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MICROSTRUCTURAL COMPOSITION OF HARDENED CEMENT PASTE EXPOSED TO FIRE

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ABSTRACT

In this study, the change of microstructural composition in hydrated cements according to the depth from the surface of a reinforced concrete (RC) column exposed to fire was examined. The remaining fractions of calcium-silicate-hydrates (C-S-H) and calcium hydroxide in hydrated cements at the surface, the depth of 40 mm and 80 mm and the center (175 mm) of the RC column exposed to a standard fire for 180 minutes were examined using thermal gravimetric analysis (TGA) and X-ray diffraction analysis (XRDA). The silicate polymerization of C-S-H in hydrated cements sampled at the corresponding depth was also evaluated using nuclear magnetic resonance (NMR). The results showed that the remaining fractions of calcium-silicate-hydrates (C-S-H) and calcium hydroxide in the hydrated cements at the center of the column are similar to those in the hydrated cements at the depth of 40 mm from the surface respectively. The highest silicate polymerization in C-S-H appears at the surface.

Keywords: Fire test, Microstructural composition, Cement, XRD, TGA, NMR

1. INTRODUCTION

When a reinforced concrete (RC) member is exposed to a fire, the temperature rise in both steel and concrete decreases the strength and stiffness of the member. Therefore, most design codes for RC structures limit temperatures in RC members subject to fire (ACI-216 1997, AS3600 2009). Alternatively, effective section areas can be considered for fire safety assessments according to its temperature while the strength or area of the concrete over 500 ℃ is ignored (AS 3600 2009). The temperature limit to ignore the concrete strength is attributed to the dehydration temperature ranges of calcium-silicate-hydrate (C-S-H) (Jain and Neithalath 2009).

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C-S-H is known as the major hydration product making up to 67% of the hydrated Portland cement paste (Diamond 1976). Therefore, it plays the most important role for the strength and fracture characteristics of hydrated cement. Moreover, most of the time-dependent mechanical properties of hydrated cement are believed to be controlled by the C-S-H microstructure (Larbi 1993, Jennings and Tennis 1994). Detailed descriptions of cement hydration and chemical compositions of cement hydration products can be found elsewhere (Taylor 1997, Mehta and Monteiro 2006).

The temperature ranges of the dehydration of C-S-H vary widely among researchers: Odelson et al. (2007) reported the range to be between 200 °C and 400°C, Alonso and Fernandez (2004) determined this range to be 100 °C to 250 °C, Alarcon-Ruiz et al. (2005) found the range to be from 180 °C to 300 °C, while Jain and Neithalath (2009) used a range from 150 °C to 400 °C.

In this study, the microstructural composition in hydrated cements sampled at the surface, the depth of 40 mm and 80 mm and the center of an RC column exposed to a standard fire was examined with the objective of understanding the significance of fire damage to the hydrated cements in the RC column. The microstructural compositions are investigated using thermal gravimetric analysis (TGA), X-ray diffraction (XRD) and ^{29}Si magic angle spinning (MAS) nuclear magnetic resonance (NMR).

2. EXPERIMENTAL STUDY

2.1. Fire test of RC column

A fire test of an RC column following ISO-834 standard fire curve (ISO-834 1975) for 180 minutes was conducted in order to obtain core samples from the specimen. It was constructed following the design specification proposed by the Korean Concrete Institute (KCI 2009). The RC column has the square section of 350 mm by 350 mm and the height of 1500 mm. The column was reinforced with 8-ϕ22 mm steel rebars longitudinally and ϕ10 mm hoop bars were placed at 300 mm spacing along the column height. Grade 420 steel rebars, which have the yield strength of 420 MPa, were used to reinforce the column.

Figure 1: Core sample from RC column after fire test.

A concrete having the 28 days characteristic compressive strength of 39.9 MPa was used for the column. The maximum aggregate size of 25 mm crushed gravel was selected for the concrete. The

slump of fresh concrete was controlled in the range from 180 mm to 220 mm. The mixture proportion of the concrete was comprised of water, cement, sand and gravel contents at 175 kg/m^3, 320 kg/m^3, 827 kg/m^3 and 939 kg/m^3 respectively. The temperatures in concrete following the standard fire curve were measured at the center section of the column located 750 mm from the bottom of the column. The time histories of temperatures following the standard fire curve for 180 minutes were measured at the surface, the depth of 40 mm and 80 mm from the surface and the center of the column section respectively. After the fire test, core samples passing through the column section as shown in Figure 1 were obtained.

2.2. Thermo gravimetric analysis (TGA)

TGA tests were performed from 25 °C to 1000 °C, heated at 10 °C/min. The mass losses at the temperature ranges from 145 °C to 400 °C, from 400 °C to 600 °C and from 600 °C to 825 °C are considered in this study for the dehydration of C-S-H, the dehydroxylation of calcium hydroxide and the decarbonation of calcite respectively.

2.3. X-ray diffraction analysis (XRDA)

XRDA is a well-known methodology in cement chemistry (Taylor 1997). Usually, it used to characterize crystalline materials. Using XRD spectra, several compositions in hydrated and unhydrated cement paste such as ettringite, calcium hydroxide, C-S-H, alite and belite can be detected. A wealth of information exists on XRD observations of cement hydration products (Taylor 1997, Mehta and Monteiro 2006).

2.4. Nuclear Magnetic Resonance (NMR)

A silicate tetrahedron having the number of n sharing oxygen atoms is expressed as Q^n where n is the number sharing oxygen atoms ranging from zero to four. The intensity of the silicate Q connections can be investigated using ^{29}Si MAS NMR technique. Using the intensity fractions of Q^ns, the average degree of C-S-H connectivity D_c, which can represent the silicate polymerization, in a hydrated cement paste is calculated as (Jupe et al. 2005)

$$D_c = \frac{Q^1 + 2Q^2}{Q^1 + Q^2} \tag{1}$$

High values of D_c represent high polymerization of C-S-H. ^{29}Si MAS NMR spectroscopy was performed in 7 mm cylinders spun at 4 kHz. Approximately 10,000 scans were performed on each sample. The ^{29}Si chemical shifts are respectively referenced relative to tetramethylsilane $Si(CH_3)_4$ (TMS) at 0 ppm, using $Si[(CH_3)_3]_8Si_8O_{20}$ (Q8M8) as a secondary reference (the major peak being at 11.6 ppm relative to TMS).

3. RESULTS AND DISCUSSIONS

The time histories of temperatures measured at the surface, the depth of 40 mm and 80 mm and the center of the column respectively are shown in Figure 2. The maximum temperatures at the end of test time of 180 minutes were observed as 932 ℃, 618 ℃, 419 ℃ and 236 ℃ at the surface, the depth of 40 mm and 80 mm and the center of the column respectively.

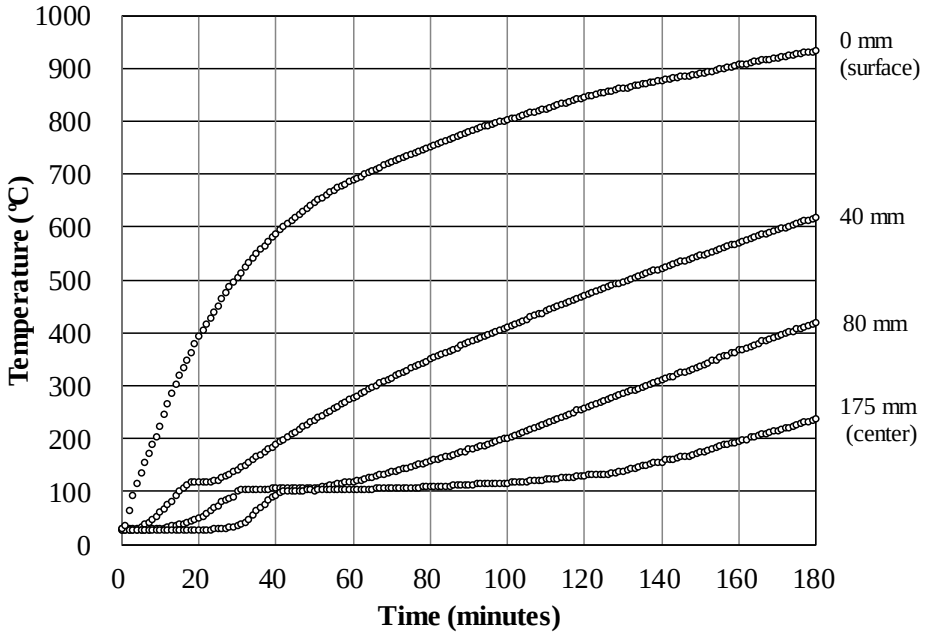

Figure 2: Temperature evolution during the fire test of RC column.

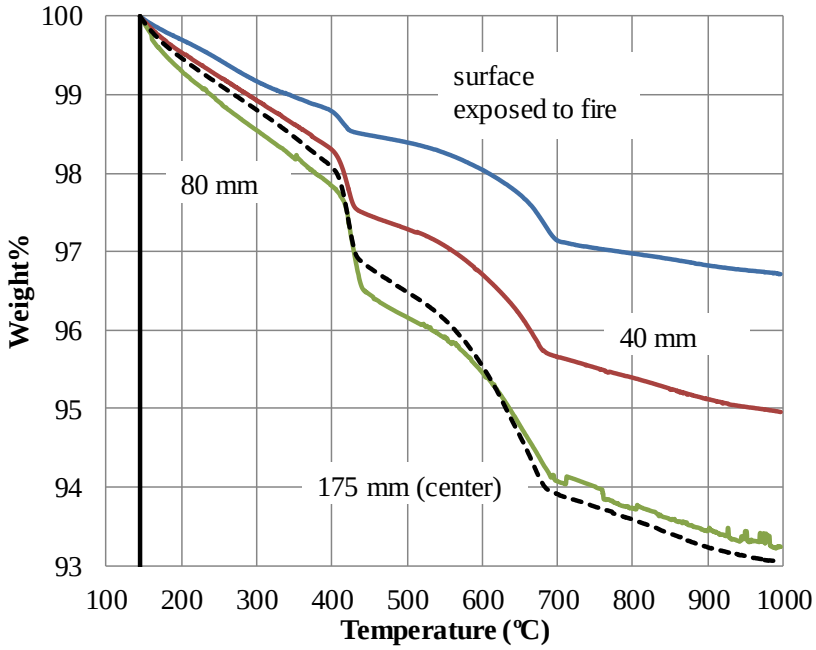

Figure 3: TGA results.

TGA curves for the hydrated cements according to the depth from the surface are shown in Figure 3. As the hydrated cement samples might absorb additional humidity prior to performing the TGA, the initial weight is taken at 145 ℃ to preclude the potential humidity absorption. The mass loss percentages for the corresponding ranges caused from the dehydration of C-S-H, the dehydroxylation of calcium hydroxide and the decarbonation of calcite are presented in Table 1. It can be seen from the TGA results that while the cements at the center of the column exposed to fire showed the highest fractions of calcium hydroxide of 2.6% and calcite of 2.1% among those at the other depth from the surface, the cements at the depth of 80 mm showed the highest fraction of C-S-H of 2.2%. The contents of calcium hydroxide at the center of the column and the depth of 80 mm, where the temperatures were 236 ℃ and 419 ℃ during the fire test, respectively, had the similar contents of 2.6% and 2.3% respectively.

Table 1: Mass loss resulted from TGA

Depth (mm)	Experienced temperature	145 ℃ ~ 400 ℃	400 ℃ ~ 600 ℃	600 ℃ ~ 825 ℃
0	932 ℃	1.2%	0.8%	1.1%
40	618 ℃	1.7%	1.6%	1.4%
80	419 ℃	2.2%	2.3%	1.8%
175	236 ℃	1.9%	2.6%	2.1%

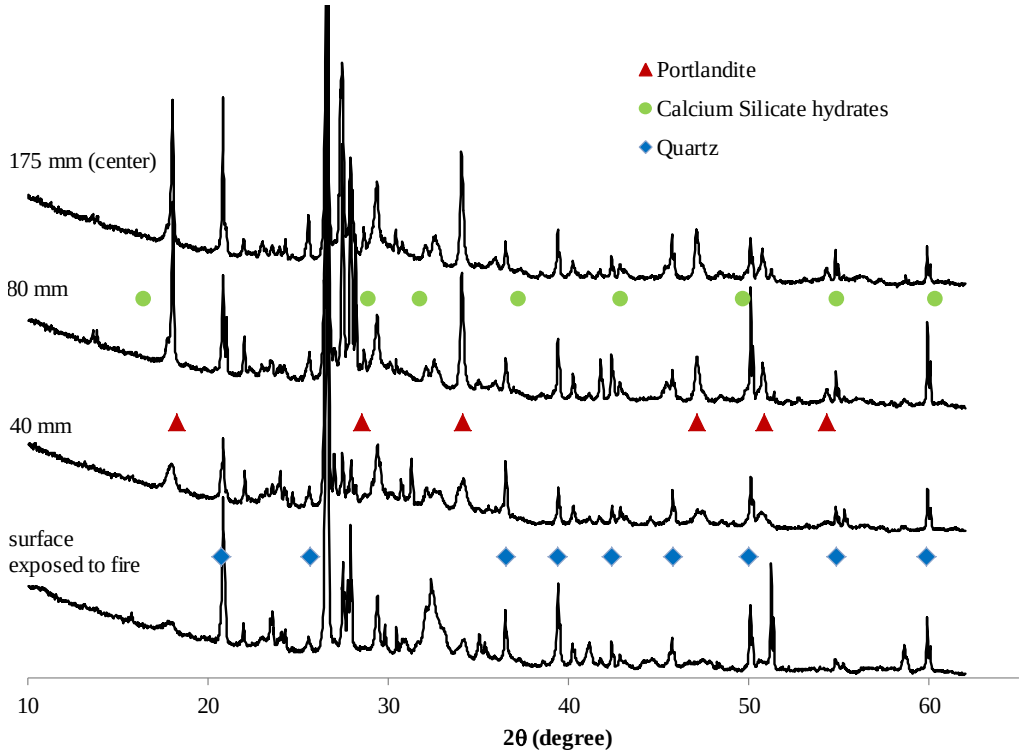

Figure 4: XRDA results.

The resulting XRDA spectra are shown in Figure 4. XRDA intensities represent calcium hydroxide peaks at 2θ of 18.2 º, 28.5 º, 34.1 º, 47.1 º, 50.8 º, 54.3 º were disappeared or decreased in the cements at the surface and the 40 mm deep from the surface.

The resulting ^{29}Si MAS NMR spectra were presented in Figure 5. The integration results of the Q^n intensities at the corresponding chemical shift range of -65 ppm ~ -75 ppm, -75 ppm ~ -82 ppm, -82 ppm ~ -90 ppm, -90 ppm ~ 102 ppm for Q^0, Q^1, Q^2 and Q^3 respectively are presented in Table 2. Q^3 level of polymerization was considered due to the inclusion of fine aggregates. Therefore, the relative fractions except Q^3 are also presented in Table 2. At the surface exposed to fire, almost no silicate connections of Q^0 and Q^1 were observed. The results showed that the silicate polymerizations in C-S-H at the center of the column and the depth of 40 mm, where the temperatures were 236 ºC and 618 ºC at the end of the fire test respectively, had the similar degree of connectivity of 1.43 and 1.45 respectively.

Table 2: Integration results of Q^n intensities (The relative fractions except Q^3)

Depth (mm)	Q^0	Q^1	Q^2	Q^3	*n*
0	56.2 (91.5)	0.4 (0.7)	4.8 (7.8)	38.5	1.92
40	21.8 (30.3)	28.6 (39.7)	21.6 (30.0)	27.8	1.43
80	15.1 (24.5)	23.6 (38.4)	22.8 (37.1)	38.6	1.49
175	21.7 (30.5)	27.1 (38.0)	22.4 (31.5)	28.7	1.45

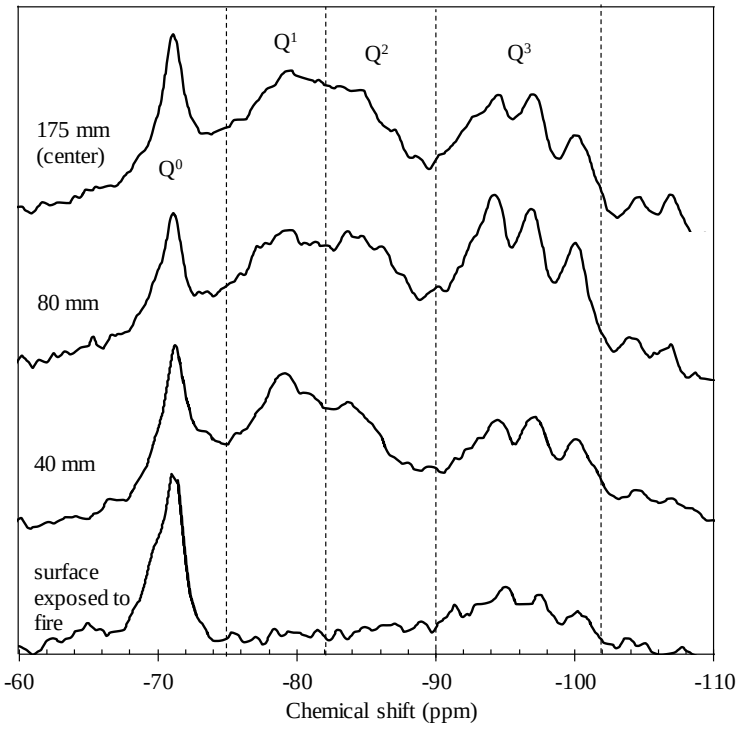

Figure 5: NMR results.

4. CONCLUSION

TGA and XRDA, ^{29}Si MAS NMR experiments were done for the cements exposed to fire to examine the microstructural compositions. The results indicated that the amount of C-S-H loss at the center of column experiencing the transferred fire temperature of 236 ℃ have been underestimated as the TGA results showed the highest C-S-H contents at the depth of 80 mm, where the transferred fire temperature is 419 ℃. Moreover, the destruction of silicate connections at the center was observed as similar as that at the depth of 40 mm, where the transferred fire temperature was 618 ℃. This might be attributed to the temperature changes during cooling time after the fire test was neglected. Due to the relatively low thermal conductivity of concrete, the high temperature, which can affect the change of microstructure in cements, will hold longer at the center of the column than other depth. Further research to generate the temperature profiles after the fire test is necessary to confirm these hypotheses.

5. ACKNOWLEDGMENTS

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REFERENCES

ACI Committee 216 (1997). Standard method for determining fire resistance of concrete and masonry construction assemblies, Am Concr Inst, Detroit.

AS3600 (2009). Concrete Structures Standards Austraillia.

Diamond S (1976). Cement paste microstructure--an overview at several levels, in: Hydraulic cement pastes; their structure and properties, Tapton Hall, University of Sheffield, pp. 2–30.

Larbi JA (1993). Microstructure of the interfacial zone around aggregate particles in concrete. Heron 38(1), pp. 1-69.

Jennings HM and Tennis PD (1994). Model for the developing microstructure in portland cement pastes. Journal of the American Ceramic Society 77(12), pp. 3161-3172.

Taylor HFW (1997). Cement Chemistry. London, Thomas Telford Publishing.

Mehta K and Monterio PJM (2006). Concrete: Microstructure, Properties and Materials, Third Edition. NY,USA: McGraw-Hill Professional.

Odelson JB, Kerr EA and Vichit-Vadakan W (2007). Young's modulus of cement paste at elevated temperatures. Cement and Concrete Research, 37, pp. 258–263.

Alonso C and Fernandez L (2004). Dehydration and rehydration processes of cement paste exposed to high temperature environments, Journal of Materials Science, 39, pp. 3015–3024.

Alarcon-Ruiz L, Platret G, Massieu E and Ehrlacher A (2005). The use of thermal analysis in assessing the effect of temperature on a cement paste, Cement and Concrete Research, 35, pp. 609–613.

Jain J and Neithalath N (2009). Physico-chemical changes in nano-silica and silica fume modified cement pastes in response to leaching. International Journal of Materials and Structural Integrity, 3, pp. 114–133.

ISO-834 (1975) Fire resistance test-elements of building construction. International Standard ISO384, Geneva.

Korean Concrete Institute (2009). Standard specification of concrete, Ministry of Land, Infrastructures and Transport, Korea.

Jupe AC, Wilkinson AP, Luke K and Funkhouser GP (2005). Class H Oil well cement hydration at elevated temperature in the presence of retarding agents: An in situ high-rnergy X-ray diffraction study. Indust Engin Chem Res, 44, pp. 5579–5584.