

Effect of elevated temperatures on chemical properties, microstructure and carbonation of cement paste

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In a fire event, it is well known that the strength of a concrete material significantly decreases, and in some cases, concrete building structures can collapse. This is mainly due to the chemical decomposition of hydration products of cement paste at elevated temperatures. This study is to provide the crucial information about how to determine the fire damaged temperatures and the damage level of cement paste. Samples were exposed to 100, 200, 300, 400, 500, 600, 700, 800, 900 and 1000 °C, respectively. After that, all heated samples were carefully collected and analyzed, in order to further investigate the variation of their thermal properties, which, in turn, can reveal a clue of the fire-damaged temperatures. X-ray diffraction, scanning electron microscope, accelerated carbonation tests were conducted to find the decomposition of hydration, collapse of pore structure, and deterioration of durability at a specific-damaged temperature. Test results showed that the higher the temperature, the more is the amounts of chemical decomposition, and the higher is the volume of pores in the cement paste samples. In conclusion, this study proposes a 'standard directory' that contains the information on the chemical variation of hydration products in cement paste at different elevated temperatures.

Key words: Fire damaged temperature, Damage level of cement paste, Carbonation tests.

Introduction

Concrete is one of the most widely used materials with outstanding performance. Although the concrete is known as a semi-permanent material, its performance can be seriously weakened when it is exposed to fire [1]. In extreme case, there is a high possibility that such damage may lead to the collapse of concrete structures. One of the key factors that deteriorate the performance of the concrete is the structural change of a cement matrix at a micro level. This is mainly because the hydration products in the cement matrix are decomposed when they are exposed to high temperature [2, 3]. This can cause the increase of pore size and thereby lead to the dramatic deterioration of durability. It is important that the condition of the fire damaged structures should be scientifically evaluated, so that the structure can be properly treated when they require the repairing.

The physiochemical, morphological and mineralogical transformations of cement paste (concrete) at elevated temperatures observed by many researchers are summarized in Table 1 [1,4-6]. As can be seen, absorbed water first evaporates at 65 °C and causes slight increase of strength, but the loss of other types of water leads to serious shrinkage and cracks. They are capillary water,

interlayer water and chemically bounded water. In particular, the desorption of the chemically bounded water from $\text{Ca}(\text{OH})_2$ at around 500 °C takes place and significantly affects the reduction of strength. Complete desiccation occurs at 600 °C. Other causes of the deterioration are the increase of the internal stresses due to water vapor starting from around 100 °C, the decrease of bonding strength between paste and aggregate due to their different thermal coefficients starting from 200 °C, and the decomposition of hydration products at various temperatures including the decomposition of C-S-H at around 700 °C.

In the literature, however, there is no widely accepted tool that can clearly evaluate the fire damaged temperature. Visual observation, Schmidt hammer, coring, UV spectrum, oxygen measurement, ultrasound and carbon dioxide measurement are some of the methods that have been tried, but they are too complicated and not concise.

Therefore, it is necessary to construct a database which includes the standard and convenient way to evaluate the damaged level of cement paste at various high temperatures. In this preliminary study, X-ray diffraction (XRD), scanning electron microscope (SEM) and accelerated carbonation tests were conducted to characterize the fundamental properties of the cement paste.

Experimental

experimental plan of this study is shown in Table 2. Water to cement ratio of the samples were 0.4 (water

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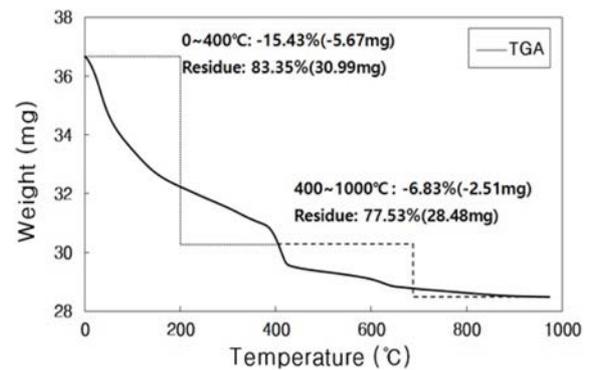
Table 1. Physicochemical transformation.

Temperature (°C)	Characteristic/cause
4-100	Desorption of evaporable water from the pores 4-80 °C: Stable hydration products and slight increase in CaO to SiO ₂ ratio 65-80 °C: Loss of absorbed water and slight development of strength 80-100 °C: Partial loss of interlay and chemically bonded water
100-200	Beginning to lose stability of cement paste mainly due to evaporable moisture 120-140 °C: Dehydration of calcium aluminosulphate hydrates, consequently destruction of ettringite 50-150 °C, 200 and 300 °C: Sequential dehydration of monosulfoaluminate
200-400	Loss of crystallinity, substantial cracks and the development of internal stresses 200 °C: Strength reduction of concrete by 30% 200-300 °C: Dehydration and compaction of C-S-H phases 300 °C: Deformed Ca(OH) ₂ crystals, strength reduction of concrete by 50%
400-600	Decomposition of hydration products and complete desiccation of pore system 450-550 °C: Transformation of Ca(OH) ₂ (Ca(OH) ₂ → CaO + H ₂ O) 500 °C: Destruction of C-S-H gels (sponge of filament-like C-S-H), strength reduction of concrete by 70%
600-900	Intermingled with voids and decarbonation of calcium carbonate 600 °C: Intensification of microcracks and starting point for disintegration of concrete structure 600-700 °C: Decomposition of C-S-H into the form of β-C ₂ S 600-800 °C: Predominance of microcracks and disruptive C-S-H phase boundaries 800 °C: Breakdown of C-S-H resulting slight increase in the residual strength 900 °C: Severe shrinkage, cracks and honeycomb-like structure
Above 1000	Melting of concrete Melting point: Cement (1200), basalt (1060), dolerite (1970), andesite (11115), diorite (1135), granite (1235), rhyolite (1260) and quartzite (1700)

Table 2. Experimental outline.

Factors considered	Detailed description
Water to cement ratio	0.4
Curing condition	·Water (28 days) + air (7 days)
Heating condition (°C)	100, 200, 300, 400, 500, 600, 700, 800, 900, 1000
Test	·Thermogravimetric analysis (TGA) ·X-ray diffraction (XRD) ·Scanning electron microscope (SEM) ·Accelerated carbonation

= 180 kg/m³ and cement = 450 kg/m³), and samples of 40 × 40 × 160 mm in size were prepared. All samples were cured in the water at 20 ± 2 °C for 28 days,

**Fig. 1.** Thermogravimetric analysis.

followed by another 7 days of curing at the atmospheric condition of 20 ± 2 °C. After the curing, all samples were exposed to elevated temperatures of 100, 200, 300, 400, 500, 600, 700, 800, 900 and 1000 °C respectively. Heated samples were stayed in a desiccator for 24 hrs and were ready to be tested. All samples were tested in triplicate for each type, and average results were used.

Ordinary Portland cement (density: 3,150 kg/m³ and fineness: 330 m²/kg) was used in this study. Fig. 1 shows the result of thermogravimetric analysis (TGA) of cement paste. As expected, the weight of the sample gradually decreased as temperature increased. It is assumed that water evaporation and chemical decomposition at elevated temperatures are the main reason for this loss. In particular, the loss of 15.43% was observed between room temperature and 400 °C, while 6.83% loss was observed between 400 and 1000 °C. Dramatic weight loss occurred at around 400 °C and 650 °C. Phenolphthalein solution of 1% was used as an indicator for an accelerated carbonation test in accordance with KS M 8238, similar to RILEM TC14 CPC 18 [7]. This solution is made by dissolving 1 g of phenolphthalein powder to 95% ethanol of 90 mL and then adding water to finally make 100 mL solution.

For a fire test, an electric furnace was used. The heating rate (R) of 4 °C/min is determined, according to RILEM TC 129-MHT [8]. This is given by

$$R = \frac{\Delta T 4D}{r^2} \quad (1)$$

where ΔT is the temperature difference between the surface and center of the sample, D is the thermal diffusivity (mm²/s) and r is the radius of the sample (mm). The targeted ΔT is set to be 20 ± 5 °C as recommended in RILEM TC 129-MHT. The thermal diffusivity of cement paste used is 0.37 mm²/s [9]. When the temperature of the furnace reached the target, they were maintained for another 20 min., followed by natural cooling (Fig. 2).

For examining the chemical change of the samples due to fire, XRD (D8 Advance by Broker) was used, and for microstructure, SEM (Quanta 400, FEI) observation was conducted.

Accelerated carbonation tests were conducted for the

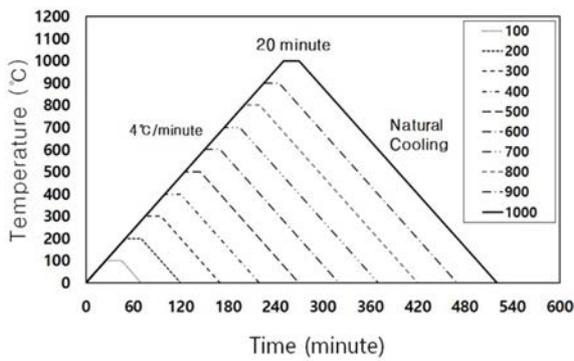


Fig. 2. Thermogravimetric analysis.

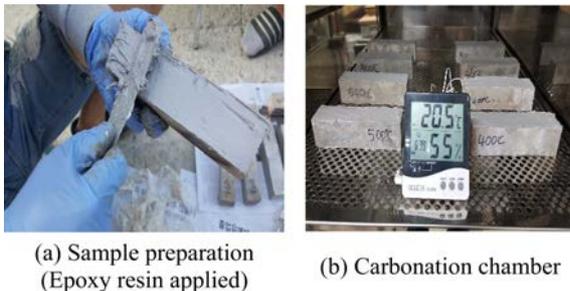


Fig. 3. Photo of accelerated carbonation test.

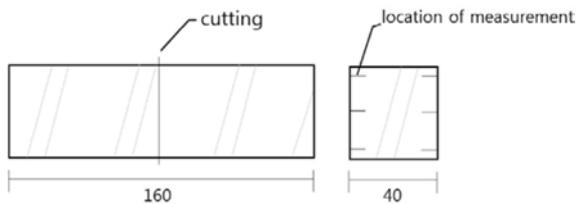


Fig. 4. Measurement of carbonation depth.

fire damaged samples in accordance with KS F 2584, similar to BS 1881-210 [10]. As can be seen in Fig. 3, epoxy resin was applied only to the top and bottom sides of the samples before commencing the test. All samples in the chamber were exposed to the carbon dioxide of $5 \pm 0.2\%$. The temperature and relative humidity in the chamber were maintained to be $20 \pm 2^\circ\text{C}$ and $60 \pm 5\%$, respectively. Carbonation depth was measured at 28 days upon start of the test. When the samples reached the target date, they were cut into the size of $40 \times 40 \times 50$ mm, and a vernier calipers was used to measure the carbonated depth after spraying the phenolphthalein solution on the cut surface as shown in Fig. 4. The solution was sprayed right after cutting the samples, and measuring was carried out between 10 min. to 2 days after the spraying, when the boundary of carbonated and non-carbonated areas was clear.

Results and Discussion

Chemical variation due to fire

As can be seen in Fig. 5, $\text{Ca}(\text{OH})_2$ started to disappear at 500°C and at 600°C , only a little trace

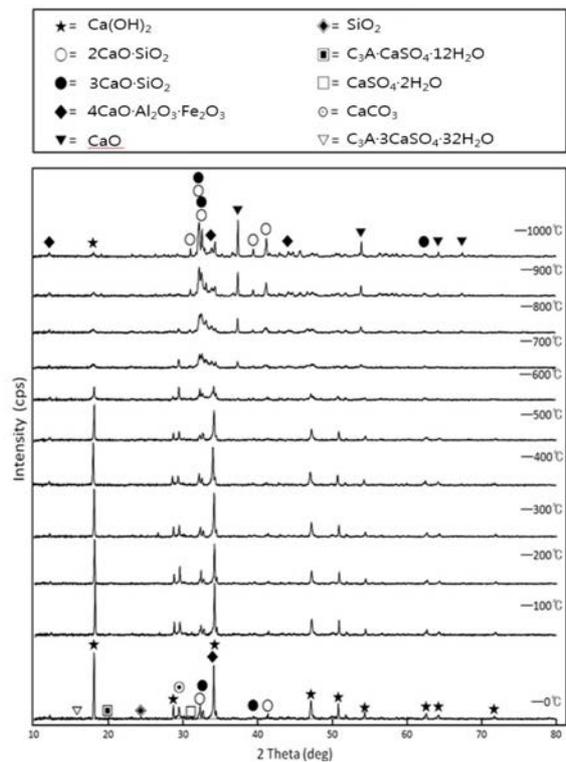


Fig. 5. X-ray diffraction analysis.

was found. This is because $\text{Ca}(\text{OH})_2$ was decomposed and converted into CaO and H_2O at this range of temperatures. It was also found that CaCO_3 dissolved into CaO and CO_2 at around 700°C . They are the two distinct phase transformation occurred in cement paste at elevated temperatures. Moreover, $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ disappeared at 300°C , and the trace of CaO found after 800°C , which is probably due to the dissolution of hydration products such as $\text{Ca}(\text{OH})_2$ and CH . In addition, it was found that $\text{C}_3\text{A} \cdot \text{CaSO}_4 \cdot 12\text{H}_2\text{O}$ was dehydrated and converted to CaO and $\text{C}_4\text{A}_3\text{S}$ at around 300°C

SEM observation

Fig. 6 is SEM observation of cement paste samples, previously heated up to 1000°C . Each sample was magnified from 5000 to 15000 times. Hence, dissolution of hydration products at elevated temperature discussed in Fig. 5 is visually proved. Etringite of acicular crystal is observed until 200°C (Fig. 6(a-d)) and disappeared after that. Mono-sulfate of plate-like shape can be seen up to 300°C (Fig. 6(a-e)), but it also disappeared at around 400°C (Fig. 6(f)). It is believed that this is due to the fact that mono-sulfate is dissolved into CaO . In addition, $\text{Ca}(\text{OH})_2$ of hexagonal plate-like shape is clearly shown at low temperature, but after 500°C , they are rarely found. C-S-H of acicular crystal is observed for longer time than other hydration products (Fig. 6(a-h)), but after 700°C , most of them were gone. Instead, there are many chances to see CaO especially after 900°C (Fig. 6(j-k)). Again, it is believed this is

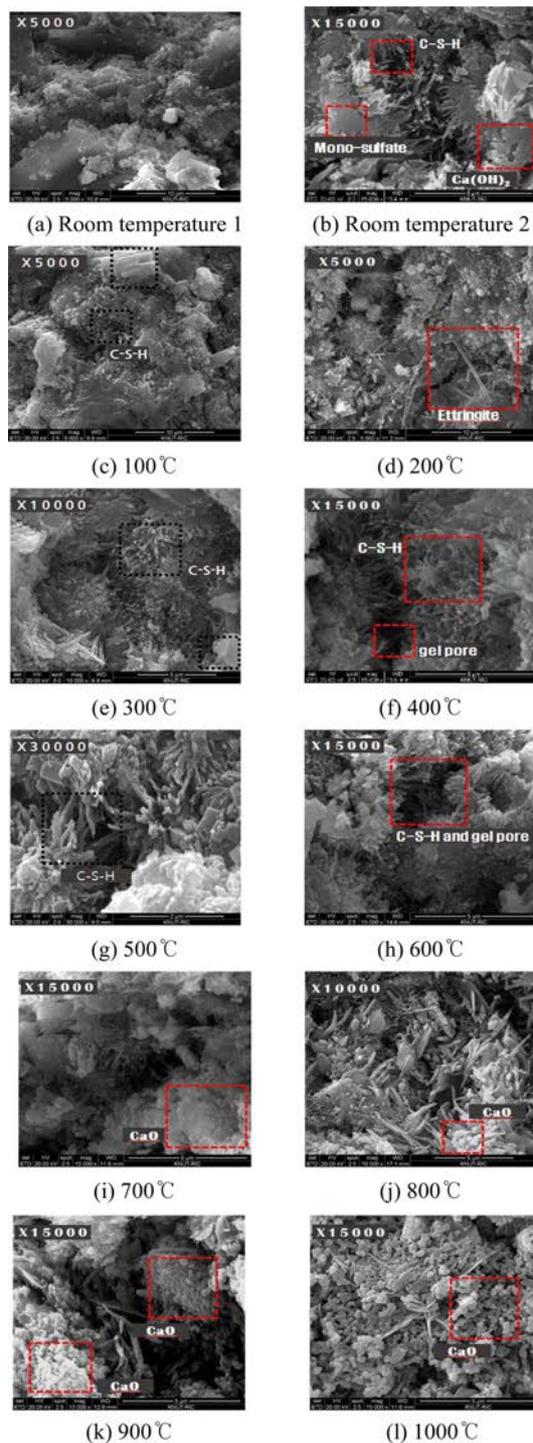


Fig. 6. SEM observation.

attributed to the dissolution of various types of hydration products.

Carbonation after fire exposure

Accelerated carbonation test is conducted to identify the effect of elevated temperatures on the diffusivity of harmful ionic species such as carbon dioxide penetrated into the cement paste samples. The results obtained from this test is important, because many of

Table 3. Standard directory on chemical variation of cement paste due to fire (XRD).

Temperature	X-ray diffraction
Room temperature (control)	–
100 °C	$3\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot 3\text{CaSO}_4\cdot 32\text{H}_2\text{O}$ ●
200 °C	$3\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot 3\text{CaSO}_4\cdot 32\text{H}_2\text{O}$ ○ $\text{CaSO}_4\cdot n\text{H}_2\text{O}$ ●
300 °C	$\text{CaSO}_4\cdot n\text{H}_2\text{O}$ ○
400 °C	–
500 °C	$\text{Ca}(\text{OH})_2$ ●
600 °C	$\text{Ca}(\text{OH})_2$ ○
700 °C	CaCO_3 ●
800 °C	CaCO_3 ○ CaO ●
900 °C	$2\text{CaO}\cdot\text{SiO}_2$ (39.4 only) ● CaO ●
1000 °C	CaO ●

- partly decomposed.
- generally decomposed.
- mostly decomposed.
- created.

fire damaged concrete structures can be misjudged when they exams only their surfaces and residual strengths that are nowadays typically prescribed in practice. However, the service life of the structures mainly influenced by carbon dioxide, and this carbonation test can provide information about the resistant level of fire damaged samples against the carbon dioxide. Fig. 7 shows the results of the accelerated carbonation test. It should be noted that all samples are cement paste, which is the same condition as other tests conducted in this study.

The carbonation depths of the samples that were exposed to 100 and 200 °C (Fig. 7(b) and 7(c)) were similar to that of a control sample (Fig. 7(a)). However, it is very interesting to note that from 300 to 500 °C, all heated samples were not carbonated, and the carbonation depths were 0 mm. Only difference is that the color of the pink is lighter than the control specimen.

At present, there is no clear evidence to prove this phenomenon, but one hypothesis is that two conflict behaviors of cement paste at elevated temperature which is first expansion (up to 200 °C) and then shrinkage (above 200 °C) can be the reason. This is because the shrinkage of the cement paste may decrease the overall size of the surface pores that can leads to block the penetration of carbon dioxide. Furthermore, the lighter pink color observed in the 300, 400 and 500 °C samples is probably due to the reduction of water and alkali source from $\text{Ca}(\text{OH})_2$.

Importantly, above 600 °C, it is not necessary to conduct the test. Because as discussed in Fig. 5, most of $\text{Ca}(\text{OH})_2$ is already decomposed at this range of temperature, and the accelerated carbonation test cannot simply distinguish whether the color change is due to the carbonation or the chemical decomposition

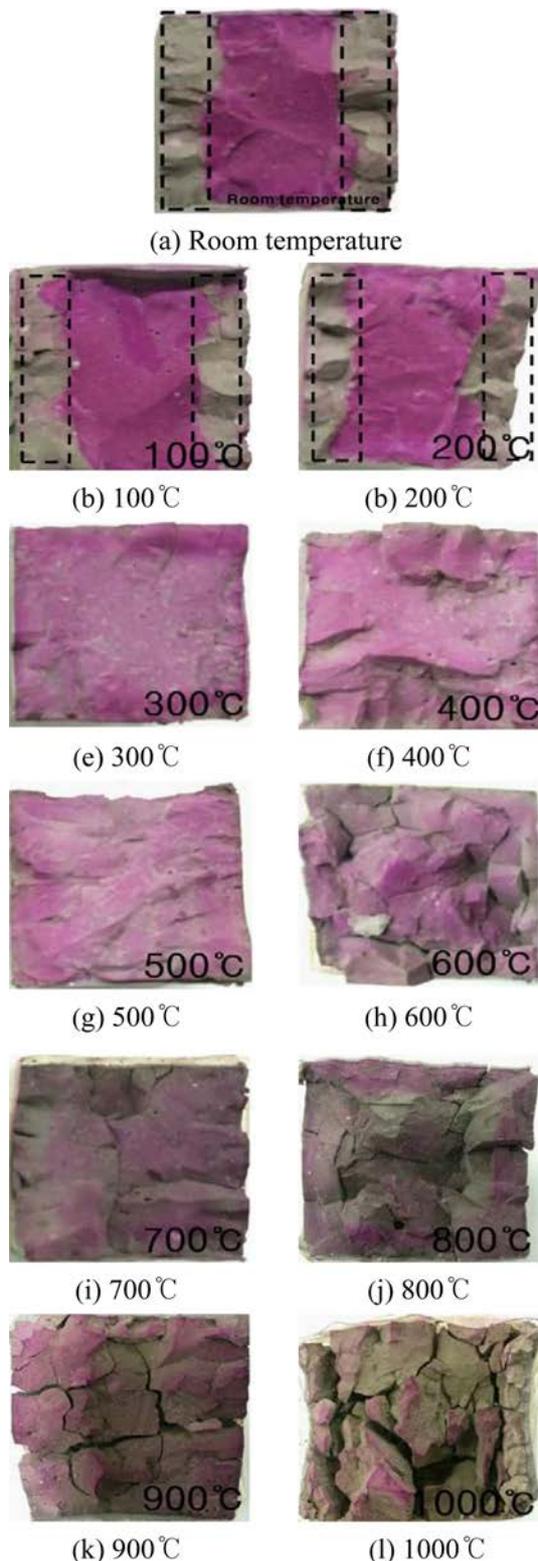


Fig. 7. Carbonation results.

of $\text{Ca}(\text{OH})_2$.

It should be noted that this test is for the samples that stored in the chamber for 28 days only. Longer curing in the chamber may results in the increase of the

carbonation depths, even in 300, 400 and 500 °C samples. Further observation is required to answer this question in near future.

The initial idea of this study is to judge the damage level of concrete structures when they are exposed to fire. The first step is to know the fire damaged temperature. This study provides the database. In Table 3, the results of XRD are summarized to clearly address the temperature effect on the chemical variation of cement paste due to fire, except for the temperature of 400 °C, which needs further examination with other chemical devices. It is believed that the standard directory made with more than one chemical device can help the investigators more clearly determined the fire damaged temperature in practice.

Conclusions

This study has investigated the effect of elevated temperatures on the properties of cement paste. Following conclusions are drawn.

1) A temperature effect on the chemical properties, pore structure and carbonation of cement paste is found to be significant. Especially, the findings from XRD analysis can clearly address the chemical decomposition and bond happened at a specific temperature.

2) It is expected that the standard directory obtained from XRD can provide the key information to determine the fire damaged temperature in practice.

3) Carbonation of cement paste after fire exposure is not clear in the present study. It needs further research to prove whether the shrinkage of cement paste contributes to delay the penetration of carbon dioxide.

Acknowledgments

This research was supported by a grant (391) from Infrastructure and transportation technology promotion research Program funded by Ministry of Land, Infrastructure and Transport of Korean government.

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