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Relationship between degradation and self-healing behavior in high strength mortar exposed to high temperatures (up to 500 °C)

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High-strength concrete exposed to fire is prone to strength reduction and possible explosive spalling due to thermo-mechanical and thermo-hydral processes; however, recovery is possible under water re-curing depending on the degree of fire damage. This research investigated the relationship between degradation and self-healing capability by examining the surface microstructure of high-strength mortar after fire in order to explore re-curing as a new repair method. Morphology properties and the shape of external and inner pores in the specimens were examined by microscopy, SEM-EDS, TG-DTA, and MIP after heating. The results show that degradation is driven by the interaction of the dehydrated zones at the surface, and spalling at the microstructure level can be attributed to build up of vapor pressure in entrained air pores. Self-healing capability was clearly observed in the dry/dehydrating and quasi-saturated zones, but is limited in dry/dehydrated, sintered areas. From these results, utilization of the dry/dehydrating and quasi-saturated zones may have high potential for a new repair method for fire-damaged concrete.

Key words: Self-healing, Degradation, Pore pressure, Fire-damaged concrete.

Introduction

Concrete generally demonstrates good resistance to high temperature exposure compared with other building materials, and has been widely used for high temperature applications. However, it does undergo a loss of performance, such as decreased strength and spalling, depending on exposure time and temperature. Explosive spalling in particular has been observed inconsistently in laboratory tests due to the large number of variables which potentially affect its mechanism [1], as well as a lack of general guidelines for fire testing to provide a unified approach for measuring the effects of these variables. Kalifa *et al*. [2] proposed a degradation mechanism involving both thermo-mechanical processes related to thermal dilation gradients in the mortar and thermo-hydral processes due to mass transfer (air, vapor, and liquid water) in the pore network. The build-up of pressure in concrete under heating exposure is illustrated in Fig. 1. As heat flux drives water vaporization, the surface becomes a dry/dehydrated zone-a brittle layer composed of sintered material which cannot undergo re-curing. In the dry/dehydrating zone, evaporation of free and chemically-bound water is occurring but the material has not yet sintered, and the quasi-saturated zone contains water under heating. Degradation of high-strength concrete has been found to be more severe than normal-strength concrete due to increased loss of strength and higher occurrence of explosive spalling, which may be attributed to the low permeability of low water-cement ratio concretes and leads to increased pore pressure and thermal stresses. Build-up of pore-pressure is driven by "moisture clog spalling," in which water vapor migration under heating generates pore pressure which, when combined with thermal processes, results in spalling when the tensile strength of the matrix is exceeded. [3, 4]

Repair of fire-damaged concrete is necessary to restore degraded performance and commonly involves the removal of damaged areas and their replacement

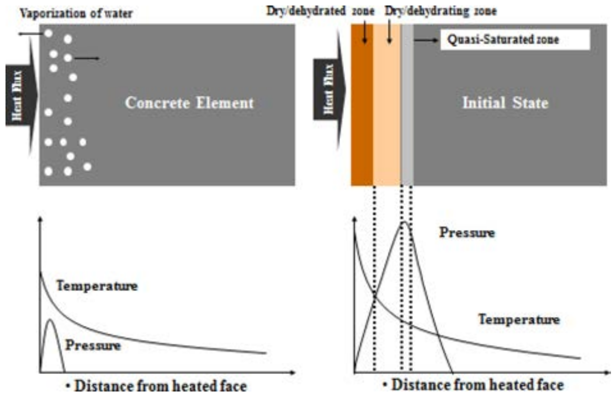

Fig. 1. The concept of the build-up of pressure on concrete by external heating (adapted from Kalifa *et al.*) [2].

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with fresh concrete or a patching material [5]. However, past research has found that re-curing fire-damaged concrete in water can restore strength and durability through the re-growth of hydration products [6, 7], development and filling of pore structure [8], and healing of cracks [9]. High-strength concrete was also found to have better recovery under re-curing due to its dense microstructure [9, 10, 11]; however, as discussed earlier, the degradation of high-strength concrete is more severe due to thermo-hydral and thermo-mechanical mechanisms, which may significantly reduce the repair effect due to re-curing. Therefore, the interaction between degradation and self-healing behavior under re-curing conditions should be clarified to further understand the potential for re-curing as a repair method.

In this paper, a study on the degradation behavior is presented in order to clarify the self-healing behavior of fire-damaged high-strength mortar during re-curing [12]. Mortar was selected for this investigation to focus on the microstructure behavior and self-healing in the cement mortar matrix. The first part investigates the degradation behavior by examining the surface microstructure of zones with different dehydration levels and considers the deterioration mechanism in terms of solid-state-sintering of entrained pores. The behavior of entrained air formed by the usage of admixtures and the local stress incompabilities between the cement paste and aggregates are also investigated by microscopy. The second part deals with self-healing behavior of fire-damaged high-strength mortar under water supply considering the differing dehydration zones. The self-healing behavior is then connected to recovery of strength and porosity as observed in an additional study.

Experimental Program

Mortar specimens

High-strength cement mortar was prepared using ordinary Portland cement (Japan Type I) at a water-binder ratio of 0.35 and Fujigawa river sand, with a maximum particle size of 4.75 millimeters, at a sand-cement ratio of 1.8. Air-entraining and super plasticizer admixtures were also utilized to satisfy workability requirements. Beam specimens (40 mm × 40 mm × 100 mm) were demolded 24 hours after casting and placed under water for 14 days at 20 °C, then air-cured at 20 °C and 60% relative humidity (RH) until high-temperature exposure at 28 days. Compressive strength at 28 days was 66.9 MPa.

Fire exposure and post-fire re-curing conditions

Specimens were exposed to high temperatures using an electric furnace. As this furnace does not have a control mechanism for the rate of heat increase, the furnace was preheated to the target temperature before beginning exposure. The temperature was set at 500 °C for one hour in order to clarify the shrinkage of cement paste and local stress behavior by mass loss of $Ca(OH)_2$ as well as free water, and was selected based on past research which found that damage at temperatures beyond 500 °C cannot be fully recovered [13]. Specimens were allowed to cool at room temperature and conditions for one hour after exposure, and then re-cured in water-submerged conditions.

Estimation methods of transport properties

Fig. 2 shows the size of pores in concrete and their methods of measurement. This investigation is focused on super plasticizer-entrained air, which falls between 10 nanometers to several millimeters, so microscopy was selected for observation. SEM (scanning electron microscope) with EDS detector were utilized to investigate the morphology and shape of fire-damaged specimens and the size of the rehydration products in order to clarify the degradation mechanism and self-healing behavior. Three-dimensional (3D) digital microscopy images were also acquired using 3D visualization software in order to identify connected pores in entrained air. Thermo-gravimetric differential thermal analysis (TG-DTA) was used to analyze the mass transport of cement paste according to degradation area, and mercury intrusion porosimetry (MIP) was conducted to clarify the self-healing behavior. All specimens were analyzed during the healing process of cracked mortar specimens, and observations were performed at each location by following the paste-aggregate bond zones and cracks.

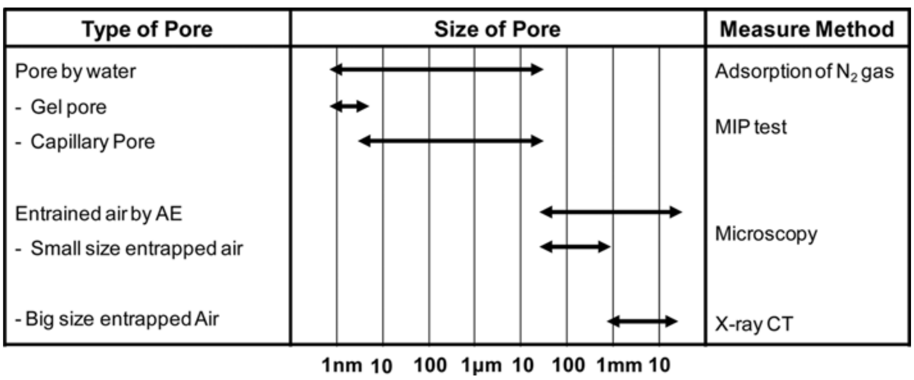

Fig. 2. Concrete pore types, sizes and associated measurement methods.

Results and Discussion

Degradation behavior of cement paste on surface area

Fig. 3 shows the surface morphology of deteriorated high strength mortar after 500 °C exposure. Degradation occurred at the surface due to shrinkage of the cement paste, similar to the solid-state-sintering effect, and the specimen surface could be divided into dry/dehydrated or dry/dehydrating zones. The deteriorated surface of the dry/dehydrated zone after heating is shown in detail in Fig. 4. This zone was almost entirely sintered, and various phenomena were observed, such as solid-state-sintering, pore shrinkage, and volcano effect driven by increasing pore pressure. Mass loss in this zone may be attributed to the reduction of $Ca(OH)_2$ and evaporation of free water in the system within the one-hour heating period.

Pore shrinkage by dehydration of combined water such as solid-state-sintering was also observed (Fig. 5). In general, the solid-state-sintering on the surface due to heating affects the grain size and shape and pore size and shape, and is driven by a reduction in surface energy. Densification occurs as excess free energy builds up on the surface of cement paste, and the release of built-up surface energy leads to the formation of coarse grains which increase in size under heating.

Fig. 6 shows the sintered and combustion traces by EDS analysis in the dry/dehydrated zone. Many coarse grains can be seen at the surface, and their chemical composition is similar to $3CaO \cdot SiO_2$ due to dehydration of the cement paste at the surface.

The dry/dehydrating zone was partially exposed after degradation of cement paste in the dry/dehydrated zone

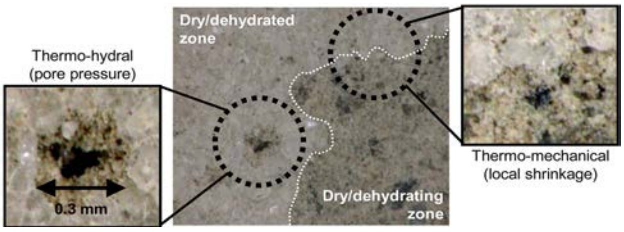

Fig. 3. Surface morphology of deteriorated mortar.

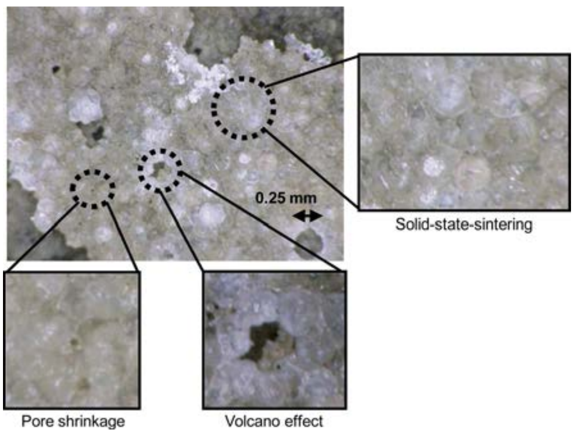

Fig. 4. Deteriorated surface of dry/dehydrated zone in detail.

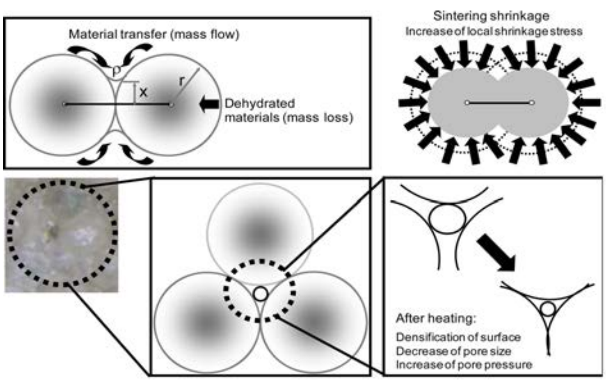

Fig. 5. Pore shrinkage by solid sintering in dry/dehydrated zone.

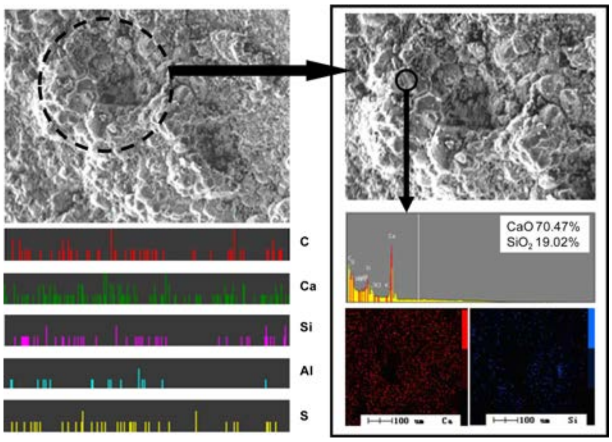

Fig. 6. X-ray spectrum of sintered mortar surface after heating.

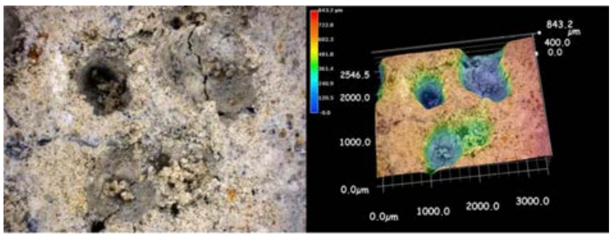

Fig. 7. Surface image and 3D visualization of surface degradation.

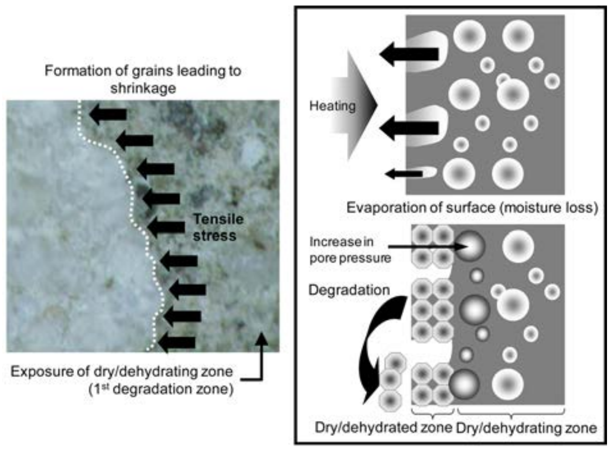

Fig. 8. Surface degradation phenomenon leading to exposure of dehydrating zone.

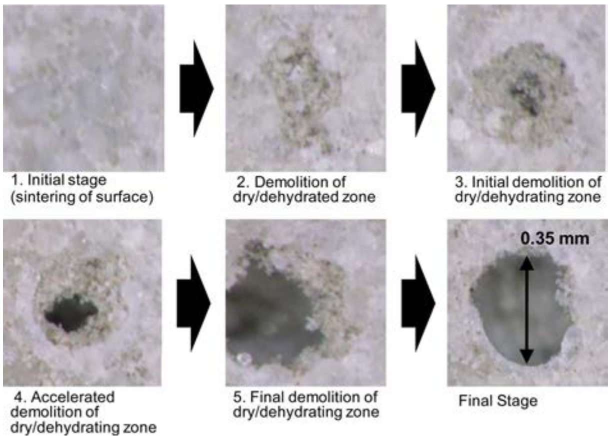

Fig. 9. Demolition process at the mortar surface by pore pressure.

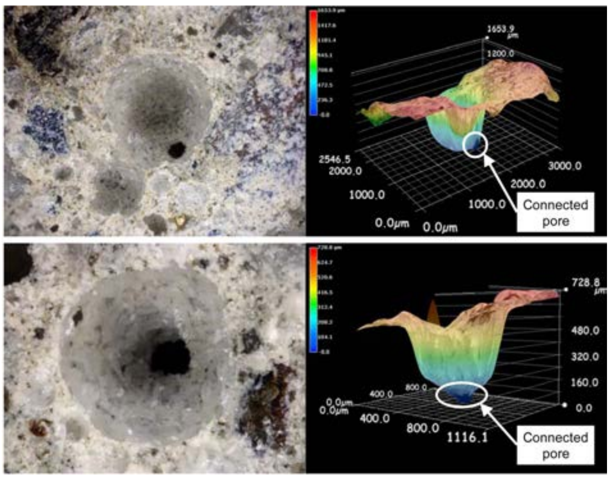

Fig. 10. Surface images and 3D visualizations of volcano effect in connected pores.

as observed visually in Fig. 7, and the mechanism is illustrated in Fig. 8. The depth of the dry/dehydrated zone was measured at 0.08 to 0.1 millimeters, but this depth is dependent on heating time and temperature. Densification of the surface layer led to a thermo-hydral degradation process (volcano effect) caused by incremental increase of pressure within entrained air. This phenomenon will be discussed in detail in the following section.

Volcano effect of entrained air by pore pressure

Observation of the mortar surface layer found deterioration of the cement paste to a depth of 0.1 millimeters. Densification of the surface through solid-state-sintering based on dehydration led to a reduction in vapor flow, causing an incremental increase of internal pore pressure within entrained air and contributing to demolition of the dry/dehydrated zone- similar to the eruption of a volcano. This volcano effect may be affected by pore size, shape, and degree of moisture content within the pore; most entrained air between 0.3 and 1.0 millimeters under this heating exposure showed volcano effects.

The demolition process of the dry/dehydrated and dry/dehydrating zones is illustrated in Fig. 9 through microscopy images, which show the degradation from surface sintering and demolition of the dry/dehydrated zone to demolition and of the dry/dehydrating zone. The volcano effect may also occur in conjunction with adjacent entrained air, where built-up pore pressure in the smaller pore exceeds the matrix strength and a connecting passageway is formed between the two pores. Pressure first drops due to larger space then increases again under heating until the volcano effect occurs at the surface, exposing both the entrained air pore as well as the adjacent, connected pore. The exposed connected pore can be clearly seen in both the surface images and 3D visualizations in Fig. 10 for two different locations where the volcano effect was observed. This section and the preceding section discussed the degradation of mortar under heating exposure and examined the mechanism considering the progress of the dry/dehydrated and dry/dehydrating zones and the build-up of pore pressure in entrained air. The following section will move towards the next step, the repair of fire-damaged mortar, by examining the self-healing behavior under water supply.

Self-healing behavior of high-strength mortar

Sintered materials lose their self-healing capability due to the sintering effect; this is clearly seen in Fig. 11, in which 28 days re-curing in water shows no effect on the sintered material. On the other hand, the dry/

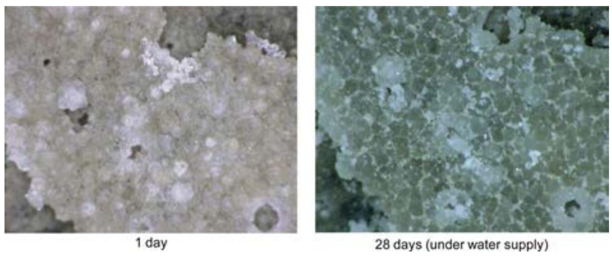

Fig. 11. Loss of self-healing capability by sintering in the dry/dehydrated zone.

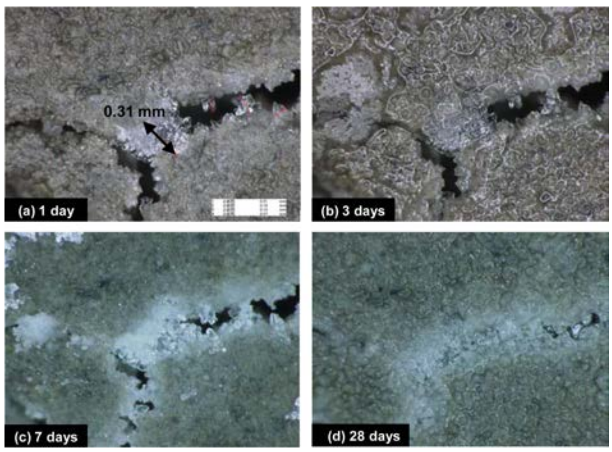

Fig. 12. Observed self-healing behavior in dry/dehydrating zone (I).

dehydrating zone is not yet sintered but in the dehydrated condition, indicating there is potential for re-curing if water is supplied to this zone. Fig. 12 shows that the self-healing effect occurs in the dry/dehydrating zone even after one day of re-curing, and by 28 days the crack was almost entirely self-healed.

The self-healing phenomenon also occurred in the entrained air structures for the dry/dehydrated, dry/dehydrating, and quasi-saturated zones. In the dry/dehydrated zone, it was found that self-healing behavior did not occur due to the pore sintering effect. For the dry/dehydrating zone, there was partial self-healing although sintering was also observed. In the quasi-saturated zone, almost complete self-healing occurred after 28 days. This demonstrates that there is high potential for fire-damaged mortar and, by extension, concrete to recover mechanical properties if re-cured under appropriate water supply conditions.

Strength and porosity recovery

A complementary investigation on self-healing under water curing was conducted by the authors but with a water-cement ratio of 0.3 and exposure temperature of 550 °C [14]. The compressive strength and porosity were examined before heating, after 1 hour of water cooling, and after 28 days re-curing, with the relationship between strength and porosity shown in Fig. 13.

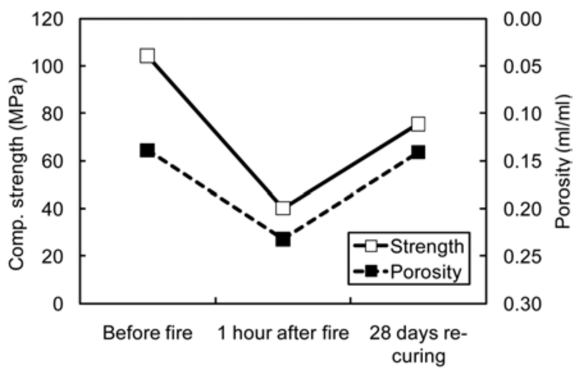

Fig. 13. Change in strength and porosity after heating and water re-curing.

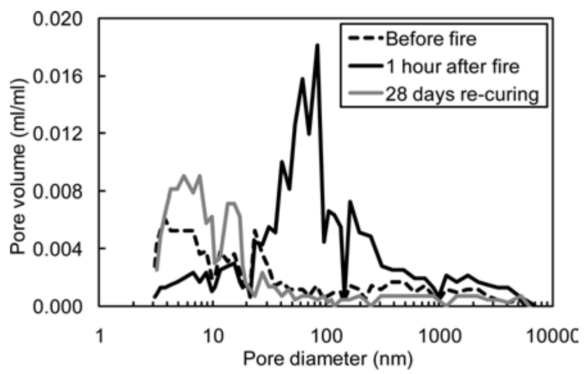

Fig. 14. Change in pore distribution after heating and water re-curing.

Recovery of both properties can be clearly observed, but strength only recovers to 72% of its original value whereas porosity is observed to completely recover after 28 days water re-curing. This discrepancy between the strength and porosity behavior may be explained by self-healing behavior observed for similar specimens in the previous section; specifically, although full crack self-healing was observed to occur after 28 days of re-curing in water (Fig. 12), the stability of this new, self-healed interface is unknown and may contribute to the lack of full strength recovery. In addition, while the porosity completely recovers by 28 days, the pore distribution is slightly different, as can be seen in Fig. 14. Pores less than 11 nanometers in size occupy a greater volume than they did before heating, with pores greater than 11 nanometers in size occupying less volume after re-curing than before heating, suggesting that re-curing in water after heating may lead to an increase in gel pores and a decrease in capillary pores relative to the pre-fired conditions.

Conclusions

In this paper, the degradation and self-healing behavior of fire damaged high-strength mortar was investigated in order to support concrete recycling and to develop a new repair method for fire-damaged concrete. Key findings are as follows:

Degradation behavior of the cement paste on the mortar surface could be related to thermo-hydral and thermo-mechanical processes under heating. Solid-state-sintering due to dehydration, pore shrinkage, and volcano effect were observed by microscopy. The volcano effect was proposed to explain degradation at the mortar surface. This phenomenon is driven by the build-up of vapor pressure in entrained air which leads to demolition of the dry/dehydrated zone. It was observed that this occurred both in single pores and connected pores near the mortar surface.

Self-healing behavior was observed in both cracks and in entrained air in the dry/dehydrating and quasi-saturated zones, which demonstrated the potential for self-healing behavior in fire-damaged high-strength mortar. No self-healing behavior was found to occur in the sintered dehydrated zone, which may limit recovery capability depending on the extent of exposure.

Secondary degradation may occur due to the weak bond between the dry/dehydrated and dry/dehydrating zones. In order to reduce this effect, the development of a chemical bonding agent for a water-based re-curing process could lead to the practical development of a new repairing method.

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References

1. V. Kodur, Fiber reinforcement for minimizing spalling in high strength concrete structural members exposed to fire, in: ACI SP-216, Innovations in Fiber-Reinforced Concrete for Value, ACI, Farmington Hills, 2003, pp. 221-236.
2. P. Kalifa, F.D. Menneteau, D. Quenard, Spalling and pore pressure in HPC at high temperatures, Cement and Concrete Research 30 (2000) 1915-1927.
3. G.R. Consolazio, M.C. McVary, J.W. Rish III, Measurement and prediction of pore pressures in saturated cement mortar subjected to radiant heating, ACI Materials Journal 95 (1998) 525-536.
4. Z.P. Bazant, Analysis of pore pressure, thermal stress and fracture in rapidly heated concrete, in: NIST SP-919, International Workshop on Fire Performance of High-Strength Concrete, Proceedings, Appendix B: Workshop Papers, B10, NIST, Gaithersburg, 1997, pp. 155-164.
5. A.K. Tovey, Assessment and repair of fire-damaged concrete structures-an update, in: ACI SP-92, Evaluation and Repair of Fire Damage to Concrete, ACI, Farmington Hills, 1986, pp. 47-62.
6. D.N. Crook, M.J. Murray, Regain of strength and firing of concrete, Magazine of Concrete Research 22 (1970) 149-154.
7. R. Sarshar, G.A. Khoury, Material and environmental factors influencing the compressive strength of unsealed cement paste and concrete at high temperatures, Magazine of Concrete Research 45 (1993) 51-61.
8. W.M. Lin, T.D. Lin, L.J. Powers-Couche, Microstructures of fire-damaged concrete, ACI Materials Journal 93 (1996) 199-205.
9. C.S. Poon, S. Azhar, M. Anson, Y.L. Wong, Strength and durability recovery of fire-damaged concrete after post-fire curing, Cement and Concrete Research 31 (2001) 1307-1381.
10. T. Kishi, T.H. Ahn, A. Hosoda, S. Suzuki, H. Takaoka, Self-healing behavior by cementitious recrystallization of cracked concrete incorporating expansive agent, in: 1st International Conference on Self-Healing Materials, Noordwijk, 2007.
11. T.H. Ahn, T. Kishi, Crack self-healing behavior of cementitious composites incorporating various mineral admixtures, Journal of Advanced Concrete Technology 8 (2010) 171-186.
12. T.H. Ahn, Development of self-healing concrete incorporating geo-materials: a study on its mechanism and behavior in cracked concrete, Ph.D. dissertation, Dept. of Civil Engineering, The University of Tokyo, Tokyo, 2008.
13. Korea Concrete Institute, KCI SP-4, Fire Resistance of Reinforced Concrete Structures, KCI, Seoul, 2005. (in Korean).
14. M. Henry, T.H. Ahn, Y. Kato, T. Kishi, Evaluation of re-curing for the recovery of high-strength mortar exposed to fire, Proc. Japan Concrete Institute 30 (2008) 435-440.