Evaluation of Steel Corrosion in Fly Ash Concrete Containing Chlorides Using Electrochemical Indexes

by

Yu-Chuan KAO*, Takao UEDA** and Chien-Kuo CHIU*

Considering the durability of fly ash concrete against the chloride attack, a quantitative evaluation of the rebar corrosion rate in concrete is necessary. In this study, reinforced concrete specimens containing premixed chlorides were prepared, using concrete with cement or fine aggregate partly substituted by fly ash. The corrosion rate of rebar in the specimen was evaluated by the polarization resistance which is an electrochemical corrosion index. The specimens were stored in the wet or dry condition at the temperature of 20 or 40 ºC. As a result, the corrosion rate of rebar was greatly suppressed by admixing fly ash with the increase of the concrete resistivity at the temperature of 20 ºC, while such suppression effect decreased with the rise in temperature to 40 ºC. The suppression effect was remarkable in the cases of fly ash addition as the substitution of fine aggregates. Moreover, the influence of a variation of the chloride content in concrete on the steel corrosion rate was significant when the specimens were stored in the dry condition. The influence of the environment temperature and the chloride content in concrete on the steel corrosion rate measured in this study could be generally evaluated by using an existing equation.

Key words:

Concrete, Fly Ash, Chloride-induced Steel Corrosion, Electrochemical Index

1 Introduction

After the Great East Japan Earthquake, the production of fly ash will continuously increase as the power supply is mainly made by thermal power plants instead of nuclear power plants. Then, the further use of fly ash as the concrete admixture is required. When fly ash is used as a concrete admixture, it has an advantage of the reduction of CO₂ emission due to the use of cement replacement material. In addition, it has been reported that properties of concrete could be improved, such as the higher fluidity of fresh concrete, the reduction of the hydration heat of cement, the higher resistance against water permeation into hardened concrete and the suppression of ASR can be expected.

On the other hand, there are some unclarified issues regarding durability of fly ash concrete. As for chloride attack, it has been pointed out that mixing of fly ash can improve the resistance of concrete against penetration of chloride ion (hereinafter Cl-) and decrease the diffusion coefficient of Cl⁻ into concrete due to the densified pore structure by mixing fly ash. However, since the pH value of the pore solution in concrete is reduced with the progress of the pozzolanic reaction, the critical Cl⁻ content in concrete for the initiation of steel corrosion may decrease compared with the case of non-fly-ash concrete. On the other hand, some past papers reported that mixing of fly ash could suppress the corrosion rate of the steel in concrete. In order to establish the durability design system of concrete structures mixing fly ash, the prediction of the damage progress after the initiation of the steel corrosion is necessary with the evaluation of the corrosion rate of steel in concrete.

In this study, the influence of fly ash mixing on the corrosion rate of steel in concrete was experimentally investigated using RC specimens containing premixed Cl⁻. Using these specimens stored in the different temperature environment, half-cell potential of rebar, electric resistance of concrete and polarization resistance of rebar were measured periodically. The corrosion rate of rebar was estimated by the measured polarization resistance considering the effect of Cl⁻ content in concrete and the environmental temperature.

2 Experimental Program

2.1 Materials

Mix proportions of concrete used in this study are shown in Table 1. Water cement ratio was 55% for all mix proportions. The base mix proportion was named N without mixing fly ash and others contained fly ash as the substitute for cement or fine aggregate in concrete. In the case of fly ash mixing as the substitute for cement, the percentage of the replacement was 20% of a mass of cement, while in the case of fly ash mixing as the substitute for fine aggregate, the percentage of the replacement was 20% of a volume of fine aggregate. Regarding the names of mix proportions shown in Table 1, II IN means type II fly ash defined in JIS A 6201 was...
admixed as the substitute for cement, while II EX and IV EX means type II and type IV fly ash was admixed as the substitute for fine aggregate respectively. Moreover, the amount of pre-mixed Cl in each kinds of concrete was set as 3.0, 5.0 or 8.0 kg/m$^3$ by dissolving NaCl in the mixing water. The water reducing agent was constantly admixed 1% to the binder content as given in Table 1 and the volume percentage of fine aggregate to total aggregate (s/a) and unit mass of water were adjusted in order to achieve the constant slump as 8 cm.

Ordinary portland cement (density: 3.16 g/cm$^3$, specific surface area: 3210 cm$^2$/g) and two types of fly ash were used. Type II fly ash (density: 2.33 g/cm$^3$, specific surface area: 4150 cm$^2$/g, ig. loss: 1.8%) and Type IV fly ash (density: 2.20 g/cm$^3$, specific surface area: 1750 cm$^2$/g, ig. loss: 0.2%) defined in JIS A 6201 were produced by a thermal power plant in Ehime prefecture. Fine aggregate (density: 2.68 g/cm$^3$, F.M.: 2.80) and coarse aggregate (density: 2.70 g/cm$^3$, F.M.: 6.60) used in this study were crushed lime stone from Oita Prefecture.

### 2.2 Preparation and curing of specimens

As presented in Fig. 1, a reinforced concrete specimen prepared in this study was 100 × 100 × 180 mm square prism with a 250 mm length deformed steel bar D13 SD345 placed at the depth of 30 mm from the concrete surface. The both end part of the embedded steel bar was coated by epoxy resin remaining the uncoated center part in concrete in the length of 100 mm. All specimens were demolded the day after casting concrete and subjected to the membrane curing for 28 days in a chamber at the constant temperature of 20 °C.

### 2.3 Various tests

All RC specimens after curing were stored in a temperature-and-humidity-controlled room. The room humidity was constantly 60 % R.H., while the room temperature was kept 20 °C for one week followed by 40 °C for one week alternately and the electrochemical indexes were measured on the last day of the storage term for one week at each temperature (refer to Fig. 2). Each RC specimen after curing was wrapped by wet cloth in a sealed plastic bag for 120 days and after that, the specimen was taken out of the bag to dry it in the room.

### Table 1 Mix proportions of concrete.

<table>
<thead>
<tr>
<th>Name</th>
<th>W/B (%)</th>
<th>s/a (%)</th>
<th>$G_{max}$ (cm)</th>
<th>SL. (cm)</th>
<th>Unit amount (kg/m$^3$)</th>
<th>NaCl</th>
<th>WRA*</th>
</tr>
</thead>
<tbody>
<tr>
<td>N</td>
<td>55</td>
<td>44.0</td>
<td>20</td>
<td>8</td>
<td>C 273 W 150 S 847 G 1088 FAH 52 FAIV 1153 52 4.94</td>
<td></td>
<td></td>
</tr>
<tr>
<td>II IN</td>
<td>55</td>
<td>41.0</td>
<td>20</td>
<td>8</td>
<td>C 210 W 144 S 793 G 1153 1153 1153 1153 8.24</td>
<td></td>
<td>B×1.0%</td>
</tr>
<tr>
<td>II EX</td>
<td>55</td>
<td>39.0</td>
<td>20</td>
<td>8</td>
<td>C 300 W 165 S 581 G 1145 1145 1145 1145 13.18</td>
<td></td>
<td></td>
</tr>
<tr>
<td>IV EX</td>
<td>55</td>
<td>39.0</td>
<td>20</td>
<td>8</td>
<td>C 309 W 170 S 575 G 1131 1131 1131 1131 1131 1131 1131 1131 1131 1131</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*WRA: Water Reducing Agent

Electrochemical measurement items for RC specimens were the half-cell potential of the steel bar, the polarization resistance of the steel bar and the concrete resistivity. The polarization resistance was measured by the AC impedance method. This method applied the low frequency (20 mHz) sine wave voltage and high frequency one (10 Hz) separately for obtaining the polarization resistance and the concrete resistivity using the impedance values in both applied frequency. In addition, the applied electric current was constantly 100 μA. The electrochemical measurement employed saturated Ag/AgCl electrode as the reference electrode and the titanium mesh as the counter electrode. These electrodes and the RC specimen were electrically connected through tap water as is presented in Fig. 1.

### 3 Compressive Strength of Concrete

Results of compressive strength test of concrete at the age of 28 days and 91 days are shown in Fig. 3. Referring to this figure, the strength of II IN containing fly ash as the substitute of cement decreases from that of N at the age of 28
days with the reduction of the amount of mixed cement.
However, at the age of 91 days, the strength of II IN reaches
the same level as that of N due to the increase of the strength
by the pozzolanic reaction of fly ash. On the other hand, the
strength of II EX containing fly ash as the substitute of fine
aggregate increases from that of N regardless of the concrete
age. This would be caused by a filler effect due to the large
specific surface area of type II fly ash in addition to the
pozzolanic reaction, while in the case of admixing type IV fly
ash with relatively coarse grain size, the strength shows the
same level as that of N.

4 Half-cell Potential of Steel in Concrete

Variation curves with time of half-cell potential during the
storage period with cyclic change of temperature is shown in
Fig. 4. In these figures, the data measured at the same
temperature are connected by lines in turns. As can be seen in
these figures, when the premixed Cl content is 3 or 5 kg/m³,
the half-cell potential values measured at 20 °C shows nobler
values than those measured at 40 °C regardless of the kinds
of concrete. This means that the higher temperature promotes
the steel corrosion in concrete. Referring to the criteria of
steel corrosion in concrete shown in ASTM C876-91, the
potential nobler than -0.09 V to saturated Ag/AgCl as
the reference electrode indicates non-corrosion with a probability
of 90% or more, the potential lower than -0.24 V indicates
corrosion with a probability of 90% or more, and the potential
between them means uncertain about the corrosion state. Fig.
4 shows that all cases measured at 40 °C in the wet condition
are classified in the corrosion range of half-cell potential.

When the premixed Cl content is 3 kg/m³, the potential
values of II IN and N show relatively low values in the
corrosion range especially in the wet condition, while the
potential data vary to nobler ones of the non-corrosion area in
the dry condition. Such a variation of half-cell potential due
to the change of the moisture condition would be caused by
the supply of the oxygen which is necessary to form the
passivation film of the steel. On the other hand, the potential
values of II EX and IV EX show remarkable effect of the
temperature and the measured data at 20 °C reach the
uncertain range even in the wet condition. As a result, it is
considered that the mixing of fly ash as the substitute of fine
aggregate can improve the steel corrosive environment if the
temperature is not so high.

When the premixed Cl content is 5 kg/m³, the potential
data in the wet condition show a general corrosion tendency
including the cases of fly ash mixed concrete, while they
move to the higher non-corrosion area in the dry condition as
presented in the cases of 3 kg/m³. In particular, the potential
values of II EX containing Cl of 5 kg/m³ are remarkably
lower than the case of 3 kg/m³ in the wet condition. The main
reason of this would be the decrease of pH value of the pore
solution by pozzolanic reaction of fly ash. In the case of IV EX, the potential maintains relatively noble values probably due to the lower pozzolanic reactivity of type IV fly ash. When the premixed Cl⁻ is 8 kg/m³, the potential values measured in the wet condition generally turn to the lower ones than the cases of 5 kg/m³ of Cl⁻, while the potential values of II EX indicate nobler values especially in the cases measured in the dry condition. The reason of this isn’t clarified but there is a possibility that the higher dosage of NaCl promoted hydration of cement and the following pozzolanic reaction of fly ash, which resulted in a dense pore structure of concrete for improving resistance against the steel corrosion.

5 Concrete Resistivity

Variation curves with time of concrete resistivity measured by using specimens containing premixed Cl⁻ of 3, 5 or 8 kg/m³ are shown in Fig. 5. Furthermore, relationship between the average values of the concrete resistivity and the premixed amount of Cl⁻ is shown in Fig. 6. The concrete resistivity is an electrical resistance of cover concrete and also an index depending moisture or Cl⁻ content in concrete, which affects the conductivity of corrosion current.

In Fig. 5, the concrete resistivity depends on the environmental temperature as given in the case of half-cell potential. The measurement at 40 °C results in the lower resistivity than the cases of 20 °C. Moreover, the resistivity data of fly ash mixed concrete are increasing with time due to the progress of the pozzolanic reaction and reached values much greater than those of non-fly-ash concrete N. Such tendency is observed most clearly in the case of II EX containing type II fly ash as the substitute of fine aggregate, subsequently the cases of II IN and IV EX are in almost same level.

Referring to Fig. 6, it is considered that the influence of the difference in Cl⁻ content on the variation of the concrete resistivity is less than that of the variation of environmental temperature or that of fly ash mixing. However, as for the case of II EX that shows relatively large resistivity, the resistivity value decreases with the increase of amount of premixed Cl⁻ from 5 kg/m³ to 8 kg/m³. It is considered that an
environment where corrosion current is liable to flow was formed due to the increase of the premixed Cl⁻ carrying electrons in the concrete. In the cases of other kinds of concrete, a change in the concrete resistivity due to the variation of Cl⁻ content in concrete was minor. In the dry condition, generally, the data of concrete resistivity become higher than those measured at 20 ºC. Most of the polarization resistance data measured at 40 ºC are less than 50 kΩ-cm² and the variation among data is small. Such a level of the polarization resistance corresponds to medium to high degree of denser pore structure and suppressed supply of oxygen or the steel position. In such situations, the Cl⁻ content at steel bar greatly affects the rate of steel corrosion 13) as the steel corrosion rate depends on the temperature and the Cl⁻ content at rebar in concrete, expressed as Equation (5).

\[ \text{loss} = \frac{k}{R_p} \]

where \( k \) is a constant, \( R_p \) is the polarization resistance, \( T \) is the environmental temperature, and \( C \) is the Cl⁻ content at rebar in concrete.

The data obtained in this study was evaluated by an empirical equation to predict the steel corrosion rate using polarization resistance, as shown in Equation (1). The equation expresses the inverse of the polarization resistance 

\[ \text{Corrosion Rate} \approx \frac{1}{R_{p,m}} \]

of measured corrosion rate to the predicted corrosion rate and the premixed amount of Cl⁻ is shown in Fig. 8. The polarization resistance \( R_{p,m} \) is known as an electrochemical index that can be used to calculate steel corrosion rate in concrete as given in Equation (1). The equation expresses that the inverse of \( R_{p,m} \) (Ω-cm²) is proportional to the corrosion current density \( I_{corr} \) (A/cm²) as the steel corrosion rate, so a quantitative estimation of corrosion progress in concrete is possible with using an appropriate constant \( k \) (V).

\[ I_{corr} = k(R_{p,m}) \]  

Referring to Fig. 7, the polarization resistance much depends on the temperature as presented in the cases of the concrete resistivity and the half-cell potential, namely, the polarization resistance measured at 40 ºC indicates the lower ones than those measured at 20 ºC. Most of the polarization resistance data measured at 40 ºC are less than 50 kΩ·cm² and the variation among data is small. Such a level of the polarization resistance corresponds to medium to high degree of the corrosion rate in the criteria of CEB 12). Whereas, in the cases of 20 ºC, the influence of fly ash mixing is significant especially, II EX and IV EX containing fly ash as the substitute of fine aggregate show the larger polarization resistance than the case of non-fly-ash concrete with the sequential increase probably caused by the progress of the pozzolanic reaction. The polarization resistance values of...
these cases generally reach over the 150 kΩ \( \cdot \) cm² corresponding to very slow corrosion rate in the criteria of the CEB. Since II IN admixing type II fly ash as the substitute of cement shows a slightly smaller polarization resistance than II EX and IV EX, the steel corrosion rate could be suppressed effectively when fine aggregates were replaced by fly ash without reducing the amount of cement.

In Fig. 8, when the measurement is made in the wet condition, the data of the polarization resistance show generally small values and the effect of premixed Cl content is not significant, while in the dry condition, there is a clear tendency that the polarization resistance values decrease with the increase of the premixed Cl content in concrete. The past paper reported that Cl content in concrete at the position of steel bar greatly affected the rate of steel corrosion as presented in the dry condition. Then, the Cl content in concrete has often used as a parameter in some equations to predict the rate of steel corrosion in concrete. In this study, the effect of Cl content on the steel corrosion rate greatly depends on the moisture content in concrete. When the Cl content is 3 kg/m³, the difference of the polarization resistance between in the wet condition and dry condition is very large, while in the case of 8 kg/m³ of Cl, such difference is not significant. When the Cl content is 5 kg/m³, II EX show the remarkably larger polarization resistance than other cases in the dry condition, which suggests the suppression of the steel corrosion rate due to admixing fly ash as the substitute of fine aggregate.

In actual situations, as chlorides penetrate from concrete surface into deeper part with the gradual rise in Cl content at the steel position. In such situations, the Cl content at steel position will be affected by the pore structure of concrete regarding the diffusion of Cl at that time. In other words, smaller Cl content at the rebar position may include the effect of denser pore structure and suppressed supply of oxygen or moisture. Correlation between the data measured in the actual situation and the data obtained in this study should be clarified by the future investigation.

7 Applicability of the Equation to Predict the Steel Corrosion Rate Using Polarization Resistance

The data obtained in this study was evaluated by an existing equation to predict the corrosion rate of steel in concrete considering the temperature and the Cl content at the steel in concrete as independent functions respectively as follows:

\[
R(T, C, D) = 0.27 \cdot C_{D}(D) \cdot R_{0} \cdot C_{T}(T) \cdot C_{C}(C) \quad \text{kg/m}^{2} \quad \text{year}^{-1}
\]

\[
C_{T}(T) = \exp\left(-2.593 \times \left(11000 \times 1/K + 8.695\right)\right)
\]

\[
C_{C}(C) = 1.93 \cdot \frac{1}{\sqrt{1 - \frac{C - 12.0}{12.0 - C_{D}^2}}}
\]

Here, \( R(T, C, D) \): steel corrosion rate (mg/cm²/year), \( C_{D}(D) \): function of concrete quality, \( R_{0} \): standard steel corrosion rate (21.33 mg/cm²/year), \( C_{T}(T) \): function of temperature, \( K \): absolute temperature, \( C_{C}(C) \): function of Cl content at rebar in concrete, \( C_{D}(D) \): Cl content at rebar in concrete (kg/m³), \( C_{0} \): Cl content for the initiation of steel corrosion in concrete (kg/m³)

Using the equations above, the steel corrosion rate as the function of the environmental temperature \( V(T) \) can be expressed as Equation (5).

\[
V(T) = a \times C_{T}(T)
\]

(5)

Moreover, the steel corrosion rate as the function of the Cl content at rebar in concrete \( V(C) \) can be expressed as Equation (6).

\[
V(C) = \beta \times C_{C}(C)
\]

(6)

Here, \( a \) and \( \beta \) are constant.

In this study, the same \( k \) value in Equation (1) is assumed regardless of the difference of the experimental condition. Then, the steel corrosion rate at 40 °C condition was predicted by Equation (5) using \( a \) calculated by substituting the average of the polarization resistance measured at 20 °C condition for \( V(T) \) in Equation (5). The ratio of the measured corrosion rate \( (I_{corr} \text{ (mA/cm²)}) \) to the predicted corrosion rate \( (V(T) \text{ (A/cm²)}) \) at 40 °C condition are shown in Fig. 9. Here, the measured corrosion rate means the corrosion rate calculated by the measured polarization resistance. In Fig. 9, when the specimens were stored in the wet condition, N and II IN show the ratio around 1.2 or 1.3 that means a relatively
accurate prediction, while II EX and IV EX containing fly ash as a substitute of fine aggregate showed grater resistance ability against the steel corrosion in concrete because such specimens indicated larger concrete resistivity and polarization resistance compared with the case of non-fly-ash concrete.

(2) The concrete resistivity and the polarization resistance are greatly affected by the variation of the environmental temperature and the measured data at 40 °C indicated a severe corrosion environment compared with the case of 20 °C.

(3) In the wet condition, the data of the polarization resistance show generally small values and the effect of premixed Cl content is not significant, while in the dry condition, there is a clear tendency that the polarization resistance values decrease with the increase of the premixed Cl content in concrete.

(4) When the Cl content is 5 kg/m³, the specimens admixing type II fly ash as the substitute of fine aggregate show the remarkably larger polarization resistance than other cases in the dry condition, which suggests the suppression of the steel corrosion rate in concrete.

(5) The influence of the environment temperature and the Cl content in concrete on the steel corrosion rate measured in this study could be evaluated by using an existing equation generally, but the specimens containing fly ash as the substitute of fine aggregate tended to be more sensitive to the temperature than the other cases.

8 Conclusions

The results of this study can be summarized as follows:

(1) Specimens containing fly ash as the substitute of fine aggregate showed grater resistance ability against the steel corrosion in concrete because such specimens indicated larger concrete resistivity and polarization resistance compared with the case of non-fly-ash concrete.

(2) The concrete resistivity and the polarization resistance are greatly affected by the variation of the environmental temperature and the measured data at 40 °C indicated a severe corrosion environment compared with the case of 20 °C.

(3) In the wet condition, the data of the polarization resistance show generally small values and the effect of premixed Cl content is not significant, while in the dry condition, there is a clear tendency that the polarization resistance values decrease with the increase of the premixed Cl content in concrete.

(4) When the Cl content is 5 kg/m³, the specimens admixing type II fly ash as the substitute of fine aggregate show the remarkably larger polarization resistance than other cases in the dry condition, which suggests the suppression of the steel corrosion rate in concrete.

(5) The influence of the environment temperature and the Cl content in concrete on the steel corrosion rate measured in this study could be evaluated by using an existing equation generally, but the specimens containing fly ash as the substitute of fine aggregate tended to be more sensitive to the temperature than the other cases.

References

Evaluation of Steel Corrosion in Fly Ash Concrete Containing Chlorides Using Electrochemical Indexes