- Technical Paper -

CARBONATION AND CHLORIDE PENETRATION INTO CONCRETE AFTER HIGH TEMPERATURE EXPOSURE

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ABSTRACT

The aim of the research is to understand how carbon dioxide and chloride penetrate into post-fire concrete which can be used without repairing, by investigating the moisture transfer in concrete. Concrete specimens with water-to-cement ratios of 0.35 and 0.45 were heated up to 350 °C. Then, the moisture transfer, and accelerated carbonation and chloride penetration depths in the specimens were measured. As a result, the carbonation and chloride penetration depths of the heated specimen were larger than the unheated specimen because of low moisture content and micro-cracks.

Keywords: Durability, Electrical resistance method, High temperature exposure, Moisture transfer

1. INTRODUCTION

Concrete structures such as tunnels and buildings are possibly exposed to fire that is one of the most extreme conditions. Generally, when concrete is exposed to high temperature lower than 100 °C, concrete is still sound. When exposed to 300 °C, the compressive strength of concrete is reduced about 15–40% because tiny cracks appear along the boundary of calcium hydroxide (CH) crystal. After exposure to 300–400 °C, CH dehydrates. When concrete is exposed to 600 °C, serious cracks in the cement paste and around aggregate particles appear. When exposed to 1,000 °C and 1,200 °C, the cracks become extensive and concrete completely loses binding properties, respectively [1, 2, 3]. As a result, post-fire concrete structures should be repaired, strengthened or demolished for recasting [4].

Normally, the use of polypropylene (PP) fiber has been recommended to reduce the risk of the explosive spalling of concrete [5]. Moreover, it was found that concrete structures after exposed to fire or high temperatures do not need repairing when they have no spalling and remain appropriate compressive strengths for using [6, 7, 8]. Although post-fire concrete seems not to need repairing, its chemical and physical properties can be changed such as dehydration, degradations of modulus of elasticity and micro cracking, resulting in easier ingress of carbon dioxide (CO_2) and chloride [9], especially for coastal concrete structures and concrete structures close to CO_2 source such as traffic tunnels and buildings. In the long term, the ingress of CO_2 and chloride may be a cause for degrading durability of concrete structures.

The purpose of this study is to understand how CO_2 and chloride penetrate into post-fire concrete which can be used without repairing. The moisture transfer in concrete after exposed to high temperature was also investigated.

2. EXPERIMENTS

2.1. Materials

Concrete was used as specimen in this study. Ordinary Portland cement, crushed stone and crushed sand were used as cement (C), coarse aggregate (G) and fine aggregate (S), respectively. Superplasticizer (SP) and air-entraining admixture (AE) were used to improve workability for casting. The target air content and target slump are 4.5±1.5% and 14.0±2.0 cm, respectively. Concrete specimens with water-to-cement ratios (W/C) of 0.35 and 0.45 were prepared. Additionally, concrete specimens with W/C of 0.35 containing PP fiber were also prepared. The PP fiber having the diameter of 48 μm and the length of 20 mm was applied at a dosage of 0.2% by volume of concrete. The target compressive strength of concrete specimen at the age of 28 days was above 50 MPa. Mixture proportions and measured properties of the concrete specimens are shown in Tables 1 and 2, respectively.

2.2. Preparation of specimens

Concrete was mixed in a mixer, and casted in molds. Prismatic specimens of 100-mm width, 100-mm height and 150-mm depth were prepared for temperature monitoring, moisture transfer examination and chloride penetration test. For temperature monitoring, thermocouples were inserted during casting at the interval of 20 mm as shown in Fig.1. The interval of 20 mm was selected in order to prevent the effect of

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Table 1 Mixture proportions of concrete

Name	W/C	kg/m^3					Percentage of cement by mass	
		W	C	S	G	PP	AE	SP
C035	0.35	170	486	651	978	-	0.001	1.5
C045	0.45	170	378	738	980	-	0.001	0.5
C035PP	0.35	170	486	651	978	1.82	0.001	1.0

Table 2 Designed and measured properties of fresh concrete

Name	Designed		Measured	
	Slump (cm)	Air content (%)	Slump (cm)	Air content (%)
C035	14.0±2.0	4.5±1.5	16.0	4.5
C045	14.0±2.0	4.5±1.5	12.0	5.0
C035PP	14.0±2.0	4.5±1.5	16.0	4.5

aggregates on temperature monitoring. The embedded depth of thermocouples was approximately 50 mm from the bottom of the specimen. For moisture transfer examination, stainless steel rods of 0.9 mm in diameter were arranged in the specimens at the interval of 20 mm as shown in Fig.2. Cylindrical specimens of 100-mm diameter and 200-mm height were prepared for compressive strength test. For carbonation examination, prismatic specimens of 150-mm width, 100-mm height and 400-mm depth were prepared.

After casting, the top surface of the mold was covered with plastic sheets and wet cloths in order to prevent water evaporation, and the specimens were stored at 20 °C and 60% of relative humidity (RH).

After demolding at the age of 24 hours, the specimens were cured in water at 20 °C for 27 days. Then, they were stored at 20 °C and 60%RH for 30 days in order to reduce free water in the capillary pores in the specimens, which causes a buildup of pore pressure during the heating test.

One day before heating, five surfaces of the specimens were covered alternately with insulating material and aluminum adhesive tape in five layers to prevent the moisture evaporation from the surfaces other than the heating surface. This operation was also conducted for simulating an actual fire accident because only one surface of concrete in an actual fire accident is generally exposed to fire. The insulating material was used for the second and fourth layers. Meanwhile, the aluminum adhesive tape was used for the first, third and fifth layers.

2.3. Heating regime

At the age of 58 days, the uncovered surface of the specimen was exposed to high temperature by placing it on a hot plate. The temperature on the hot plate was raised up to 350 ˚C at a rate of approximately 20 ˚C/min, kept at 350 ˚C for 15 minutes, and then the specimens were removed from the hot plate for the designed tests.

2.4. Compressive strength test

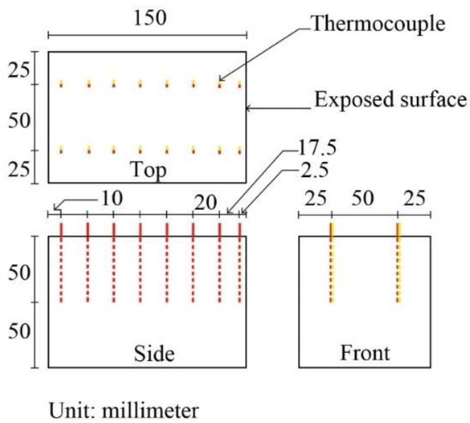

Fig. 1 Specimen configuration for temperature monitoring

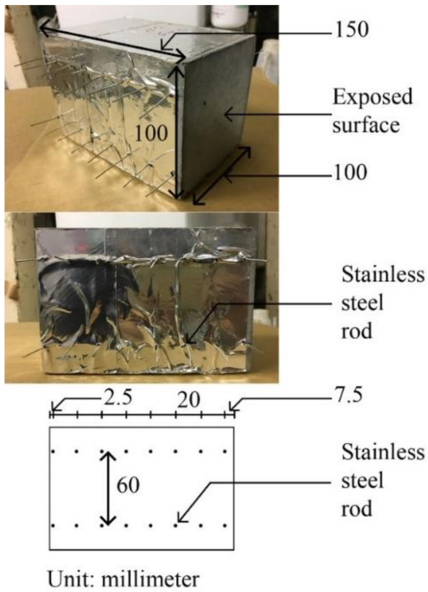

Fig. 2 Specimen configuration for moisture transfer

Compressive strength test was conducted at the ages of 28 days and 58 days, as per JIS A 1108 (Method of test for compressive strength of concrete). At the age of 58 days, the compressive strength test was carried out before and after heating. As for the specimen after heating, all insulating material and aluminum adhesive tape were removed from the specimen, and then the specimen was cooled down naturally before the compressive strength test.

2.5. Moisture transfer examination

Fujioka et al. [10] and Bui et al. [11] reported that electrical resistance measurement in hardened cement using stainless steel rods could determine the internal relative humidity through a correlation between the electrical resistivity and internal relative humidity of the hardened cement. Therefore, the electrical resistivity was used in this study to explain the moisture transfer in the concrete specimens.

After heating, insulating material and aluminum adhesive tape except for the first layer of aluminum adhesive tape were removed from the specimen. Next, the specimen was stored at 20 °C and 60%RH and its electrical resistance was immediately measured. The electrical resistance at each depth of the specimen was assessed at the specific times. Then, the electrical resistivity was calculated from Eq. (1).

$$\rho = \frac{\pi \times l}{\log\left(\dfrac{d}{a}\right)} \times R \qquad (1)$$

where,
ρ: resistivity (kΩ·cm)
R: resistance (kΩ)
l: depth of electrode (cm)
d: interval of electrode (cm)
a: electrode radius (cm)

2.6. Accelerated carbonation test

The prismatic specimen sealed with the first layer of aluminum adhesive tape was cooled down naturally at 20 °C and 60% RH for 8 hours. Then, the specimen was stored at 20 °C, 60% RH and 5% concentration of CO_2 for accelerated carbonation test according to JIS A 1153 (Method of accelerated carbonation test for concrete). The carbonation depths were measured by using phenolphthalein indicator solution. The average value of the 20 measurements was recorded as the carbonation depth of the specimen at the accelerated carbonation periods of 1, 4, 8, 13 and 26 weeks.

2.7. Accelerated chloride penetration test

After heating and removing all insulating material and aluminum adhesive tape, the specimen was cooled down naturally at 20 °C and 60%RH for 8 hours. Then, five surfaces of the specimen were coated with epoxy resin so that the chloride penetrates into the specimen one-dimensionally. The specimen was immersed in 3mass% of sodium chloride solution for 1 day before being dried at 20 °C and 60%RH for 6 days. This wet and dry operation was repeated 30 times.

The chloride penetration depth of the specimen was measured at the fifteenth and thirtieth cycles by using silver nitrate solution. The average value of the 20 measurements was recorded as the chloride penetration depth of the specimen.

3. Results and discussion

3.1. Temperature history

Figs. 3-5 show the temperature history of the hot plate and the internal temperature of the specimens. The temperature history of the hot plate is slightly different in each mixture because the heating test was

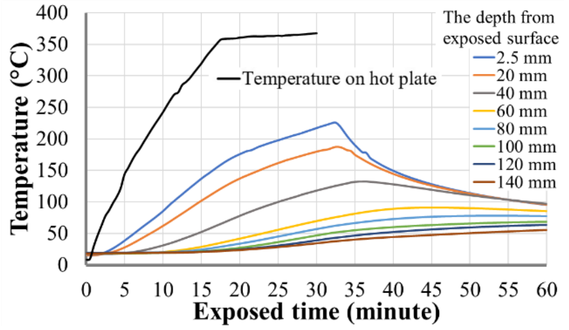

Fig. 3 The temperature history of hot plate and the internal temperature of C035

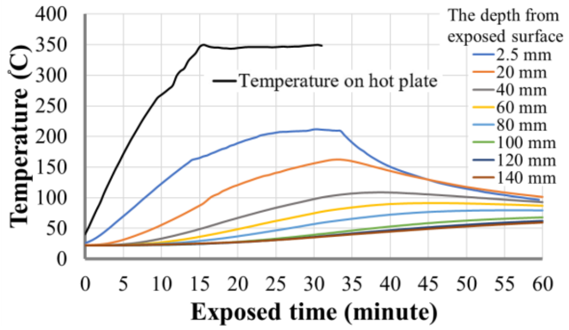

Fig. 4 The temperature history of hot plate and the internal temperature of C045

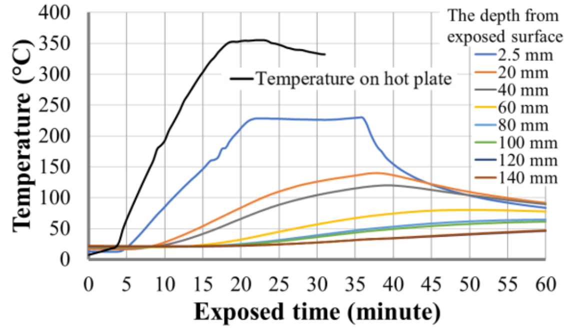

Fig. 5 The temperature history of hot plate and the internal temperature of C035PP

conducted manually and separately in each mixture. The temperature at the depth of 2.5 mm from the exposed surface of C035PP specimen fluctuated around 150 to 180 °C in the period of exposed time between 15 to 20 minutes. This fluctuating was not observed in C035 and C045 specimens. This should be affected by the melting of the PP fibers in the specimen since the melting point of the PP fibers used in this study is around 160 °C. The rates of temperature increase at the depths of 2.5, 20 and 40 mm from the exposed surface are shown in Table 3. Although the rate of temperature increase at the depth of 2.5 mm from the exposed surface for C035PP specimen is higher than that for C035 specimen, the rates of temperature increase at the depths of 20 and 40 mm for C035PP specimen are lower than those for C035 specimen. Heating energy may be consumed by the melting of the PP fibers in C035PP specimen.

3.2. Compressive strength

The compressive strengths of C035, C045 and C035PP specimens are shown in Table 4. After heating, the compressive strengths decreased and the residual compressive strength of C035, C045 and C035PP specimens were 75, 82 and 85% of the compressive strength before heating, respectively. The reduction might be due to the micro-cracks caused by the pore pressure. It is known that the pore vapor pressure depends on the porosity of mortar [5, 12, 13]. Generally, high-strength concrete with a low W/C has low permeability and the water vapor cannot migrate easily through the pore structure. In other words, the reduction of W/C would enhance pore pressure [13]. That is the reason why the residual compressive strength of C045 specimen was higher than that of C035 specimen. Meanwhile, when C035PP specimen is exposed to high temperature, the PP fibers are melted at the temperature of 160 °C. Thus, the porosity of concrete containing PP fibers is increased and the water vapor pressure is mitigated [14,15]. Finally, the residual compressive strength of C035PP specimen is higher than that of C035 specimen.

3.3. Moisture transfer

The electrical resistivity at each depth of C035, C045 and C035PP specimens is shown in Figs 6-8, respectively. It was observed that the electrical resistivity at the depth of 7.5 mm from the exposed surface for all heated specimens were much higher than that of the unheated specimens. Meanwhile, the electrical resistivities at the depths of 27.5, 47.5, 67.5 and 87.5 mm from the surface for the heated specimens were lower than those for the unheated specimens, and those at the other depths for the heated specimens were almost the same as the unheated specimens.

Jansson [16], Ozawa and Morimoto [15], Anderberg [17] and Zdenek [18] reported that the free water in concrete is evaporated when the elevated temperature reaches to 100 °C and the evaporation process is continuing. Naturally, the conductivity is decreased at a low water content. Therefore, according to the result of the electrical resistivity of the heated specimens, it is found that the moisture at the depth close to the exposed surface (i.e. at the depth of 7.5 mm) for the heated specimens was evaporated out of the specimens during heating at the high temperature of approximate 230 °C. A part of water vapor migrated to the inside of the specimen whose temperature was lower than 180 °C, resulting in condensation of the vapor. That was the cause of the decrease in the electrical resistivity at the depths far from the exposed surface (i.e. at the depths of 27.5, 47.5, 67.5 and 87.5 mm). The moisture content in the deeper area than 100 mm from the exposed surface did not change. The temperature at those depths was lower than 80 °C, which was not enough for evaporation of water and the water vapor from the exposed surface could not reach to this area.

The electrical resistivity at every depth from the exposed surface of the heated specimen except for the depth of 7.5 mm was increased with time, and the electrical resistivity at the depth of 7.5 mm from the

Table 3 Rate of internal temperature increase

Name	Increasing rate at the depth from exposed surface (℃/min)		
	2.5 mm	20 mm	40 mm
C035	7.50	6.23	3.85
C045	6.47	5.13	2.84
C035PP	8.96	4.34	3.37

Table 4 Compressive strength of specimens

Name	Compressive strength (MPa) (S.D.)		
	28 days	58 days	
		Before heating	After heating
C035	66.98 (0.29)	75.01 (1.32)	56.10 (0.85)
C045	59.86 (0.80)	63.66 (2.23)	52.45 (1.92)
C035PP	69.20 (3.36)	82.48 (0.58)	70.52 (2.17)

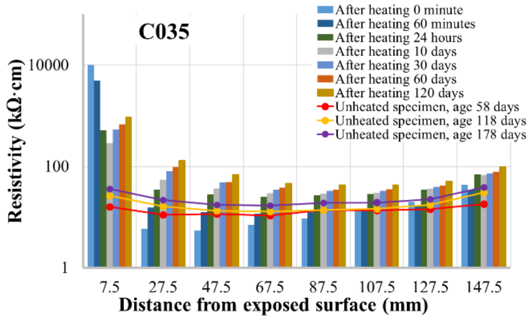

Fig. 6 Electrical resistivity of C035

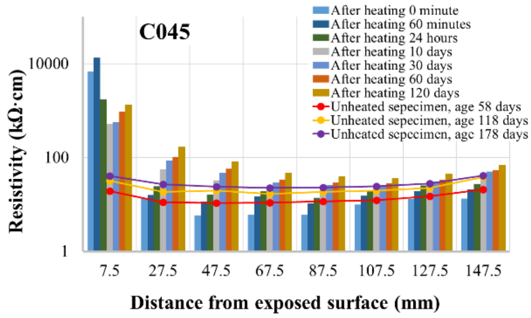

Fig. 7 Electrical resistivity of C045

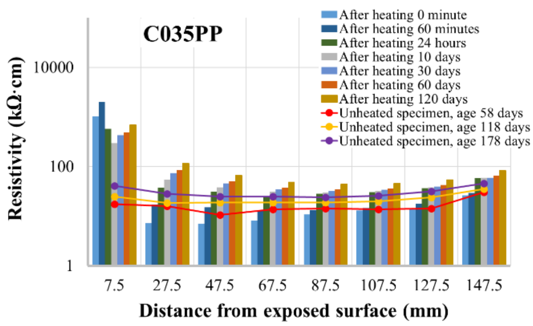

Fig. 8 Electrical resistivity of C035PP

surface was decreased for 10 days after heating. The electrical resistivity in the unheated specimens was also constantly increased with time.

The continuous increase in the electrical resistivity for 120 days for the unheated specimens showed that they were gradually drying at 20 °C and 60 %RH [19]. In the meanwhile, this tendency was also observed for the heated specimens, especially at the depth of approximate 0-50 mm from the exposed surface. This area had very low moisture content compared with the unheated specimen. However, in the case of the heated C035 specimen, it seems to be completely dry.

3.4. Carbonation depth

Fig. 9 shows the carbonation depths and carbonation rates of the heated and unheated specimens for C035, C045 and C035PP. Unheated C035 and C035PP specimens were not carbonated during this period, while carbonation of unheated C045 specimens was observed 1 week after exposed to CO_2. Concrete with a low W/C is more difficult to be carbonated than that with a high W/C because of dense microstructure of concrete [21]. The addition of PP fibers can also improve the carbonation resistance of concrete [22].

On the other hands, all heated specimens for C035, C045 and C035PP were carbonated one week after the start of accelerated carbonation test and the carbonation depth increased with the CO_2 exposure time. It indicates that CO_2 penetrated into the heated specimen more easily than into the unheated specimen, regardless of the W/C. The results of the compressive strength test showed the possibility of micro-cracks in concrete and the generation of pores due to the melting of PP fibers for the heated specimens, while the results of the moisture transfer measurement showed the formation of very low moisture condition at the depth closer to the exposed surface due to heating. Considering these results, it is supposed that micro-cracks and low moisture content accelerated carbonation of the heated specimens. The carbonation depth of C035PP specimens was almost the same as that of C035 specimen although the pores would be increased in C035PP specimens due to the melting of PP fibers. Melted PP may cover the hardened cement, resulting in contribution to the protection against carbonation.

3.5. Chloride penetration

The chloride penetration depth of the specimens is shown in Fig. 10. The chloride penetration depth of the unheated specimens for C035 and C035PP was not observed because of dense microstructure of concrete, while the chloride penetration depth of unheated C045 specimen at the age of 30 cycles was approximately 12 mm.

The chloride penetration depths of heated specimens for C035, C045 and C035PP were approximately 21, 31 and 25 mm at 30 cycles, respectively. Similar to the results of the carbonation test, the chloride penetration depths of the heated specimens were larger than those of the unheated specimens. However, the chloride penetration depth of the heated specimen for C035PP was larger than that for C035. The generation of pores due to the melting of PP fibers affected the chloride penetration. Besides, the rates of chloride penetration for the heated

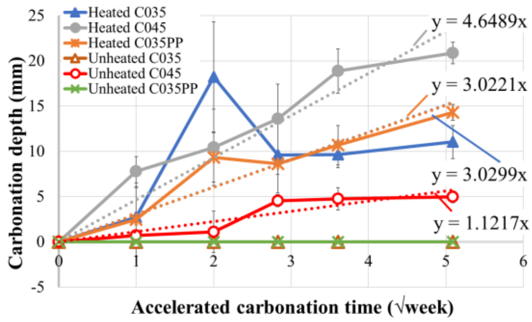

Fig. 9 Carbonation depth of specimens

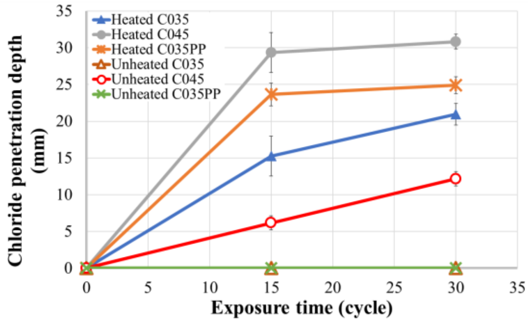

Fig. 10 Chloride penetration depth of specimens

specimens were different between 0-15 cycles and 15-30 cycles, while the chloride penetration depth of the unheated specimen for C045 was almost proportional to the cycle number. This must be related to the influence region of heating, which means the depth of micro-cracks. Also from the difference in the changes of the chloride penetration rates between C035 and C045, the influence region of heating may be different in both mixtures. From the internal temperature profile of C035PP specimen shown in Fig. 5, PP fibers up to the depth of 10 or more millimeters must have been melted. Therefore, chloride penetrated earlier in C035PP specimen than in C035 specimen up to the depth around 20 mm.

4. Conclusion

The conclusions from the experimental results obtained in this study are as follows:

(1) The compressive strengths of C035, C045 and C035PP after exposed to high temperature were reduced by 25, 18 and 15%, respectively.

(2) CO_2 can penetrate more easily into heated concrete than unheated concrete. Low moisture content and micro-cracks in heated concrete caused easier CO_2 penetration, while the melting of PP fibers did not affect it very much.

(3) Chloride can also penetrate into heated concrete than unheated concrete. Micro-cracks in heated concrete and the melting of PP fibers in heated concrete containing PP fibers caused easier chloride penetration.

The residual compressive strength of the heated concrete might be appropriate to use without repairing, but even so, its durability is worse than the unheated concrete, especially concrete with high W/C and concrete containing PP fiber.

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