- Technical Paper -

# INVESTIGATION ON THE CARBONATION RESISTANCE AND RECOVERY OF THE CONCRETE EXPOSED TO HIGH TEMPERATURE

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## ABSTRACT

The effects of cooling method and elapsed time after heated on the carbonation resistance of the concrete subjected to high temperature were investigated by an accelerated carbonation test. The results indicate that the carbonation depth of the concrete increased with raising the heating temperature for any cooling methods, and was smaller when the concrete was cooled in the air than by water. The longer the elapsed time after subjected to the high temperature, the lower the carbonation resistance. And the application of the performance-modifying agent (PMA) of concrete to the surface of heated concrete could improve the carbonation resistance of the concrete.

Keywords: concrete, carbonation resistance, recovery, cooling method, high temperature, performance-modifying agent

#### 1. INTRODUCTION

The properties of concrete deteriorate when it is subjected to a fire, because the chemical/physical transformations in aggregates and cement paste occur at high temperature. Fire-damaged concrete structures are generally repaired based on the strength and durability assessments to decide what the repairing methods should be used.

Up till now, the properties of concrete subjected to a fire have been widely studied. Some investigations have been focused on the mechanical behaviors of the concrete exposed to fire, such as the compressive strength, modulus of elasticity, and how to avoid the spalling [1-5]. It was reported that the mass of the concrete specimen reduces gradually as the temperature rises up to 800°C, but sharply reduced beyond 800°C [1]. Reference [4] concluded that concrete exposed to up to 100°C is normally considered as healthy. At 300°C, strength reduction would be in the range of 15-40%. Above 400°C, concrete lost their strength rapidly and the rate of strength losses was more for high strength concrete. At 550°C, reduction in compressive strength would typically range from 55% to 70% of its original value. The effects of high temperatures are generally visible in the form of surface cracking, and for a rapid heating rate, spalling will occur because of a steep thermal gradient between the surface and the inside of heated concrete.

Other investigations have been focused on the microcosmic changes in the chemical composition and physical structure of the concrete exposed to high temperature [6,7]. The main chemical process resulted in the internal damage of concrete is an alteration of hydrates. Below 200°C, possible evolution of hydration of anhydrous is pointed out. The maximum transformation occurs primarily in the hardened cement

paste starting from the dissociation of calcium hydroxide at 400°C. When the temperature surpasses  $500^{\circ}$ C, the alterations produced by high temperature are more evident. At this temperature level, most changes experienced by concrete can be considered irreversible. At 750°C, the calcium silicate hydrate (C-S-H) gel has completely disappeared.

In the references [8-11], an attention was put on the pore structure of concrete after high temperature exposure, which helps to understand the mechanism of concrete deterioration. The changes of pore amount and volume after high temperature exposure, proved by means of mercury porosimetry, would cause an increase in concrete permeability, and worsen the permeabilityrelated durability.

Due to these changes, concrete gradually and sometimes sharply loses its mechanical strength and durability. And the durability loss is usually higher than the mechanical strength loss in concrete. However, there is very few research works focused on the durability loss of the concrete exposed to high temperature, which reduces the remaining service life of the structure very rapidly. It was reported that high-strength pozzolanic concretes had a severe loss in permeability-related durability than the compressive strength loss [12]. Poon et al. [13] reported that all high strength concrete specimens had a very low permeability at 20°C. However, as the temperature was increased, a severe loss in impermeability was observed. Janotka and Bagel indicated that the permeability of concrete increased greatly with the increase in the temperature [14].

As one of the major aspects of the durability of concrete, carbonation is a complex physicochemical process that slowly deteriorates reinforced concrete structure in the course of time. The deterioration is generally caused by a reduction in the alkalinity of

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concrete due to a chemical reaction between  $CO_2$  from the air and the hydration products of cement. The corrosion of the reinforced bars in the concrete occurs when the concrete alkalinity becomes low.

There are many literatures that deal with carbonation resistance of concrete at normal temperature. Several mathematical models have been developed to predict the carbonation depth of concrete [15-19]. The concrete, which suffered a fire to cause thermal micro-cracks and the alteration in chemical composition, may have a different carbonation characteristic from that of normal concrete. However, there exist few literatures that refer to the effect of high temperature on carbonation resistance and post-fire-recovery of concrete [20]. We do not yet find the investigation on the effect of cooling method and post-fire-curing condition on carbonation resistance of concrete exposed to high temperature.

In this study, we investigate the extent and influencing factors of the carbonation of concrete exposed to high temperature. The concrete specimens are exposed to high temperatures of  $200^{\circ}$ C,  $450^{\circ}$ C and  $750^{\circ}$ C for 150min, and then cooled in the air or by water jet. The accelerated carbonation tests are performed after the concrete specimens exposed to the high temperatures are cured in the air at room temperature for 0 day, 4 weeks, 7 weeks, and 9 weeks. Carbonation depths are measured after the CO<sub>2</sub> exposure in the accelerated carbonation chamber for 7 days.

## 2. TEST PROGRAMS

## 2.1 Materials and Preparation of Specimens

The cement used in this study was ordinary portland cement, of which the specific gravity is 3.16 g/cm<sup>3</sup>. Coarse aggregate of crushed stone with a maximum size of 20mm was used. The density at saturated surface dry condition, and water absorption ratio of coarse aggregate were 2.73 g/cm<sup>3</sup>, and 0.40%, respectively. Fine aggregate was sea sand with density of 2.59 g/cm<sup>3</sup> at saturated surface dry condition, water absorption ratio of 1.60%, and fineness modulus of 2.57. Water reducing admixture air-entraining (AE) agent was also used in a dosage of 1.1% by mass of cement. Also, polypropylene fiber with a length of 12 mm at 0.2% per 1 m<sup>3</sup> concrete was used to improve the spalling resistance of concrete during heating.

Mix proportions of concrete used were 1 (cement) : 0.50 (water) : 2.42 (sand) : 2.78 (coarse aggregate) by mass. Unit weight of cement is 346 kg/m<sup>3</sup>. 44 concrete cylindrical specimens with diameter of 100mm and length of 200mm were produced.

After demoulding at 1 day, the specimens were cured in  $20^{\circ}$ C water for 7 days, and then moved to a room to cure naturally for 56 days. The compressive strength of the concrete at 28 days is 40MPa.

# 2.2 Heating and Cooling Regimes

The concrete specimens were heated up to different temperatures in an electric furnace, of which

inside temperature was controlled to follow the ISO834 standard fire temperature curve. The heating temperatures were monitored by thermocouple set up in the electric furnace. After the concrete suffered to the heating at each predetermined high temperature level for 2.5 hours, they were taken out from the electric furnace and cooled down to the room temperature in the air or by a water jet.

After being cooled, we applied the performance -modifying agent (PMA) to the surfaces of some of the specimens with brush. The PMA is viscous liquid, usually used to the surface of concrete to strengthen it and lower its water permeability. The PMA can react with Ca(OH)<sub>2</sub> in concrete to form CSH when the water exists. The reaction product fills into the pores and the cracks in the concrete. The surfaces of the specimens were moistened with water before applying the PMA. Then the surfaces were sprinkled with water about 1 lit/m<sup>2</sup> after the PMA on the surfaces was dried naturally. The total amount of used PMA was about 0.3 kg/m<sup>2</sup>. The specimens with the application of the PMA were cured with sprinkling water about 1 lit/m<sup>2</sup> twice every day for 7 days.

The accelerated carbonation tests were carried out at 0 week, 4 weeks, 7 weeks and 9 weeks after exposed to high temperature.

# 2.3 Accelerated Carbonation Testing

The diffusion rate of carbon dioxide mainly depends on the moisture and the temperature of environment. The rate of neutralizing is usually slow due to low  $CO_2$  concentration. Hence, the accelerated carbonation test with higher  $CO_2$  concentration is practically used to estimate the carbonation depth.

At the age of scheduled curing time, the specimens were directly put into the accelerated carbonation apparatus named Asahi Neutralization Test Chamber with environmental conditions of  $20^{\circ}$ C and 60% R.H.

After all the concrete specimens were exposed to  $CO_2$  of 10% concentration for one week. Then, they were taken out and the depths of carbonation were immediately measured by spraying onto the surface of a freshly broken concrete specimen, which has been cleaned of dust and loose particles with a pH indicator that was 1% solution of phenolphthalein in 70% ethyl alcohol.

The phenolphthalein test is a simple and rapid method of measuring carbonation depth. Phenolphthalein is a colorless acid, but it will turn purple when the pH is above a certain value in the range of 8.4-9.8, that is, higher alkaline areas of concrete turn vivid purple. If getting discolored, the carbonation has taken place, and thus the depth of the carbonation is the thickness of the discolored concrete layer.

An average carbonation depth was taken from the broken surfaces. For each specimen, at least four measurements were made on each of the splitting surfaces, excluding the places where were blocked by aggregate particles. The average value of the eight measurements for two splitting surfaces was recorded as the final carbonation depth of the concrete.

## 3. TEST RESULTS AND DISCUSSION

Figs. 1-4 demonstrate the effects of various parameters on the carbonation depth of the concrete specimens.

## 3.1 Effect of Temperature

The test results of the carbonation depth for the concrete specimens exposed to different temperatures are shown in Fig. 1. It is observed from this figure that the carbonation depth increased with the increase of the heating temperature.



Fig.1 Effect of temperature on the carbonation depth

The increase of the carbonation depth of the specimens heated up to  $200^{\circ}$ C was smaller than to  $450^{\circ}$ C and  $750^{\circ}$ C. The reduction in carbonation resistance is mainly attributed to a decline in the permeability with increasing temperature. The higher the heating temperature, the greater the carbonation depth.

Although the increment of carbonation depth of the specimen subjected to high temperature of 200°C was rather small, but a remarkable increase of the carbonation depth could be observed in comparison with that of the specimen not suffered the high temperature. This can be interpreted through the evaporation of free water, which leads to many gas channels in the concrete, but they are not sufficient to notably reduce the permeability.

High temperature of 450 °C leaded to a great increase in the carbonation depth. It may be considered that with increasing temperature, the decomposition of hydrates and destruction of the gel structure occur, and lead to the changes of the micro pore structure of concrete.

The heating at the high temperature of  $750^{\circ}$ C resulted in a further increase of carbonation depth. The depth of carbonation was up to 50mm, that is, the concrete was completely neutralized. Compared with the carbonation depth at 450 °C there was an extremely great increase. This is probably because that a very great increase in permeability would take place above

 $750^{\circ}$ C. This is attributed to the formation and connection of pores and gas channels in large quantities.

#### 3.2 Effect of Cooling Method

Fig. 2 shows the carbonation depths of the concretes cooled by different methods after exposed to high temperatures. It is clear that the carbonation depth of the concretes was greatly affected by the cooling method.

When heating temperature was 200 °C, water cooling reduced slightly the carbonation resistance, compared to the air cooling. However, the effect of cooling method was remarkable when the concretes were exposed to 450 °C. Also, all the specimens, no matter cooled in the air or by water jet, got carbonated completely after they were exposed to 750 °C.

The fact that the carbonation depth of concrete cooled by water was larger than that of cooled in the air can be attributed to two reasons. First, sudden cooling produced many micro-cracks in concrete. When the specimens were immediately cooled by water jet right after exposed to  $200^{\circ}$ C or  $450^{\circ}$ C, the temperature of the surface of the specimen dropped suddenly, while the inside temperature was still high. This would result in many cracks in out side of the concrete.

Second, at the temperature of 200°C, all the free water and part of the bound water have escaped from the concrete in form of vapor. At 450°C, water comes out from the dehydrated portlandite. At 750°C, the calcite decomposes to generate CO<sub>2</sub>. However, if cooled by water, the dehydrated cement paste in the specimens would rehydrate, and the CaO would participate in rehydration process with water to form new portlandite, which expand to aggravate the damage of the pore structure in concrete. It becomes easy to react with CO<sub>2</sub> after CaO transforms to Ca(OH)<sub>2</sub>. In addition, the coarsened pores were filled with water in case of the water cooling, which accelerates CO<sub>2</sub> to penetrate into concrete and dissolve in the pore solution, where reacts with the Ca<sup>2+</sup>/OH<sup>-</sup> to form CaCO<sub>3</sub>.

In short, water cooling reduced carbonation resistance of heated concrete, no matter what temperature the heating was at. Hence, fire fighting with water would further harm the durability of concrete structure suffered to a fire.

### 3.3 Effect of Elapsed Time after Heated

The influence of elapsed time after heated on the carbonation depth of concrete is demonstrated in Fig. 3. It can be seen that the varying trend of the carbonation depth with the elapsed time was dependent on the extent of high temperature-damage in the concrete.

The carbonation depth of the specimens subjected to the temperature of  $200^{\circ}$ C decreased a little with the elapsed time. This shows that to some extent, the carbonation resistance of the concrete subjected to  $200^{\circ}$ C recovered with post-fire-time. Because the rehydration of cement, which increases with time decreases the porosity and permeability of concrete heated at  $200^{\circ}$ C, which reduces CO<sub>2</sub> diffusion into the







Fig.3 Effect of elapsed time after heated on the depth of carbonation

## concrete specimens.

However, it can be seen from Fig. 3 that the longer the elapsed time after exposing the concrete specimen to the temperature of  $450^{\circ}$ C, the greater the carbonation depth. The heating at  $450^{\circ}$ C caused more severe damage to concrete than  $200^{\circ}$ C, so that the

carbonation resistance cannot recover as the case of 200°C, which was also observed in the case of 750°C. Moreover the carbonation resistances of the specimens cooled by water jet were lower than those cooled in the air, because that the specimens cooled by water jet were damaged more seriously.

#### 3.4 Effect of Application of PMA

As shown in Fig. 4, the use of the PMA had a significant effect on the improvement of the carbonation resistance of the concrete subjected to high temperatures. The carbonation depth of the specimens applied the PMA was substantially smaller than that of those without using the PMA.

The application of the PMA greatly reduced carbonation depth of the concrete specimens not suffered high temperature, exposed to  $200^{\circ}$ C, and  $450^{\circ}$ C. It was due to that the reaction products of the PMA and the constituents in the concrete obstruct the diffusion of CO<sub>2</sub> into the concretes.

However, if exposed to 750°C, even applying the PMA to the surfaces of the specimens, the carbonation depths were still 50 mm because the reaction products of the PMA cannot repair perfectly the cracks in the specimens, caused by the high temperature, which make  $CO_2$  to diffuse into the specimens easily. And maybe the alkalinity of concrete already lost completely during heated at 750°C.

In short, for the concrete exposed to temperatures



Fig.4 Effect of application of PMA on the depth of carbonation

 $200^{\circ}$ C and  $450^{\circ}$ C, the PMA can increase the carbonation resistance and then improve the durability of reinforced concrete. However, it is useless for the concrete exposed to temperatures of  $750^{\circ}$ C and above.

## 3. CONCLUSIONS

In this study, we investigated the carbonation resistance of the concrete after exposed to fire, and the influencing factors of its recovery by measuring the carbonation depth. The test results show that heating temperature, cooling method, elapsed time after heated, and the application of the performance modifying agent of concrete, produced a large effect on carbonation resistance of heated concrete. The obtained conclusions are as follows.

(1) The carbonation depth of concrete increased with raising the heating temperature. The increase of the carbonation depth of the specimens heated up to 200°C was smaller than to 450°C and 750°C. The concrete exposed to 750°C was neutralized completely.

(2) Compared to the concrete cooled in the air, a remarkable reduction in the carbonation resistance was observed when the concrete, which was heated at 200 °C and 450 °C, was cooled by water.

(3) The recovery degree of the carbonation resistance changes with the elapsed time after heated. The carbonation resistance of the concrete subjected to high temperature of  $200^{\circ}$ C increased slightly with elapsed time after heated. However, if the heating temperature was above  $450^{\circ}$ C, the carbonation resistance decreased with the elapsed time.

(4) PMA can improve the carbonation resistance of the concrete specimens that not suffered high temperature, exposed to  $200^{\circ}$ C, and  $450^{\circ}$ C. The carbonation depth of these concretes applied the PMA were certainly smaller than that of the concretes without using the PMA. However, PMA is useless for the concrete exposed to temperatures of  $750^{\circ}$ C.

As a further work of this study, we continue to examine the influences of elapsed time after heated and the application of the PMA on the carbonation resistance of concrete exposed to high temperature.

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