

Theoretical Approach to Calculate Surface Chloride Content C_s of Submerged Concrete under Sea Water Laden Environment

Yoon, In-Seok^{*} Ye, Guang^{**} Copuroglu, Oguzhan^{***} Shalangen, Erik^{****} Breugel, Klaas van^{*****}

ABSTRACT

The ingress of chloride ions plays a crucial role for service life design of reinforced concrete structures. In view of durability design of concrete structures under marine environment, one of the most essential parameters is the surface chloride content of concrete. However, on the basis of the results of in-situ investigation, this value has been determining in the numerous studies on the durability design of concrete structures. Hence, it is necessary to confirm the range of the surface chloride content in order to establish a unified durability design system of concrete.

This study suggests a rational and practical way to calculate the maximum surface chloride content of submerged concrete under marine environment. This approach starts with the calculation of the amount of chloride ingredients in normal sea water. The capillary pore structure is modeled by numerical simulation model HYMOSTRUC and it is assumed to be completely saturated by the salt ingredients of sea water. In order to validate this approach, the total chloride content of the mortar and concrete slim disc specimen was measured after the immersion into the artificial sea water solution. Additionally, the theoretical, the experimental and in-situ investigation results of other researchers are compiled and analyzed.

Based on this approach, it will follow to calculate the maximum surface chloride content of concrete at tidal zone, where the environment can be considered as a condition of dry-wetting cycles.

1. Introduction

The deterioration of concrete structures due to chloride diffusion is now a growing problem in many countries. It is well known that the main cause of reinforcement corrosion of concrete exposed to marine environment is chloride diffusion. Therefore, the durability design of concrete structures under marine environment is regarded as a prerequisite in order to create durable concrete and it is also a criterion for the mix proportion and cover depth optimization.

The literatures have been flooded with methodological approaches to carry out the durability design of concrete, since 1980s. In the process of durability design, the surface chloride content, C_s , has been regarded as one of the crucial parameters. At the same time, the surface chloride content is considered as a standard parameter to define environmental degree of chloride laden concrete. However, many researchers and engineers have determined this value empirically. Because it is not easy to define the value due to time variation with elapsed time, environmental condition, and especially microclimatic condition at concrete surface. In this study, a rational and practical way is suggested for the calculation of the maximum C_s in the submerged portion.

* KCI Member, Microlab, CiTG, TU Delft, Postdoctoral fellow

** Microlab, CiTG, TU Delft, Senior researcher

*** Microlab, CiTG, TU Delft, Ph.D candidate

**** Microlab, CiTG, TU Delft, Associate professor

***** Foreign member, Microlab, CiTG, TU Delft, Professor

2. Significance and Approach to Calculate C_s

C_s depends on many parameters such as the ingredient of sea water, the geographical location, and the exposure condition with water level. Many researchers have confirmed this value, based on the result of in-situ investigation of old concrete structure.

The concrete sections exposed to marine environment are mainly divided into three parts: atmospheric zone, tidal zone, submerged zone. The origin chloride sources of concrete are air borne chloride carried from sea for atmospheric zone, brackish water or sea water for tidal zone, and sea water for submerged zone, respectively. For this reason, equivalent chloride concentration, C_{env} can be expressed as maximum equivalent surface chloride content which is described by Eq. (1).

$$C_{env} = C_{seaf}(h) \quad (1)$$

In the tidal zone where intermittent drying-wetting cycles occur, chloride ingredients can be accumulated at the surface of concrete if sea water is dried out. The evaporation can increase C_s of concrete in the tidal zone to a higher value than the chloride content of sea water. In submerged zone, C_s does not increase infinitely because the value is governed by the degree of saturation. That is, the C_s initially will fluctuate about a steadily rising level and then increase with elapsed time slowly and continuously. Finally, this value will stagnate if it equals the concentration of sea water approximately. Maximum C_s can be regarded as an imperative parameter to predict a service life of concrete for long term and a constant value after a certain short period has elapsed. Thus, in order to characterize the chloride build-up, the rational expression can be depicted by [1]:

$$C_s(t) = C_{max} (1 - e^{-at}) \quad (2)$$

C_s depends on the amount of chloride ingredient in sea water. Table 1 shows the major constituents of normal sea water. The amount of competitive salt can be calculated as:

$$C_c = Q_c W_c \quad (3)$$

NaCl, MgCl₂ are mainly considered in this study, since they are the major competitive salts of sea water. The quantity of NaCl, MgCl₂ can be calculated as 27.47 g/l, 3.82 g/l, respectively and the mass fraction, Ω_c , can be obtained if total salt ingredients are assumed to be 35.0 %.

If it is assumed that concrete is completely saturated with sea water, the chloride content in concrete can be calculated theoretically. To begin with, all the capillary pores are assumed to be filled with sea water and the salt quantity (Q_c) is calculated by the following equation:

$$Q_c = \Omega_c \rho_c \phi_{cap} \quad (4)$$

The value should be translated into a quantity of total Cl⁻ to consider an atomic weight of ingredients of salt as:

$$Q_c^{Cl} = Q_c \frac{W_{Cl}}{(W_c + W_{Cl})} \quad (5)$$

Total quantity of Cl^- composition can be simply calculated as:

$$Q_{\text{Total}}^{\text{Cl}} = Q_{\text{NaCl}}^{\text{Cl}} + Q_{\text{MgCl}_2}^{\text{Cl}} \quad (6)$$

Now, we can calculate how much the chloride would be accumulated at the surface of submerged concrete under seawater laden environment.

Table 1 Chemical element of sea water [2]

Chemical Element (e)	Cl	Na	Mg	SO_4	K	Ca	HCO_3
Volume (m mol/ l)	548	470	54	28	10	10	2

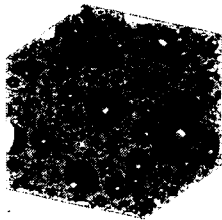


Fig. 1 Microstructure modeling

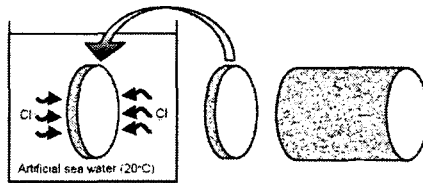


Fig. 2 Chloride immersion testing

Table 2 Mix pro. of mortar or con'c

Unit weight (kg/m^3)			
Water	Cement	Sand	(Gravel)
185	411	706	(1001)
185	370	720	(1021)
185	336	732	(1038)

() is not contained in mortar

2. Experiment and Discussion

The C_s of the mortar disk and concrete disk is calculated and presented in Table 2. At the end of the 20 °C water curing period, the top 2 mm of the specimens was sawn and then immersed in artificial sea water with same composition as given in Table 1. Total chloride ion content in the specimens was measured in accordance with the technique described in ASTM C1152-97 and expressed as a weight ratio of chloride to concrete ($g_{\text{cl}} / g_{\text{conc}}$) for mortar and concrete specimens.

Fig. 3 shows the calculation results of capillary pore according to the numerical simulation model HYMOSTRUC model. Because the HYMOSTRUC model can calculate the microstructural properties of hardened cement paste, these values should be converted to the capillary porosity of concrete to consider volumetric portion of cement, water, sand and coarse aggregate, respectively.

Fig. 4 and Fig. 5 present comparisons of measured C_s and calculated C_s in mortar and concrete, respectively. For concrete, accurate relationship between experiment and calculation is not formulated because of skin effect and sporadic existence of coarse aggregates. However, it should be noticed that predicted values of C_s are approximately in reasonable agreement with the measured values in case of mortar. More than anything else, maximum C_s theoretically depends on w/c ratio because dense concretes have finer pore structures and should absorb less chloride in view of build-up rate of chloride, according to this result.

Fig. 6 depicts the result of comparison of this result and other studies.[3]~[6] As shown in this figure, C_s depends on w/c ratio but is mostly in range of 5.5 to 7 × 10⁻³ $g_{\text{cl}} / g_{\text{conc}}$, which coincides with the result of in-situ investigation of Takeda and calculated result of Bazant approximately.

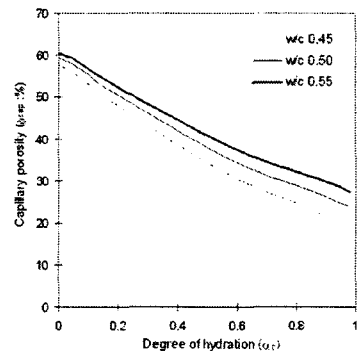


Fig. 3 Capillary pore with various stage of hydration

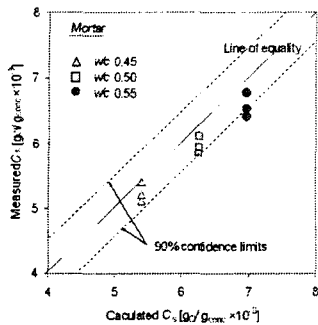


Fig. 4 Comparison of calculated and measured C_s (in mortar)

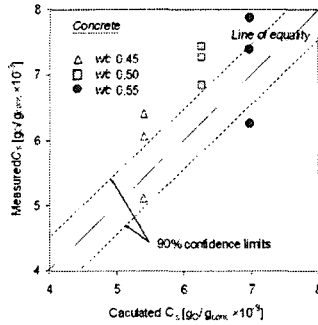


Fig. 5 Comparison of calculated and measured C_s (in concrete)

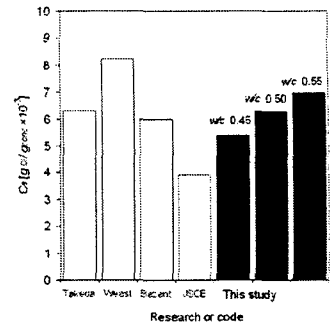


Fig. 6 Comparison of this result and other studies

3. Conclusions

The accuracy of this approach is dependent on pore structural properties of concrete and the microclimatic condition at near surface concrete. C_s is mainly an environmental parameter, however, that is also a little governed by material properties of concrete such as w/c ratio, weight of cement, and the type of cement. For these reasons, it is not easy to define this value of C_s in concrete deterministically.

This approach is theoretically based on the ingredient and amount of seawater, and microstructural characteristics of cementitious materials. This result can be used for reasonable durability design of concrete structure. On the basis of the approach suggested, the calculation of C_s in tidal concrete will be followed.

References

1. P. Arora, B.N. Popov, B. Haran, M. Ramasubramanian, S. Popova, and R.E. White, "Corrosion Initiation Time of Steel Reinforcement in a Chloride Environment - A One Dimensional Solution," *Corrosion Science*, Vol.39, No.4, pp.739-759, 1997.
2. E.H. Lieb, A. Gianguzza, S. Sammartano, E. Pelizzetti, *Chemistry of Marine Water and Sediments*, Springer, 2002.
3. N. Takeda, S. Sogo, S. Sakoda, and T. Idemitsu, "An Experimental Study on Penetration of Chloride Ions into Concrete and Corrosion of Reinforcing Bars in Various Marine Environment," (in Japanese language) *Journal of JSCE*, No.599, No.40, 1998.8.
4. "CRC Handbook of Chemistry and Physics," R.C. Weast and M.J. Astle (Eds.), 63rd, pp.299, CRC Press, Boca Raton, FL, F-154, 1982.
5. Z.P. Bazant, "Physical Model for Steel Corrosion in Concrete Sea Structure - Application," *Journal of Structure, Div., ASCE*, No.105, Vol.6, pp.1137-1153, 1979.
6. JSCE, Concrete Standard Specification, Part of Durability (in Japanese language), 1999.

Notations

C_{max} : maximum surface chloride content,	$f(h)$: function of height above tidal zone,
C_{sea} : concentration of chlorides in the seawater,	Q_e : quantity of chemical element e ,
C_{env} : equivalent chloride concentration,	Q_c^{Cl} : quantity of Cl^- in competitive salts c
Ω_c : mass fraction of competitive salt c of seawater,	a : rate of coefficient of chloride accumulation,
ϕ_{cap} : volume of capillary pores,	W_e : atomic weight of element e ,
t : elapsed time,	ρ_c : density of the competitive salt c of seawater