Basic Study on Chloride-induced Steel Corrosion in Concrete Subjected to Heating up to 300 °C

by

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It has been reported that the mechanical properties of concrete would be severely damaged due to the thermal stress and the high vapor pressure when the concrete is subjected to a high temperature environment over 500 °C especially in the cases of the high strength concrete. However, in the cases of the normal strength concrete subjected to the heating up to 300 °C could be generally used after the fire damage, although the durability of such concrete members has not been clarified enough. In this study, the chloride-induced corrosion of steel in concrete subjected to the heating up to 300 °C was investigated. As a result, it was clarified that when the heating temperature exceeded 100 °C, the increase of the porosity of the heated concrete resulted in the decrease of the compressive strength and that the CI⁻ penetration into concrete accelerated by the heating over 150 °C resulted in the promotion of the chloride-induced steel corrosion in the heated concrete due to not only the increase of the porosity but also the decrease of the CI⁻ fixing ability of the concrete.

Key words: Concrete, Residual properties after heating, Chloride-induced steel corrosion, Electrochemical index

1 Introduction

Concrete is the most widely used construction material for building infrastructures, while concrete structures have been sometimes damaged by fire. It has been reported that the mechanical properties of concrete would be damaged due to the thermal stress and the high vapor pressure when the concrete is subjected to a high temperature environment\(^{16,2}\). Such damages become serious when the temperature rises over 500 °C especially for the high strength concrete. However, in the cases of the concrete subjected to the high temperature below 500 °C, the damaged concrete still can be used after proper strengthening and rehabilitation\(^{2} \) because the reduction of the compressive strength due to the fire damage is not severe. Some researchers also reported that the residual compressive strength of the concrete slightly increased by the heating around 300 °C compared with the compressive strength of the un-heated concrete. The reason is that the water in concrete will be vaporized and the cement paste will be re-hydrated by the steam curing effect around 300 °C\(^{15-16}\).

On the other hand, chloride-induced corrosion of the steel bars embedded in concrete is the main cause of the deterioration of reinforced concrete (RC) members\(^{7-9}\). Even the reduction of the compressive strength of the fire damaged concrete could not be serious if the heating temperature is not so high, the micro-cracks in concrete would be formed and connected due to the high vapor pressure of the steam in concrete and the thermal stress\(^{10}\). Such a change in the micro-structure of concrete will decrease the resistance performance against the penetration of CI⁻ and will accelerate the steel corrosion in concrete\(^{11}\). Past researches showed that the damage by the heating accelerated the chloride permeability of concrete and the carbonation rate of concrete after the heating\(^{11,12}\). However, there is almost no related researches directly focused on the steel corrosion situation in concrete after heating.

In this study, the chloride-induced corrosion of steel in concrete subjected to the heating up to 300 °C was investigated. Reinforced concrete specimens were prepared for the heating followed by the cyclic immersion into salt water and drying for accelerating steel corrosion. Electrochemical corrosion indexes were measured during the acceleration period. After the accelerated steel corrosion test, the distributions of chloride ions (CI⁻) in concrete and the weight loss of the steel bar in concrete were measured. Moreover, micro-structure of the concrete was observed by SEM (Scanning Electron Microscope) observation.

2 Experimental Program

2.1 Materials

Mixture proportions of concrete used in this program are shown in Table 1. Water to cement ratios (W/C) were set to 45% and 60% respectively. Ordinary portland cement (density: 3.16 g/cm\(^3\), \(\text{R}_2\text{O}: 0.56\%\)), fine aggregate (crushed sand, fineness modulus: 2.63, water absorption rate: 1.77\%, density: 2.57 g/cm\(^3\)) and coarse aggregate (crushed gravel, fineness modulus: 6.39, water absorption rate: 1.55\%),
the heated concrete resulted in the decrease of the compressive strength and that the Cl- penetration into concrete accelerated enough. In this study, the chloride-induced corrosion of steel in concrete subjected to the heating up to 300 ºC was could be generally used after the fire damage, although the durability of such concrete members has not been clarified cases of the high strength concrete. However, in the cases of the normal strength concrete subjected to the heating up to 300 ºC4)-6).

On the other hand, chloride-induced corrosion of the steel bars embedded in concrete is the main cause of the reduction of the compressive strength due to the fire

The concrete is subjected to a high temperature environment1), 2). Concrete is the most widely used construction material density: 2.57 g/cm³) were used in this program, the volume rate of sand to total aggregate (s/a) was 48% and the maximum size of coarse aggregate (Gmax) was 15 mm. Water reducing agent (WRA) and air entraining agent (AEA) were also used in this program to satisfy the requirements of the fresh concrete. The data of slump and concrete air are shown in Table 1.

### 2.2 Preparation of specimens

Two kinds of specimens were prepared in this program and the details are shown in Fig. 1. The RC prism specimens, each of which contained a deformed steel bar D13 at the center of the square section were prepared to investigate the chloride-induced steel corrosion in concrete after the heating test, while cylinder specimens without steel bar were prepared to measure the residual compressive strength after the heating. The list of the specimens is shown in Table 2. Three thermocouples were embedded in one specimen of each experimental group in order to measure the temperature in concrete during the heating as shown in Fig. 1. All specimens were subjected to the wet curing in a room controlled constantly at 20 ºC for 28 days before heating.

### 2.3 Method of heating

The specimens were heated using an electric oven. The temperature rising rate was set to 5 ºC/min and the temperature was kept constant for 5 hours after the oven temperature reached the target temperature. The top and bottom surfaces of the specimens were covered with ceramic fiber blanket (Fig. 2 (a)) during the test in order to protect the top and bottom surface of concrete with the exposed part of the steel bar, and to make sure that the heat was transferred through the side surface of the specimens. The residual compressive strength of the cylinder specimens and the porosity of the prism specimens were also measured after the specimens were cooled in air for 24 hours.
The porosity was calculated by Eq. (1), where \( P \) is the porosity of the concrete specimen, \( W_t \) and \( W_s \) are the water submerged mass of the concrete specimen in air and in water, \( W_d \) is the oven dry mass of the concrete specimen in air.

\[
P = \frac{W_t - W_d}{W_t} \times 100
\]

The RC prism specimens were subjected to the cyclic immersion into salt water and drying in order to accelerate the chloride-induced steel corrosion.

### 2.4 Cyclic immersion into salt water and drying

The top and bottom surfaces of the RC prism specimens were coated with epoxy resin (Fig. 2 (b)) before the test in order to make \( Cl^- \) penetrate through the side surface. The cycles of immersing the specimens in 10% NaCl solution for 4 days followed by drying the specimens in air for 3 days repeated for 90 days, both the NaCl solution and the air were kept at 20 °C constantly during the test. The half-cell potential, polarization resistance and concrete resistivity of the specimens were measured regularly during the test to monitor the rebar corrosion situation. As a reference electrode for these electrochemical monitoring, saturated silver chloride (Ag/AgCl) was used. Polarization resistance was measured by the rectangular wave electric current polarization method, as the deference of impedances at 800 Hz and 0.1 Hz of electric current frequency. Concrete resistivity was obtained as the impedance at 800 Hz of electric current frequency.

The distribution profiles of \( Cl^- \) content in the concrete specimens were measured after the test using the powder samples grinded from the each of five plates in a specimen as shown in Fig. 3. \( Cl^- \) content was measured by following to JIS A 1154. SEM observation of split concrete surface and the measurement of weight loss of steel due to corrosion were also carried out after the cyclic immersion test. The weight loss of steel was measured by following to JCI-SC1.

### 3 Results and discussion

#### 3.1 Temperature in concrete during heating

As shown in Fig. 1, three thermocouples were embedded in a specimen at the different depth respectively. However, since the differences among the data measured by these three thermocouples were not remarkable, it can be said that the temperature was almost uniformly distributed in the concrete during the heating. In addition, as the temperature differences between the cylinder specimens and prism specimens were also small, the average temperature values of cylinder and prism specimens during the heating are shown in Fig. 4.

It can be seen from the curves that the rising rate of the temperature in concrete decreases after 100 °C because of the consumption of the heat for the evaporation of the water in concrete. Moreover, in the cases of 45 % W/C concrete, the rising rate of temperature is higher than that of the cases of 60% W/C concrete for the 100 and 200 °C heated specimens, whereas this phenomenon is not found for the 300 °C heated specimens. The reason would be that since the amount of water in 60 % concrete is more than the case of 45 % concrete, the rising rate of temperature in 60 % concrete becomes relatively low when the surrounding temperature is
100 or 200 °C, whereas in the cases of 300 °C heated specimens, the effect of water evaporation becomes minor due to the relatively early convergence of the water evaporation.

3.2 Residual compressive strength of concrete

There were no obvious cracks and other changes on the concrete surface of all heated specimens after the heating test as shown in Fig. 5. The residual compressive strength of concrete and the porosity of concrete after the heating are shown in Fig. 6 and Fig. 7 respectively.

It can be seen from Fig. 6 that the compressive strength of the concrete decreases when the heating temperature exceeds 100 °C whereas the additional decrease of the compressive strength when the temperature reaches around 300 °C is relatively small. The similar results have been reported with the possible mechanisms of re-hydration due to the steam curing in concrete subjected to the heating to around 300 °C[9,13,14]. In addition, the decrease of compressive strength of 60% W/C concrete is larger than that of 45% W/C concrete. As shown in Table 1, the cement content of the 45 % W/C concrete is larger than that of the 60 % W/C concrete, then the steam curing during the heating in the 45 % W/C concrete could be more effective than the case of the 60 % W/C concrete. On the other hand, the damage of the 60 % W/C concrete due to the micro-cracks formed by the high vapor pressure of the moisture in concrete and the thermal stress would be remained after the heating and affect the mechanical properties significantly.

From Fig. 7, the porosity increases when the heating temperature exceeds 100 °C whereas the additional increase of porosity observed around 200 °C to 300 °C is not significant. Such a tendency of the porosity increase with the rise in temperature is agree with the tendency of the decrease of the compressive strength shown in Fig. 6.

The cylinder specimens after the compressive strength test were also sprayed with phenolphthalein solution to investigate the carbonation due to the heating but the carbonation of concrete was not observed in all specimens as shown in Fig. 8. From this result, it can be said that the component of Ca(OH)₂ in the concrete didn’t be decomposed by the heating conducted in this study.

3.3 SEM observation of concrete

Results of SEM observation of the concrete (the sampling point in a specimen is shown in Fig. 3) after the
heating and the cyclic immersion into salt water and drying are shown in Fig. 9.

Compared with the concrete section of the un-heated specimens, concrete section heated to over 100 ℃ ((a) and (b) in Fig. 9) became rough and small cracks were observed, and the concrete section heated around 300 ℃ ((c) and (d) in Fig. 9) became porous and larger cracks were observed. The results of the SEM observation indicate that the micro-structure of concrete changed to porous and micro-cracks were introduced even if the affected temperature was around 150 ℃. Such damage of concrete micro-structure would cause the decrease of compressive strength as shown in 3.2 and could affect the resistance performance of concrete against the penetration of ions and steel corrosion behavior described in the following parts.

### 3.4 Distribution of Cl⁻ in concrete

Distribution of water soluble Cl⁻ content, total Cl⁻ content and the ratio of water soluble Cl⁻ to total Cl⁻ content in concrete after the cyclic immersion into salt water and drying are shown in Figs. 10 to 12 respectively.

According to Fig. 10 and Fig. 11, the specimens heated to around 200 ℃ (P245 and P260) or 300 ℃ (P345 and P360) show the relatively higher Cl⁻ content compared with the cases of un-heated specimens (PA45 and PA60) or specimens heated to lower than 100 ℃ (P145 and P160). Especially in the cases of specimens of 60 % W/C heated to around 200 ℃ or 300 ℃, the declination of Cl⁻ content with the depth around the steel bar becomes mild and then the Cl⁻ content around the steel bar becomes relatively high.

Generally, Cl⁻ ions penetrate from the concrete surface as the apparent diffusion process with the fixing of a part of free Cl⁻ to the cement hydration products. However, in the cases of concrete heated to around 200 ℃ or 300 ℃, the penetration of Cl⁻ seems different from the usual diffusion process observed in the general cases. Similar Cl⁻ profiles in concrete subjected to the heating to around 300 ℃ were reported in the past researches. Such Cl⁻ profiles will promote the steel corrosion in concrete. Moreover, Cl⁻ content values in 200 ℃ heated specimens are higher than those in the 300 ℃ heated specimens for both 45% W/C and 60% W/C concrete. The reason of this is considered that the 300 ℃ heated specimens were cured to some extent by the hot steam which was vaporized from the water in concrete and the resistance performance of concrete against Cl⁻ penetration was increased. Regarding W/C of concrete, the Cl⁻ content values in the 60% W/C concrete were higher than those in the 45% W/C concrete regardless of the heating temperature.

From Fig. 12, the ratios of water soluble to total Cl⁻ content increase with the rise in the heating temperature, which means that the concrete ability of fixing Cl⁻ ions in the hydration products like Friedel’s salt was significantly decreased by the heating of the concrete. From these results, it can be suggested that the promotion of Cl⁻ penetration into concrete affected by the heating to around 200 or 300 ℃ shown in Fig. 10 and Fig. 11 would be caused not only by the damage of the micro-structure in the heated concrete but also by the decrease of the Cl⁻ fixing ability of the concrete due to the heating. Such phenomena would accelerate not only Cl⁻ penetration into concrete but also steel corrosion in concrete after the heating.

### 3.5 Apparent diffusion coefficient of Cl⁻ in concrete

Variation curves of apparent diffusion coefficients of Cl⁻ obtained by using with the heating temperature are shown in Fig. 13:

$$C_i(x,t) = C_e \left[ 1 - erf \left( \frac{x}{2D_i^{1/2}t} \right) \right]$$

(2)

where $C_i(x,t)$ is the Cl⁻ concentration at distance $x$ from the exposed concrete surface after time $t$, $C_e$ is the original Cl⁻ concentration, $C_i$ is the Cl⁻ concentration of the exposed
concrete surface, \( x \) is the distance from the exposed concrete surface, \( t \) is the exposure time, \( D \) is the Cl\(^-\) diffusion coefficient and \( erf \) is the error function.

From Fig. 13, the diffusion coefficient values increase with the heating up to around 200 °C but it turns to decrease with the heating to around 300 °C. When the concrete is heated to around 300 °C, the steam-curing would be effective to reduce the diffusion coefficient of the heated concrete as described in 3.2. However, as shown in 3.4, considering the change in the Cl\(^-\) fixing ability of the concrete due to the heating, it may be difficult to explain the Cl\(^-\) penetration property of concrete after heating by using the diffusion process. In fact, there were relatively large errors between some of the measured Cl\(^-\) profiles shown in Fig. 10 and those obtained by using Eq. (2). Therefore, the detailed mechanism of Cl\(^-\) penetration into the heated concrete should be investigated in the future research works.

### 3.6 Electrochemical indexes

Variation curves of half-cell potential, polarization resistance and concrete resistance of RC specimens during the cyclic immersion into salt water and drying are shown in Figs. 14 to 16 respectively.

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. These criteria are also shown in Fig. 14.

From Fig. 14, it can be seen that the half-cell potential values of the non-heated and 100 °C heated specimens decrease slowly during the period of the accelerated steel corrosion and almost keep the range of the uncertain area. On the other hand, the half-cell potential values of the 200 or 300 °C heated specimens rapidly decrease due to the cyclic immersion into salt water and drying. These cases are classified to the corrosion area in the ASTM criteria but the half-cell potential values of 45 % W/C cases are relatively nobler than the cases of 60 % W/C. These results are consistent to the results of the porosity or the Cl\(^-\) content profiles in concrete.

The polarization resistance \( R_p \) is known as an electrochemical index that can be used to calculate the steel corrosion rate in concrete as shown in Eq. (3).

\[
I_{corr} = 2.5 / (R_p)
\]  

(3)

The equation expresses that the inverse of \( R_p \) is proportional to the corrosion current density \( I_{corr} \) as the steel corrosion rate, so a quantitative estimation of corrosion progress in concrete is possible with using an appropriate constant \( k \).

From Fig. 15, the polarization resistance values of the specimens heated to around 200 or 300 °C are all decreasing during the period of the accelerated steel corrosion whereas those of the un-heated specimens maintained almost constant. From this, the steel corrosion rates of the specimens heated to...
respectively. According to Fig. 16, it can be seen that the concrete resistivity values measured before starting the cyclic immersion into salt water and drying increase with the heating due to the drying of concrete. After starting the immersion into salt water, the concrete resistivity values decrease with the penetration of salt water and the 200 °C heated 60% W/C specimen (P260) shows gradual decrease of the concrete resistivity while 300 °C heated 45% W/C specimen (P345) shows gradual increase of the concrete resistivity during the period of the accelerated steel corrosion.

These results suggest that P260 specimens got the heaviest damage of the micro-structure in concrete due to the heating and P345 got the largest effect of the steam curing, which are confirmed by the results of porosity, chloride penetration tendency and other electrochemical indexes.

3.7 Weight loss of steel in concrete due to corrosion

The corrosion situation and the weight loss data of steel bars removed from the specimens after the cyclic immersion into salt water and drying are shown in Fig. 17 and Fig. 18 respectively.

From Fig. 17, the corrosion degree of all steel bars is not serious as a whole. However, from Fig. 18, the weight loss values of the steel in concrete significantly increase when the heating temperature exceeds 100 °C and maintain the relatively severe corrosion level from around 200 °C to 300 °C regardless of the difference of the concrete W/C, which is consistent with the results of the Cl- distribution and electrochemical indexes. Namely, when the heating temperature exceeds 100 °C and rise to 200 or 300 °C, the damage of the concrete micro-structure and the decrease of the Cl- fixing ability of the concrete accelerated the Cl- penetration after the heating, which results in the acceleration of the steel corrosion in concrete. Considering the results of this study, even if the decrease of the compressive strength with the heating is not so significant, the corrosion resistance performance of concrete after the heating could be severely decreased. So, the serviceability of the fire-damaged concrete structure should be judged including the reduction of the durability after the heating.

4 Conclusions

The results of this study can be summarized as follows:

(1) The compressive strength of the concrete decreased when the heating temperature exceeded 100 °C whereas the additional decrease of the compressive strength when the temperature reached around 300 °C was relatively small. In addition, the decrease of compressive strength of 60% W/C concrete was larger than that of 45% W/C concrete.

(2) The porosity increased when the heating temperature exceeded 100 °C whereas the additional increase of porosity observed around 200 °C to 300 °C was not significant. Such a tendency of the porosity increase with the rise in temperature was agree with the tendency of the decrease of the compressive strength.

(3) The Cl- penetration into concrete after the heating to around 200 or 300 °C was accelerated not only by the damage of the micro-structure in the heated concrete but also by the decrease of the Cl- fixing ability of the concrete due to the heating.

(4) The steel corrosion rates of the specimens heated to around 200 or 300 °C increased with the accelerated steel corrosion compared with the cases of the un-heated specimens. On the other hand, the decrease of the polarization resistance of the specimens heated to around 200 °C is larger than that of the specimens heated to around 300 °C. Such a tendency is also observed in the results of the concrete resistivity especially in the cases of the 45 % W/C concrete.

(5) When the heating temperature exceeded 100 °C and rose to 200 or 300 °C, the weight loss of the steel in concrete due to the chloride-induced corrosion was accelerated.

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