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Theoretical Time Evolution of Critical Chloride Content in Concrete

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Abstract: The critical chloride content for corrosion initiation is a crucial parameter in determining the durability and integrity of reinforced concrete structures, however, the value is still ambiguous. Most studies reporting the critical threshold of the chloride content have involved experimental measurements of the average amount of the total chloride content at an arbitrary time. Although carbonation can significantly impact on critical threshold chloride content, the majority of the researches have not dealt with this issue in combination with carbonation of concrete. Furthermore, many studies have tried to define the critical chloride content within the scope of their experimental concrete mix proportion at arbitrary time. However, the critical chloride content for corrosion initiation is known to be affected by a lot of factors including cement content, type of binder, chloride binding, concentration of hydroxyl ions, and so on. It is necessary to define a unified formulation to express the critical chloride content for various mix proportions of concrete. The purpose of this study is to establish an analytical formulation of the critical chloride content of concrete. In this formulation, affecting factors, such as mix proportion, environment, chemical evolution of the pore solution with elapsed time, carbonation of concrete and so on are taken into account. Based on Gouda's experimental results, the critical chloride content is defined as a function of $[Cl^-]$ vs. $[OH^-]$ in the pore solution. This is expressed as the free chloride content per unit of mass to consider time evolution of $[OH^-]$ content in the pore solution using the numerical simulation program for cementitious materials, HYMOSTRUC. The results are compared with other experimental studies and with various codes. It is believed that the approach suggested in this study could provide a good solution to determine the critical chloride content with the original source of chloride ions, for example, marine sand at initial time, and sea water penetration later on.

Keywords: Critical chloride content, Free chloride, Deterioration, Carbonation of concrete

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1 Introduction

Over the past few decades, a considerable number of studies on the deterioration of concrete due to chloride penetration have been carried out extensively. It is well known that the reinforcement passivity is broken when a certain quantity of chloride is present in the pore solution and that one of the crucial parameters to determine the service life of concrete is the critical chloride content. In order to define the chloride content that initiate reinforcement corrosion, the concept of a chloride threshold level has to be dealt with. This can be defined as the level of critical chloride content. The critical chloride content is required when identifying the cause of the observed deterioration of structures and when chloride induced corrosion is likely to be the failure mechanism. In the latter cause, the prediction of service life is given by the time required for transport processes to raise the chloride content at the level of the reinforcement to the critical chloride content.

Many researchers have tried to define the critical chloride content as a specific value[1~15]. The studies reporting on the critical chloride content have involved the experimental measurement of the average amount of the total chloride content. The studies have tried to define the critical chloride content within the scope of their experimental concrete mix proportion at arbitrary time. However, there is no agreement on its value, because the critical chloride content for corrosion initiation is affected by many factors. It has been recognized that critical chloride content cannot be unified as a specific value because many affected factors exist. The critical chloride content should be constant originally, based on the unified mechanism of reinforcement corrosion due to chlorides. It is necessary to define a unified formulation to express the critical chloride content as a function of these many factors, if it is impossible to express the critical chloride content as a unified specific value.

Meanwhile, another issue of our concern is the effect of carbonation of concrete on the critical chloride content. The majority of researches which studied the critical chloride content didn't deal with this issue in combination with the carbonation of concrete, although the carbonation of concrete can significantly affect the critical threshold chloride content.

The purpose of this study is, therefore, to establish a unified solution of the critical chloride content of carbonated concrete as well as non-carbonated concrete. The affecting factors mentioned above are taken into account in the analytical formulation and the time evolution of the critical chloride content is computed theoretically, based on the theory of cement chemistry for hydration. It is expected that this study may provide a fundamental approach for a unified durability design system, based on the knowledge of cement science and concrete technologies.

2 Research Significance

There is no attempt to integrate the formulation of the critical chloride content to deal with coupling between the affecting factors and the critical chloride content, based on the knowledge of hydration of cement. It is now necessary to formulate theoretically as one of material parameter for defining critical chloride content in the service life modeling of marine concrete structures. In this respect, the improvement should be taking into account the various affecting factors such as chemical development of cement due to hydration, pH of pore solution, water content in the pore of the concrete, carbonation, and so on. It is believed that critical chloride content should be depicted as a time function because of the physico-chemical development of concrete as time elapsed.

3 Theoretical formulation

3.1 Literature review

The value of the critical chloride content has been derived from experimental methods. The reported critical chloride content was collected and analyzed with the aim of identifying what in theory is the reasonable formulation of expressing the critical chloride content.

Table 1 shows literature reviews on the critical chloride content. The critical chloride content is varied widely between different concretes, as shown in reported values[1~15]. The reason for this is because the critical chloride content is influenced by numerous factors: (a) direct factors affecting the electrical potential of reinforcement such as the type of chloride accompanying cation, oxygen availability, relative humidity insides the pores and temperature, (b) factors of material properties such as the degree of hydration of cement, C_3A of cement, porosity with w/c ratio, type of cement or admixture and its replacement ratio, (c) condition of reinforcement such as its surface finishing and metallurgical composition, and so on. The relationship between these factors and corrosion is extremely complex. The factors influence the nature of the passive layer, which in turn determines the electrical potential exhibited by the reinforcement. In this respect, to adopt a specific single value for the purpose of specification or service life prediction seems not to be appropriate. Nevertheless, it has become common practice to limit the permissible chloride content of reinforced concrete as a percentage of the cement, values of 0.40 % (acid-soluble) or 0.15 % (water-soluble) by mass of cementitous material being commonly used in Europe and (North) America, respectively.

One of the fundamental approaches to define the critical chloride content is to express the content in chemical pore solution. Earlier research on the solution studies argued that, in theory, the critical chloride content should be expressed as a ratio of the chloride concentration to hydroxyl concentration or free chloride concentration in the concrete pore solution. This hypothesis has been perpetuated by current discussion which includes (a) the stated assumption that only free chloride presents a corrosion risk, (b) reporting free chloride or chloride to hydroxyl concentration ratio but omitting total chloride contents in threshold level studies, and (c) attributing significant changes in the threshold level solely to change in the free chloride and hydroxyl concentration.

Unfortunately, the ratio of chloride concentration to hydroxyl concentration is also not clear in spite that the proposed chloride content to lead to local breakdown of the passive layer formed in the alkali solution can be expected to have good agreement to each other, in comparison with concrete. One of the reasons is because the value depends on pH of the pore solution[16]. It is necessary to formulate the critical chloride content, based on the knowledge of pore solution in cement paste with pH value.

3.2 Porosity of hardened cement paste

Affecting factors about the water content of cement paste are mix proportion, degree of hydration, porosity and so on. The used chemical and physical properties of cement and mix proportion of concrete, as an example for calculation of hydroxyl concentration and pore water, are shown in **Table 2** and **Table 3**, respectively. The used cement is confined to ordinary Portland cement in this study.

Figure 1 shows the porosity of cement paste simulated by the numerical simulation program for cementitious material, HYMOSTRUC[Breugel, 1991]. The porosity of cement paste can be converted into that of concrete as;

$$\phi_{pore}(con'c) = \phi_{pore}(cp) \cdot V_{cp} \tag{1}$$

where,
$\phi_{pore}(con'c)$: porosity of concrete,
$\phi_{pore}(cp)$: porosity of cement paste,
V_{cp}: volumetric fraction of cement paste in unit volume of concrete.

3.3 Hydroxyl concentration in cement paste

Hydroxyl concentration also changes continuously with hydration, like the capillary water content. The hydroxyl concentration of cement paste during the hydration is calculated, based on the study of Eijk and Browers[2000]. It should be introduced briefly in this section. First, the total number (Na_T) of moles of Na^+ and K^+ available per mass of cement and the amount of readily soluble sulfate

Table 1: Literatures about critical chloride content of cementious materials[1−15]

Researcher	Condition	$[\mathrm{Cl}]_f^*$	$[\mathrm{Cl}]_t^{**}$	[Cl]/[OH]	Condition
Hausman, 1967	Solution			0.60	Solution simulating the concrete
Gouda, 1970	Solution			∼ 0.35	Solution simulating the concrete
Goni, 1990	Solution			0.25 ∼ 0.8	Steel in alkaline solution with chloride
Gouda & Halaka, 1990	OPC BFSC			2.42 1.21	Mortar suspension
	OPC BFSC OPC		3.04 1.01 1.60		Concrete with added chloride
Andrade & Page, 1986	OPC BFSC			0.15 ∼ 0.69 0.12 ∼ 0.44	OPC and BFSC (chloride added)
Hansson & Sorensen, 1988	OPC mortar		0.6 ∼ 1.4		100 % RH 50 % RH (external chloride)
Lambert, Page, Vassie, 1991	Concrete			3.00	Concrete exposed to external chloride
Kayyali & Haque, 1995	MS HS HSS HSSFA	1.15 0.85 0.80 0.45			Medium strength Conc. (MS) High strength Conc. (HS) HS + Supplement (HSS) HSS + Fly ash
Hussain , Al-Musallam, Al-Gattani, 1995	Concrete		0.14 0.17 0.22	0.35 0.62 1.00	Cement with C_3A C_3A content = 2.43 % C_3A content = 7.59 % C_3A content = 14.00 %
Schiessl , Breit, 1996	OPC BFSC FA		0.5 ∼ 1.0 1.0 ∼ 1.5 1.0 ∼ 1.5		Concrete with admixed chloride and externally exposed to chloride
Thomas, Matthews, Hayners, 1990			0.5		Concrete prisms at marine exposure
Thomas, 1996	Concrete		0.70 0.65 0.50 0.20		FA at marine exposure FA = 0 % FA = 15 % FA = 30 % FA = 50 %
Hope, IP, 1987	OPC		0.097∼0.19		Concrete slabs with added chloride in various exposure conditions
Oh, Jang, Shin, 2003		0.11 ∼ 0.13	0.45 ∼ 0.93	0.17 ∼ 0.26	I, V type of cement, Half-cell potential and pore solution measurement

* $[\mathrm{Cl}]_f$: free chloride content (% by weight of cement),

** $[\mathrm{Cl}]_t$: total chloride content (% by weight of cement).

Table 2: Physical and chemical properties of OPC cement

Chemical composition (%)							Specific gravity	Blain (yd^2/lb)
SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	Ig.loss		
19.88	4.87	3.11	61.56	2.95	2.82	1.0	3.14	184.5

Table 3: Mixing proportion of concrete

Mix symbol	w/c	Unit weight, kg/m^3			
		Water	Cement	Sand	Gravel
OPC-45	0.45	185	411	706	1001
OPC-50	0.50	185	370	720	1021
OPC-55	0.55	185	336	732	1038

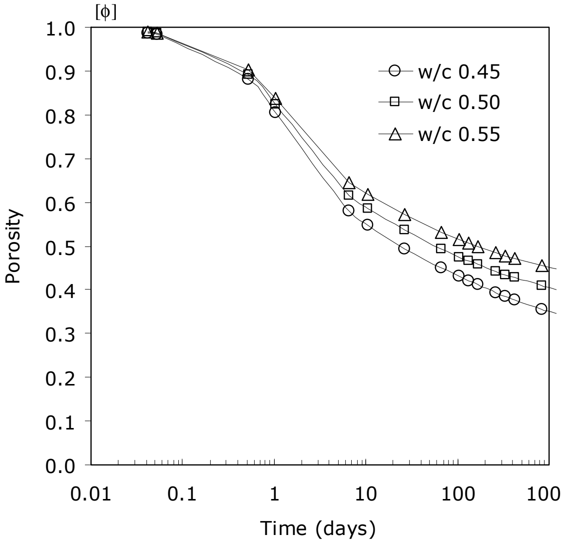

Figure 1: Time evolution of porosity in OPC cement

($[Na^+]_{sulfate}$) immediately after contact with water are written, as:

$$Na_T = \frac{f_{Na_2O} \cdot 2}{MW_{Na_2O}} \tag{2}$$

where,

Na_T: total Na content [mol/g (= × 453.7 mol/lb)],

f_{Na_2O}: Na_2O mass fraction [g/g],

MW_{Na_2O} : molar mass of Na_2O [g/mol (= × 2.204 $\times 10^{-3}$ lb/mol)].

The alkalis in the cement are partly present as readily soluble sulfates at the surface of the cement grains and partly bound in the clinker mineral. The amount of readily soluble sulfates Na^+ released immediately after contact with water can be calculated as;

$$[Na^+]_{sulfate} = \frac{f_{Na,sulfate} \cdot Na_T \cdot m_c}{\phi_w(\alpha)} \tag{3}$$

where,
$[Na^+]_{sulfate}$: released from clinker,
α : degree of hydration of cement phase,
$f_{Na,sulfate}$: fraction of Na present as sulfate,
$\phi_w(\alpha)$: actual absolute volume of capillary water in the paste.

The amount of Na^+ released from the clinker, $[Na^+]_{clinker}$, can therefore be determined as;

$$[Na^+]_{clinker} = \frac{(1 - f_{Na,sulfate}) \cdot Na_T \cdot \alpha \cdot m_c}{\phi_w(\alpha)} \tag{4}$$

Because the degree of hydration increases, more alkalis will be dissolved in the pore water and water is taken out of the system due to this hydration reaction. Both influences will affect the increase of the alkali concentration in the pore water. The total number of Na becomes Eq.(5).

$$[Na^+]_{released} = [Na^+]_{sulfate} + [Na^+]_{clinker} \tag{5}$$

The amount of uptake of Na^+ ions by the hydration products, CSH and AFm is considered to be proportional to the concentration present in the solution and the quantity of the hydration products formed. Binding factors of 0.31 and 0.20 m mol per gram of hydrated cement for Na^+ and K^+ can be used, respectively. From this, the amount of consumed Na^+ per liter (1 liter = 1.308 $\times 10^{-3}$ yd^3) of pore solution can be determined as;

$$[Na^+]_{consumed} = \frac{b_{Na} \cdot \alpha \cdot m_c \cdot [Na^+]_{released}}{m_w} \tag{6}$$

in which, b_{Na} is the binding factor. The difference between the amounts of alkalis released and the amount of alkalis consumed provides the actual alkali concentration in the cement pore water.

$$[Na^+ + K^+] = [Na^+]_{released} - [Na^+]_{consumed} + [K^+]_{released} - [K^+]_{consumed} \tag{7}$$

$$k_{CH} = \frac{k^o_{CH}}{\gamma_{ca}\gamma^2_{OH}} = [Ca^2] + [OH^-]^2 \tag{8}$$

in which, γ_{ca}= 0.43, = 0.80. In a solution that contains CH, the molar solubility is S_{CH}. [OH$^-$] ion in solution originates both from the dissolution of CH and from the total amount of alkalis [Na$^+$ + K$^+$] released into the pore water. As long as CH is present in the solution, it holds that:

$$[Ca^{2+}] = S_{CH} \tag{9}$$

$$[OH^-] = 2S_{CH} + [Na^+ + K^+] \tag{10}$$

With respect to the water ionization, the [OH$^-$] and [H$^+$] are related as Eq.(12). Calcium concentration of the pore water can be also calculated as Eq. (13).

$$k_w = [H^+][OH^-] = 10^{-14} \tag{11}$$

$$[Ca^{2+}] = \frac{([Na^+ + K^+] - X)^2}{6X} \tag{12}$$

in which, $X = \sqrt[3]{[Na^+ + K^+]^3 + 27k_{CH} + 3\sqrt{3} \cdot \sqrt{k_{CH}} \cdot \sqrt{2[Na^+ + K^+]^3 + 27k_{CH}}}$.

Figure 2 represents development of hydroxyl concentration in the simulated pore solution with the procedures mentioned above.

Figure 3 represents the pH value of the simulated pore solution in cement paste. Based on the calculation of the hydroxyl concentration in the pore solution of **Figure 2**, the development of pH of the pore solution can be calculated from;

$$pH = 14 + \log[OH^-] \tag{13}$$

3.4 Capillary water content in cement paste

The water content in the capillary pore system of concrete is also one of the affecting factors of the critical chloride content. The critical chloride content might decrease for concrete with a high water content because a high water content leads to dilution of chemical concentration of hydroxyl in concrete. The change of water content presented in capillary pore system of concrete should be taken into account in the computation of critical chloride content as time elapsed.

Figure 4 illustrates a pore structural system of cement paste corresponding with water content schematically. The pore system of cement paste consists of volumetric portion of air, $\phi_{\ vapor}$, and volumetric portion filled with mixing water, $\phi_{W(cap)}$. Total Saturation (S) can be expressed as a summation of internal saturation (S_i) and

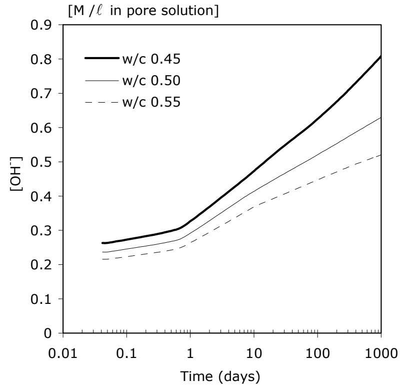

Figure 2: Development of [OH$^-$] concentration in OPC cement

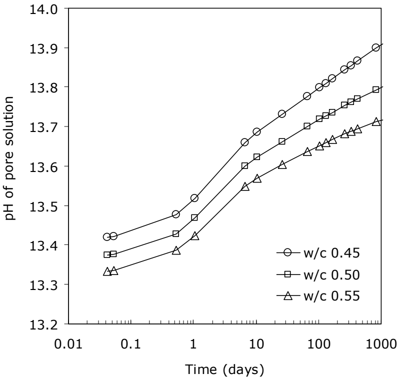

Figure 3: pH value of pore solution in cement paste with elapsed time

external saturation (S_o). Internal saturation (S_i) and external saturation (S_o) depend on capillary water content and water flow from external environment, respectively. Van Breugel[17] proposed Eq. (15) as a volume of the capillary water presented in sealed cement paste. If it is assumed that cement paste is sealed, evaporation of water and external source to supply water such as relative humidity or raining or sea water can be disregarded. This means that Eq. (15) is available for assessing degree of internal saturation.

$$\phi_{W(cap)}(\alpha) = \frac{\rho_{ce}}{\rho_w + \rho_{ce} \cdot w/c}(w/c - 0.4\,\alpha) \cdot V_{cp} \tag{14}$$

where,
α : degree of hydration of cement,
ρ_{ce} : specific mass of cement,
ρ_w : specific mass of mixing water,
w/c: w/c ratio.

For concrete under outdoor conditions to flow external water, thus, the degree of external saturation increases gradually. For submerged concrete, degree of saturation in pore system becomes a full saturated condition eventually. Based on what mentioned above, the degree of saturation can be written, as;

$$\phi_{pore} = \phi_{W(cap)} + \phi_{vapor} \tag{15}$$

$$\phi_{W(cap)} \leq \phi_W \leq \phi_{pore} \tag{16}$$

$$S_i(= \frac{\phi_{W(cap)}}{\phi_{pore}}) \leq S \leq 1(= \frac{\phi_W(= \phi_{pore})}{\phi_{pore}} \tag{17}$$

Figure 5 shows capillary water content presented in cement paste with elapsed time. The volume of capillary water equals that of cement paste at initial time, however, that decreases with elapsed time because mixing water is consumed by hydration with cement.

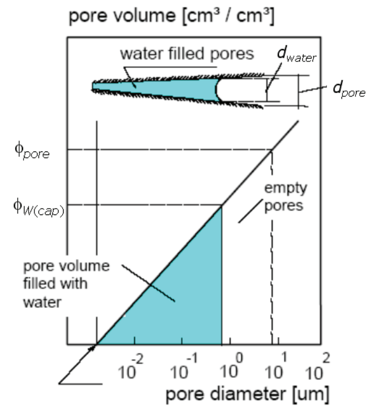

Figure 4: Schematic representation of the pore size system with emphasis on the state of the pore water in the actual pore volume[17]

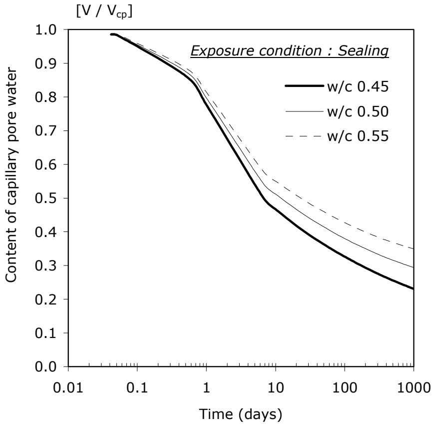

Figure 5: Content of capillary pore water in unit volume of cement paste

3.5 *Effect of carbonation on critical chloride content*

The critical chloride content of non-carbonated concrete has been studied for a long time and there have been arguments for the issue ceaselessly as well. However, for carbonated concrete, there is no established knowledge or experimental data to define the critical chloride content, although many concrete structures have suffered corrosion damage due to the double deterioration of carbonation and chloride ion simultaneously. According to the CEB[1992], the critical chloride content of non-carbonated concrete is recognized as 0.4 % by weight of cement, as shown in **Figure 6**. For carbonated concrete, they only supposed that critical chloride content might be smaller than 0.4 %. This is not clear, and worse still, it is also not easy to define critical chloride content of carbonated concrete by an experimental program at arbitrary time. In this section, the effect of carbonation on the critical chloride content is examined theoretically.

As regards the role of chlorides influencing the nature of the passive layer on reinforcement in pore solution, carbonated concrete is more complicated than non-carbonated concrete. The decrease of the pH value in the pore solution is induced by the carbonation of concrete. The decreased pH value might significantly affect the critical chloride content, although the mechanism has not been adequately demonstrated. The pH value in the pore solution of non-carbonated concrete is normally known to range between 13.0 and 14.0. For carbonated concrete, the pH value of the pore solution decreases and reinforcement corrosion occurs at pH of 11.5[Broomfield, 1997]. The concentration of hydroxyl due to carbonation can be calculated by Eq. (14), based on the assumption that the pH value in the pore solution of carbonated concrete may range between 11.5 and 13.0.

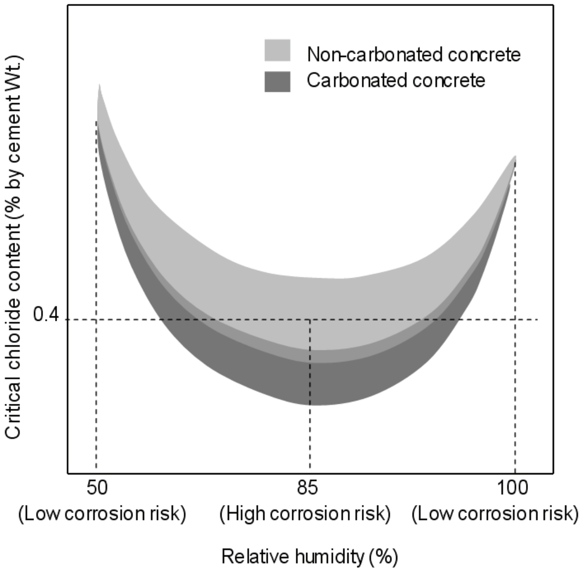

Figure 6: Critical chloride content of (non)carbonated concrete

3.6 Cl^- concentration vs. OH^- concentration

The ratio of [Cl^-] / [OH^-] has been achieved by assessing the experimental evidence showing the effect of chloride binding or hydroxyl concentration, as well as the effect of the presentation of the chloride threshold level. The ratio of [Cl^-] / [OH^-] is favored by the availability, simple means to derive experimental data, some of which are documented in standard.

Hausmann[1967] suggested 0.60 and Gouda[2] proposed a threshold ratio of [Cl^-] / [OH^-] to be about 0.35. This value should be confirmed by assessing the experimental results showing the effect of pH on the ratio of [Cl^-] / [OH^-]. In this study,

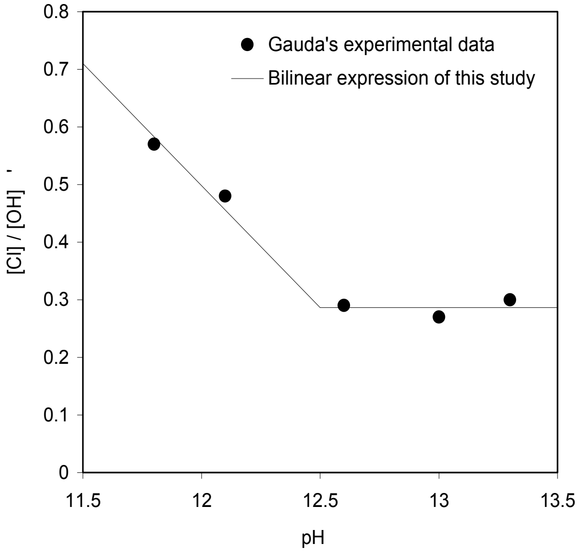

Figure 7: Relation between pH and [Cl$^-$]/[OH$^-$]

a new formulation for the ratio of [Cl$^-$] / [OH$^-$] vs. pH is derived from Gouda's experimental results[1970] (see **Figure 7**), as:

$$[Cl^-]=\begin{cases}(5.588-0.424pH)[OH^-] & \text{for } 11.5<pH<12.5\\ 0.287[OH^-] & \text{for } pH\geq 12.5\end{cases} \tag{18}$$

The limit of scope, 12.5 of Eq. (19) is approximately identical with the research of Hausmann who proposed 0.60 for this ratio within 12.4 of pH. Goni[3] also suggested 0.25 $\sim$ 0.80 for this ratio, and this range is within Eq.(19).

Based on what was mentioned above, a formula of chloride threshold level is constructed, as shown in Eq.(20). After the time evolution of OH and a change of pore water are obtained by the HYMOSTRUC, these are inputted into this formulation.

$$\left[Cl^-(aq)\right]_{cr}=\frac{\begin{cases}-\left(0.348\ +\ 0.424\log\left[OH^-\right]\right)\ \left[OH^-\right] & for\,pH<12.5\\ 0.287\left[OH^-\right] & for\,pH\geq 12.5\end{cases}}{\phi_W\cdot V_{cp}\cdot W_{conc}}\,\frac{MW_{OH}}{MW_{Cl}} \tag{19}$$

where,

$[\mathrm{Cl}^-(aq)]_{cr}$: critical chloride content (g/g_{conc}),
V_{cp} : volumetric fraction of cement paste in unit volume of concrete,
W_{conc} : unit weight of concrete (= 2,350 kg/m^3),
MW_{OH} : molar mass of OH (= 17.01 g/mol),
MW_{Cl} : molar mass of Cl(= 35.45 g/mol),
ϕ_W :water content in pore system of concrete.

4 Results and discussion

4.1 Critical chloride content under minimum degree of saturation

Figure 8 represents calculated results of critical chloride content of sealed concrete for different w/c ratio. Although the difference of w/c ratio between maximum and minimum is 10 %, the critical chloride content is different in a great measure and this is very obvious as time elapsed. The critical chloride content of concrete with high w/c ratio is higher than that of concrete with low w/c ratio. Two examinations should be discussed in this result. First, the critical chloride content is not a constant. The critical chloride content continues to increase remarkably, because of the time development of the OH^- concentration in the pore solution. This means that the concrete will have better resistance against corrosion as time elapsed. Second, the critical chloride content at initial time, computed in this study, is much less than generally expected. It should be emphasized that even with low chloride concentration, reinforcement corrosion might occur. Therefore, concrete should be completely isolated from any sources of chloride from the initial mixing time. Marine sand or admixtures, added with chlorides, should be prohibited from mixing in concrete.

Meanwhile, the critical chloride content of concrete is within the scope of ACI Committee 222, 0.15 % by weight of cement. Especially, the critical chloride content of concrete at 28 days is 0.11 % to 0.145 % and this value is well tantamount to the scope of ACI committee 201, 0.10 % to 0.15 % by weight of cement. Accordingly, this study is expected to provide a fundamental solution to calculate rational critical chloride content for various original sources of chloride ions, for example, marine sand at initial time and sea water penetration later on. For the former, this study can offer a criterion to assess the quality of sand and fresh concrete in the field. For the latter, the study can also help in-situ investigation to estimate the integrity of old concrete structures, when subjected to chloride penetration.

Figure 9 shows a comparison of this study with the JSCE code. According to the concrete standard specification suggested by JSCE code[24], the critical chloride content is regarded as 0.051 % to 0.102 % by weight of concrete (1.2 kg/m^3 to 2.4 kg/m^3). This scope is approximately similar to the long term range for concrete with ranging between w/c 0.50 and w/c 0.55.

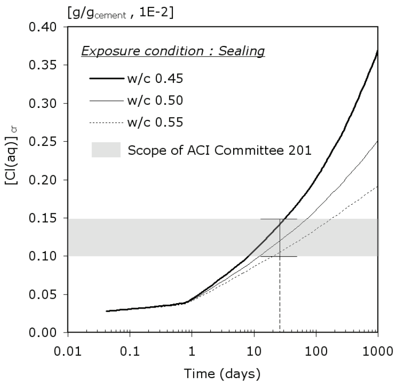

Figure 8: Time evolution of critical threshold chloride content of sealed concrete

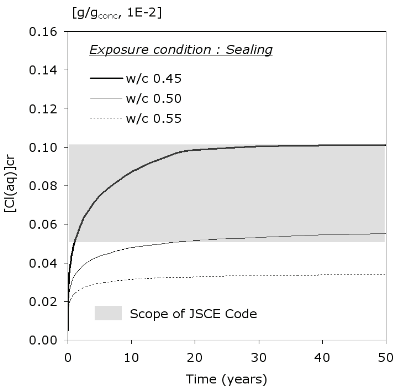

Figure 9: Time evolution of critical threshold chloride content of sealed concrete

4.2 Critical chloride content under maximum degree of saturation

For saturated concrete, the hydroxyl concentration can be diluted because of the extra water content supplied from the outside. This leads to a decrease of the critical chloride content of concrete.

Figure 10 shows the critical chloride content of saturated concrete for different w/c ratio. Compared with that of sealed concrete (see **Figure 9**), the critical chloride content of saturated concrete decreases because of the external water. This trend is obvious for concrete with a high w/cratio, because high pore volume can be a space filled with water. For further study, it is necessary to compute the critical chloride content with various degrees of saturation.

4.3 Critical chloride content in carbonated concrete

Figure 11 to **Figure 13** show the critical chloride content of carbonated concrete. The figures show that the carbonation of concrete leads to a significant reduction of the critical chloride content. This is seems to be typical for concretes with low w/c ratio, as its OH^- concentration is lower than that of concrete with a high w/cratio. This has occurred even with a slight drop of the pH value (to 13.0). Eq.(14) states that if pH of the pore solution is lower than 13.0, the OH^- concentration of concrete decreases dramatically. Furthermore, the critical chloride content for the carbonated concrete becomes extremely low, and reaches almost zero if the pH value of

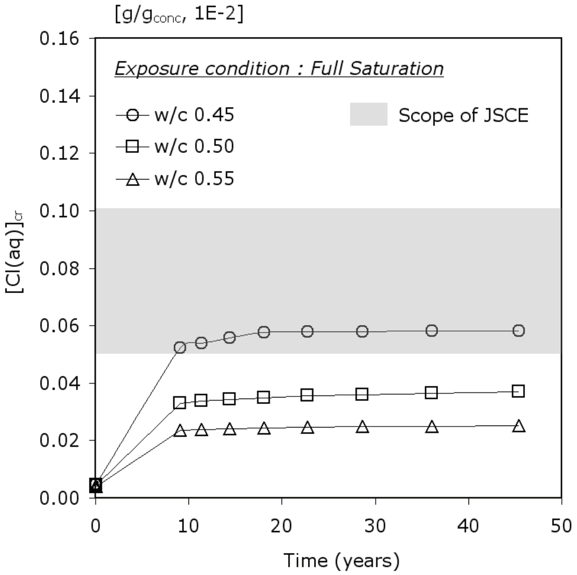

Figure 10: Time evolution of critical chloride content of fully saturated concrete

the pore solution decreases to about 11.5. In that range, the critical chloride content for carbonated concrete is not significant any more and therefore, attention should be drawn more to the rate of reinforcement corrosion due to the double deterioration environment of carbonation and chloride.

According to the above mentioned results, this study contributes to the discussion on why different results of the determination of the critical chloride content are usually reported in literatures. It is expected that this study is useful in establishing various scenarios for service life predictions of concrete structures exposed to the double deterioration environment of carbonation and chlorides. The study could be regarded as a prerequisite to calculate the service life prediction of concrete if the initiation time to corrosion wants to be computed accurately.

Meanwhile, for an extension of this approach, it is necessary to apply for the calculation of the critical chloride content of blended concrete. According to literature[25], the use of mineral admixtures, for example, fly ash or granulated blast furnace slag, is known to increase the chloride binding capacity of hydrates, thus reducing the level of the critical chloride content in the pore solution. This also might influence hydroxyl concentration in concrete. It can be realized to express the time evolution of the critical chloride content of blended concrete to consider the effect of the admixtures on the hydroxyl concentration in this approach.

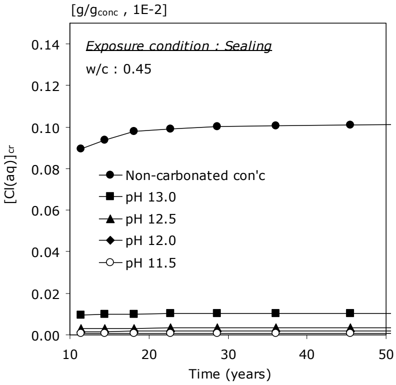

Figure 11: Effect of carbonation on critical chloride content of concrete with *w*/*c* 0.45

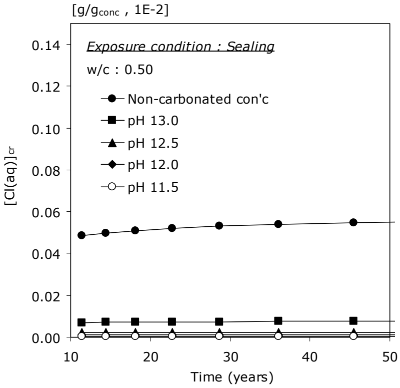

Figure 12: Effect of carbonation on critical chloride content of concrete with *w*/*c* 0.50

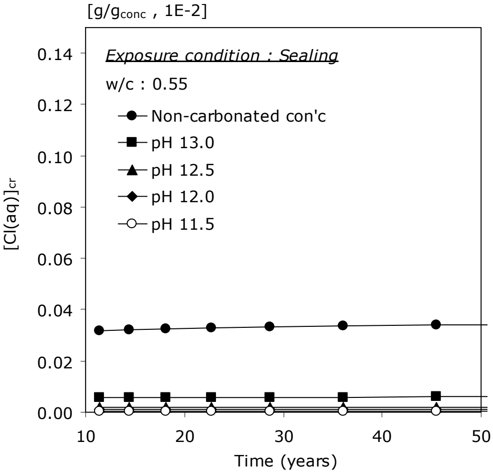

Figure 13: Effect of carbonation on critical chloride content of concrete with *w*/*c* 0.55

5 Conclusions

The critical chloride content is one of the most important aspects in the durability performance of reinforced concrete structures exposed to chlorides. The critical chloride content that causes the initiation of corrosion is of particular importance in the calculation of service life and the investigation of the integrity of concrete structures. The purpose of this study is to establish the critical chloride content that cause active corrosion initiation of reinforcement in concrete, and to examine its time evolution. To this end, a comprehensive approach for the formulation is constructed, considering many affecting factors. The following conclusions have been drawn from this study.

1. Time evolution of the critical chloride content is manipulated by the physico-chemical development of cement paste. Many affecting factors such as mix proportion, water content, and chemical pore solution are taken into account in the formulation. The critical chloride content increases as time elapsed because hydration of cement can foster more alkali chemical properties than initial condition.

2. The critical chloride content in the simulated pore solution of concrete is dependent on the time development. Thus, the time evolution expression, based on a change of chemical pore solution for the critical chloride content, can provide us with the understanding why in previous works researchers have found significant differences.

3. At 28 days, the critical chloride content calculated in this study is completely identical with ACI committee 201. Furthermore, the calculated critical chloride content of old concrete with w/c 0.50 below has good agreement with JSCE code.

4. Carbonation of concrete leads to a decrease of the critical chloride content significantly. This is obvious for concrete with low w/c ratio, as its OH^- concentration is lower than that of concrete with high w/cratio. For carbonated concrete with pH of 11.5, the critical chloride content is extremely low.

5. This study presents a fundamental approach for the critical chloride content at arbitrary time and the results show that the critical chloride content is influenced by time as well as by mix proportion and carbonation. Time evolution of the critical chloride content can provide a fundamental approach to calculate the rational critical chloride content for various original sources of chloride ions, for example, marine sand at initial time, and sea water penetration later on.

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References

ACI Committee 222R-01 (2002): Protection of Metals in Concrete against Corrosion, Manual of Concrete Practice, ACI.

ACI Committee 201 (2002): Durability of Concrete, Manual of Concrete Practice, ACI.

JSCE (1999): Concrete Standard Specification (written in Japanese), Part of Durability.

Alonso, C.; Andrade, C.; Castellote, M.; Castro, P. (2000): Chloride Threshold Values to Depassivate Reinforcing Bars Embedded in a Standardized OPC Mortar, *Cement and Concrete Research*, Vol.30, pp.1047-1055.

Andrade, C.; Page, C. L. (1986): Pore Solution Chemistry and Corrosion in Hydrated Cement System Containing Chloride Salt, *Cement and Concrete Research*, Vol.21, pp.49-53.

Breugel, K. van (1991): Simulation of Hydration and Formation of Structures in Hardening Cement-Based Materials, Ph.D Thesis, TU Delft, the Netherlands.

Broomfield, J. P. (1997): Corrosion of Steel in Concrete, E&FN SPON, London, UK.

CEB (1992): Durable Concrete Structures: Design Guide, 2^{nd} Edition, Thomas Telford, London.

Diamond, S. (1986): Chloride Concentrations in Concrete Pore Solutions Resulting from Calcium and Sodium Chloride Admixtures, *Cement, Concrete, and Aggregate*, Vol.8, No.2, pp.97-102.

Dhir, R. K.; Jones, M. R. (1990): Corrosion of Reinforcement in Concrete Construction, Page, C. L. (Ed.), Elsevier Applied Science, London, pp.227-236.

Eijk, R. J. van; Brouwers, H. J. H. (2000): Prediction of Hydroxyl Concentrations in Cement Pore Water using a Numerical Cement Hydration Model, *Cement and Concrete Research*, Vol.30, pp.1801-1806.

Goni, S.; Andrade, C. (1990): Synthetic Concrete Pore Solution Chemistry and Rebar Corrosion Rate in the Presence of Chlorides, *Cement and Concrete Research*, Vol.20, pp.525- 539.

Gouda, V. K. (1970): Corrosion and Corrosion Inhibition of Reinforcing Steel, *British Corrosion Journal*, Vol.5, pp.198-203.

Gouda, V. K.; Halaka, W. Y. (1970): Corrosion and Corrosion Inhibition of Reinforced Steel, *British Corrosion Journal*, Vol.5, 1970, pp.204-208.

Hansson, C. M.; Sorensen, B. (1988): The Threshold Concentration of Chloride in Concrete for Initiation of Reinforcement Corrosion, Corrosion Rates of Steel in

Concrete, ASTM Spec Tech Publish, pp.3-16.

Hausmann, D. A. (1967): Steel Corrosion in Concrete. How does it occur?, *Journal of Materials Protection*, Vol.5, pp.19-23.

Hope, B. B.; Ip, A. K. C. (1987): Chloride Corrosion Threshold in Concrete, *ACI Materials Journals*, July-August, pp.306-314.

Hussain, S. E.; Al-Gahtani, A. S.; Rasheeduzzafar (1996): Chloride Threshold for Corrosion of Reinforcement in Corrosion, *ACI Material Journal*, Vol.93, No.6, pp.1-5.

Hussain, S. E.; Al-Musallam, R. A.; Al-Gahtani, A. S. (1995), Factors Affecting Threshold Chloride for Reinforcement Corrosion in Concrete, *Cement and Concrete Research*, Vol.25, pp.1543-1555.

Kayyali, A.; Haque, M. N. (1995): The Ratio of Cl^-/OH in Chloride Contaminated Concrete, *Magazine of Concrete Research*, Vol.47, pp.235-242.

Lambert, P.; Page, C. L.; Vassie, P. R. W. (1991): Investigation of Reinforcement Corrosion Electrochemical Monitoring of Steel in Chloride Contaminated Concrete, *Material Structures*, Vol.24, pp.351-358.

Oh, B. H.; Jang, S. Y.; Shin, Y. S. (2003): Experimental Investigation of the Threshold Chloride Concentration for Corrosion Initiation in Reinforced Concrete Structures, *Magazine of Concrete Research*, Vol.55, No.2, pp.117-124.

Schiessel, P.; Breit, W. (1996): Local Repair Measures at Concrete Structures Damaged by Reinforcement Corrosion, Proceedings of the Fourth International Symposium on Corrosion of Reinforcement in Concrete Construction, SCI, Cambridge, pp.525-534.

Thomas, M. (1996): Chloride Thresholds in Marine Concrete, *Cement and Concrete Research*, Vol.26, 1996, pp.513-519.

Thomas, M. D. A.; Matthews, J. D.; Haynes, C. A. (1990): Chloride Diffusion and Reinforcement Corrosion in Marine Exposed Concretes Containing PFA, Corrosion of Reinforcement in Concrete, Elsevier, Warwickshire, UK, pp.198-212.