Evaluation of Chloride Penetration Characteristics using a Colorimetric Method in Concrete Structures

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ABSTRACT

When, for a long time, concrete structures are exposed to the marine condition, the corrosion possibility of the steel in concrete increases due to the ingression of chloride ions from the outside. Because the damages of corrosion caused by the chloride ion are very serious, many researches have been performed. In addition, the silver nitrate colorimetric method that can measure easily penetration depth of chloride ion has been widely executed. Currently, however, characteristics of the method were not fully verified. The aim of this paper is to estimate the applicability of colorimetric method; for this purpose, influencing factors and reaction mechanism of the method were investigated.

From the test results, it is noted that, when $AgNO_3$ was sprayed in split sections, two reactions (i.e., white reaction of AgCl and brown reaction of AgOH) were shown. And, the response velocity of white reaction was faster than that of brown reaction by 3240 times and, when $AgNO_3$ solution is used, more than 0.05N concentration shall be sprayed.

INTRODUCTION

One of the merits of using reinforced concrete (RC) is its high durability. After formation of cracks in concrete structures, however, corrosion of reinforcing bars becomes a problem. When concrete structures are exposed to chlorides from seawater, deicing chemicals, salt, salt water, brackish water, or spray from these sources, reinforcing bar in RC is more vulnerable to corrosion. This phenomenon occurs due to penetration of chloride ion through inner voids in concrete. Hardened concrete shows strong alkalinity between pH 12.6 and 13.5. Under the alkaline environment, a passive film formed between concrete and reinforcing bar plays a role in protecting corrosion of reinforcement embedded in concrete from moisture and oxygen. If a concrete construction suffers deterioration by penetration of chloride ion and/or carbonation, the passive film is broken and corrosion is begun by contacting with additional moisture and oxygen. With progress of corrosion, the volume dilation of steel occurs and, due to the expansion pressure, micro-cracks are happened in the surrounding region of the steel. As the results, the bond strength and stiffness are decreased and durability is also decreased because of damages such as cracks, eventual falling of concrete cover, and eventual decrease of cross-sectional area etc.

Penetration of chloride ions is mainly preceded through diffusion in concrete. In general, the diffusion coefficient of concrete is used to decide the penetration speed of chloride ions. Diffusion coefficient has important meaning in point that it makes possible to predict the starting time of corrosion. Many test methods such as immersion test and electrical-chemical acceleration test have been introduced to determine the diffusion coefficient. However, there are some difficulties in applying such test methods to the field. In order to determine the diffusion coefficient, it is necessary to obtain the chloride amount with distance from the surface of concrete and the analysis using the data obtained from sampling has to be performed in a laboratory. In case of electrical-chemical acceleration test method, however, it is difficult to directly compare the test results.

Recently, to solve this problem, a silver nitrate colorimetric method, which can easily measure the penetration depth of chloride ions, has been proposed. However, up to date, various applications of the method are not sufficiently examined. The purpose of this study is to experimentally investigate the mechanism and its various influencing factors of the method in concrete structures.

The corrosion problem considered in this study is also significant to a RC member of nuclear power plant (NPP) structures. In NPP structures, the corrosion shall not occur. Namely, when considering the specialty (i.e., radiation leakage and durability deterioration etc.) of NPP structures, engineers (more specifically, the nuclear engineer) shall consider corrosion problems as major issues.

MECHANISM OF COLORIMETRIC METHOD

Penetration depth measurement of chloride ion using silver nitrate colorimetric method is firstly introduced by Otsuki et al.[1]. Silver nitrate colorimetric method used the principle of which a white deposit is formed through reaction of silver ion (Ag^+) and chloride ion (Cl^-). If colorimetric method is continuously applied to concrete structures suffered the penetration of chloride ion, additional precipitation reaction beside white-precipitation reaction happens. That is, after creating of calcium hydroxide ($Ca(OH)_2$) resulting from the hydration of cement, hydroxide ions that exist within voids make brown-precipitation reaction with silver ion. Fig. 1 shows diagram for the principle of colorimetric method and Eq. (1) indicates reaction equation of colorimetric method.

$$Ag^+ + Cl^- \Rightarrow AgCl \qquad \text{(White reaction)}$$
$$Ag^+ + OH^- \Rightarrow AgOH \qquad \text{(Brown reaction)} \qquad (1)$$

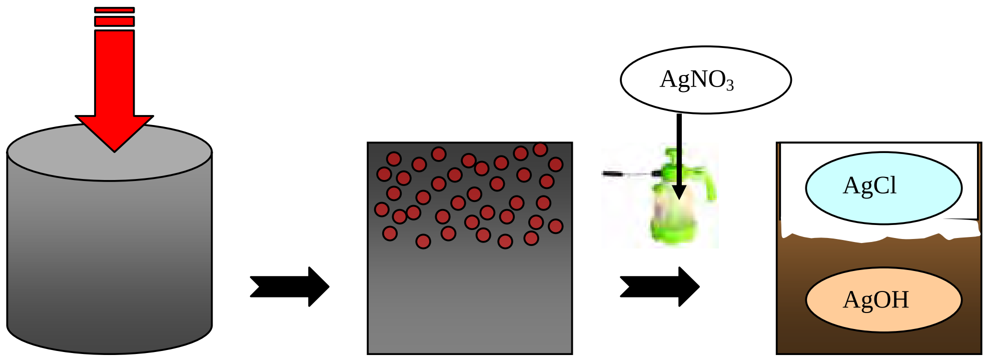


Fig. 1 Diagram of Colorimetric Method

EXPERIMENTAL PROGRAM

Test Variables

The purpose of this study is to review the mechanism of the colorimetric method and to investigate the influencing factors, which effects on the colorimetric method. For influencing factors, reaction velocity and Cl:OH ratio in color-changed border were investigated. Also, it was also necessary to decide the most suitable spray concentration of silver nitrate and the amount of chloride ion in color-changed border. Using silver nitrate solution of some selected concentrations, chloride ion penetration depths were measured for concrete specimens immersed in seawater. Chloride diffusion coefficient was determined based on penetration depth. Table 1 shows test variables adopted in this research.

Table 1. Test Variables

Test Items	Contents	Details
Optimized $AgNO_3$ concentration	pH	10, 11, 12, 13
	NaCl concentration (kg/m^3)	0.1~1.0
	$AgNO_3$ concentration (kg/m^3)	0.03N, 0.04N, 0.05N, 0.1N
Reaction velocity constant	Ag^+: Cl^-: OH^-	1:1:0.05, 1, 10, 50, 100
Concrete applicability estimation	Indoor test	Cl^- concentration of border Chloride penetration depth

Concrete Mixture Proportioning and Test Procedure

When colorimetric method was applied to concrete, concrete specimens were prepared to investigate penetration depth and diffusion coefficient of chloride ion. Chloride ion was penetrated into concrete specimens by immersing in seawater. Mixture proportions are shown in Table 2. Specimens were immersed for 6 months in seawater after water curing for 7 days. During test period, the penetration depth and concentration of chloride were measured.

Table 2. Mixture Proportions of Concrete

w/c	s/(s+g)	Unit weight (kg/m^3)			
		w	c	s	g
0.4	0.43	170	425	721	1022
0.5	0.45	172.5	345	782	1021
0.6	0.46	175	292	816	1024

TEST RESULTS AND EVALUATION

Reaction Velocity Constant

Reaction velocity constant was determined using Eq. (2)[2].

$$\frac{\{Cl^-\}_0 - \{AgCl\}}{\{Cl^-\}_0} = \left(\frac{\{OH^-\}_0 - [\{AgNO_3\} - \{AgCl\}]}{\{OH^-\}_0} \right)^K \Rightarrow Y = X^K \qquad (2)$$

where, $\{Cl^-\}_0$ is the initial amount of Cl^- (mol), $\{OH^-\}_0$ is the initial amount of OH^- (mol), $\{AgNO_3\}$ is the initial amount of $AgNO_3$ (mol), and $\{AgCl\}$ is the amount of Cl^- (mol) reacted with Ag = [initial amount of Cl^- (mol)] – [remaining amount of Cl^- (mol)]. Fig. 2 shows relationship between Y and X in Eq. (2).

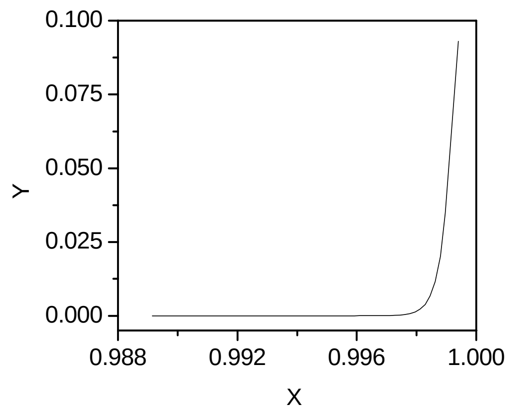
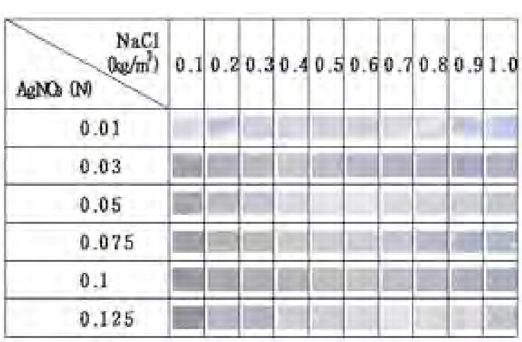


Fig. 2 Relationship between Y and X in Eq. (2)

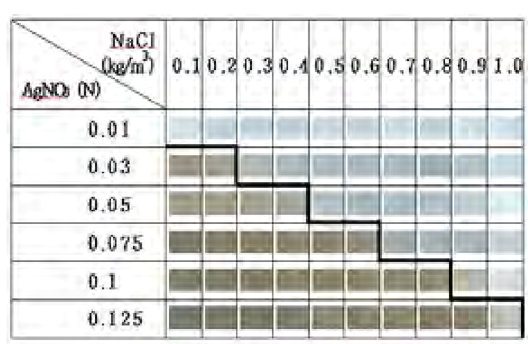
From regression analyses using the Eq. (2) and test data, reaction velocity constant (K) of 3240 was obtained. It means that chloride ion (Cl^-) penetrated into concrete reacts with silver ion by the velocity of 3240 times compared to hydration ion (OH^-) when silver nitrate solution was sprayed. In other words, when silver nitrate was sprayed in chloride parts of concrete, reaction with chloride ion is faster than that of hydration ion and the white color part is firstly represented.

Color-change with Cl:OH Ratio and pH

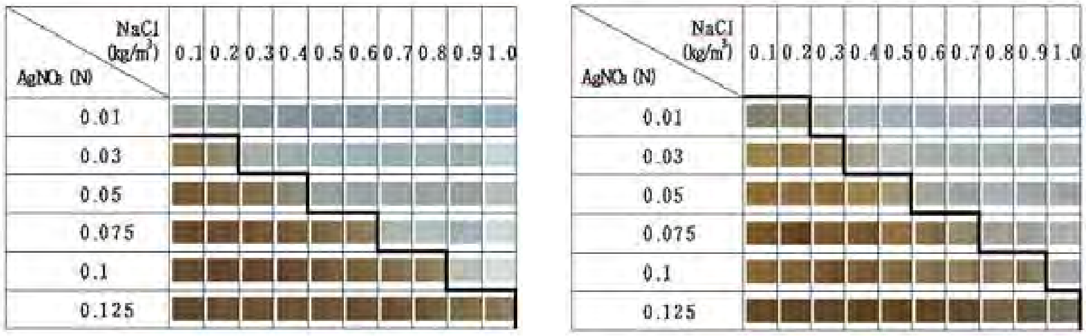
In order to compare the chemical color-change with Cl:OH ratio and pH of concrete specimens, color reaction tests were performed. Figs. 3(a)~(d) show color-changed results with Cl:OH ratio and pH.



(a) pH 10



(b) pH 11



(c) pH 12 (d) pH 13

Fig. 3 Changes of Color with pH, NaCl, and $AgNO_3$ Concentration.

Optimum $AgNO_3$ Concentration

According to the results, it is noted that color-changed border can be changed with concentration of $AgNO_3$ and AgCl:AgOH ratio in color-changed border exists in the range of approximately 1:3～5. However, when pH of concrete is below 10, the measurement of penetration depth by colorimetric method was not easy. When concrete structure is exposed to chloride attack and carbonation condition, additional research for applicability of colorimetric method would be needed. When investigators measure penetration depth of chloride ion, it is reasonable to use the optimized $AgNO_3$ solution, which can observe distinct color-changes and detect as low chloride ion amount as possible. Fig. 4 shows color-change of concrete with concentration of $AgNO_3$. According to the results, as the concentration of $AgNO_3$ increases, the distinct change of color was observed. Since the color-change is not clearly observed in low-concentration including 0.03 and 0.04N, the presenting possibility of errors is higher than that of high-concentration. Therefore, when the penetration depth of chloride ion is measured, it is recommended that silver nitrate concentration more than 0.05 N has to be used.

0.03N 0.04N 0.05N 0.1N

Fig. 4 Color-change of Concrete with $AgNO_3$ Concentration

Chloride Ion Concentration in Color-changed Border

Many research results for the chloride ion concentration in color-changed border have been presented. However, the additional researches are required because there is no consensus about these discussions. Otsuki et al.[1] found that although the total chloride ion content at the color-changed border varied from approximately 0.4–0.5% for cement paste, 0.8% for mortar, and 0.5% for concrete, the corresponding soluble chloride concentration was relatively constant and was in the order of 0.15% by weight of cement for the investigated cement paste, mortar, and concrete with different water/cement ratios. However, it was not extensively discussed about accuracy of chloride ion concentrations detected. Earlier work carried out at CSIRO by Sirivivatnanon and Khatri[3] on a limited number of concrete samples immersed in 3% NaCl solution and then sprayed with 0.1N $AgNO_3$. The result showed that the concentration of water-soluble chloride at the border varied from 0.84% to 1.69% by weight of the binder. The average detectable level was around 1.2% by weight of the binder. This level was almost 10 times higher than that found by Otsuki et al.[1].

Fig. 5 shows free chloride and total chloride amounts in color-changed border when 0.1N $AgNO_3$ was sprayed in concrete. According to the test results, free chloride amount in color-changed border is between 85 and 100 ppm and total chloride amount is between 165 and 180 ppm. Converting this free chloride to amount (%) per weight of cement, the value indicates between 0.28% and 0.33%. And, water-cement ratio shows minor effect on amount of free chloride and total chloride measured in color-changed border.

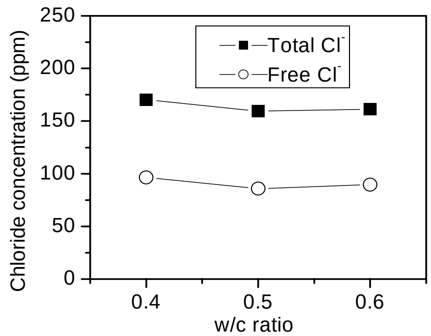


Fig. 5 Free and Total Chloride Concentrations in Color-changed Border

Chloride Penetration Depth and Chloride Diffusion Coefficient

To evaluate the applicability of the silver nitrate colorimetric method in concrete, the penetration depth and diffusion coefficient of chloride ion are compared for specimens immersed in seawater for 6 months. Fig. 6 and Fig. 7 show, respectively, penetration depth and diffusion coefficient with $AgNO_3$ concentration.

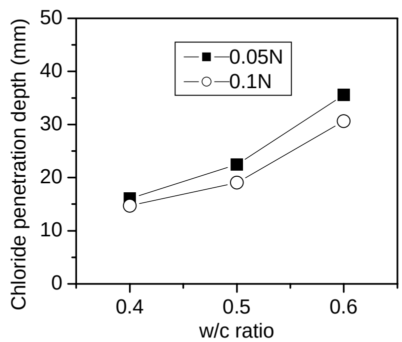


Fig. 6 Chloride Penetration Depth with $AgNO_3$ Concentration and w/c

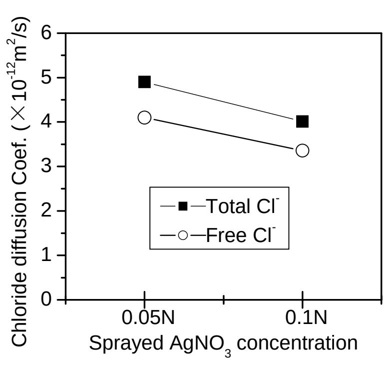


Fig. 7 Chloride Diffusion Coefficients with $AgNO_3$ Concentration

According to the test results, as w/c increases, penetration depth of chloride increases and penetration depth of 0.05N

$AgNO_3$ was detected the deeper depth than that of 0.1N $AgNO_3$. The reason is because the color-changed border was formed in the low chloride amount as the sprayed $AgNO_3$ concentration decreases and, as the result, the depth increases. Also, there was any difference in diffusion coefficients (Da) of chloride ion obtained by penetration depths for each 0.05N and 0.1N solution. In this study, the chloride concentration profile by immersion test[4] was also investigated. And, on the basis of this concentration profile, the diffusion coefficient (Dc) was calculated. Fig. 8 displays relationship between Dc and Da. These results indicate that test methods reflected well the influence of w/c and a little difference between diffusion coefficients with test method was present.

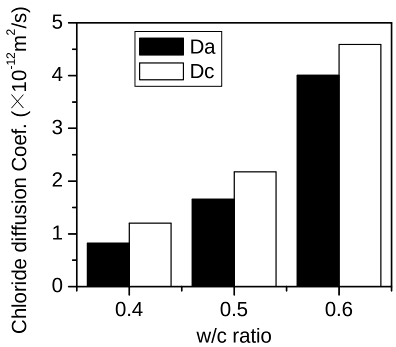


Fig. 8 Chloride Diffusion Coefficients with Test Method

CONCLUSIONS

The colorimetric method consists of two reactions (i.e., white reaction (AgCl) and brown reaction (AgOH)). These reactions have an effect on velocity constant. According to the results, chloride ion (Cl^-) penetrated into concrete reacts with silver ion by the velocity of 3240 times compared to hydration ion (OH^-) when silver nitrate solution is sprayed. Also, when the colorimetric method is applied in concrete, it is recommendable that silver nitrate concentration more than 0.05 N has to be used in measuring penetration depth of chloride ion. However, when pH value of concrete is below 10, the measurement of penetration depth by colorimetric method was not easy. Thus, when concrete structure is exposed to chloride attack and carbonation condition, additional research for applicability of colorimetric method would be needed. Free chloride ion amount in color-changed border is between 85 and 100 ppm and total chloride ion amount is between 165 and 180 ppm. Converting the free chloride ion to amount per weight of cement, it indicated the value between 0.28% and 0.33%.

ACKNOWLEDGEMENTS

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