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Airborne chloride penetration into mortar specimens with different mix proportions in Phuket, Thailand

Pakpoom Limtong[1*], **Rungrawee Wattanapornprom**[2], **Withit Pansuk**[3]

[1,3] Department of Civil Engineering, Faculty of Engineering, Chulalongkorn University
254 Phaya Thai, Wang Mai, Patumwan, Bangkok, 10330, THAILAND

[2] Department of Civil Engineering, School of Engineering, University of Tokyo
7-3-1 Hongo, Bunkyo-ku, Tokyo, 113-8656, JAPAN

[*]E-mail: ohm.stife@gmail.com

***Abstract*:** A concrete structure in hot and humid marine environments, like in the southern Thailand, has the deterioration due to the corrosion of the steel reinforcement which is accelerated by airborne chloride. Thus, some structures are needed to be repaired or reconstructed before their designed service life, even though the structures are not directly contacted with the seawater. Airborne chloride intensity in each area varies due to different environmental conditions, and very few airborne chloride data are available in Thailand. Thus, gathering the quantitative data of airborne chloride intensity and penetration into various mix proportions of concrete specimen in a risk area is necessary to come up with a proper standard specification for durable concrete under airborne chloride condition in Thailand. In this study, two sets of mortar specimens with three mix proportions had been used for the experiment; one was exposed to airborne chloride, the other was immersed in salt water. After 5 months exposure, the specimens were tested for the total chloride content at each depth from the concrete surface. The airborne chloride mechanism between two kinds of exposure is discussed, together with the airborne chloride intensity at site, meteorological data from Thailand Meteorological Department, and existing standard specification for durable concrete design. The airborne chloride mechanism is more complicated than the salt-water immersion case, because the penetration rate also differs depending on the concrete mix proportion, the chloride concentration on the concrete surface, temperature, and relative humidity. The airborne chloride penetration data into the mortar specimens in Phuket should be potentially useful for a better sustainable infrastructures design and maintenance of concrete structures under marine environments in Thailand.

Keywords: airborne chloride, penetration, durable concrete design

1. Introduction

Durability of concrete structures can be reduced by being exposed to marine environments. In a marine environment, chloride penetration causes reinforcement steel corrosion which is the major reason of concrete cracking. In consequence, those concrete structures are

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required to be reconstructed. The southern part of Thailand located in a hot and humid zone has a high tendency to face such deterioration. Some concrete structures were investigated as shown in Figure 1.1. Even though the structures are not directly contacted with the seawater, airborne chloride, also known as the sea aerosol traveling in the atmosphere, can cause such serious deterioration. For sustainable development, a suitable standard specification of durability design of concrete structure in a marine environment in Thailand is necessary to strengthen durability performance.

Figure 1.1 Deterioration from airborne chloride

Chloride deterioration in marine environments can be deteriorated due to combined effects of chemical action, such as crystallization pressure of salts within concrete when it is subjected to wetting and drying process, or corrosion of embedded reinforcing steel, and physical action, such as dynamic load of wave [1]. Concrete exposed to a marine environment can be divided into two categories. First, the direct exposure can be both fully and partially contacted seawater, such as structures in tidal zone and splash zone. Second, the indirect exposure, when structures are exposed to airborne chloride as shown in Figure 1.2.

Airborne chloride deterioration can be represented by the following processes: i) airborne chloride generation, ii) transportation, iii) surface adhesion, and iv) ingression through concrete pores [2] as shown in Figure 1.3 [3]. The amount of airborne chloride penetration depends on various factors, such as environmental conditions, climate, the chloride concentration on the surface, and effects from the rainfall [2-4]. Airborne chloride deterioration mechanism has high complexity because different areas have different characteristics, and research about airborne chloride in Thailand marine environmental conditions is still limited. Therefore, study about airborne chloride penetration in Thailand is necessary. From the previous research [3] compared the result between OPC and OPC+FA Class F 15%; however, fly ash from Mae-Moh Thailand is Class C, which has no information.

In this study, on-site exposure in Phuket, Thailand and salt-water immersion of mortar specimens have been conducted, together with on-site measurement of airborne chloride intensity in the atmosphere [5]. After 5 months of exposure, the specimens have been collected and tested to determine the total chloride content at each depth from the concrete surface.

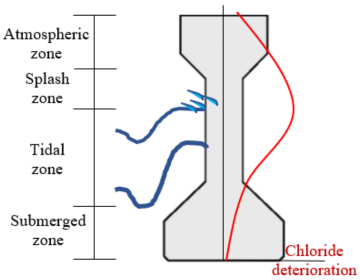


Figure 1.2 Concrete in a marine environment [1]

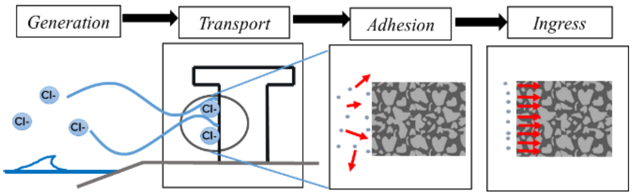


Figure 1.3 Deterioration from airborne chloride [3]

1.1 Objectives

The objectives of this study are to study the characteristics and collect the quantitative data of airborne chloride penetration into various mix proportions of mortar specimens from the on-site exposure in Southern Thailand, The Andaman Sea side, compared to those submerged in salt water, and to suggest factors needed to be considered for a design code of durable concrete under the airborne chloride condition in Thailand marine environments.

2. General knowledge about airborne chloride

2.1 Airborne chloride generation and transportation

Airborne chloride generates as the wave begins to break. The amount and particle size produced depend on coastal topologies and wave conditions. It has been reported that if the coastline is the obstacle coast, more and larger airborne particles have a high tendency to be produced due to wave smashing than that of the beach coast. The particle size distribution at the initial point vary from 10 μm to 5,000 μm [2]. As airborne chloride is generated, the horizontal wind and residual wave energy after breaking transport airborne chloride upward at a certain height, then it is moved into inland by the wind flow while falling due to the gravity force [6].

Previous research [2] conducted an experiment to collect airborne chloride particle sizes distribution at different heights and different distances in two different coastal topologies by using the water-sensitive paper, as shown in Figure 2.1. The result shows that larger particles present at a lower elevation, but they drop faster while traveling farther than the smaller ones. Thus, smaller particles can reach farther and higher distances.

Past researcher [7] conducted experiment about airborne chloride transportation and deposition using wet candle collection method in a tropical region in the northeast of Brazil, at five monitoring stations placed at 10, 100, 200, 500 and 1100 m from the sea to characterize inland transportation of airborne chloride. The result shows an abrupt reduction in the presence of marine salt in the first 100 m from the sea, as shown in Figure 2.2. Among other factors, wind speed plays a very important role, due to its relation with airborne chloride generation and inland transportation. Strong winds are capable to carry larger salt particles to longer distances before settling by gravitational force. Higher salt deposition can be observed at the same distance from the seashore when wind speed increases, but the effect weakens as the distance goes farther.

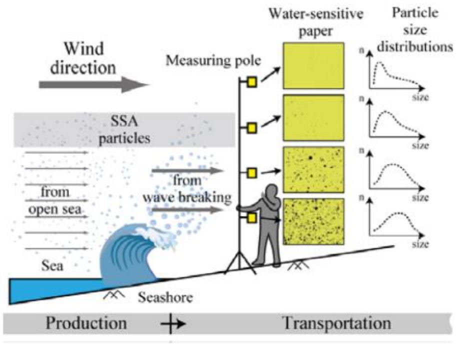


Figure 2.1 Particle size distribution measurement by using the water-sensitive paper [2]

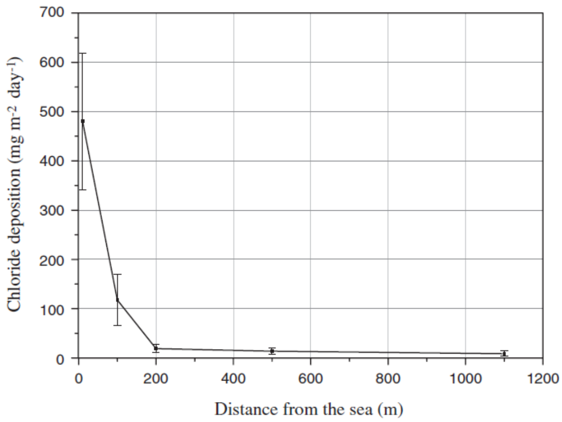


Figure 2.2 Chloride deposition on the wet candle at each monitoring position [7]

2.2 Airborne chloride adhesion and ingression

Airborne chloride attaches to cementitious materials such as C-S-H gel, C-A-H, C-A-F-H, and ettringite [8]. Many research have reported that concrete with lower porosity (low w/b ratio) tends to have lower chloride penetration, and the chloride concentration is intense on the surface because the higher amount cementitious materials has hydrated, the more binding capacity the concrete has. It can be concluded that the chloride binding capacity depends on concrete mix design, curing time and exposure period. After adhesion, both chloride ions and water ingress into the concrete. Generally, the total chloride in the concrete increases when the amount of airborne chloride on the concrete surface increases from Fick's 2nd law of diffusion, as shown in Eq. 2.1. The chloride concentration on the concrete surface subjected to airborne chloride is not constant because some parts are wet, but some parts remain dry. Consequently, chloride ingression is not uniformly distributed. Airborne chloride ingression mechanisms can be described as follows [3, 9].

$$C_d = C_0\left(1 - erf\left(\frac{x}{2\sqrt{Dt}}\right)\right) \qquad \text{Eq. (2.1)}$$

2.2.1 Chloride ion transport mechanism

Chloride ions from the thin layer of water ingresses into concrete pores by: i) advection or capillary suction, and ii) diffusion as shown in Figure 2.3. Advection describes the process of absorption of water containing chloride ion into pores. Diffusion is the movement of chloride ions due to the different concentration gradient from high to low. With these mechanisms, it can be inferred that moisture transport affects the degree of chloride penetration. Therefore, moisture transport is needed to be considered.

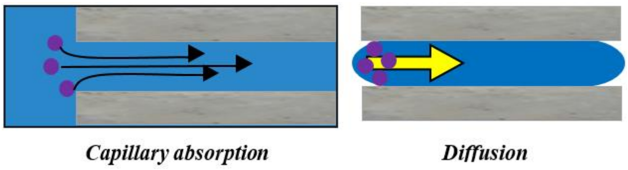


Figure 2.3 Chloride ion transport mechanism

2.2.2 Moisture transport mechanism

In marine environments, moisture transportation in porous media plays an important role in invasion of water and ions into concrete structures. Marine exposure environments can be divided into two conditions [10]: i) humid moist environment where RH is nearly saturated, and moisture diffuses into pores by the concentration gradient; ii) submerged environment when a concrete structure is submerged in the sea, the main transportation is the capillary suction of liquid water. In the actual exposure, structures can be exposed to both conditions.

Typically, when concrete structures are exposed to airborne chloride, the boundary condition is closer to the humid moist environment; however, when they are subjected to rainfall or splash covering the concrete surface, the boundary condition is closer to the submerged environment.

2.2.3 Washout effect from the rainfall

In the actual environments, precipitation is needed to be considered. The water from the rainfall or snow can dilute the chloride concentration on the concrete surface which leads to the diffusion of the chloride concentration inside concrete.

Past researcher [3] assumed that the washout effect fully occurs when the concrete is subjected to heavy rainfall (>= 5 mm/hr). At this stage, chloride concentration on the concrete surface becomes zero, and chloride ions inside the concrete diffuse out, as shown in Figure 2.4. A numerical model has been proposed to calculate airborne chloride concentration on concrete surfaces with the washout effect, and was verified by both experiments in laboratory and at site. For the laboratory experiment, the prepared mortar specimens were coated with epoxy and submerged in 3% sodium chloride solution for 90 days. After that, the specimens were placed on the 30 degrees incline and exposed to water with the flow rate of 85 mL/min (equal to 5 mm/hr), as shown in Figure 2.5. For the on-site experiment, mortar specimens were placed and exposed to airborne chloride conditions with the rainfall environment. The environmental data at site were provided by AMEDAS of the Japan Meteorological Agency to be used as boundary conditions for the analysis. The results of both experiments are shown in Figure 2.6 and Figure 2.7 respectively.

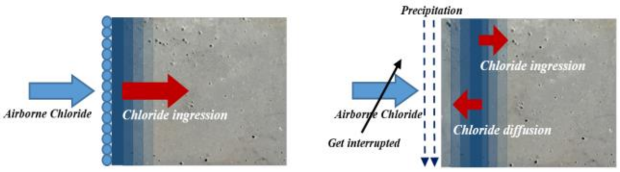


Figure 2.4 Washout effect from the rainfall [3]

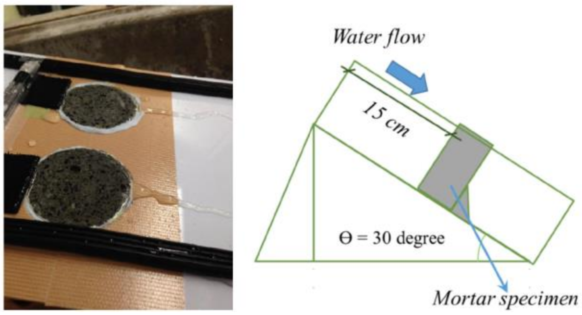


Figure 2.5 Washout effect laboratory experiment [3]

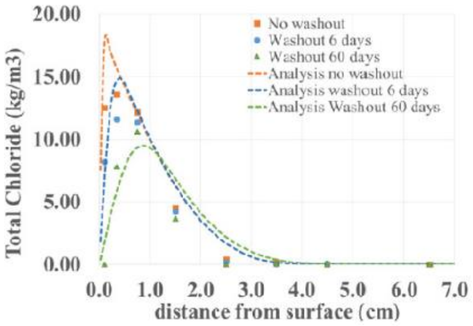


Figure 2.6 Total chloride result from the lab test [3]

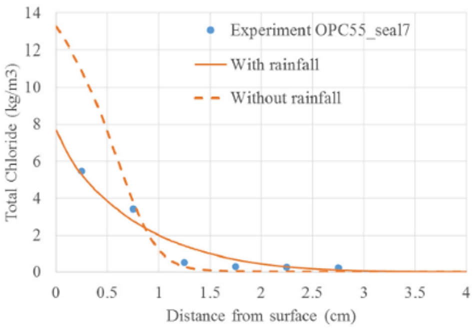


Figure 2.7 Total chloride result from the on-site exposure [3]

2.3 Airborne chloride collection methods

2.3.1 Tank collector

This method was developed by Public Works Research Institute of Japan (PWRI). All parts of the tank are made of stainless steel. Airborne particles accumulate on the capture board (size 10 x 10 cm^2) which is connected by the tube to the plastic container, as shown in Figure 2.9. Airborne chloride on the capture board is washed into the plastic container by distilled water.

Figure 2.9 Tank collector [12]

2.3.2 Mortar chip

Mortar chip, or thin-plate mortar, is an effective method to collect the amount of airborne chloride at a specific position [13]. However, the result is affected by the properties from the mix proportion, thickness, and washout effect from the rainfall.

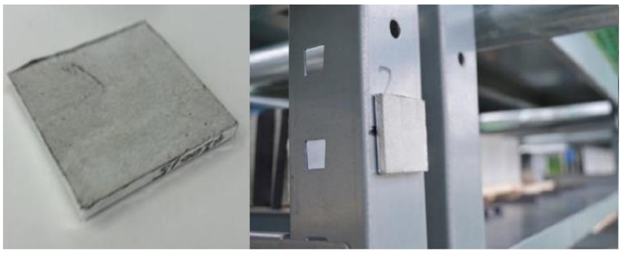


Figure 2.10 Mortar chip collection method [12]

In this study, these two methods were used to collect the airborne chloride at site. From past experiment [12], mortar chip and tank provide almost the same result, but mortar chip is more convenient.

2.4 Exposure site in Phuket, Thailand

Southern Thailand is surrounded by the ocean; Andaman Sea covers west coast, and Gulf of Thailand covers east coast. Thailand is influenced by the annual South-West monsoon from May to October, and North-East monsoon from November to January [14], as shown in Figure 2-11. In the West-coast areas, such as Phuket and Phang-Nga, the South-West monsoon carrying moist wind from Indian Sea. On the other hand, the cold dried wind from the North-East monsoon cannot fully reach due to Gulf of Thailand. Concrete structures in the areas, are exposed to a harsh marine environment, with a hot and humid moist climate throughout the years. These conditions stimulate the deterioration from chloride attack.

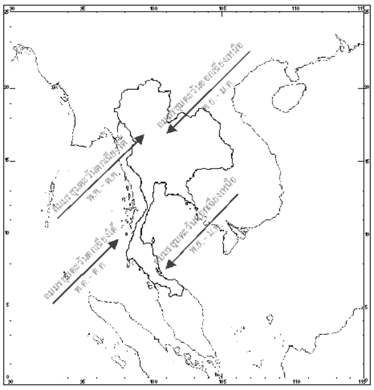


Figure 2.11 The annual monsoon in Thailand [14]

2.5 Durable concrete design code in Thailand

According to Thailand standard of concrete durability performance, designers should take the corrosion of embedded steels due to chloride penetration into account for the concrete structures located within 1 kilometer from the seashore [15].

In Thailand, standard specifications of concrete structure against marine environments are written by Department of Public Works and Town and Country Planning (DPT 1332-55). Concrete structures exposed to chloride conditions must be designed to prevent chloride from reaching the critical level at the exterior face of steel bars for service life [15].

$$C_d \le C_{lim} \qquad \text{Eq. (2.2)}$$

Where C_{lim} is the critical chloride content (% w/w of binder). See Table 2.1**;** C_d is the chloride content at the surface of steel, is calculated by

$$C_d = (C_s - C_0)\left[1 - erf\left(\frac{c}{2\sqrt{D_a t_r}}\right)\right] + C_0 \qquad \text{Eq. (2.3)}$$

C_0 is the chloride content in concrete at the beginning (% w/w of binder), can be determined by ASTM C-1152. See Table 2.2; C_s is the chloride content at the surface of concrete (% w of binder), can be determined by Table 2.3 and Eq. 2.5; t_r is the specified service of life of the structure (year), erf is the error function, $erf(z) = \frac{2}{\pi}\int_0^z e^{-n^2}dn$; D_a is the apparent chloride diffusion coefficient (cm^2/year), is used for the design of concrete mix proportion; c is the required concrete covering

To calculate Eq. 2.3, $C_{s'}$ from Table 2.3 must be converted to %w/w of binder from Eq. 2.5,

$$C_s = C_{s'} \cdot \frac{\rho_{concrete}}{b} \qquad \text{Eq. (2.4)}$$

Where $C_{s'}$ is the chloride content at concrete surface from Table 4; $\rho_{concrete}$ is the unit weight of concrete; b is the unit weight of binder.

Without consideration of the crack of the concrete, the durable concrete mix design for chloride (w/b) at service life can be calculated by the following Eq. 2.5 and Eq. 2.6.

Only OPC; $D_{a,c} = (w/b)^3 \times 13.5(\frac{1}{t_r})^{0.40}$ Eq. (2.5)

OPC + Fly Ash; $D_{a,fa} = D_{a,c} \times \alpha_{fa}$ Eq. (2.6)

Table 2.1 Critical chloride (C_{lim}) [15]

Type	**C_{lim} (%w/w of binder)**
OPC	0.45
- % w/w Fly Ash to binder < 0.15	0.45
- % w/w Fly Ash from 0.15 to less than 0.35	0.35
- % w/w Fly Ash from 0.35 to 0.55	0.30

Table 2.2 Maximum acceptable chloride content in concrete at the beginning (C_0) [15]

Structure	**C_0 (%w/w of binder)**
1. Prestressed concrete	0.08
2. Concrete exposed to chloride i.e. sea-retaining walls	0.20
3. Concrete with protection from moisture	1.00
4. Others	0.30

Table 2.3 Chloride content at concrete surface considering the distance from the seashore [15]

Service Life (year)	**Chloride content at concrete surface, $C_{s'}$ (%w/w of concrete)**				
	Distance from the seashore (m)				
	0	**100**	**250**	**500**	**1,000**
10	0.299	0.135	0.061	0.041	0.040
20	0.389	0.176	0.079	0.054	0.052
30	0.453	0.205	0.092	0.063	0.060
40	0.506	0.229	0.103	0.070	0.067
50	0.551	0.249	0.112	0.076	0.073

3. Methodology

To study airborne chloride ingression mechanisms, 2 sets of 10 x 10 x 10 cm^3 mortar specimens with 3 different mix proportions are casted and cured by submerging in water in laboratory. The procedure is shown in Figure 2.12. The mix proportions are shown in Table 7 below. After curing the mortar specimens by water immersion for 28 days, coat 5 surfaces of each specimen with epoxy, leave 1 surface to get exposed in order to analyze one-dimensional chloride penetration, as shown in Figure 2.13, 2.14 and 2.15, respectively.

One of the specimen sets is submerged in the 3% sodium chloride (NaCl) solution which imitates seawater containing sodium chloride about 3 – 3.5 % [10]. Another set is placed at site and get exposed under actual environment. After 5 months, both sets of the specimens will be drilled to get the powder of each depth, and titrated with silver nitrate solution ($AgNO_3$) to determine the chloride concentration at each depth.

Kalim beach at the Andaman Sea coast has been the chosen place to collect the quantity of airborne chloride. The site is located about 30 meters from the sea. Airborne chloride tank collector, mortar chip and mortar specimens were installed on the rooftop, as shown in Figure 2.15. There is no obstacle, providing the specimens and equipment clearly exposed to the wind flow.

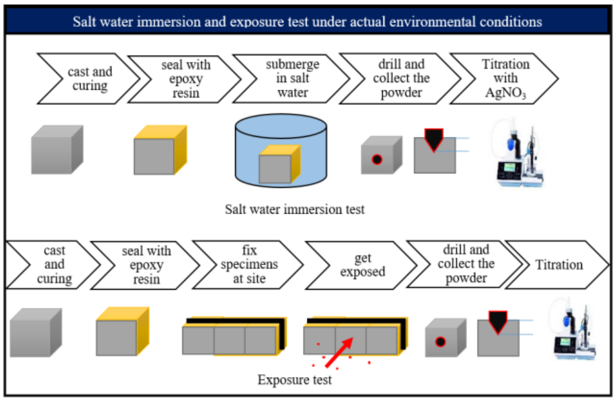
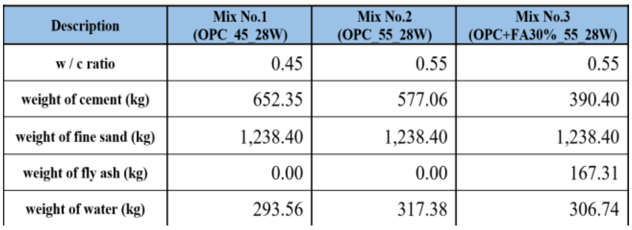


Figure 2.12 Outline procedure of the experiment

Table 3.1 Mix proportions of the mortar specimens



Description	Mix No.1 (OPC_45_28W)	Mix No.2 (OPC_55_28W)	Mix No.3 (OPC+FA30%_55_28W)
w / c ratio	0.45	0.55	0.55
weight of cement (kg)	652.35	577.06	390.40
weight of fine sand (kg)	1,238.40	1,238.40	1,238.40
weight of fly ash (kg)	0.00	0.00	167.31
weight of water (kg)	293.56	317.38	306.74

Figure 2.13 the mortar specimens coated with epoxy

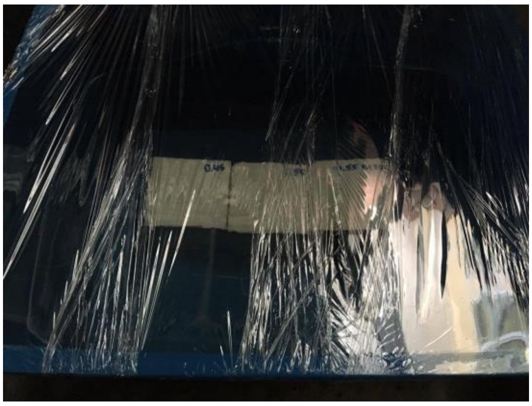


Figure 2.14 Salt-water immersion set

Figure 2.15 On-site exposure set

The percentage of total chloride content by weight of the sample is calculated from Eq. 3.1 [16]

$$\%Cl = \frac{3.545 \times (V_1 - V_2) \times N}{W} \qquad \text{Eq. (3.1)}$$

Where V_1 is millitres of $AgNO_3$ solution used for sample titration, V_2 is millitres of $AgNO_3$ solution used for blank titration, N is exact normality of prepared $AgNO_3$ solution, and W is mass of sample in gram.

For calculating kilograms of chloride per cubic metre of concrete sample, multiply percent chloride by the density of concrete sample to the nearest 0.1 kg/m^3.

$$Cl^- \left[\frac{kg}{m^3} \right] = \%Cl \cdot \frac{AirDryDensity}{100} \qquad \text{Eq. (3.2)}$$

For the airborne chloride intensity data assimilation, from the mortar chip and the tank collector, the value from Eq. 3.2 will be converted into sodium chloride (NaCl) in mg/dm^2/day to represent the amount of sea salt aerosol in the atmosphere by the following equation.

$$NaCl[\,mdd\,] = \left(\frac{5.844}{3.545} \right) \left(Cl^- \left[\frac{kg}{m^3} \right] \right) \left(\frac{1}{days} \right) \qquad \text{Eq. (3.3)}$$

Table 3.2 Exposure period

No.	Exposure period	Duration (days)
1	Jan 19 – Feb 19, 2017	31
2	Feb 19 – Mar 19, 2017	29
3	Mar 19 – Apr 08, 2017	21
4	Apr 08 – May 21, 2017	44
5	May 21 – June 21, 2017	31

4. Results and discussions

[5] collected airborne chloride intensity in Phuket, by mortar chips during January – June 2017, the results at elevation 15.5 meters where the mortar specimens were placed are shown in Figure 4.1**.** The airborne chloride intensity data captured by mortar chips changed monthly due to different climate.

The results of airborne chloride penetration from on-site measurement and chloride penetration from salt-water immersion are shown in Figure 4.2, 4.3 and 4.4. Chloride penetration from salt-water immersion gives a higher and smoother decreased value. It is because chloride uniformly ingress into pores by capillary absorption. The total chloride concentration becomes dramatically lesser as deeper because while specimens are submerged in salt water, the unhydrated cement continues hydrating and the effect of capillary absorption becomes less. However, on-site exposure yields lower value of airborne chloride concentration at each depth because airborne chloride partially attached to the mortar surface, some parts are wet but some parts are dry. Therefore, there are both capillary absorption and diffusion.

The airborne chloride concentration around 0 – 0.5 cm depth is lower than that of 0.5 – 1.0 cm depth for all three specimens. It is because the mortar surfaces were washed out by the rainfall during exposure. Moreover, the slope is not steep which means that chloride can ingress deeper, because no more curing is giving for mortar specimens at site.

The submerged mortar specimen with cement-fly ash paste contains higher total chloride content at the surface than the ordinary Portland cement specimens, because it can bind more chloride ion due to more cementitious components from both hydration and pozzolanic reaction after gradually curing under the water. In contrast, the one at site contains comparatively lower chloride content.

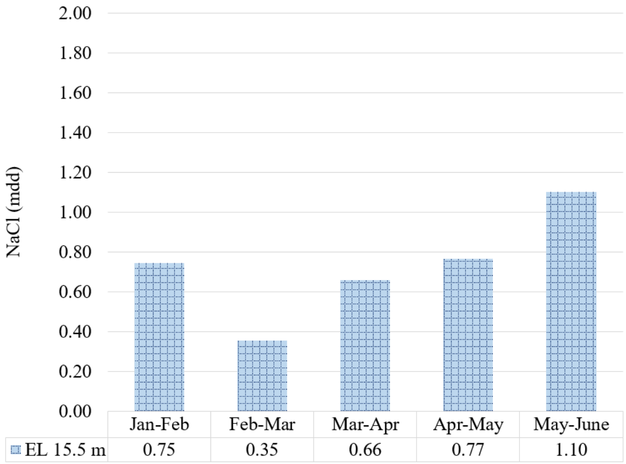


Figure 4.1 Airborne chloride intensity captured by mortar chips at elevation 15.5 m [5]

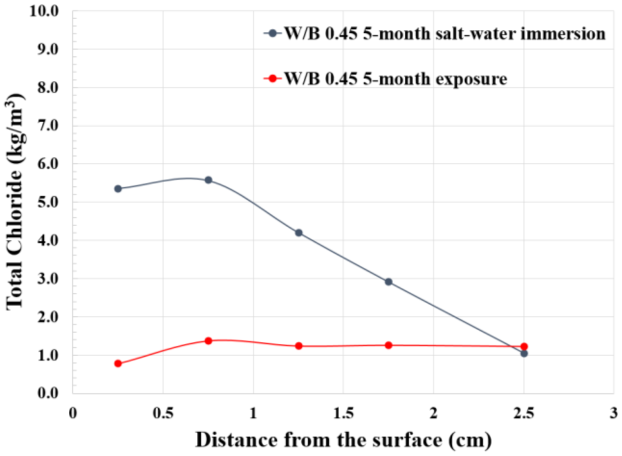


Figure 4.2 Chloride penetration for W/B 0.45 mortar

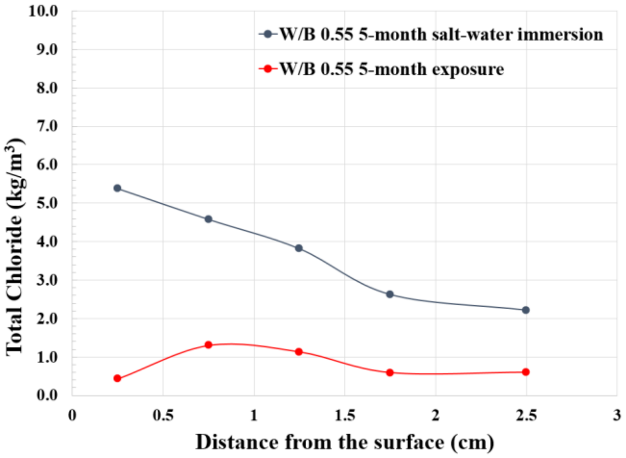


Figure 4.3 Chloride penetration for W/B 0.55 mortar

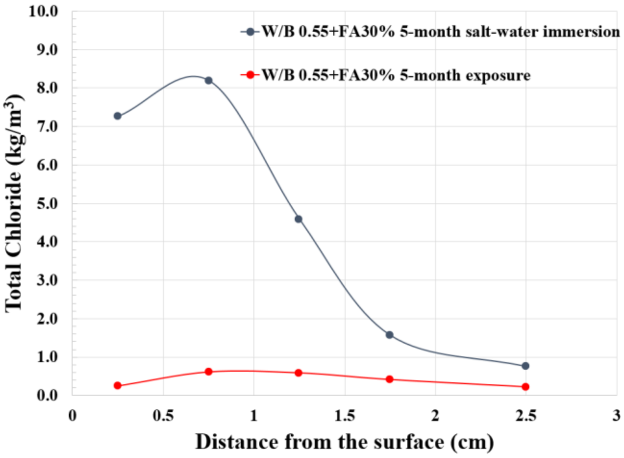


Figure 4.4 Chloride penetration for W/B 0.55 + Fly Ash 30% mortar specimen

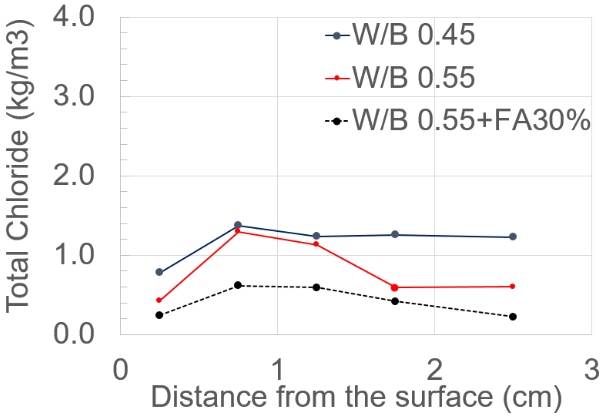


Figure 4.5 Comparison of airborne chloride penetration among each mix design

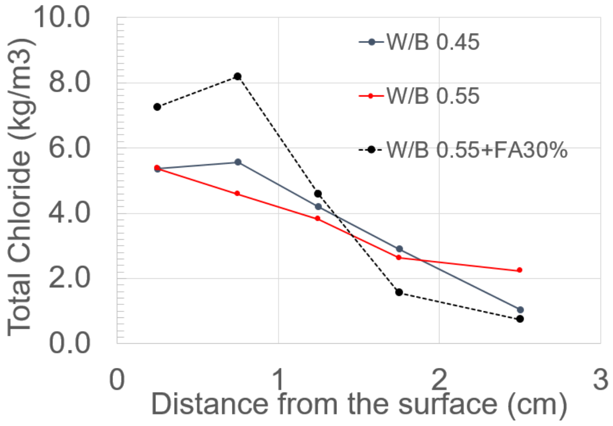


Figure 4.6 Comparison of salt-water penetration among each mix design

According to the surveying in the exposure site, the concrete slab has concrete covering of 1.0 cm. From Table 2.1, the critical chloride content (C_{lim}) at the exterior surface of steel compared to chloride content from 0.5 – 1.0 cm depth of each mortar specimen is shown below.

Table 4.1 Comparison of C_{lim} and C_d from exposure (%w/w binder)

Specimen	C_{lim}	Experiment C_d
W/B 0.45	0.45	0.21
W/B 0.55	0.45	0.22
W/B 0.55+FA30	0.35	0.11

After only 5 months of exposure, the chloride content is almost half of the critical chloride content. The chloride content at the concrete surface ($C_{s'}$) from Table 2.3 might not be enough with the actual airborne chloride environment in Thailand. Therefore, concrete structures in Phuket are risk to encounter airborne chloride deterioration, if durable design does not take into account.

Further experiment of airborne chloride penetration into various concrete mix designs, including airborne chloride intensity collection for long-term condition should be held in Thailand.

5. Summary

The mechanism of penetration under airborne chloride condition differs from submerged, tidal and splash condition. Airborne chloride on the concrete surface is affected by environmental conditions, and washout effect from the rainfall. According to Figure 4.5 and Figure 4.6, different mix proportions have different chloride binding capacity which affects the chloride concentration on the concrete surface. Concrete with cement-flyash should be used in marine environments, due to less porosity after a proper curing. Chloride at the concrete surface should consider concrete mix design, lower W/B has higher Chloride at the concrete surface because chloride cannot penetrate inside. A proper durable concrete design standard specification under airborne chloride condition should be developed to include chloride at the concrete surface and concrete mix design.

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