for free chloride or total chloride, in cement paste or mortar, with whatever W/B, and whether mineral admixtures are added, or the exposure time is 36d or 84d. This finding is consistent with the results of mass researches about chloride distribution in immersion. It can be concluded that under immersion condition with diffusion as the dominating mechanism for chloride transport, chloride maximum phenomena cannot be induced.
3.2 Wetting and drying regime B

Fig. 6 shows the total chloride distribution of paste specimens under regime B using IC. It can be observed that maximum phenomena appear in chloride profiles of W40 and W50 but not in profile of W30. As for the absence of maximum phenomenon in W30, there are two possible reasons. One is that the matrix of W30 is denser for its lower W/B, and thus it needs more time for the maximum phenomenon to come into being. The second is that maximum phenomenon perhaps has already formed in W30 and locates within 0–1.0 mm (chloride content at 0.5 mm and 1.0 mm approximates very much), but the testing interval of 0.5 mm is too large for maximum phenomenon in W30 to be tested.
Figure 6. Chloride distribution in surface layer of specimens under wet-dry regime B measured by method of IC

To better explain the results in Fig. 6, EPMA was employed to report chloride distribution continuously within 0~5.0mm of W40 and W30 [35], presented in Fig. 7. From Fig. 7(a), it can be seen that the densest range of

Figure 7. Chloride distribution of specimens under wet-dry regime B measured by EPMA(orientation of penetration is from left to right): (a) W40-N (b) W30-N
chloride appears in depth 1.5~4.0mm from the exposed surface, which conforms to the position of maximum phenomenon in W40 in Fig. 6 and further verifies the existence of maximum phenomenon in surface layer. As is presented in Fig. 7(b), chloride is the densest in depth of 0~1.0mm, and is denser than that in the outermost surface, and it suggests that maximum phenomenon does exist in somewhere within 0~1.0mm, which validates the conjecture above about maximum phenomenon of W30 existing in 0~1.0mm from surface in Fig. 6. Thus, it can be concluded that the absence of maximum phenomenon in W30 in Fig. 6 blames for the testing method that is not exact enough to present the exact position of maximum. For example, if the maximum phenomenon occurs at depth 0.3mm, the testing intervals of 0.5mm or 1.0mm or even larger apparently can easily omit its appearance. In conclusion, mere wetting and drying under regime B can incur different degrees of maximum phenomena presented by various methods in paste specimens with different W/B.

3.3 Wetting and drying regime C

Fig. 8 shows chloride distribution in the surface layer of specimens under wetting and drying regime C tested by IC and SNT. It can be seen that, maximum phenomena appear in chloride profiles of specimens with whatever W/B and in either free or total chloride under regime C. Comparing Fig. 8(a) with Fig. 8 (b), it is clear that though

![Figure 8](attachment:image.png)

Figure 8. Chloride distribution of specimens under wet-dry regime C measured by: (a) IC (b) SNT

the tested chloride change law of W40 and W50 is basically the same, the presented chloride content by IC and SNT of them differs a lot. The chloride content obtained by IC is significantly lower than
that by SNT, and it can be ascribed to the dilution process of IC which abates the accuracy of tested chloride content. However, the trend of chloride changing with depth tested by IC remains unaffected. Note that due to insufficient samples of W30, only total chloride content of it is presented by IC. Generally, it can be concluded that mere wetting and drying under regime C can also incur varying degrees of maximum phenomena presented by different methods in paste specimens with different W/B.

3.4 Wetting and drying regime D

Fig. 9 presents chloride distribution in the surface layer of specimens under regime D using SNT. It can be observed that significant maximum phenomena appear in chloride profiles of specimens with whatever W/B and in either free or total chloride, and free chloride content is slightly lower than total chloride content but the change trend of them is identical. Therefore, it can also be concluded that mere wetting and drying under regime D can incur varying degrees of maximum phenomena in paste specimens with different W/B. Besides, the evaluation law of maximum phenomena under regime D is clearly presented, that is, the higher the W/B is, the more significant the maximum phenomenon is.

![Figure 9. Chloride distribution of specimens under wet-dry regime D](image)

3.5 Wetting and drying regime E

Fig. 10 shows free chloride distribution in the surface layer of specimens under regime E using SNT. It is clear that maximum phenomena occur in all specimens under regime E, no matter in paste or mortar, with or without SL and FA. Therefore, it can be drawn that mere wetting and drying under regime E can also incur chloride maximum in either paste or mortar specimens with different W/B. It can also be observed that the maximum phenomena in specimens with SL or FA is more significant than that in specimens without mineral admixtures.

![Figure 10. Chloride distribution of specimens under wet-dry regime E](image)
4. Discussion
The results of chloride distribution in the surface layer of specimens with different W/B detected by SNT, IC and EPMA show that chloride maximum phenomena occur under four different wetting and drying regimes, in either paste or mortar specimens, in free or total chloride, and with or without SL or FA. It suggests that mere wetting and drying action can lead to the appearing of chloride maximum phenomena when skin effect and rain washing effect are excluded, though sometimes the depth of maximum cannot be clearly presented limited by the accuracy of testing method.

Diffusion, capillary adsorption/moisture evaporation, and carbonation all play a role in determining chloride transport during wetting and drying. Diffusion drives chlorides transferring from high concentration places to low concentration places. Capillary adsorption carries external chlorides into matrix and forces the original chlorides there to move into deeper positions. Moisture evaporation decreases water content and makes chlorides deposit in the form of crystals. Carbonation, on the one hand, affects chloride transport rate through changing pore structures of matrix, though it has been reported that its influence to pore structure cannot decide the occurring of chloride maximum phenomena [8]; on the other hand, carbonation controls chloride transport by decomposing Friedel’s salt, Kuzel’s salt and C-S-H gel and releasing chemical and physical bound chloride into pore solution [36]. Therefore, the formation of chloride maximum phenomenon under cyclic wetting and drying can be attributed to the combined effect of diffusion, capillary adsorption/moisture evaporation and carbonation. To put it into details, at the beginning of wetting, salt solution enters into surface part of matrix and elevates water and chloride content there rapidly, and then during drying, the water decrease in surface concentrates pore solution, further increases chloride concentration there (kg Cl/m3 pore solution), and drives chloride to transport into deeper positions, which consequently decreases the actual chloride content in surface (kg Cl/kg sample) and increases the actual chloride content in deeper places. Meanwhile, CO2 enters into matrix and carbonation reaction occurs, which releases surface bound chloride and decreases bound chloride content there. And in the next wetting, those released chloride ions will again be brought into deeper positions. As a result, after several repeating, the free and bound chloride content in surface decreases gradually while that in deeper positions increases constantly, and when chloride content at a certain deeper position surpasses that in surface, the chloride maximum phenomenon is formed.

5. Conclusions
The chloride distribution in the surface layer of specimens with different W/B detected by SNT, IC, and EPMA presents a fact that: chloride maximum phenomena appear in all specimens under four wetting and drying regimes, no matter in paste or mortar, in free or total chloride, and whether with SL and FA or not. The result suggests that mere wetting and drying action can incur the forming of maximum phenomenon even without the attendance of skin effect and rain washing. However, the position of maximum phenomena sometimes can not be presented confined by the accuracy of testing method. The formation of chloride maximum phenomenon under mere wetting and drying can be ascribed to the combined effect of diffusion, capillary adsorption/moisture evaporation and carbonation.

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References
[1] Anna V. Saetta, Roberto V. Scotta, Renato V. Vital iani, Analysis of Chloride Diffusion into Partially Saturated Concrete. Ameri. Concr. Inst. Mater. J. 90. 5 (1993)
[2] Zhiwu Yu, Ying Chen, Peng Liu, Weilun Wang, Ac celerated simulation of chloride ingress into concrete under drying-wetting alternation condition chloride environment. Constr. Build. Mater. 93 (2015)
[3] Chanakya Arya, Samira Bioubakhsh, Perry Vassie, Modelling chloride penetration in concrete subjected to cyclic wetting and drying. Mag. Concr. Res. 66, 7 (2014)
[4] P. Castro, O.T. De Rincon, E.J. Pazini, Interpretation of chloride profiles from concrete exposed to tropical marine environments. Cem. Concr. Res. 31 (2001)
[5] G.R. Meira, C. Andrade, I.J. Padaratz, C. Alonso, J.C. Borba Jr, Chloride penetration into concrete structures in the marine atmosphere zone–Relationship between deposition of chlorides on the wet candle and chlorides accumulated into concrete. Cem. Concr. Compos. 29 (2007)
[6] Rob B. Polder, Willy H.A. Peelen, Characterization of chloride transport and reinforcement corrosion in concrete under cyclic wetting and drying by electrical resistivity. Cem. Concr. Compos. 24 (2002)
[7] Honglei Chang, Song Mu, Deqing Xie, Penggang Wang, Influence of pore structure and moisture distribution on chloride “maximum phenomenon” in surface layer of specimens exposed to cyclic drying-wetting condition. Constr. Build. Mater. 131 (2017)
[8] Honglei Chang, Song Mu, Pan Feng, Influence of carbonation on “maximum phenomenon” under cyclic wetting and drying condition. Cem. Concr. Res. 103 (2018)
[9] C. Andrade, M. A. Climent, G.de Vera, Procedure for calculating the chloride diffusion coefficient and surface concentration from a profile having a maximum beyond the concrete surface. Mater. Struct. 48 (2015)
[10] Honglei Chang, Pan Feng, Jian Liu, Zuquan Jin, Kai Lv, Qiaoling Liu, Chloride maximum phenomenon near the surface of cement paste induced by moisture evaporation and carbonation. Mater. Struct. 51 (2015)
[11] H. Ye, N. Jin, X. Jin, C. Fu, Model of chloride penetration into cracked concrete subject to drying–wetting cycles. Constr. Build. Mater. 36 (2012)
[12] K. Hong, R.D. Hooton, Effects of cyclic chloride exposure on penetration of concrete cover. Cem. Concr. Res. 29 (1999)
[13] Chanakya Arya, Perry Vassie, Samira Bioubakhsh, Chloride penetration in concrete subject to wet/dry cycling: influence of moisture content. Struct. Build. 167, SB2 (2014)
[14] Carmen Andrade, Jose Miguel Díez, Cruz Alonso, Mathematical Modeling of a Concrete Surface “Skin Effect” on Diffusion in Chloride Contaminated Media. Adv. Cem. Mater. 6, 6 (1997)
[15] Xu Ke, Properties of Chloride IonsTransportation in Concrete under Different Drying-wetting Cycles. Master thesis, Three Gorges University, China, (2012)
[16] K. Hong, R.D. Hooton, Effects of fresh water exposure on chloride contaminated concrete. Cem. Concr. Res. 30, 9 (2000)
[17] H. Kuosa, R.M. Ferreira, E. Holt, M. Leivo, E. Vesi kari, Effect of coupled deterioration by freeze–thaw, carbonation and chlorides on concrete service life. Cem. Concr. Compos. 47, 9 (2014)
[18] H. Ye, C. Fu, N. Jin, X. Jin, Influence of flexural loading on chloride ingress in concrete subjected to cyclic drying-wetting condition. Compos. Concr. 15, 2 (2015)
[19] Joško Ožbolt, Filip Orsancić, Gojko Balabanic, Modelling influence of hysteretic moisture behavior on distribution of chlorides in concrete. Cem. Concr. Compos. 63 (2016)
[20] Amor Ben Fraj, Stéphanie Bonnet, Abdelhafid Khel ijd, New approach for coupled chloride/moisture transport in non-saturated concrete with and without slag. Constr. Build. Mater. 35 (2012)
[21] Bamforth PB. The derivation of input data for modelling chloride ingress from eight-year UK coastal exposure trials. Mag. Concr. Res. 51, 2 (1999)
[22] Zibara Hassan, Binding of external chloride by cement pastes. PhD thesis. Department of Building Materials, University of Toronto, Canada, (2001)
[23] Goni S. Guerrero A, Accelerated carbonation of Friedel’s salt in calcium aluminate cement paste. Cem. Concr. Res. 33, 1 (2003)
[24] Jonathon Backus, Danny McPolin, Muhammed Basheer, Adrian Long, Niall Holmes, Exposure of mortars to cyclic chloride ingress and carbonation. *Adv. Cem. Res.* **25**, 1 (2013)

[25] Qiang Yuan, Caijun Shi, Geert De Schutter, Katrien Audenaert, Dehua Deng, Chloride binding of cement-based materials subjected to external chloride environment—A review. *Constr. Build. Mater.* **23** (2009)

[26] D. McPolin, P.A.M. Basheer, A.E. Long, K.T.V. Grattan, T. Sun, Obtaining progressive chloride profiles in cementitious materials. *Constr. Build. Mater.* **19** (2005) [27] Chunhua Lu, Yuan Gao, Zhaowei Cui, Ronggui Liu, Experimental Analysis of Chloride Penetration into Concrete Subjected to Drying-Wetting Cycles. *J. Mater. Civil Eng.* **27**, 12 (2015)

[27] M.D.A. Thomas, J.D. Matthews, Performance of pfa concrete in a marine environment—10-year results. *Cem. Concr. Compos.* **26** (2004)

[28] G.R. Meira, C. Andrade, I.J. Padaratz, C. Alonso, J.C. Borba Jr, Chloride penetration into concrete structures in the marine atmosphere zone—Relationship between deposition of chlorides on the wet candle and chlorides accumulated into concrete. *Cem. Concr. Compos.* **29** (2007)

[29] Majid Safehian, Ali Akbar Ramezanianpour, Assessment of service life models for determination of chloride penetration into silica fume concrete in the severe marine environmental condition. *Constr. Build. Mater.* **48** (2013)

[30] Honglei Chang, Song Mu, Detecting water soluble chloride distribution of paste in a high-precision way. *J. Visual. Exper.* 129e56268 (2017)

[31] Jian-Guo Dai, Y. Akira, F.H. Wittman, H. Yokota et al, Water repellent surface impregnation for extension of service life of reinforced concrete structures in marine environments: The role of cracks. *Cem. Concr. Compos.* **32** (2010)

[32] H. Ye, Y. Tian, N. Jin, X. Jin, C. Fu, Influence of cracking on chloride diffusivity and moisture influential depth in concrete subjected to simulated environmental conditions. *Constr. Build. Mater.* **47** (2013)

[33] Henrik Wall and Lars-Olof Nilsson, A study on sampling methods for chloride profiles: simulations using data from EPMA. *Mater. Struc.* **41** (2008)

[34] Honglei Chang, Song Mu, Jianzhong Liu, Chloride Distribution Feature in Surface Layer of Cement Paste under Cyclic Drying-Wetting Condition. *Key Eng. Mater.* **711** (2016)

[35] Honglei Chang, Chloride binding capacity of pastes influenced by carbonation under three conditions. *Cem. Concr. Compos.* **84** (2017)