MODELING OF THE SURFACE CHLORIDE REDUCTION DUE TO EXCESS ABSORBABILITY

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ABSTRACT: The chloride attack on concrete structures in the atmospheric marine environment depends on the mechanism of aerosol chloride particles which are transported to the structural members. Many literatures expressed the level of severity on chloride attack based on the available aerosol chloride content at a certain location. The amount of aerosol chloride particles decreases with distance from seashore under the exponential equation. The proposals of severity were also referred to this empirical trend. However, this model is proposed a mechanism to against former conclusion by clarifying the statement of 'Not overall aerosol chloride can be penetrated into concrete'. This means that the total amount of absorbed aerosol chloride ions is not equaled to the total chloride ions in concrete. This model is explained about the limitation of aerosol chloride ions penetration due to the saturated degree of moisture which is able to transport in concrete in a period of time. During a big typhoon, a lot of aerosol chlorides particles are transported to the concrete surface, however this phenomenon can also result the surface soaking from too much aerosol chloride ions on the surface. Whenever, concrete can not absorb total water on the surface, the surface is saturated and droplets will be formed. A location where is located very near to seashore, might have a surface soaking many times in a year. A structure near seashore might be very severe for chloride attack, but the severity is also limited by the environmental itself. This phenomenon can be thought as similar as the effect of rain-induced surface chloride dissolution.

KEYWORDS: Aerosol chloride, Surface chloride, Excess absorbability, Surface dissolution

1. INTRODUCTION

The model of chloride penetration is referred to the Fick's 2nd law of diffusion, and advection of free chloride ions as theoretically expressed in **Eq.1**. The chloride penetration in the atmospheric structure due to aerosol chloride ions is different from the mechanism of them in the submerged condition. In submerged condition, the exposed salt concentration is constantly averaged 3% of NaCl. The structure in land will be subjected with aerosol chloride particles which depend on the environmental loads such as wind, sea wave, distance, temperature, atmospheric pressure, and rain. The calculation for this kind of structure must be assumed that transported aerosol chloride ions are primarily installed within this layer. The concrete surface at 2mm depth is defined as a boundary layer as shown in **Figure 1**.

$$\frac{\partial C_{free(x,t)}}{\partial t} = \frac{\partial F_{free(x,t)}}{\partial x} \qquad (1)$$

where, $C_{free(x,t)}$ is free chloride at a depth and time (mol/l)

$F_{free(x,t)}$ is flux of free chloride at a depth and time (mol/dm^2/hr)
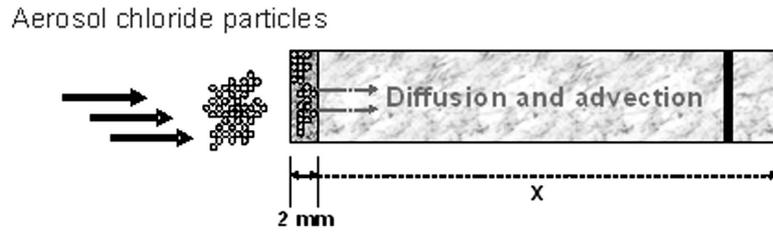
Figure 1 Definition of 2mm surface layer for storing all aerosol chloride particles

The total surface chloride content is calculated by

$$C_{total(0,t)} = \frac{W_{(h,x)}}{10^5 \cdot M_{cl} \cdot \phi \cdot S_{(0,t)} \cdot \Delta x} \qquad (2)$$

where, $C_{total(0,t)}$ is total chloride concentration on surface layer at a certain time (mol/l)

$W_{(h,x)}$ is the transported aerosol chloride at a certain height and depth (mg/dm^2)

M_{cl} is molecular weight of chloride ion

ϕ is concrete pore ratio

$S_{(0,t)}$ is surface saturation

Δx is surface layer of 2mm which has consistent chloride concentration [Swatekititham 2004].

Flux of free chloride content is calculated by ions diffusion and the advection due to moisture gradient. The flux due to diffusion is calculated by the multiplication of diffusion coefficient and free chloride gradient. Another flux is chloride movement together with the moisture flux. The combination of free chloride flux is expressed as follows;

$$F_{free(x,t)} = D_t \cdot \left[\frac{\partial C_{free(x,t)}}{\partial x}\right] + D_w \frac{\partial S_{(x,t)}}{\partial x} \cdot C_{free(x,t)} \quad (3)$$

where, D_t is chloride ions diffusion coefficient in concrete (dm^2/day)

$S_{(x,t)}$ is degree of saturation in concrete

D_w is moisture diffusion coefficient in concrete (dm^2/day) [Saeki T. et al, 1990]

The diffusion coefficient, D_t is calculated by the following expression as follows [Swatekititham 2006],

$$D_t = D_{cl} \cdot \phi \cdot S_{(x,t)} \cdot e^{[2285(\frac{1}{293} - \frac{1}{273+T_k})]} \qquad (4)$$

where, D_{cl} is diffusion coefficient of chloride ions in pore water [Ishida 1999]

T_k is concrete temperature in Kelvin.

Maruya et al, 1998 proposed the relationship between total chloride and fixed chloride and the proposal is used for determining the free chloride concentration at any depths in concrete for this study.

2. MECHANISM OF EXCESS CHLORIDE IONS ABSORBABILITY

Referred to **Figure 2**, the aerosol chloride particles which transport to concrete surface will be accumulated on 2mm surface layer. Considering on this surface layer, the limitation of aerosol chloride penetration is due to the rate of moisture flux transport. Thus, the surface soaking criteria can be explained by **Eq.5**.

$$F_{in\text{-}water} > F_{out\text{-}water} \qquad (5)$$

where, $F_{in\text{-}water}$ is flux in the surface layer due to aerosol chloride (water particles containing 3% salt)

$F_{out\text{-}water}$ is flux out the surface layer due to water penetration in concrete
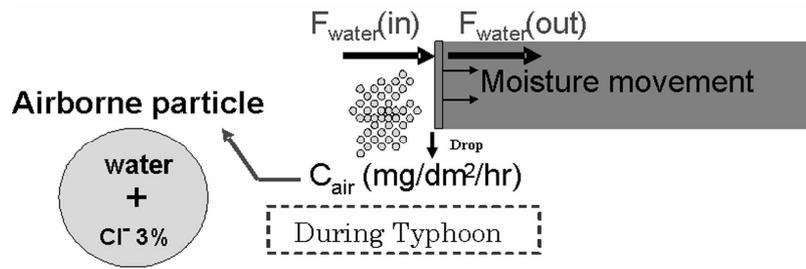
Figure 2 Modeling of salt water drop due to excess moisture absorbability
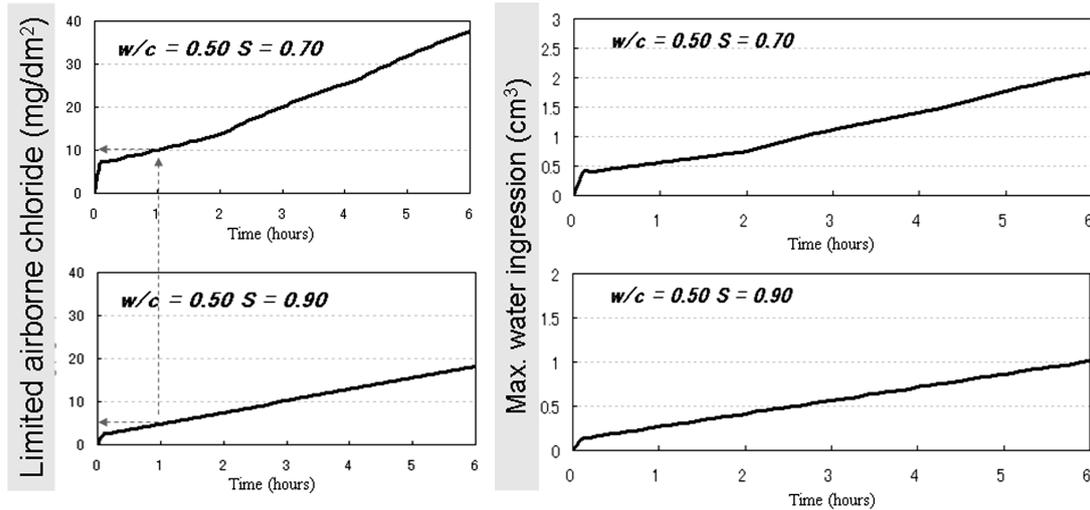

Figure 3 Calculation of maximum water ingression (cm^3) and conversion to the limitation of aerosol chloride (mg/dm^2) with time-dependent (hours)

For a structure far from seashore, this criterion is happened only in a huge typhoon. For a structure near seashore, it can be happened more frequent either small-size typhoon or during windy period. When concrete surface is soaked, the salt water layer is formed and the droplets of salt water are occurred.

2.1 Modeling on moisture transport in concrete

The moisture flux out of surface layer is necessary to calculate as the rate of absorbability. Referred to Saeki et al's model, 1990 of moisture transport in concrete, the amount of moisture transport with time is calculated under the condition that surface layer is saturated. The amount of moisture which can transport in concrete depends on the pore volume and existed degree of saturation. The calculation

examples were done in 2 cases; case1: w/c = 0.50 and saturation 0.70, case 2: w/c = 0.50 and saturation 0.90 for whole depth as illustrated in **Figure 3**. The maximum water ingression is converted into the limited aerosol chloride under the assumption of 3% salt concentration consistently. The limited aerosol chloride in low saturated level in concrete is higher than that in high saturated level due to the residual free-pore space for water storage. For example, maximum water ingression, in the case of w/c = 0.50 and S = 0.70, is approximately 0.52 cm^3. This amount of water is come from the aerosol chloride particles which have 3% salt concentration. The limited aerosol chloride contents were calculated as equaled to 10 (mg/dm^2) for the first hour.

2.2 The surface chloride dissolution model

In general, chloride concentration in the 2mm surface layer is increased due to the amount of transported aerosol chloride ions. Without the consideration of excess absorbability, the surface chloride is gradually increased through the structural life. For long-term exposure, the surface chloride concentration is increased much higher than the aerosol salt concentration of 0.51mol/l. If the surface is soaked during a typhoon, the equilibrium of free chloride concentration in surface layer and outside salt concentration is taken. Afterward, the surface soaking effect is able to limit the surface chloride content to a certain level. The parameter affecting the times of surface soaking per year is the distance from seashore and location. This phenomenon is also able to explain why the chloride concentration at the surface layer of structures in tidal and splash zones are not dramatically different from it in the atmospheric zone near seashore. Structures exposed directly to seawater are also subjected to the desalination out of surface layer.

$$\frac{\lim}{t \to t_i}[C_{total(0,t)}] = 3\% \, NaCl_{(sea)} \qquad (6)$$

where, t_i is time to equilibrium state depending on the surface depth (for 2mm surface depth, t_i is within 1-2 hours)

$3\% \, NaCl_{(sea)}$ is sea salt concentration which the average is 3% for overall Japan seashore.

2.3 Simulation of chloride penetration for Ananai Bridge (Kochi 150m from seashore)

According to the calculation in above model using the environmental condition in Kochi prefecture in 2003, aerosol chloride particles can cause the surface soaking only once a year. The surface chloride concentration is fluctuated due to the aerosol chloride content attached occasionally and the degree of surface saturation is so scattered. However, the tendency of the surface chloride content might be either the inversion of exponential function or the logarithm of time as expressed in **Figure 4**.
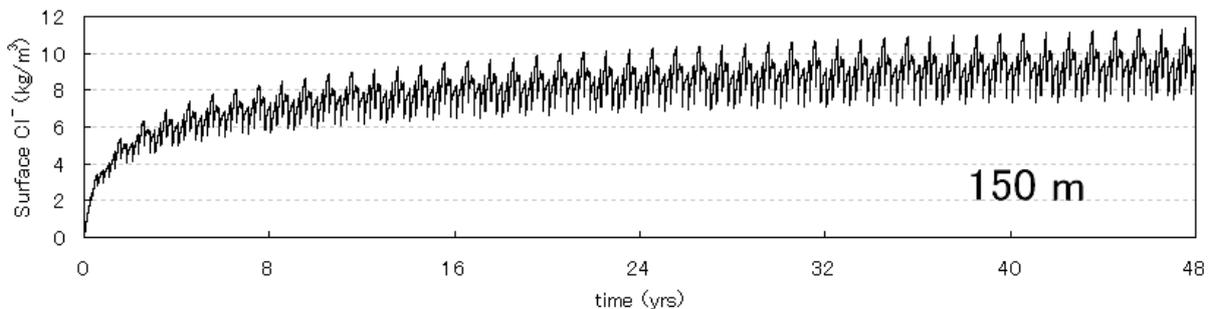

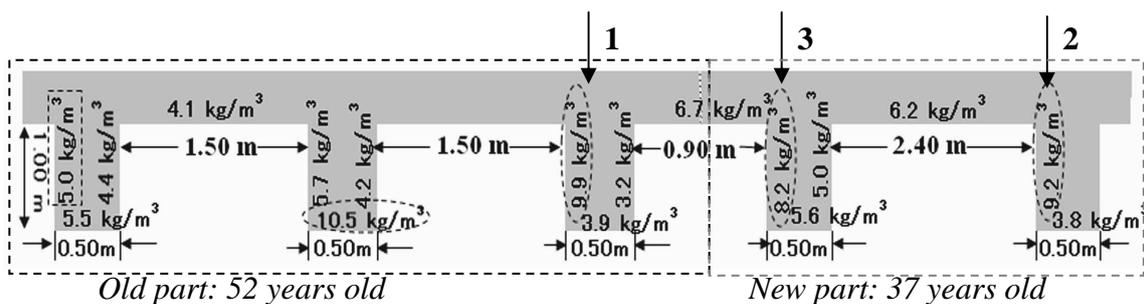**Figure 4** The surface chloride simulation for Ananai Bridge (150m from seashore)

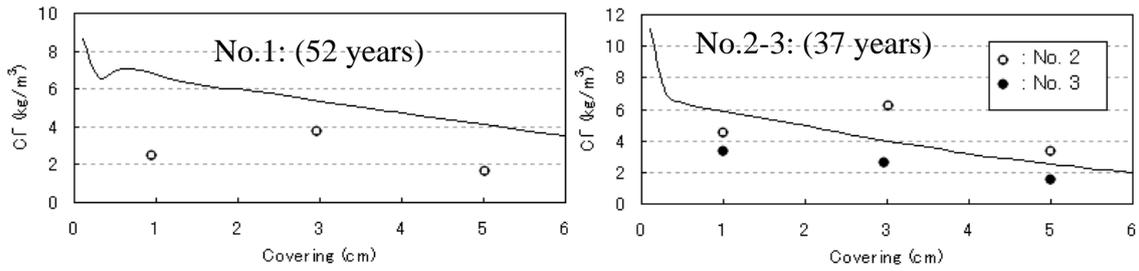**Figure 5** The investigation on surface chloride content of Ananai Bridge

Figure 6 Comparison between data and computational results of members No.1-3
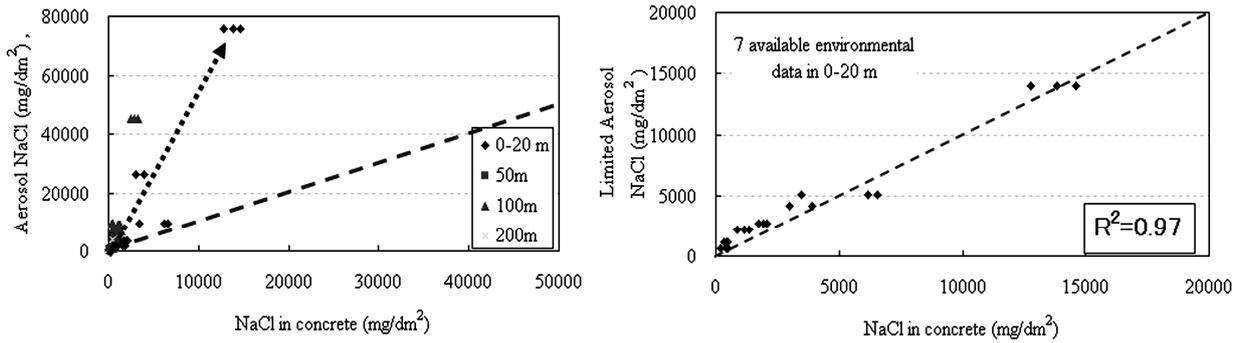

Figure 7 Comparison between PWRI data and computational results

Next, the further comparison of chloride profile in concrete is essentially proved the accuracy of chloride penetration model including this effect. The investigation of surface chloride content of this bridge has been done as shown in **Figure 5**.

According to the data of chloride distribution in concrete, there are some concrete specimens were cored from this bridge. The variety of surface chloride distribution for each member is not well understood yet, thus only 3 data of similar surface chloride content can be compared. The compressive strength of 3 selected members is 42, 40.8 and 39.3 (N/mm^2), respectively. The comparison between data and calculation is expressed in **Figure 6**, respectively. The calculation for member No.1 is largely overestimated at 52 years, but it is slightly deviated for members' no. 2 and 3 at 37 years

2.4 Verification by PWRI investigated data (1985)
The investigation of aerosol salt by 10x10cm plate

and chloride content in 3 types of concrete specimens was done all over Japan. The results of aerosol salt measured by plate and concrete are compared. The aerosol salt collected by plate near seashore is much larger than that in concrete specimens as illustrated in **Figure7 (left)**. By applying this phenomenon of excess absorbability for 7 data in 0-20m from seashore, the limitation of maximum aerosol chloride which is able to absorb in concrete is calculated and the comparison is shown in **Figure7 (right)**.

Referred to JSCE design specification in 1999 and modified diffusion coefficient in 2002, the calculation of corrosion initiation time under the chloride threshold value at 1.2 kg/m^3 at 5cm covering depth is expressed as 6.8 years for this bridge which has w/c = 0.55 and constant surface chloride content of 3.8 kg/m^3 for distance 150m from seashore. Comparing with the irregular surface chloride increment including excess of absorbability
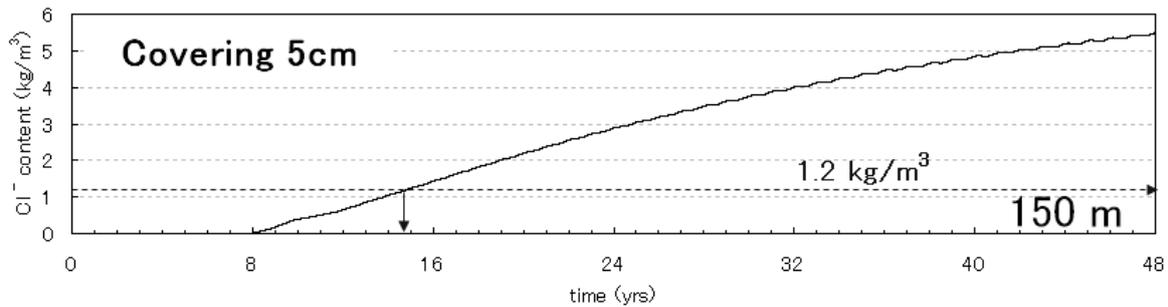
Figure 8 The increment of chloride content at w/c = 0.55 and covering depth 5cm in 150m from seashore in Kochi Prefecture, Japan

and the result of chloride distribution at the same covering depth in **Figure 4 & 8**, the corrosion is initiated after 14.8 years of exposure. The surface chloride concentration to reach 3.8 kg/m^3 takes 30 years of exposure. This mechanism can help calculate time of corrosion initiation more appropriate than the current specification.

3. SUMMARY

The current state of simulation model is able to calculate the chloride profile in concrete due to the amount of transported airborne chloride. The limitation of airborne chloride absorbability is thought as the surface soaking phenomenon due to the excess of airborne chloride on the concrete surface layer. This phenomenon is proved the statement that the total transported airborne chloride is not always equaled to the amount of chloride in concrete. The development of the diffusion coefficient model and the fixed-free chloride ratio is done recently; therefore this might help the calculation be more precise. Generally, structures near seashore will have possibility to occur surface soaking many times and the surface chloride is limited to a certain level through a long-term exposure. According to the excess absorbability, the time of corrosion initiation is retarded by lessening flux of surface chloride concentration.

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