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Repair of Fire-Damaged Concrete: Improvement of Carbonation Resistance

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ABSTRACT

The effects of heating temperature, cooling method and elapsed time after heating on the carbonation resistance and recovery of fire-damaged concrete was investigated. The concrete specimens were heated to 750 °C, followed by an accelerated carbonation test. Some of the specimens were embrocated with a performance-modifying agent (CS) before the accelerated carbonation test. The phenolphthalein test was conducted to measure the carbonation depth. 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 recovery of carbonation resistance was found when the temperature was lower than 450 °C, however, the longer the elapsed time after being subjected to the higher temperatures above 450 °C, the lower the carbonation resistance of the heated concrete.

INTRODUCTION

The mechanical properties and durability of concrete deteriorate when it is subjected to a fire, because the chemical composition and physical structure transformations in aggregates and cement paste occur at high temperature. How to repair fire-damaged concrete structure should be decided based on the strength and durability assessments. Up till now, the properties of concrete subjected to a fire have been widely studied. Some of them are about the mechanical behaviors of the concrete exposed to fire, such as the compressive strength, modulus of elasticity, and how to avoid the spalling [Arioz 2007; Khandakar 2006; Han et al. 2009; Georgali and Tsakiridis 2005; Hertz and Sorensen 2005]. It was reported that the mass of concrete reduces gradually as the temperature rises up to 800 °C, but sharply reduces above this temperature [Arioz 2007]. Reference [Georgali and Tsakiridis 2005] concluded that concrete exposed to up to 100 °C is still healthy. At 300 °C, the strength of the concrete would reduce 15-40%. Above 400 °C, the concrete lost its strength rapidly and the reducing rate of strength was greater for high strength concrete. At 550 °C, the reduction in compressive strength would typically range from 55% to 70% of its initial value. The effects of temperature are generally found in the form of surface cracking, and for a rapid heating rate, the spalling would occur.

Others have been focused on the changes in the chemical composition and physical structure of the concretes exposed to high temperature [Alonso and Fernandez 2004; Kim et al. 2002]. The main chemical process resulted in internal damage of concrete is an alteration of hydrates. Below 200 °C, possibly anhydrous hydration increases. 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 °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 [Chan et al. 1999, 2000; Lion et al. 2005; Rostasy et al. 1980], 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 permeability- related durability.

Due to these changes, concrete gradually and sometimes sharply loses its mechanical strength and durability. And the durability loss of heated concrete is usually higher than its mechanical properties. However, there is very few research works on the durability loss of the concrete exposed to high temperature, which shorts the 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 [Poon et al. 2001]. Poon et al. [Poon et al. 2003] 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 [Janotka and Bagel 2003].

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 concrete due to a chemical reaction between CO_2 from the air and $Ca(OH)_2$ - a hydration product of cement. The corrosion of the reinforced bars in the concrete would occur 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 [Wang and Lee 2009; Papadakis et al. 1991; Isgor and Razaqpur 2004; Roy et al. 1999; Lo et al. 2008]. 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 or improvement of concrete [Suzuki et al. 2008]. The investigation on the effects of cooling method and post-fire-curing method on the carbonation resistance of concrete exposed to high temperature was not found. This is an important problem to be solved. If the carbonation resistance of the fire-damaged concrete can recovered by itself or by using admixture, it will greatly simplify the repairing of concrete structures exposed a fire.

In this study, we investigate the extent and influencing factors of the carbonation of concrete exposed to high temperature. The concrete specimens are heated to different temperatures and lasted for 150 minutes. Then, they are cooled in the air or by water jet. To study the carbonation depth of the concrete specimens before the accelerated carbonation test, the carbonation depths of concrete specimens are measured when the specimens are cooled to room temperature. 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, 28 days, 56 days, and 90 days. Carbonation depths are measured after the CO_2 exposure in the

accelerated carbonation chamber for 7 days. The objective of the present study was to investigate the application of CS on fire-damaged concrete to increase carbonation resistance of the concrete itself. The carbonation resistance of concrete specimens coated with CS to protect against carbonation was compared with the carbonation resistance of the uncoated plain concrete specimens.

EXPERIMENTAL INVESTIGATION

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^3 . Coarse aggregate of crushed stone with a maximum size of 20 mm was used. The density at saturated surface dry condition, and water absorption ratio of coarse aggregate were 2.73 g/cm^3 , and 0.40%, respectively. Fine aggregate was sea sand with density of 2.59 g/cm^3 at saturated surface dry condition, water absorption ratio of 1.60%, and fineness modulus of 2.57. Water reducing admixture air-entraining agent was also used at a dosage of 1.1% by mass of cement. Also, polypropylene fiber with a length of 12 mm at 0.1% (in volume fraction) per cubic meter of concrete was used to prevent concrete from spalling during heating.

Mix proportions of concrete used were 1 (cement) : 0.50 (water) : 2.01 (sand) : 2.48 (coarse aggregate) by mass. Unit weight of cement is 370 kg/m^3 . The concrete cylindrical specimens with diameter of 100mm and length of 200mm were produced.

The specimens were demolded 24 hours after the casting and cured in a water tank at 20 °C for 28 days, and then kept in a room to cure naturally for 56 days. The compressive strength of the concrete at 28 days is 40MPa.

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. At the same time, the temperatures in the concrete specimen were monitored by thermocouples to ensure that the inside temperature of the concrete also rises up to the desired temperature. After suffered to the predetermined high temperatures for 2.5 hours, the concrete specimens were taken out from the electric furnace and cooled down to the room temperature in the air or by a water jet for 15 minutes.

Properties of performance-modifying agent (CS)

In order to develop a technology to improve the properties of heated concrete, after the heated specimens were cooled, some of them were embrocated with the CS on their surfaces, using brush.

The CS is a patented product with silicate system material produced in Japan. It is a viscous liquid, and it is usually used on the surface of concrete to strengthen it or repair cracks to lower the water permeability. The CS reacts with $Ca(OH)_2$ and others in concrete to form C-S-H when the water exists. The reaction product fills into the pores and cracks in the concrete. The reaction mechanism of CS is shown in figure 1.

The surfaces of the specimens were moistened with water before applying the CS. Then the

surfaces were sprinkled with water about 1 lit/m^2 after the CS on the surfaces became dry naturally. The total amount of embrocated CS was about 0.3 kg/m². The specimens with the application of CS were cured with sprinkling water about 1 lit/m^2 twice every day for 7 days.



Fig.1. Effect Reaction Mechanism of CS

The reactions in figure 1 are as follows:

 $\begin{array}{ll} \mbox{Reaction 1:} \\ \mbox{Ca(OH)}_2 + H_2O + CO_2 \rightarrow Ca(OH)_2 + H^+ + HCO_3 \rightarrow CaCO_3 + 2H_2O & (1) \\ \mbox{Reaction 2:} \\ \mbox{Na}_2SiO_3 \cdot nH_2O + Ca(OH)_2 + nH_2O \rightarrow CaSiO_3 \cdot nH_2O + 2NaOH & (2) \\ \mbox{Reaction 3:} \\ \mbox{2}{3CaO \cdot SiO}_2 + 6H_2O \rightarrow 3CaO \cdot 2SiO_2 \cdot 3H_2O + 3Ca(OH)_2 & (3) \\ \end{array}$

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 (10%) is practically used to shorten the test period.

In order to measure the variation of carbonation depth of concrete with elapsed time, the accelerated carbonation tests were carried out at 0 day, 28 days, 56 days and 90 days after exposed to high temperature. At the age of scheduled curing time, the specimens were directly put into the accelerated carbonation apparatus, named Asahi Neutralization Test Chamber, at a temperature of 20 $^{\circ}$ C and a relative humidity of 60%.

After the concrete specimens were exposed to CO_2 at a concentration of 10% for 7 days, 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.

For each specimen, 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.

RESULTS AND DISCUSSIONS

Effect of heating temperature

The carbonation depths of the concrete specimens exposed to different temperatures are shown in figure 2, which were measured immediately after cooled to room temperature. It can be seen that the concrete has been carbonated after it exposed to high temperature. When the specimens were cooled in the air, the carbonation depth increased with the increase of the heating temperature. However, the carbonation depths of the concrete specimens were 0 mm when they were cooled by water jet. This is maybe because pH kept higher, benefiting from the re-hydrating, the Ca(OH)₂ reformed after water cooling.

Figure 2(b) shows the carbonation depths of the concrete specimens, which were placed in the accelerated carbonation apparatus for 7 days. From figure 2(b), it is clear that the carbonation depths of the concrete increased with heating temperatures for both of the cooling methods. Although the increment of carbonation depth of the specimen subjected to high temperature of 200 °C was rather small, compared to other specimens suffered to the high temperature above 200 °C, but a remarkable increase of the carbonation depth could be observed in comparison with the normal specimen. 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.

And the increment of the carbonation depth of the specimens heated up to 200 °C and 300 °C was smaller than to 450 °C, 600 °C and 750 °C. The carbonation increased clearly from the heating temperature of 450 °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.

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 600 °C and 750 °C resulted in a further increase of carbonation depth. The depth of carbonation was up to 50mm, that is, the concrete was completely neutralized. This is probably because that a very great increase in permeability would take place above 750 °C, due to the formation and connection of pores and gas channels in large quantities.



Fig.2. Effect of Temperature on the Carbonation Depth

Effect of cooling method

Figure 3 shows the carbonation depths of the concrete specimens cooled by different methods

after exposed to high temperatures. From this figure we can see that, the carbonation depth of the specimens cooled by water jet was greater than those cooled in the air for the same heating temperature. The carbonation resistance of the concrete specimens cooled by water jet is obviously lower than that of those cooled in the air for all the elapsed time.



Fig.3. Effect of Cooling Method on the Carbonation Depth

When heated at 200 °C and 300 °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 and 600 °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 has two reasons. First, sudden cooling produces many micro-cracks in concrete. When the specimens were immediately cooled by water jet right after exposed to 200 °C or 300 °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 and 300 °C, all the free water and part of the bound water have escaped from the concrete in form of vapor. At 450 °C and 600 °C, some water comes out from the dehydrated portlandite. At 750 °C, the calcite decomposes to generate CO_2 . However, if the concrete cooled by water, the dehydrated cement paste 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_2 after CaO transforms to $Ca(OH)_2$. In addition, the coarsened pores were filled with water in case of the water cooling, which accelerates CO_2 to penetrate into concrete and dissolve in the pore solution, where reacts with the Ca^{2+}/OH^- to form $CaCO_3$. In short, water cooling reduced carbonation resistance of heated concrete, no matter at what heating temperature. Hence, fire fighting with water would further harm the durability of concrete structure.





Fig.4. Depth of Carbonation of the Specimens Embrocated CS on Their Surfaces

As shown in figure 4, the use of the CS had a significant effect on the improvement of the carbonation resistance of the concrete subjected to high temperatures.

It is obviously that, for both of the two cooling methods and all of the elapsed times after heated, compared to the carbonation depths of the concrete specimens uncoated with CS, the carbonation depths of the concrete specimens applied the CS were substantially smaller after exposed to temperatures of $200 \,^{\circ}$ C, $300 \,^{\circ}$ C, $450 \,^{\circ}$ C and $600 \,^{\circ}$ C.

The application of the CS also greatly reduced carbonation depth of the concrete specimens not suffered high temperature. It was due to that the reaction products, inducing by the CS, obstruct the diffusion of CO_2 into the concretes.

However, if exposed to 750 °C, even applying the CS to the specimens' surfaces, the carbonation depths were still 50 mm, probably because the alkalinity of concrete already lost completely during heated at 750 °C, and the re-hydrating reactions caused by the CS do not easily take place. In short, for the concrete exposed to high temperatures 200 °C, 300 °C, 450 °C and 600 °C, the CS can improve the carbonation resistance. However, it is invalid for the concrete exposed to temperatures of 750 °C and above.

Effect of elapsed time after heated

The influence of elapsed time after heated on the carbonation depth of concrete is demonstrated in figure 5. It can be seen that the varying trend of the carbonation depth with the elapsed time was dependent on the heating temperature and cooling method. The CS also played an important part on the recovery of the carbonation resistance of the concrete specimens subjected to high temperatures.

The carbonation depth of the specimens, heated at 200 °C and 300 °C decreased a little with the elapsed time. It is suggestive that to some extent, the carbonation resistance of the concrete subjected to temperatures below 300 °C can recover naturally with time. Because the re-hydrate would decrease the porosity and permeability of concrete heated at 200°C and 300 °C. Because the concrete specimens cooled by water were damaged seriously than those cooled in the air as stated above, the carbonation resistance of the water-cooled specimens recovered slowly than those cooled in the air. This consideration also may be applied to the concrete specimens embrocated with CS. Although the CS was embrocated to the concrete specimens, the carbonation depths of the seriously damaged concrete specimens recovered less than those damaged slightly.

However, it can be seen from figure 5 that the carbonation depth of the concrete specimens heated at 450 °C did not reduce with the elapsed time. It means that, when the heating temperature rose up to 450 °C, the carbonation resistance can't recover as those heated at 200 °C and 300 °C. The reason is that the heating at 450 °C caused more severe damage, including chemical and physical transforms, than at 200 °C and 300 °C.

The carbonation resistance can't recover as the case of $300 \,^{\circ}$ C, which was also observed in the case of $600 \,^{\circ}$ C. The carbonation depth of the concrete specimens heated at the temperature of $600 \,^{\circ}$ C increased with the elapsed time.

When the concrete specimens were heated at the temperature of $750 \,^{\circ}$ C, the carbonation depths of the specimens kept at 50 mm, and did not vary with the elapsed time even if the CS was used.

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.



Fig.5. Effect of Elapsed Time after Heated on the Depth of Carbonation

CONCLUSIONS

In this study, for developing repairing technology for fire-damaged concrete, the carbonation resistance of the concrete exposed to fire was investigated, the accelerated carbonation tests were carried out for the concrete exposed to different temperatures and then cooled in the air or by water, the influencing factors of its recovery and the effects of embrocating the performance-modifying agent were discussed by measuring the carbonation depth. The obtained conclusions are as follows.

(1) The carbonation depths of all the concrete cooled to room temperature by water were nearly 0mm. That is because the value of pH is kept higher due to the $Ca(OH)_2$ reformation after water cooling.

(2) The carbonation depth of concrete increased with raising the heating temperature. The carbonation depth of the specimens heated up to 200 °C and 300 °C were smaller than to 450 °C, 600 °C and 750 °C. The concrete exposed to 750 °C was neutralized completely.

(3) Compared to the concrete cooled in the air, a remarkable reduction in the carbonation resistance was observed when the concrete was cooled by water for any of the heating temperatures. The difference in the carbonation resistance between the two cooling methods is more obvious when the heating temperature was above $450 \,^{\circ}$ C.

(4) CS could improve the carbonation resistance of the concrete specimens if heating temperature is not higher than 600 $^{\circ}$ C. The carbonation depths of the concretes embrocated with the CS were certainly smaller than those without using the CS.

(5) The recovery degree of the carbonation resistance varies with the elapsed time after heated. The carbonation resistance of the concrete subjected to temperature of 200 °C and 300 °C increased slightly with elapsed time after heated. However, if the heating temperature was above 450 °C, the carbonation resistance decreased with time.

As a further work of this study, we will continue to examine the influences of lasting time of high temperature and the application of the CS on the carbonation resistance of heated concrete. In order to improve the carbonation resistance of the fire-damaged concrete, the dosage of CS and the curing conditions will also continue to discuss.

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