

EFFECT OF CYCLIC WETTING-AND-DRYING CONDITION ON CARBONATION-INDUCED CORROSION

Luge CHENG^{*1}, Takufumi NOGUCHI^{*2}

ABSTRACT

Most concrete buildings are exposed to variable environment, the moisture content inside concrete may be changeable under natural weather characterized by sunshine and rainfall. In addition, such concrete buildings always suffered from carbonation especially for the buildings out of service life. The changing moisture content inside the concrete may promote the steel corrosion and increase the deterioration risk. This study investigated the effect of cyclic wetting-and-drying condition on corrosion behavior of carbonated and chloride-attacked mortar. The comparison of corrosion rate and corrosion potential among noncarbonated, carbonated mortar and chloride-contained mortar were made. Corrosion parameters of reinforcing steel bar were measured with electrochemical device. The results indicated that under cyclic wetting-and-drying condition, steel corrosion rate varies with moisture content. Steel corrosion of carbonated mortar is less susceptible to water content than that of noncarbonated ones due to the higher porosity.

Keywords: steel corrosion, carbonation, moisture content, cyclic wetting and drying

1. INTRODUCTION

Many concrete buildings exposed to variable natural environments deteriorated by various external factors such as carbonation or chloride attack during use inevitably. Under environmental conditions, water content penetrate into the concrete layer when rainy weather occurs, and evaporate on sunny days. Considering the environmental change and destructive substance attack, the steel corrosion of concrete constructions is serious.

It is general agree that moisture is the most important parameter controlling the risk of degradation of concrete constructions in spite of which, there are scarce works in which water content of its evolution when changing the external conditions. Parrott [1] have measured the relative humidity in cavities made in concrete specimen surface. Andrade [2] have measured it in real structures. Nevertheless, natural weather is characterized in general by a constant evolution during the day-night and seasonal cycles. Environmental conditions are unstable due to weather events like raining and sunshine, which relate to the moisture content of concrete structures. Regarding the studies of corrosion behavior of concrete exposed to the variable external moisture conditions, they are still scarce, in particular with respect of monitoring of moisture content and corrosion rate successively.

The purpose of this study is to analyze the impact of cyclic changes of moisture conditions maintained for a

few-day cycles, on corrosion rate of reinforcing steel bar in carbonated mortar specimens, and find the most serious condition of corrosion process. Non-carbonated mortar specimens were tested under the same external condition acted as control group and chloride-containing mortar specimens were also tested in this study. Corrosion rate measurement conducted by Linear Polarization Resistance technique. The measurement of moisture content and corrosion rate were carried out in a continuous mode on the mortar.

2. RESEARCH METHOD

2.1 Materials

Ordinary Portland cement (OPC) was used, clean river sand having a maximum diameter of 5mm (fineness modulus of medium sand=2.66) was used as fine aggregate. Table 1 presents the details of the mortar mixes used. A lean mix with a high W/C ratio and low cement content was used to increase the carbon dioxide diffusion rate, which could shorten the time required for the carbonation front to reach the surface of steel bars. Also, mortar with high water cement ratio will have high porosity, which makes the effect of water change more obvious.

2.2 Specimen and the testing condition

*1 Dept. of Architecture, Tokyo University, JCI Student Member

*2 Prof., Dept. of Architecture, Tokyo University, JCI Member

Table 1 Mixture proportion of concrete

W/C (%)	S/C	W (kg/m ³)	C (kg/m ³)	S (kg/m ³)
70	3	321.9	459.84	1379.69

All the mortar specimens were casted in steel mould by size of 144mm×88mm×40mm. Fig. 1 depicts the specimen configuration. A steel bar (SS400D, Φ=10mm) and a stainless steel bar (SUS304, Φ=10mm) were embedded into the mortar specimen with mortar cover of 8mm.

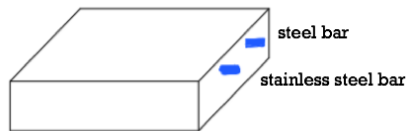


Fig. 1. Specimen configuration

Before casting, in order to position these two bars at the predetermined area, two 8mm thick plastic plates with two holes were placed at both sides of the steel mould to insert two bars. After 24 hours, demoulded the specimen and removed the plastic plates. Two bars extend 8mm from mortar specimen surface to connect with electrochemical device. Then submitted these specimens to curing room of 70% RH and 25°C for one week. All the specimens were covered by preservative film to avoid water evaporation, and extended steel reinforcing bars were covered by waterproof to inhibit the corrosion behavior in the air which affect the evaluation of corrosion process of steel reinforcing bar in mortar.

Three test series were fabricated in the same size with different corrosion conditions. Mortar specimens without any additives were divided into 2 series. Series 1 are three noncarbonated mortar specimens without any additives, and three mortar specimens in series 2 were carbonated to initiate corrosion process and also the main research object of this study. The specimens containing 3% chloride content which belonged to series 3 were also fabricated. In addition, three plain mortar specimens of the same size were casted used as reference specimens (R1,2,3) to measure the carbonation depth. A small mortar specimen (144mm×42mm×40mm) is also casted, embedded a miniature moisture sensor (WD-3-WET-5YG) inside to monitor the moisture content of mortar successively.

After curing period, the three mortar specimens which belong to series 2 and three reference specimens were covered by epoxy resin except top surface, thus carbon dioxide only penetrated into the specimens from one direction. Then transferred these six specimens to the accelerated carbonation chamber where their temperature was set to maintain the same temperature as the specimens casting and curing, had 60% relative humidity, contain 0.5% CO₂. Exposure to accelerated carbonation lasted for 60 days. Determination of the carbonation depth in the reference mortar specimens at 30, 45 and 60 days was made using the phenolphthalein test. In this study, the indicator solution was prepared using 1% phenolphthalein

powder and 99% ethyl alcohol. Carbonation depth test was performed by spraying the indicator solution on the surface of freshly broken reference mortar specimens free from dust. If the mortar was carbonated, its color remained the same, if it was not carbonated, the color of the mortar change to purple color. The depths of carbonation in the specimens were measured by tracking the edges of the color changes. The measuring of carbonation depth of reference mortar specimens at 60 days is shown at Fig. 2. Table 2 shows the average value of carbonation depths. The corrosion of steel rebar may initiate as the carbonation front has reached to the depth of embedded steel rebar.

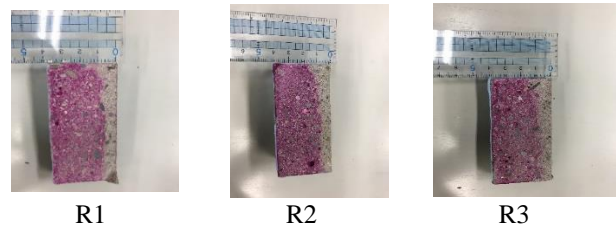


Fig. 2 Measuring of carbonation depth of reference mortar specimens at 60 days

Table 2 Carbonation depth results (unit: mm)

Number	Measuring value					Average value
R1	13	10	8	7	6	8.8
R2	8	8	7	7	8	7.6
R3	9	8	8	8	7	8
Average carbonation depth						8.1

R: reference mortar specimen

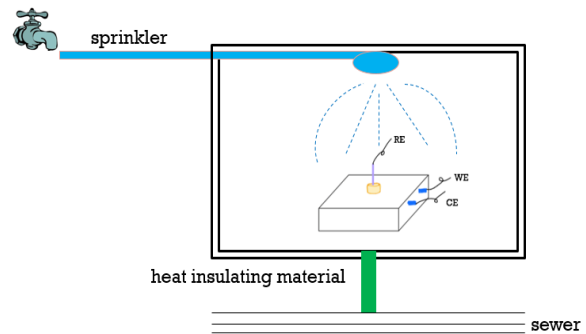


Fig. 3. Experimental layout

During testing period, all these three series mortar specimens were submitted to cyclic wetting and drying conditions which corresponding to 1 day and 2 days respectively. Such cyclic wetting and drying conditions were used to simulate raining and sunshine environmental conditions. In this study, such cyclic condition had three cycles and lasted nine days. Fig. 3 shows the experimental layout, a box made by insulation materials to keep the temperature relative stable, a sprinkler was inserted into the box through a small hole, installed above the specimen. A hole was drilled at the bottom of the box to connect with a hose to flow water to sewer. During the wetting period, turn on the tap and spray water to the mortar specimens to simulate rainfall event. During the drying period, turn off the tap, so that the water inside the

specimens evaporate naturally in the laboratory environment.

In addition, the small size mortar specimen which embedded by moisture sensor inside was also submitted to the same condition to monitor the moisture content change inside mortar specimen during cyclic wetting and drying condition successively.

2.3 Electrochemical measurement

The electrochemical technique used to measure the instantaneous corrosion rate is Linear Polarization Resistance technique (LPR). The corrosion of steel in mortar is a dynamic electrochemical process involving an exchange of ions between passive and active locations on the surface of a steel reinforcing bar. A small polarization perturbation is applied to the steel reinforcing bar from the surface of the mortar and the resulting response is measured after a suitable time delay for equilibrium to be established. The polarization resistance, R_p , was obtained from the slope of linear part of a polarization curve from -10 mv to +10 mv around the corrosion potential at a sweep rate of 0.1mv/sec. Both over and under potentials are applied in order to maximize current while minimizing the disturbance to the corrosion system. The rate of active corrosion is inversely proportional to polarization resistance (R_p). The corrosion intensity was estimated from the polarization resistance determination. Stern-Geary's equation was employed:

$$i_{\text{corr}} = \frac{\beta_a \beta_c}{2.3(\beta_a + \beta_c)} \frac{\Delta I}{\Delta E} = \frac{B}{R_p}$$

B can be determined empirically by from the β_a and β_c which are anodic and cathodic Tafel coefficients respectively. Value of B is normally assumed to be 26mv for actively corroding steel in concrete and 52mv [3] when no significant corrosion develops. ΔI and ΔE are current value and potential value respectively.

LPR measurements are normally made using a three-electrode system. The reinforcing steel bar acts as a working electrode and the stainless steel bar acts as a counter electrode. A stable reference electrode (Ag/AgCl) enables the corrosion potential and over-potential of the steel to be measured between the reinforcing steel bar and stainless steel bar. A damped sponge was placed between reference electrode and the surface of mortar specimen to conduct electricity between them. LPR measurement can be shown to be an effective mean of directly evaluating the rate of corrosion activity [4]. A point should be noticed is that electrochemical measurement equipment (HZ-7000) is very sensible to the noise, so the experiment should be processed in a quiet place.

3. RESEARCH RESULTS

3.1 Moisture content change during testing period

Fig. 4 presents the moisture content inside the mortar monitored by the moisture sensor embedded in the mortar specimens during cyclic wetting and drying condition. Moisture content is evaluated by volume

standard using moisture sensor (WD-3-WET-5YG) in this study. moisture content was obtained using following equation:

$$\text{volumetric moisture content} = \frac{\text{water volume}}{\text{air} + \text{water} + \text{solid}} \times 100\%$$

Since the W/C ratio of mortar is 0.7, high porosity makes it easier for water to penetrate and evaporate. When the mortar specimens were sprayed by water, the moisture content increase gradually due to the penetration of water, then rise to high point and peak in 41.4%. When stop spraying water to the specimens, the moisture content value drops rapidly initially because of the evaporation of water, then decrease progressively, and fall to the lowest value of 36.3%. A point should be noticed is that the average value of moisture content changed during wetting period in each cycle increased gradually, and moisture content behave similarly during drying period. This phenomenon is corresponding to corrosion behavior that also applied to subsequent figures.

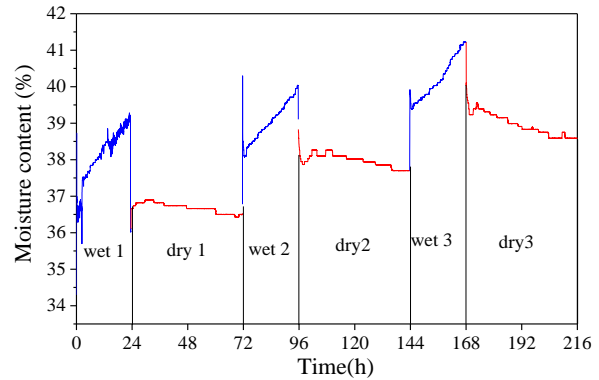


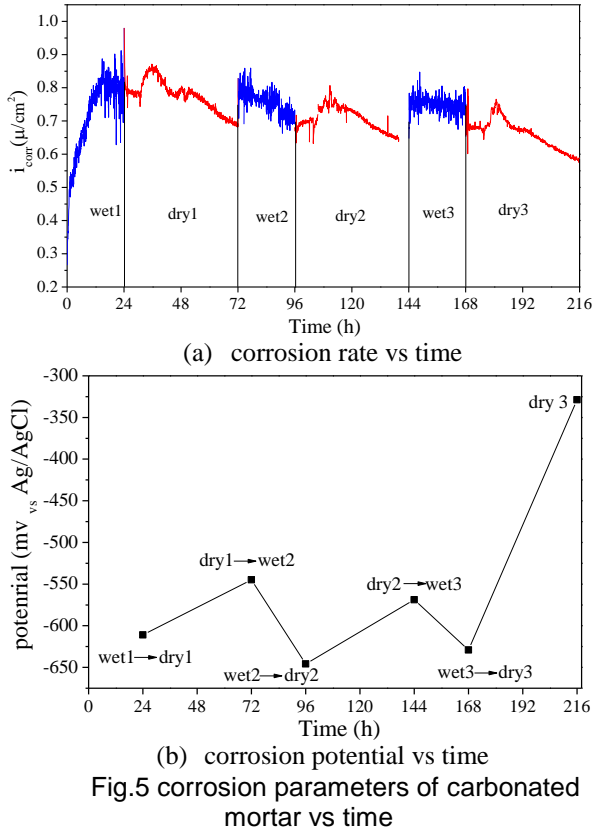
Fig. 4 moisture content vs time

3.2 Corrosion parameters of carbonated specimens

The evolution of the i_{corr} and E_{corr} of the reinforcing steel bars embedded in the carbonated mortar specimens are given in (a) and (b) in Fig 5. Each point is the arithmetical mean of values from three specimens. During wetting period, the graph shows that there has been a marked rise of i_{corr} values. The average value of corrosion current density is about $0.75 \mu\text{A}/\text{cm}^2$. After stopping spraying water to the specimens, i_{corr} values decrease slowly. The rate of specimens during drying period being is about $0.70 \mu\text{A}/\text{cm}^2$. It is obvious that the corrosion rate during wetting condition is higher than that during drying condition in general.

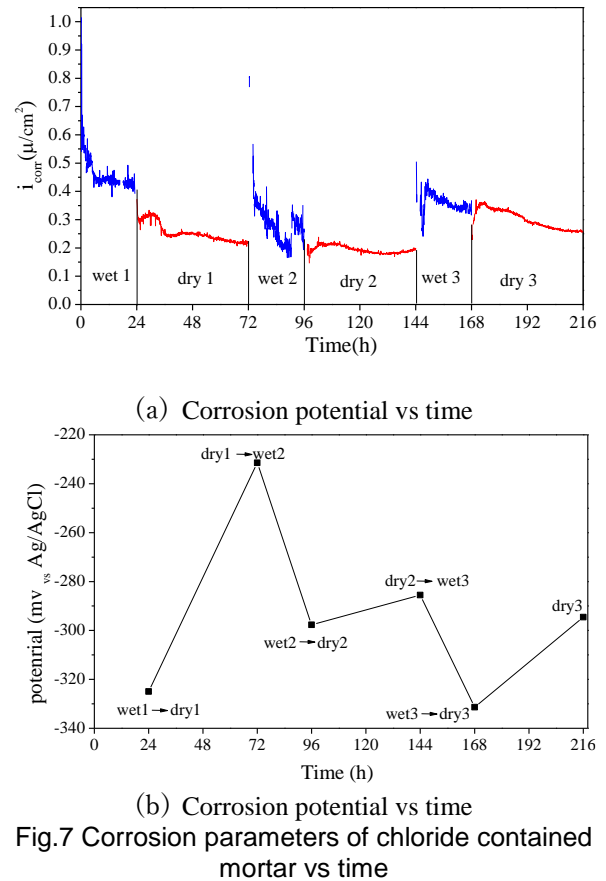
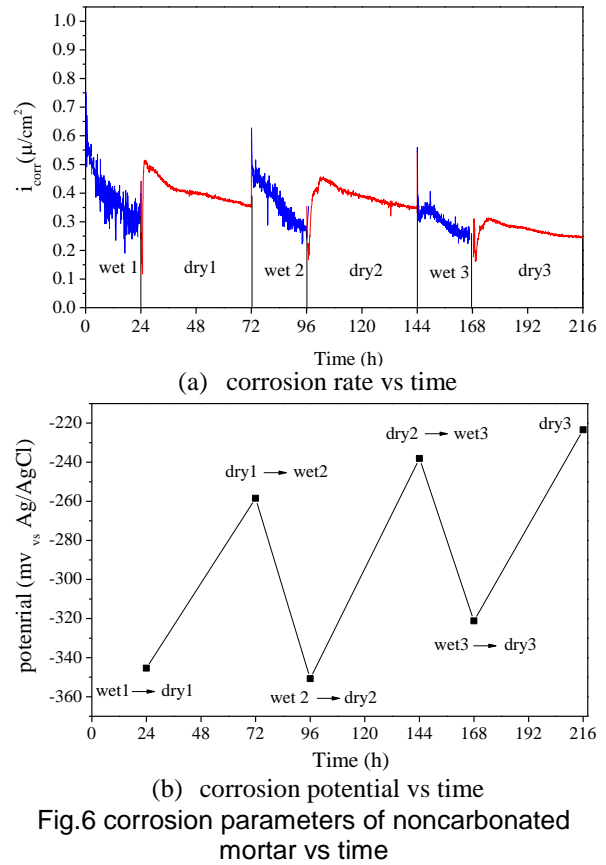
Specifically, corrosion rate varies with moisture content inside mortar during cyclic wetting-and-drying condition. When the environmental condition change to wetting, the moisture content increases as shown in Fig. 4. The corrosion rate increases rapidly and reaches the maximum value. However, as time goes on, the corrosion rate decreases gently. Similar behaviors were showed in each cycle. When environmental condition transfer to drying period later, the corrosion rate maintains stability for a period of time, then increases to reach a relatively high value, but gradual declines to the lower value later.

In addition, the maximum and minimum value of corrosion rate of each cycle decrease during the testing period. Fig. 6(b) shows the corrosion potential change during testing time. It could be observed that the corrosion potential during wetting period was more negative but more positive during drying period.



3.3 Corrosion parameters of noncarbonated specimens without additives and specimens containing chloride content

As the control series, the corrosion parameters of noncarbonated mortar specimens are demonstrated in Fig. 6. The trend of corrosion rate during cyclic wetting-and-drying condition was similar with that of carbonated ones. Compared with carbonated specimens, noncarbonated specimens showed relative lower corrosion rate with the increase of time. However, the average value of corrosion rate of noncarbonated specimens during wetting period is $0.351\mu\text{A}/\text{cm}^2$; during drying period, which is $0.372\mu\text{A}/\text{cm}^2$. In this situation, the corrosion rate of drying condition was higher than that of wetting condition. Such phenomenon is different with the corrosion situation of carbonated mortar. In addition, at early stage of wetting period, corrosion rate increases rapidly, when condition transfers to drying, after a short time of decline, corrosion rate increases to the maximum value immediately. Therefore, corrosion rate is more susceptible to environmental changes in this case. It can be seen from the Fig. 6(b) that the trend of corrosion potential change is same as that of carbonated specimens, which is that more negative potential corresponds to higher corrosion rate.



In this study, mortar specimens containing 3% chloride content were also monitored under the same condition. The results of the corrosion parameters of chloride mortar are set out in Fig. 7. Corrosion rate of chloride containing specimens is lower than carbonated specimens and noncarbonated specimens during testing period. Corrosion potential shows the similar trend with the others.

4. DISCUSSION

4.1 Analysis of moisture content change during test period

Moisture content increases rapidly at wetting period but decreased gradually at drying period as shown in Fig. 4. Considered the fact the diffusion coefficient depends on the moisture content. In this study, the moisture diffusion coefficient significantly decreased when the moisture content decreased to below 37.5% to 36.5%.

Although the trend of moisture content in each cycle was similar, the average value of moisture content during wetting or drying period of each cycle increased as time went on. This is presumably because that 24-hour wetting period is insufficient to saturate the mortar specimens completely, and 48-hour drying period is not enough to dry the specimens to the state before wetting period. After drying period of first cycle, there was still liquid water remained in the specimens. So, when the second wet-dry cycle began the moisture content in the specimens rose again and reached a higher value than the previous cycle. This explanation is also proved by the higher value of the third cycle, and the phenomenon that the average value of moisture content increased during drying period in each cycle.

4.2 Relationship between moisture content and corrosion rate

When carbonation front reaches to the surface of reinforcing steel bar, the passive oxide film is dissolved due to the drop of PH value of the surrounded mortar. The corrosion behavior could be initiated later if electrolyte present on the surface of steel reinforcing bar. The corrosion reaction that are usually considered as a simplified description of the overall corrosion process are:

Cathodic reaction: $1/2 O_2 + H_2O + 2e^- \rightarrow 2OH^-$

Anodic reaction: $Fe \rightarrow Fe^{2+} + 2e^-$

Mortar is a composite of particles of aggregate of various size in a matrix of cement paste. Since the resistivity of the aggregate are several orders of magnitude higher than that of the water in the pores, it can be concluded that mortar can be considered as being nonconducting aggregate particles embedded in an ionically conducting cement paste matrix. When water penetrate into the mortar through the air voids and capillary pores, the ions could be transferred by mobile water. The resistivity of mortar decreases with an increase in free and mobile water, but increases when liquid water loss from mortar. The resistivity of mortar mainly governs the current distribution between anode and cathode. The

corrosion current density is approximately inversely proportional to the mortar resistivity, calculated by Stern-Geary equation illustrated in 2.3.

The results shown in Fig. 5(a) indicate that when water content increased during wetting period, corrosion rate also increased and reached to the maximum value when moisture content is about 38.3%. However, when water content inside specimens continues to rise, the diffusion of oxygen through the concrete is reduced considerably. Corrosion cathodic reaction on the steel surface is inhibited when supplied oxygen is insufficient, thus inhibit the corrosion process. Based on this theory, it could be seen in Fig. 5(a) obviously that after corrosion rate reached to the maximum value during wetting period, then decreased progressively. However, during drying stage, with the evaporation of water, oxygen penetrates to the surface of reinforcing steel bar to promote corrosion process. Therefore, after a period of stability, corrosion rate increased and rose to the maximum value with moisture content of 37.3% after drying cycle begins. As water content inside specimens evaporates continuously, resulting in insufficient water on the surface of steel reinforcing bars, thus inhibit the corrosion reaction. After reaching the maximum value, corrosion rate decreased to lower value as Fig. 5(a) showed.

With regard to the change of corrosion rate during transformation of two different conditions (drying to wetting or wetting to drying). It is well known that mortar acts like a sponge and it keeps water for longer time, absorbs water quickly but it gets out slower. This behavior is appreciated in Fig. 5(a), where the corrosion rate suddenly increased when the moisture content also did, but it slowly decreased when moisture changed to lower value. Similar behavior was observed in noncarbonated mortar specimens (Fig. 6 (a)) and specimens containing chloride content (Fig. 7 (a)).

Comparing the corrosion rate change during test period of carbonated mortar and noncarbonated mortar. Carbonated specimens show less susceptible to water content change due to the higher porosity than noncarbonated ones. Higher porosity of carbonated mortar makes it difficult for water to penetrate or evaporate.

4.3 Corrosion parameters of three series

Three series specimens were monitored through testing period. The maximum, minimum and average value of corrosion rate of three series mortar are summarized in Table 4 at wetting and drying period.

The average corrosion rate of carbonated specimens is higher than the others, which means the corrosion activities are more active when mortar is carbonated. The maximum corrosion rate occurs during wetting stage of carbonated specimens, which attributes to the dissolve of passive film and supplied water content. One unanticipated finding was that the minimum value presented in the drying stage of 3% chloride containing mortar specimens. This is different from previous research that suggested that chloride-induced corrosion is more active than carbonation-induced corrosion. It seems possible that these results are due to the time of wetting period and drying period. Chloride content penetrate by

diffusion of ions in the water. Due to insufficient wetting time, it is not enough to move sufficient chloride ions to the surface of reinforcement steel bar. During drying period, pure water evaporates, the salts being left behind. Thus, the concentration of salts increases near the surface of the mortar. The concentration gradient drives the chloride ions in the water near the surface towards the zones of lower concentration, i.e., inwards. However, the water evaporates with a high rate because of the high porosity of mortar. A small amount of water left behind inhibits the concentration gradient movement of chloride ions.

The following broad criteria for corrosion have been developed from field and laboratory investigation given in Table 5[5]. During cyclic wetting and drying condition, carbonated specimens showed moderate to high corrosion, noncarbonated specimens and chloride-containing specimens showed the low to moderate corrosion. However, although judging from the Table 5, the corrosion risk of chloride-containing specimens is smaller than that of the other two, the actual corrosion is serious from the surface condition of the steel rebar.

Table 4 Corrosion rate of three series

series	condition	$i_{corr \max}$	$i_{corr \min}$	Average i_{corr}
1	W	0.782	0.190	0.351
	D	0.628	0.117	0.372
2	W	0.980	0.266	0.740
	D	0.980	0.58	0.714
3	W	1.014	0.166	0.369
	D	0.372	0.146	0.250

1-Noncarbonated mortar specimens without additives Unit: $\mu\text{A}/\text{cm}^2$
 2-carbonated mortar specimens
 3-chloride-containing mortar specimens

Table 5 Corrosion current vs. condition of the rebar

Corrosion current (i_{corr})	Condition of the rebar
$i_{corr} < 0.1 \mu\text{A}/\text{cm}^2$	Passive condition
$i_{corr} 0.1-0.5 \mu\text{A}/\text{cm}^2$	Low to moderate corrosion
$i_{corr} 0.5-1.0 \mu\text{A}/\text{cm}^2$	Moderate to high corrosion
$i_{corr} > 1.0 \mu\text{A}/\text{cm}^2$	High corrosion rate

Table 6 Corrosion condition related with OCP values

OCP values ($\text{mv}_{vs} \text{Ag}/\text{AgCl}$)	Corrosion condition
<-650	Steel corrosion
-650 to -360	High (<90% risk of corrosion)
-360 to -230	Intermediate corrosion risk
>-230	Low (10% risk of corrosion)

OCP: open circuit potential

It is agreed that more negative E_{corr} corresponds to higher i_{corr} . Corrosion situation could be evaluated by corrosion potential. However, data about the relationship between E_{corr} that use silver and silver chloride electrode as reference electrode and corrosion condition are limited. In this study, according to the evaluation of corrosion rate, Table 6 provides the relationship between E_{corr} and corrosion condition could be obtained roughly.

However, as shown in Fig. 5, the average i_{corr} values change trend of carbonated mortar specimens during wetting or drying condition is different from the E_{corr} values change trend at the corresponding environmental stages. Similar behaviors also showed at the noncarbonated mortar specimens and mortar specimens without additives shown in Fig. 5 and Fig. 6 respectively. In general, corrosion rate is higher at wetting condition than which at drying condition, and the potential tested at the end of wetting condition is negative than which at the end of drying condition. But no obvious quantitative relationship showed between E_{corr} and i_{corr} . E_{corr} is more affected by mortar resistivity which related to the moisture content of mortar.

5. CONCLUSIONS

During cyclic wetting and drying condition which simulated the changeable natural environment.

- (1) In carbonated mortar, the cathodic reaction of corrosion process is promoted by supplied moisture during wetting period. Corrosion rate increases with increase of moisture content and reaches the maximum value when moisture content of 37.3% to 38.3%. However, decrease trend shows when moisture content over 38.3% due to the insufficient oxygen on the surface of steel rebar. When moisture content inside mortar decreases during drying period, oxygen penetrates into the mortar to promote corrosion reaction, after a short time of stability, corrosion rate increases rapidly. With continuous evaporation of moisture content, water content near the reaction location could not satisfy the cathodic reaction, thus inhibits the corrosion process.
- (2) The corrosion rate change of carbonated mortar shows less susceptible to water content than noncarbonated ones due to the higher porosity.
- (3) Although E_{corr} could evaluate the corrosion condition, no obvious quantitative relationship exist between E_{corr} and i_{corr} .

REFERENCES

- [1] L.J.Parrott, Advance in Cement Research, 1988, 1,No.3, July,pp.164
- [2] C.Andrade, J.Sarria, C.Alonso, "Fourth Int. Symposium on Corrosion of Reinforcement in Concrete Construction," July 1996, Cambridge, SCI, London, J.Figg, C.L.Page,P.Bamforrg, pp.233-242
- [3] Hladky K, Geary AL, "Electrochemical polarization: a theoretical analysis of the shape of polarization curves," J Electrochem Soc 1957; pp.56-63.
- [4] C. Alonso and C. Andrade. "Corrosion of steel reinforcement in carbonated mortar containing chlorides," Advances in Cement Research Vol.1, No.3, July 1988
- [5] C.Andrade, M.C.Alonso, J.A.Gonzalez, "An initial effort to use corrosion rate mwasurents for estimating rebar durability corrosion rates of steel in concrete," ASTM STP 1065, N.S.Berke et al. editors. ASTM, Philadelphia 1990, pp.29-37