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Fire resistance and residual strength of reactive powder concrete Using metakaolin

Hongseok Jang, Jebang Yi and Seungyoung So*

Department of Architectural Engineering, Research Center of Industrial Technology, Jeonbuk National University, 567 Baekje-daero, deokjin-gu, Jeonju 54896, Republic of Korea

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Abstract. This study investigates the fire resistance characteristics of reactive powder concrete according to changes in the cement content per unit area, mixing ratio of metakaolin (MK), and content of polypropylene fiber. A fire test was conducted, and the resulting residual strength characteristics were investigated through flexural and compressive strength measurements, as well as condition rating classification based on visual evaluation. MK effectively reduced the initial high content of calcium hydroxide, thereby reducing the water vapor pressure generated during pyrolysis and slowing spalling. Furthermore, the pore structure and loose tissue were effective for relieving the water vapor pressure in the event of a fire.

Keywords: reactive powder concrete; metakaolin; pozzolanic activity; spalling properties; fire resistance

1. Introduction

Compared with many other structural materials, concrete has a lower thermal conductivity and better energy dissipation capacity until complete collapse (Asadi *et al.* 2018). It is well-known as a material with excellent fire resistance, maintaining performance for long periods in fire without emitting harmful gases or smoke (Rix 2009). However, prolonged exposure of concrete structural members to high temperatures can severely affect part of or the entire structural system (Yang *et al*. 2019, Bingöl and Gül 2009, El-Hawary and Hamoush 1996, Felicetti *et al*. 2009, Haddad and Shannis 2004, Lin *et al*. 1996, Poon *et al*. 2001, Yang *et al*. 2016, Seitllari and maser 2019). In recent years, the spalling phenomenon in high-strength concrete has emerged as a source of concern because the damage is more severe than in ordinary concrete, and high strength concrete is becoming the material of choice for the construction of high-rise buildings and large-scale structures (Georgali and Tsakiridis 2005, Zhang *et al*. 2020). Hence, as concrete is enhanced to high-strength and ultra-high strength, fire safety can be anticipated as a potential social problem (Tang 2017, Tang 2018). Since ultra-high-strength concrete is particularly used in high-rise apartments, hotels, and office skyscrapers, fire-safe concrete design is needed to prevent the possibility of very serious injury as a result of these trends.

While no common standard exists for ultra-high strength concrete, it is generally classified on the basis of being lower or higher than 100 MPa. A compressive strength of 40–100 MPa is classified as high strength, while a compressive strength greater than 100 MPa is classified as ultra-high strength concrete (Šerelis *et al*. 2016). The production of ultra-high strength concrete is largely classified into two types. The first is primarily for in-situ casting using pozzolans and special admixtures, and coarse aggregates are generally used (Bastos *et al*. 2016). The second type is reactive powder concrete (RPC), which incorporates metal fibers to increase toughness; this method uses reactive powders such as silica fume (SF), a fine aggregate, and pozzolan for concrete without coarse aggregates (Sarika and John 2015).

RPC is based on filling the micropores of cement hydrates with ultrafine fillers using SF and pozzolans such as micro quartz and precipitated silica, thereby minimizing the pores and creating a tight structure (Banerji *et al.* 2020, Hiremath and Yaragal 2018, Peng *et al*. 2015), and resulting in extremely low permeability (two orders of magnitude lower than the conventional normal strength concrete) as reported by Li *et al.* (2018) and Shi *et al*. (2015). To achieve this, a large amount of SF is used, and a high temperature, high pressure physical curing method is applied to activate the pozzolanic reaction (Dashti Rahmatabadi 2015, Kushartomo *et al*. 2015), and the unit cement quantity reaches 950 kg m^{-3}, utilizing sub mixtures containing a high proportion of cement (Bakiş 2017).

It has been reported that adding SF increases the density of concrete (So *et al*. 2014). The reason for the decreasing porosity is that SF produces more calcium silicate hydrate (C-S-H), which is produced when SF reacts with calcium hydroxide (a basic cement hydrate) in the material. The volume of C-S-H is larger than that of SiO_2 and $Ca(OH)_2$ (CH) because C-S-H also contains water (Lagerblad 2001). While producing high-strength RPC, the unit cement quantity is inevitably increased and unreacted CH remains.

When exposed to high temperatures, CH dehydrates, decomposing into water and lime (at approximately 450–500°C) (KISC 2010). It is known that the large amount of water generated at this stage is converted to high water

*Corresponding author, Professor
E-mail: archiso@jbnu.ac.kr

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Table 1 Chemical and physical properties of raw materials.

Type	Oxide composition (%)							Specific gravity	Blain fineness (cm^2 g^{-1})
	SiO_2	CaO	Al_2O_3	Fe_2O_3	SO_3	MgO	TiO_2		
OPC	20.57	63.03	5.48	3.18	2.23	3.41	-	3.15	3,267
SF	91.92	0.32	0.20	0.10	0.18	0.3	-	2.12	200,000
MK	83.82	0.22	8.89	0.30	-	-	0.09	2.50	10,500

vapor pressure, thereby accelerating spalling and leading to explosive spalling. Hence, the fire resistance of RPC remains a concern, particularly with regards to explosive spalling (Liu *et al*. 2010).

As a pozzolan used in concrete, metakaolin (MK) has properties similar to SF. MK (active kaolin) is formed by calcining kaolin minerals at approximately 600–800°C (Joshaghani *et al.* 2017) and then pulverizing to activate the kaolin. MK is a highly reactive material with a higher fineness than conventional blast furnace slag (BFS) or fly ash (FA), making it possible to manufacture dense concrete by filling the pores of the concrete (Lee 2008). Research has shown that MK with a high fineness can be used as a substitute for SF because it has very similar physical properties (Tafraoui *et al*. 2009). Most importantly, at the similar performance, MK is more competitive than SF in terms of price owing to its abundant reserves globally.

MK, as a dehydrated clay mineral, is inherently fire resistant and has a faster reaction rate than SF. Thus, through the initial rehydration process, it is known that CH is effectively reduced by the conversion of a large proportion into C-S-H or calcium aluminate hydrate (C-A-H). Moreover, since MK (10,500 cm^2 g^{-1}) has a lower fineness than SF, the cement matrix becomes less dense and the pores increase in size and quantity to a higher degree relative to using only SF. Consequently, the large pores and a more open matrix as a result of using MK are expected to be more effective at relieving steam pressure in the event of a fire.

If the raw materials and quality are stabilized, the pozzolan MK can replace SF. Numerous studies have used MK as an admixture for concrete; however, most studies applied it to general concrete such as FA or BFS, thereby intermixing the materials. Research on the fire performance and thermal explosion of RPC using MK exposed to high temperatures is still lacking.

This study assessed the pozzolanic reactivity of MK and compared it with the conventional RPC manufactured using only SF. The physical properties including the strength and explosive spalling behavior of the MK-incorporated RPC were also analyzed, as well changes in the internal pores and CH before and after fire testing.

2. Materials and methods

2.1 Materials

MK was prepared by calcining domestic low-grade halloysite kaolin. Unrefined SF was used as received. Ordinary Portland cement (OPC) was used as specified in the Korean standard L 5201. Table 1 lists the chemical composition and physical properties of these materials.

Two types of domestic silica sand (particle sizes of 0.3–0.5 mm and 0.15–0.3 mm) with a density of 2.65 g cm^{-3} and SiO_2 content of $\geq$ 82% were used. Quartz fine powder with an average particle size of approximately 45 μm was used as a filler. The grade of steel fiber used consisted of a highly elastic steel fiber with a diameter, length, specific gravity, and tensile strength of 0.5 mm, 15 mm, 7.8, and 1,195 MPa, respectively. Polypropylene (PP) fiber with a length, diameter, specific gravity, and melting temperature of 13 mm, 20 μm, 0.91, and 165 °C, respectively was used to reduce the build-up of internal vapor pressure in the concrete, and to control explosive spalling. A high-performance superplasticizer was used in accordance with the ASTM C494 standard (Erdoğdu *et al.* 2019). A 1.05 g cm^{-3} density polycarboxylic acid system developed by the Korean Company S was incorporated for ultra-high strength. The flow table rate of the mixture was set in the range of 120–140 mm and the mixing water was adjusted.

2.2 Mixing ratio and curing method

Prior to this study, an investigation was conducted on spalling in RPC produced using SF (So *et al*. 2014). All RPC specimens exhibited explosive spalling when the SF/cement ratio exceeded 30%. Therefore, the reactive powder in this study was set to 30% relative to the cement weight. A combination of steel fibers and PP fibers in RPC is effective for preventing explosive spalling. A suitable PP content was determined to be at least 0.5 vol.% of the cement weight, hence, the mixing ratio of PP fibers was set to 0.1–1 vol.% of the cement weight as the basic mix. The steel fiber/cement ratio was fixed at 20%. In this study, the mixing ratios listed in Table 2 were employed to investigate the basic properties and spalling of RPC as a function of the unit cement content (700 kg m^{-3}, 800 kg m^{-3}, 950 kg m^{-3}), as well as the SF/MK mixing ratio and the applicability of MK as an RPC material.

All specimens were mixed using a forced mixer capable of stirring up to 10 L. The binder (OPC, SF, and MK), quartz fine powder, and silica sand were dry mixed for 5 min; water and admixture were added, and the mixture was kneaded for 5 min. Steel fibers and PP fibers were then added and stirred for approximately 5 min, after which the flow table value was measured. For each mixing ratio, one 100 × 200 mm size specimen and two 40 × 40 × 160 mm

Table 2 RPC mixing ratios and flow table value

Mix Type	Unit weight (kg m^{-3})								Flow table (mm)
	OPC	SF	MK	Q_s	Q_p	PP	S	W	
70C-30SF-00MK-10PP		210	-	924				238	134
70C-15SF-15MK-10PP	700	105	105	945	210	7	160	238	120
70C-00SF-30MK-10PP		-	210	907				266	125
80C-30SF-00MK-10PP		240	-	728				219	138
80C-15SF-15MK-10PP	800	120	120	752	240	8	160	219	128
80C-00SF-30MK-10PP		-	240	668				266	143
95C-30SF-00MK-10PP		285	-	501				285	122
95C-15SF-15MK-10PP	950	143	143	527	285	10	160	285	115
95C-00SF-30MK-10PP		-	285	478				319	122
80C-15SF-15MK-0PP						-			140
80C-15SF-15MK-1PP						1			138
80C-15SF-15MK-3PP	800	120	120	752	240	2	160	219	140
80C-15SF-15MK-5PP						4			135
80C-15SF-15MK-10PP						8			128

*OPC: ordinary Portland cement, SF: silica fume, MK: metakaolin, Q_s: quartz sand (silica sand), Q_p: quartz powder, S: steel fiber, PP: polypropylene fiber, W: water

size specimens were tested. A total of 42 samples were used for the fire test, and the experimental value was expressed as the average value of the 40 × 40 × 160 mm size specimens. The specimens were steam cured, excluding paste specimens for constituent structural analysis by age. Ultra-high strength concrete is generally applied using precast or prestressed methods. Therefore, steam curing was applied to mold the test piece specimens, after which they were subject to a constant temperature and humidity room for 1 h, demolded, placed in a steam curing machine, and cured at 90°C for 72 h.

2.3 Evaluation of pozzolanic activity

The assessed pozzolanic-activity index (API) test proposed by Yamamoto *et al*. (2006) is based on the pozzolanic reaction mechanism that produces C-S-H gels by the reaction of CH in Portland cement with the ions of pozzolans Si and Al. The API test refers to the amount of Ca^{2+} consumed by the pozzolanic reaction between cement and the sample, and it was conducted using the following procedure.

We added 1.5 g of the sample, 1.5 g of OPC, and 50 ml of distilled water to the reaction bottle and stirred for 1 h to prevent settling at the bottom of the container. The sealed container was placed in an 80 °C reactor for 18 h. The sample and liquid were separated by filtering through a 0.2 μm glass fiber filter, after which the Ca^{2+} ion concentration of the liquid was measured and calculated using Eq. (1).

$$API = \frac{Ca_{cement} - Ca_{(cement+sample)}}{Ca_{cement}} \quad (1)$$

2.4 Fire test

To determine the spalling behavior of the test specimens, fire test was conducted in accordance with the standard heating time-temperature curve with reference to the KS F 2257-1 (2005) and FILK Standard FS 019-1990 (1990). The heating rate was set to 10 °C /min. When the temperature inside the furnace reached 1,100°C, this temperature was maintained for 2 h to render the specimens temperature homogenous (Zheng *et al*. 2012). After the fire test, the specimens were visually inspected for spalling and judged as presented in Table 3. For the specimens in which spalling did not occur, or only partial damage occurred but the overall shape was still intact, the mass reduction rate was measured by comparing the mass before and after the fire test. The residual strength (compression, flexure) was measured to obtain the residual strength ratio using a specimen in sound condition.

2.5 RPC hydrate analysis

The crystallinity of the hydrates was analyzed using X-ray diffraction, and the pore structure was analyzed using the mercury intrusion technique. In explosive spalling of RPC, vaporization of free and chemically bonded water at increasing temperature is a crucial factor in determining the water vapor pressure in the capillary pores. It is generally known that four degradation mechanisms and the corresponding temperature ranges are observed for hardening cement pastes (EI-Jazairi and Illston 1980).

Accordingly, thermal (TG-DTA) analysis measurements were performed on the specimens for each temperature range using the existing SF-RPC thermal analysis method by So *et al*. (2014).

Table 3 Rating according to damage and spalling after fire test

Condition	Rating	Exterior shape and sample condition	Recovery
Sound	A	Sound state: Appearance of a sound state, shape maintained, fine seeping and cracking, strength maintained	Partial recovery possible
Seeping out	B	Damage from seeping out: Seeping out of molten steel fiber and PP fiber, balloon-like swelling due to internal vapor pressure, overall shape maintained, strength maintained	Partial recovery possible after repair
Partial	C	Partial failure: Seeping out of molten solution and partial peeling, peeling failure, overall shape maintained, strength partially maintained	Dismantling
Cutting	D	Cutting spalling: Strength lost, shear failure, partial shape remaining	Unrecoverable
Full width	E	Full spalling: 50% or more spalling failure, shattered state, shape cannot be confirmed	Unrecoverable

CH, which is most closely associated with concrete spalling, undergoes pyrolysis at 450–500°C and decomposes into calcium oxide (CaO) and water (H_2O), in a 1:1 mole ratio (EI-Jazairi and Illston 1980). The weight loss observed in the TG-DTA analysis at 450–500°C was due to dehydration of CH; thus, the CH content was quantified using the weight loss value. The molecular weights of CH and H_2O are 74.09 g mol^{-1} and 18.02 g mol^{-1}, respectively, hence, the conversion factor of 74.09/18.02 = 4.11 was multiplied by the weight loss due to dehydration of the quantified CH content. This is described in Eq. (2).

$$\text{CH content} = \text{weight loss at 450–500 °C} \times 4.11 \tag{2}$$

3. Result and discussion

3.1 Pozzolanic reactivity evaluation of raw materials

MK was produced by calcining domestic low-grade halloysite kaolin at 650–800°C, which contains active amorphous silica and alumina (Parveen *et al*. 2019). This reacts rapidly with the cement hydrates to produce C-A-H and C-S-H, producing a dense, hydrated cement matrix material (Lee 2008).

MK is known to be a highly reactive material with a relatively high fineness compared with the conventional BFS or FA. It has been reported that if the fineness is high (100,000–200,000 cm^2 g^{-1}), MK can be used as a substitute for SF or cement as their properties are very similar (Tafraoui *et al.* 2009, Mustafa *et al.* 2017). Larbi *et al.* (1990) also found that the pozzolanic activity of SF and MK was apparent after 2 h, whereas FA exhibited low pozzolanic activity before 28 days. The similar test results were obtained in this study.

Fig. 1 shows the results of the pozzolanic reactivity evaluation of MK using the API test. This test compared SF, FA, and BFS, which are all well-known pozzolans. The API of MK was found to be 89%, slightly below that of SF, and approximately 20% higher than that of FA.

The production of MK is performed at a moderate temperature range of 650–800°C, unlike OPC, which is calcined at high temperatures of approximately 1,450°C, as the interlayer water of the halloysite mineral is dehydrated even by weak heating (Wikipedia 2019). Kaolinite transforms into MK with a two-dimensional glass structure at these intermediate dehydration temperatures (Sperinck *et al*. 2011).

When kaolin is activated by heat treatment at 650–800°C, it transforms to a high energy state with enhanced reactivity. Subsequently, when the powder is exposed to moisture, the hydration reaction is hardly progressed, instead converting to MK, which exhibits hydraulicity under alkaline conditions (Lee 2009).

3.2 RPC strength improvement using MK

The MK constituents, amorphous alumina and silica, react with cement hydrates to produce additional C-A-H and C-S-H, thereby forming a dense hydrated matrix. As a result, in the short term, the formation of ettringite and the activation of tricalcium silicate in cement increase the early strength. In the medium and long term, the compressive strength and durability are improved by the reaction of CH and pozzolanic reaction of cement (El-Diadamony *et al.* 2015, Wild *et al.* 1996).

MK was used alone as the reactive powder, yielding a compressive strength of 80–100 MPa, which is below the 100 MPa standard for ultra-high strength concrete. In addition, it has a very high initial hydration reactivity, which is attributed to its Al_2O_3 phases, and generates heat

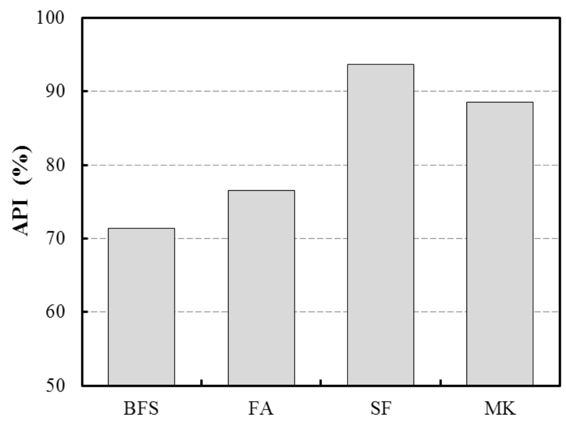
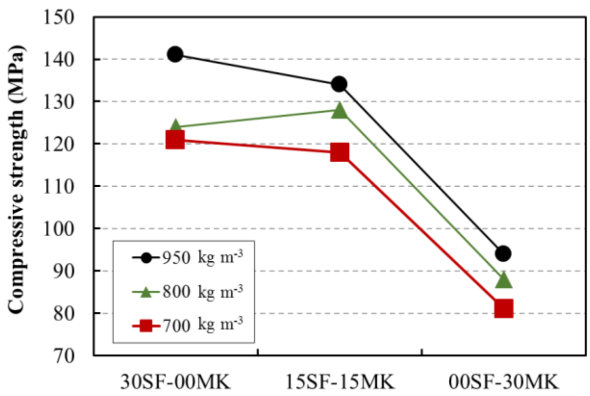


Fig. 1 Pozzolanic activity index measured by API Test

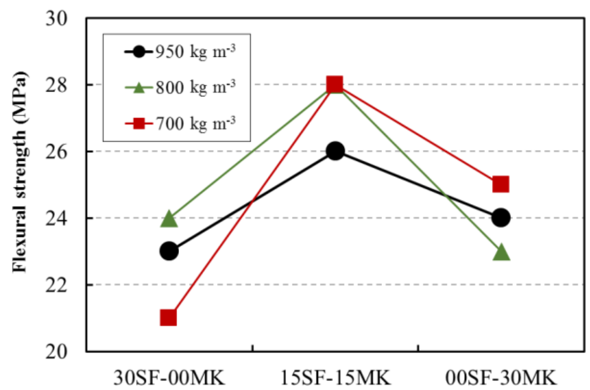
(Curcio *et al.* 1998, Ambroise *et al.* 1994). To ensure workability, a relatively large unit quantity of water is required compared with a mixture using only SF. In fact, the water to cement ratio increased from 3% up to 5% when MK was used, as presented in Table 2. The extra water addition reduced the final strength of the MK-only concrete.

The compressive strength increased by approximately 6% when 15% MK and 15% SF (15SF-15MK) are mixed at a unit cement content of 800 kg m^{-3} compared with the test specimen with only 30% SF. Moreover, the flexural strength was higher for all three-unit cement contents. These results demonstrate that SF and MK can be mixed at a ratio of approximately 1:1 and still be effective in terms of retaining or improving the flexural and compressive strengths when the powder content is 30% (Fig. 2).

Analysis of the hydrated 80C-15SF-15MK paste containing MK showed that at the beginning of hydration, the Type 1 C-S-H phase was produced together with the C-A-H and ettringite; after 7 days of age, calcium aluminum silicate hydrate (C-A-S-H) was produced, and after 28 days of age, hydrated phases expressing strength, such as the Type 4 C-S-H phase and AFt (Al_2O_3-Fe_2O_3-tri) phase, were observed. In particular, before 7 days of age, the CH peak gradually decreased primarily due to the reaction of CH with Al_2O_3, resulting in ettringite and C-A-H.

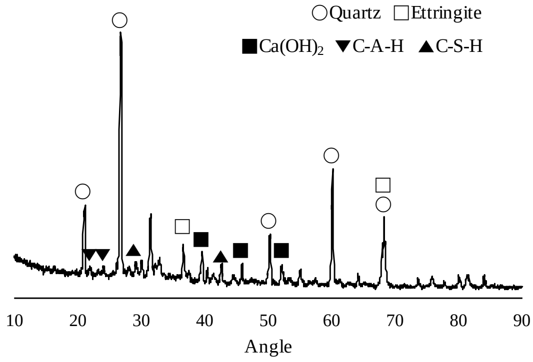


(a) Compressive strength

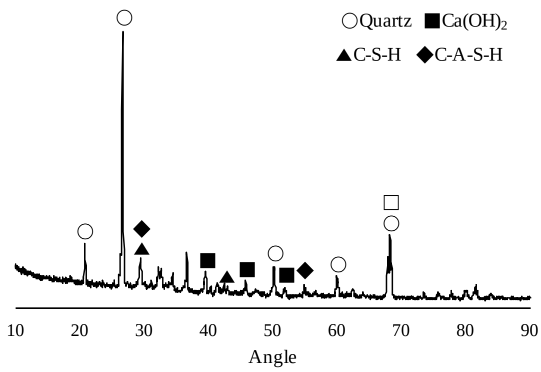


(b) Flexural strength

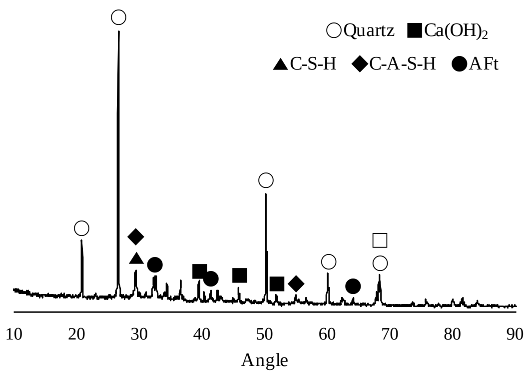
Fig. 2 RPC strength according to unit cement content and composition ratio of SF and MK (a) Compressive strength, (b) Flexural strength



(a) 3-days



(b) 7-days



(c) 28-days

Fig. 3 Hydrated tissue by age of 80C-15SF-15MK RPC specimen

These hydrates exhibited high compressive and flexural strength at early ages due to their fast hydration rate (Fig. 3).

3.3 Fire resistance evaluation

3.3.1 Visual inspection after fire test

The 95C-30SF-00MK-10PP specimen consisting of 30% SF with 950 kg m^{-3} cement exhibited spalling in which shear failure occurred at the top after the fire test. Molten steel fibers and synthetic fibers swelled outwards, and corrosion and seeping out of the steel fibers occurred. However, both 95C-15SF-15MK-10PP and 95C-00SF-30MK-10PP maintained sound condition (Fig. 4).

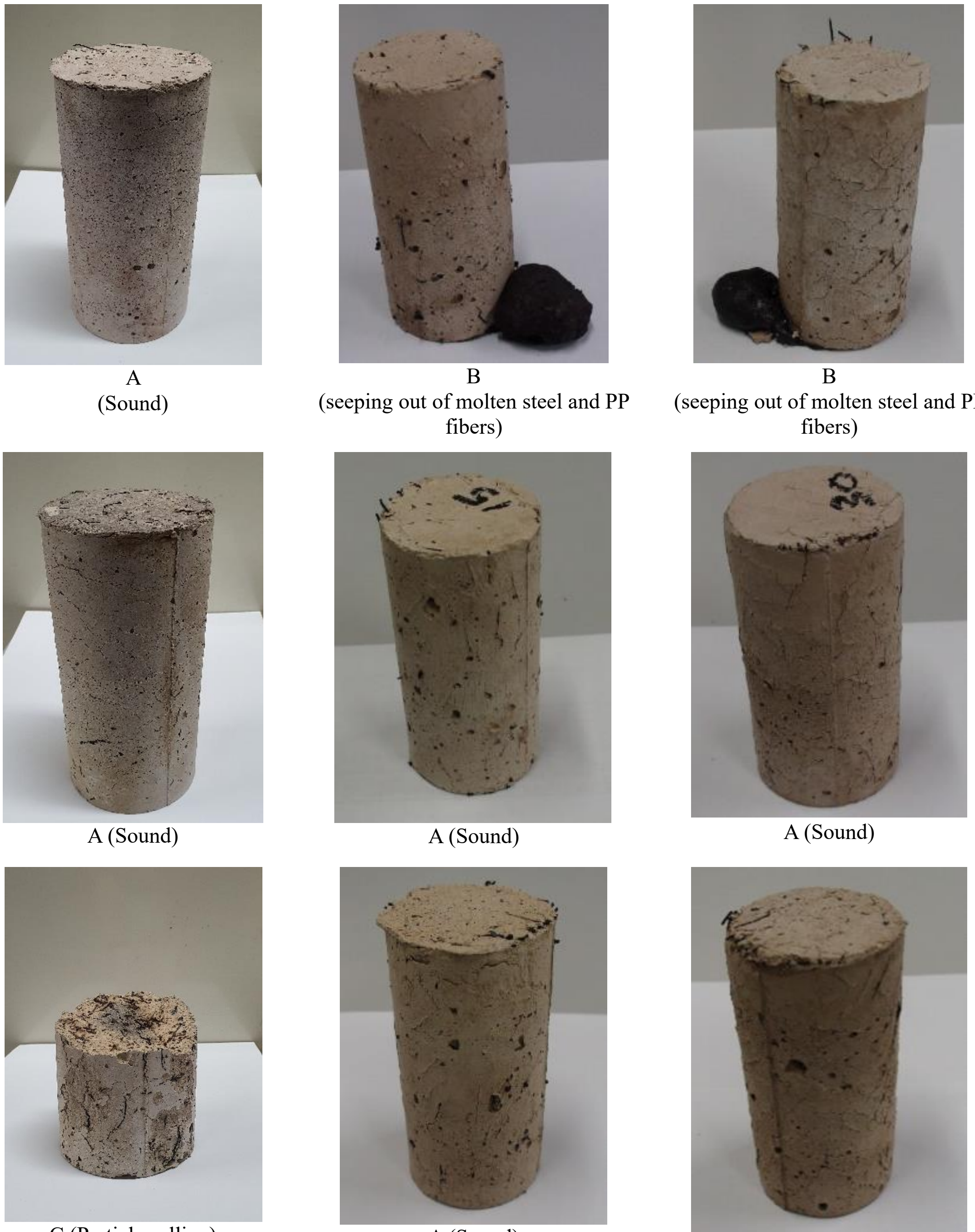


Fig. 4 Explosive spalling properties and rating of RPC specimens according to SF and MK composition.

Under the condition of 800 kg m^{-3} cement, the specimens remained sound at all composition ratios. Under the condition of 700 kg m^{-3} cement, 70C-30SF-00MK-10PP exhibited cracking and thermal corrosion but remained sound. In contrast, in both composition ratios, molten material seeped to the outside in 70C-15SF-15MK-10PP and 70C-00SF-30MK-10PP. This is because the lower the cement content per unit area, the less loose is the tissue.

This is advantageous for spalling but may lead to seeping out of the molten liquid. Spalling intensively occurred in the range of approximately 400–500°C at a cement content of 950 kg m^{-3}, whereas the specimen with SF exhibited only partial spalling accompanied by noise and debris collision. The more the unit binder content was lowered, the more spalling was alleviated. This is because the larger the SF mixing rate, the denser the internal

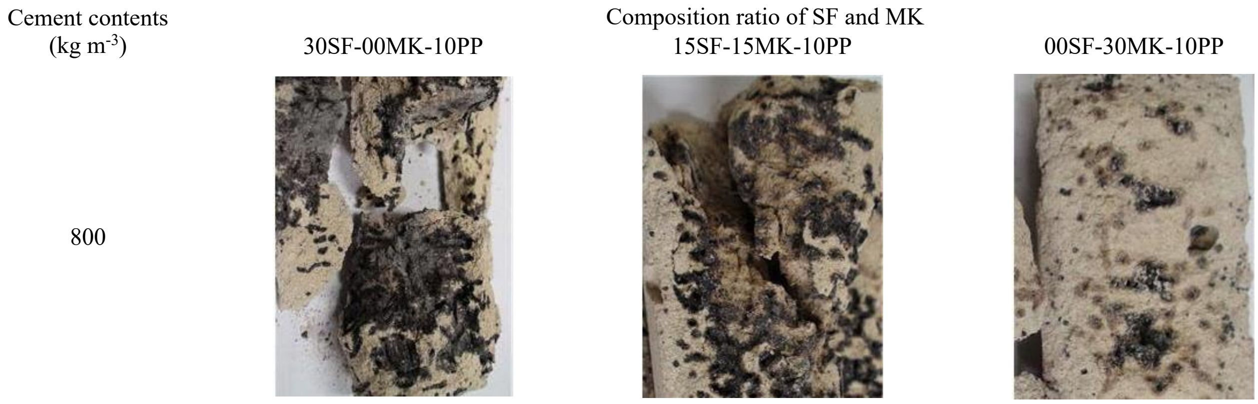


Fig. 5 Internal structure of RPC specimens after fire test according to SF and MK composition.

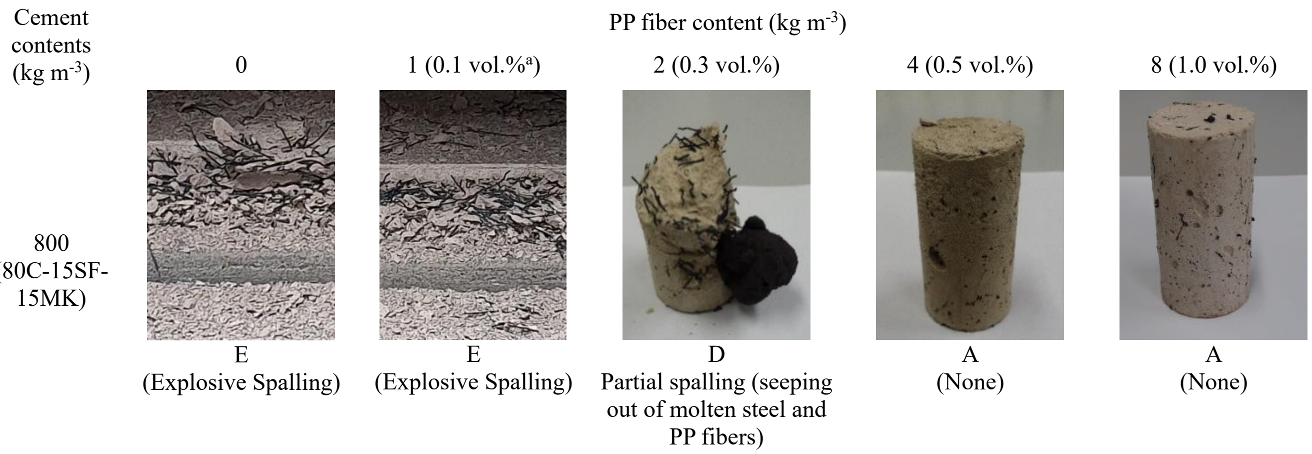


Fig. 6 Spalling properties of 80C-15SF-15MK RPC according to PP fiber content.

structure and the greater the resulting compressive strength. Spalling was exacerbated by the amplification of the internal steam pressure due to the small size of the unit pores.

As shown in Fig. 5, as the mixing rate of MK increased, the more yellow and brown spotted the molten steel fibers and PP fibers in the inner tissue became. This is attributed to the MK structure loosening at high temperatures and absorbing the molten materials and water vapor pressure through the sponge effect. Thus, RPC with MK partially replacing SF exhibited better strength and alleviation of spalling.

Fig. 6 shows the damage and spalling state after the fire test on RPC containing PP fiber content according to the 80C-15SF-15MK ratio. After the fire test, the specimens with 0 or 0.1 vol.% PP fiber were completely shattered via explosive spalling, and the 0.3 vol.% PP specimens were cut and exhibited spilling out of the dissolved steel and PP fibers with the water vapor and gas of the matrix. The results indicate that the combination of ≥0.3 vol.% PP fibers in RPC mixed steel fibers is effective for preventing the occurrence of explosive spalling. According to results previously reported by So *et al*. (2014), the minimum content of PP fibers required to prevent spalling was 0.5 vol.%, similar to that of SF alone.

3.3.2 Strength change before and after fire resistance

The samples that did not exhibit complete spalling were selected and tested for residual strength, focusing on compressive strength. In the residual strength test according to the PP fiber content of the 80C-15SF-15MK specimens, all the 9 specimens with PP fibers of 0 kg m^{-3}, 1.0 kg m^{-3}, and 2.0 kg m^{-3} exhibited complete explosive spalling. In addition, the 95C-30SF-00MK-10PP specimens exhibited partial spalling after the fire test, but it was not possible to measure their residual strength. On the other hand, it was possible to measure the residual strength of the other mixing ratio specimens after the fire resistance test.

The strength of the demolded specimen and the strength after the fire resistance test were measured to obtain the residual strength ratio. The ability to perform a residual strength measurement indicates that the specimens did not exhibit spalling and maintained their shape before the fire test at high temperatures of ≥1000°C. Moreover, a high residual strength ratio suggests that the change in the internal structure of the RPC was small, and that it maintained its resistance to stress even after exposure to high temperatures; therefore, it exhibits fire resistance.

The residual compressive strength ratio and flexural strength ratio were 15–25% and 20–30%, respectively,

Table 4 Residual strength of RPC according to mixing rate of SF and MK after fire testing

Mix Type	Compressive strength			Flexural strength		
	Before fire test C_b (MPa)	After fire test C_a (MPa)	Relative to the residual strength, C_r^* (C_a/C_b) (%)	Before fire test F_b (MPa)	After fire test F_a (MPa)	Relative to the residual strength, F_r^* (F_a/F_b) (%)
70C-30SF-00MK-10PP	121	30	25	21	5	24
70C-15SF-15MK-10PP	118	26	22	28	6	21
70C-00SF-30MK-10PP	81	15	19	25	5	20
80C-30SF-00MK-10PP	124	26	21	24	5	21
80C-15SF-15MK-10PP	128	31	24	27	8	30
80C-00SF-30MK-10PP	88	13	15	26	6	26
95C-30SF-00MK-10PP	141	-	-	23	-	-
95C-15SF-15MK-10PP	134	33	25	26	7	27
95C-00SF-30MK-10PP	94	14	15	24	6	25

Table 5 Residual strength of RPC according to mixing rate of PP fiber in 80C-15SF-15MK specimen after fire test

Mix Type	Compressive strength			Flexural strength		
	Before fire test C_b (MPa)	After fire test C_a (MPa)	Relative to the residual strength, C_r^* (C_a/C_b) (%)	Before fire test F_b(MPa)	After fire test F_a(MPa)	Relative to the residual strength, F_r^* (F_a/F_b) (%)
80C-15SF-15MK-0PP	118	Spalling	-	20	Spalling	-
80C-15SF-15MK-1PP	121	Spalling	-	21	Spalling	-
80C-15SF-15MK-3PP	125	Spalling	-	23	Spalling	-
80C-15SF-15MK-5PP	121	35	29	25	6	29
80C-15SF-15MK-10PP	128	31	24	27	8	30

demonstrating a substantial difference according to the cement content and the mixing ratio of SF/MK (Table 4). The MK-incorporated specimens exhibited higher flexural strength both before and after the fire test compared with the specimens incorporating only SF. Most notably, the 15SF-15MK specimen had the highest residual compressive strength and residual flexural strength after the fire test at unit cement contents of 950 kg m^{-3} and 800 kg m^{-3}. In contrast, the residual strength of the 95C-30SF-00MK-10PP specimen could not be measured due to partial spalling after the fire test.

Table 5 shows that the residual strength of RPC exposed to high temperatures increased as the PP fiber content increased. All the RPC specimens with PP fiber of 0 kg m^{-3}, 1.0 kg m^{-3}, and 2.0 kg m^{-3} were shattered. However, the RPC specimens with PP fiber of 4 kg m^{-3} and 8 kg m^{-3} were sound, with residual compressive strengths of 24–29% and residual flexural strengths of 29–30%. Thus, incorporating PP fibers was effective for preventing explosive spalling, with a minimum incorporation content of 4.0 kg m^{-3} (0.5 vol.%) (Atkinson 2004, Nishida and Yamazaki 1995).

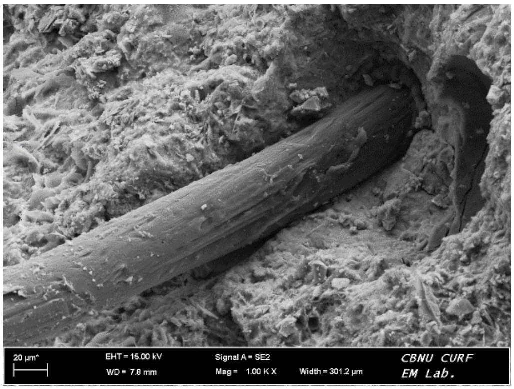
PP fiber melts at 165–170°C and forms a pathway for gas. Therefore, it contributes to create a more permeable network than the matrix, which allows the outward migration of gas and results in the reduction of pore pressure (Kalifa *et al*. 2001). Furthermore, with respect to the amount of fiber needed to prevent spalling, it has been reported that 1–3 kg m^{-3} of PP fiber is required to mitigate the occurrence of spalling (Bilodeau *et. al*. 2004). Fig. 7 shows the SEM micrographs of the RPC specimen with PP fiber before and after the fire test. It can be confirmed that the PP fiber melted after the fire test and created a fine pathway (Fig. 7(b)).

3.3.3 Mass loss and CH content by temperature range

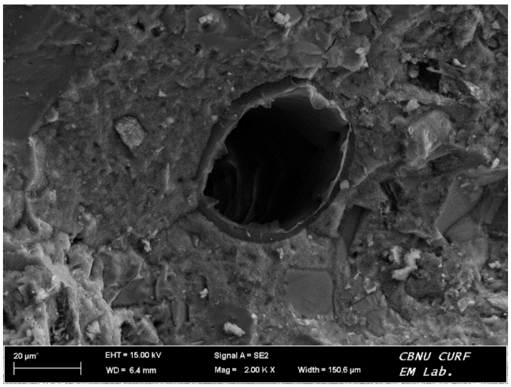
Table 6 presents the mass loss and CH content according to the temperature range of each specimen. The experimental results show that the unit cement content and CH content are proportional to each other. The CH contents were reduced in all MK-incorporated mixtures, consistent with MK having rapidly reacted with CH and becoming stabilized with calcium silicate hydrate at the early stage.

Table 6 TG-DTA analysis of RPC specimens according to SF and MK content

Mix Type	Weight loss ratio (%)			Predicted contents of $Ca(OH)_2$ (%)
	W_{t1} 25–200°C	W_{t2} 200–450°C	W_{t3} 450–500°C	
70C-30SF-00MK-10PP	6.460	2.537	0.2717	1.117
70C-15SF-15MK-10PP	6.137	2.363	0.2458	1.010
70C-00SF-30MK-10PP	5.799	2.190	0.2119	0.871
80C-30SF-00MK-10PP	6.137	3.419	0.2964	1.218
80C-15SF-15MK-10PP	6.566	2.843	0.2700	1.110
80C-00SF-30MK-10PP	6.371	2.573	0.2723	1.119
95C-30SF-00MK-10PP	4.830	4.845	0.3571	1.468
95C-15SF-15MK-10PP	5.002	4.718	0.3363	1.382
95C-00SF-30MK-10PP	5.876	3.042	0.3070	1.262



(a) Before fire test



(b) After fire test

Fig. 7 SEM micrographs of RPC specimen with PP fiber before and after the fire test

Poon *et al*. (2001) reported that at early ages, the rates of CH consumption in MK-blended cement pastes were higher than in SF- or FA-blended cement pastes. Janotk *et al*. (2020) explained that the efficiency of MK as a pozzolan in cement and concrete is mainly determined by the high content of SiO_2 and Al_2O_3. Curcio *et al*. (1998) reported that the higher initial reactivity of MK can be attributed to its Al_2O_3 phases, which are known to contain 4- and 5-coordinated Al and Al_2O_3 involved in the fast formation of C_2ASH_8 (gehlenite), and a small amount of the crystalline C_4AH_{13} phase.

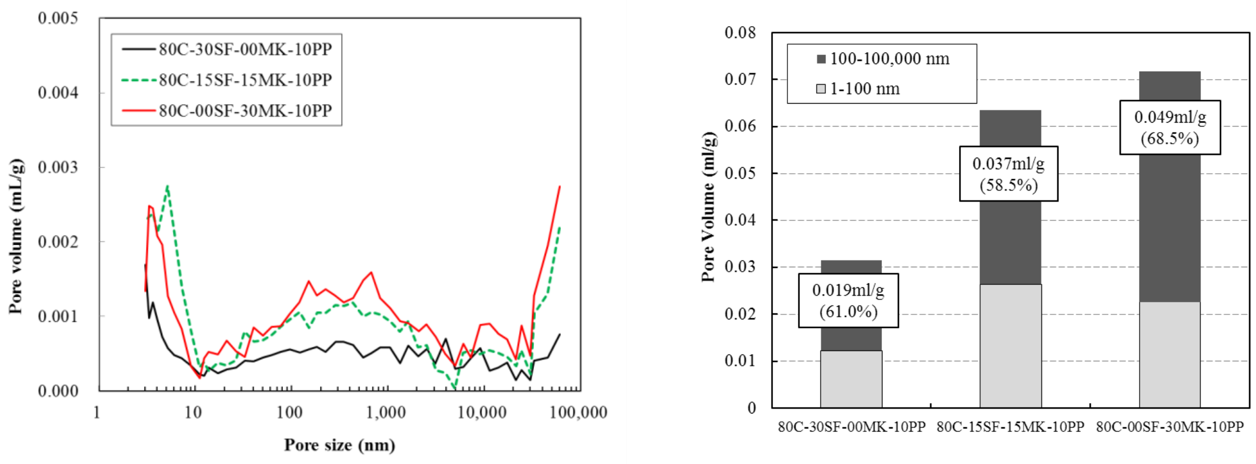
In our study also, it can be inferred that MK exhibited higher reactivity than SF since the SF only mixtures had the highest CH contents. Thus, through the initial rehydration process, the CH content was effectively reduced by conversion into C-S-H or C-A-H. The CH remaining in the cement matrix dehydrates above 450–500°C (Gamal *et al*. 2019), generating steam pressure in the concrete, thereby accelerating spalling. Hence, the incorporation of MK reduces the CH content and mitigates spalling.

3.3.4 Analysis of pore structure of RPC before and after fire test

This study used mercury intrusion porosimetry (MIP) to measure the porosity and pore size distributions of various RPC specimens with different SF and MK contents before and after the fire test. The effect of the MK content on spalling of RPC was also investigated.

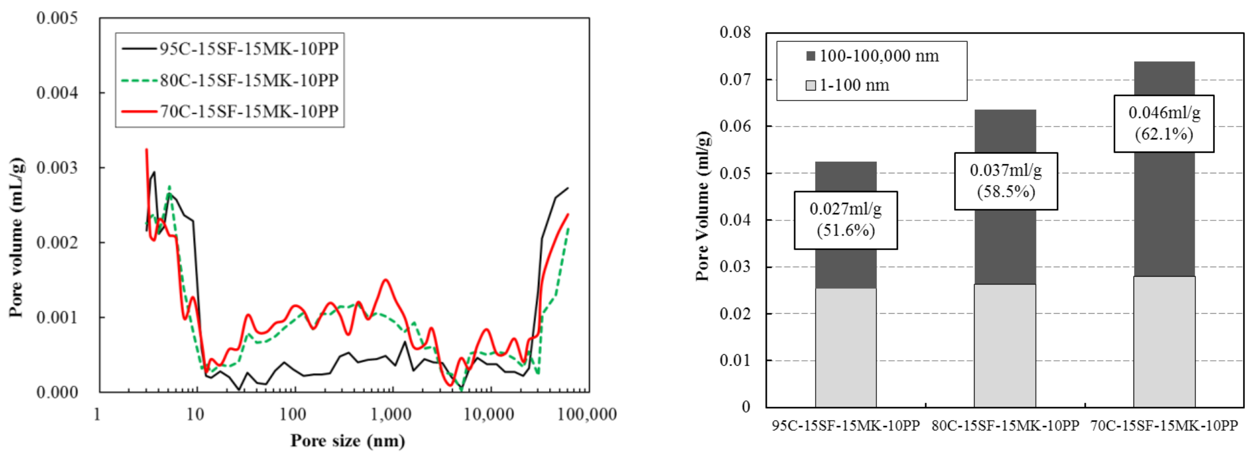
Fig. 8(a) shows the pore distribution of specimens with different SF/MK mixing ratios with a cement content of 800 kg m^{-3}. The pore distribution was largely divided into 1–10 nm, 10–10,000 nm, and >10,000 nm. The 80C-30SF specimen exhibited the lowest pore volume in all ranges. At 1–10 nm, there were no significant trends according to the mixing ratio. However, at pore distributions of 10–10,000 nm and >10,000 nm, the pore volume clearly increased as the mixing rate of MK increased.

Fig. 8(b) shows the composition ratio for the 100–100,000 nm size pores. In a study that compared the spalling results and pore structural analysis results, So *et al*. (2014) found that the factors affecting spalling were related to the composition ratio of the micropores rather than the overall porosity. They reported that if the porosity ratio increases above the standard pore of approximately 100 nm for the release of water vapor pressure, it becomes a relatively open matrix and steam pressure is released smoothly, which is advantageous for mitigating spalling.



(a) Pore distribution (b) Ratio of total pores to 100–100,000 nm pores

Fig. 8 Pore distribution and ratio according to SF and MK content of RPC



(a) Pore distribution (b) Ratio of total pores to 100–100,000 nm pores

Fig. 9 Pore distribution and ratio according to unit cement content of 15SF-15MK RPC

The results of this study have also demonstrated that as the pore size increased above 100 nm, the effect on spalling was more advantageous. In the MK-incorporated 80C-15SF-15MK-10PP and 80C-00SF-30MK-10PP specimens, the pore volumes were 0.037 ml g^{-1} and 0.049 ml g^{-1} in the pore range of 100 nm or more, and spalling did not occur after the fire test. However, the 80C-30SF-00MK-10PP specimen incorporating only SF exhibited a pore volume of 0.019 ml g^{-1}, that is, less than half that of the corresponding MK specimens, and it exhibited partial spalling after the fire test.

Fig. 9(a) shows the pore distribution of 15SF-15MK RPC with varying cement content. Micropores with a pore size of >100 nm proportionately decreased as the cement content per unit area increased. For the RPC with a cement content of 950 kg m^{-3}, pores >100 nm comprised 51.6% of the total pore volume, whereas the RPC with 800 kg m^{-3} comprised 58.5%. However, the 700 kg m^{-3} RPC showed a high total pore volume, and pores >100 nm also comprised a high ratio (62.1%). RPCs with the 15SF-15MK composition ratio did not exhibit spalling, though the 700

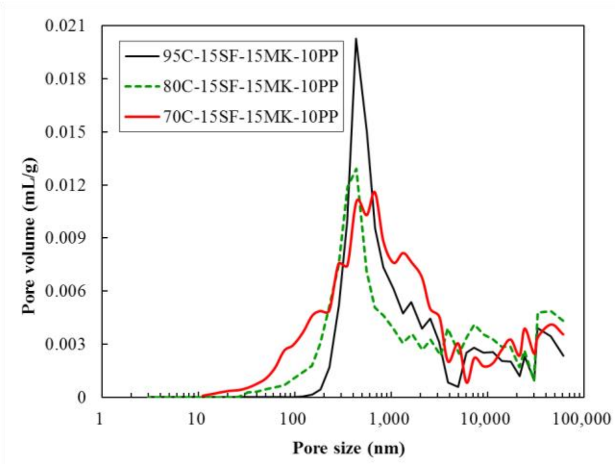


Fig. 10 Pore distribution according to unit cement content of 15SF-15MK RPC after fire test

kg m^{-3} RPC with the highest number of pores exhibited partial molten steel and PP fiber seeping through the loose matrix.

Fig. 10 shows changes in the porosity and pore size distribution of the RPC specimens according to the mixing ratio of OPC, SF, and MK after the fire test. The porosity of the RPC specimens increased by a factor of 2 (27.7–30.5%) compared with the RPC specimens before the fire test. In particular, the pore volume of 100–10,000 nm significantly increased in all RPC specimens, contributing to the release of water vapor accumulated in the RPC matrix.

4. Conclusions

Results of the evaluation of the pozzolanic reactivity of MK indicate that the API was 89%, almost equivalent to that of SF, and approximately 20% higher than that of FA and BFS. Furthermore, MK reacts rapidly with the cement hydrates to produce C-A-H and C-S-H, yielding a dense hydrated matrix and enabling the production of high-strength concrete. Since MK rapidly reacted with CH and was stabilized with C-S-H, CH was actively consumed, hence the generation of water vapor was reduced during fire conditions. The pore volume of 100–100,000 nm is relatively high compared with the conventional RPC using only SF, which is advantageous for spalling, as the water vapor pressure is released smoothly through the loose structure. However, concrete incorporating only MK as a reactive powder was unable to yield a strength of over 100 MPa. When the powder content was 30%, RPC with a 1:1 ratio of SF and MK exhibited a compressive strength of over 100 MPa regardless of the unit cement content, and exhibited the highest residual flexural and compressive strength. It was observed that incorporating PP fibers was very effective for preventing explosive spalling. In the RPC specimens incorporating MK, the minimum PP fiber content required to prevent spalling was 0.5 vol.% of the cement weight.

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References

Alireza, J., Mohammad, A.M. and Mohammad, B. (2017), “Evaluation of incorporating metakaolin to evaluate durability and mechanical properties of concrete”, *Adv. Concr. Constr.*, **5**(3), 241-255. https://doi.org/10.12989/acc.2017.5.3.241.

Ambroise, J., Maximilien, S. and Pera, J. (1994), “Properties of metakaoling blended cements”, *Adv. Cem. Based Mater.*, **1**(4), 161-168. https://doi.org/10.1016/1065-7355(94)90007-8.

Asadi, I., Shafigh, P., Bin Abu Hassan, Z.F. and Mahyuddin, N.B. (2018), “Thermal conductivity of concrete – a review”, *J. Build. Eng.* **20**, 81-93. https://doi.org/10.1016/j.jobe.2018.07.002.

Atkinson, T. (2004), “Polypropylene fibers control explosive spalling in high-performance concrete”, *Concrete.*, **38**(10), 69-70.

Bakiş, A., Işik, E., El, A.A. and Ülker, M. (2017), “A study on the mixture ratio of pumice powder concrete on the concrete pavement and the construction of building”, *IOSR-JMCE.*, **14**(3), 83-90. https://doi.org/10.9790/1684-1403068390.

Banerji, S., Kodur, V. and Solhmirzaei, R. (2020), “Experimental behavior of ultra high performance fiber reinforced concrete beams under fire conditions”, *Eng. Struct.*, **208**(1) 110316. https://doi.org/10.1016/j.engstruct.2020.110316.

Bastos, G., Patiño-Barbeito, F., Patiño-Cambeiro, F. and Armesto, J. (2016), “Admixtures in cement-matrix composites for mechanical reinforcement, sustainability, and smart features”, *Materials (Basel).*, **4**(12), 972. https://doi.org/10.3390/ma9120972.

Bilodeau, A., Kodur, V.K.R. and Hoff, G.C. (2004), “Optimization of the type and amount of polypropylene fibres for preventing the spalling of lightweight concrete subjected to hydrocarbon fire”, *Cem. Concr. Res.*, **26**, 163-174. https://doi.org/10.1016/S0958-9465(03)00085-4.

Bingöl, A.F. and Gül, R. (2009), “Effect of elevated temperatures and cooling regimes on normal strength concrete”, *Fire Mater.*, **33**(2), 79-88. https://doi.org/10.1002/fam.987.

Bingöl, A.F. and Gül, R. (2009), “Residual bond strength between steel bars and concrete after elevated temperatures”, *Fire Saf. J.*, **44**(6), 854-859. https://doi.org/10.1016/j.firesaf.2009.04.001.

Curcio, F., Deangelis, B.A. and Pagliolico, S. (1998) “Metakaolin as a pozzolanic microfiller for high-performance mortars”, *Cem. Concr. Res.*, **28**(6), 803-809. https://doi.org/10.1016/S0008-8846(98)00045-3.

Dashti Rahmatabadi, M.A. (2015), “Mechanical properties of reactive powder concrete under pre-setting pressure and different curing regimes”, *Int. J. Civ. Struct. Eng. Res.*, **4**(4), 354-358. https://doi.org/10.18178/ijscer.4.4.354-358.

El-Diadamony, H., Amer, A.A., Sokkary, T.M. and El-Hoseny, S. (2015), “Hydration and characteristics of metakaolin pozzolanic cement pastes”, *HBRC J.*, **14**(2), 150-158. https://doi.org/10.1016/j.hbrcj.2015.05.005.

El-Hawary, M.M. and Hamoush, S.A. (1996), “Bond shear modulus of reinforced concrete at high temperatures”, *Eng. Fract. Mech.*, **55**(6), 991-999. https://doi.org/10.1016/S0013-7944(96)00049-5.

EI-Jazairi, B. and Illston, J.M. (1980), “The hydration of cement paste using the semi-isothermal method of derivative thermogravimetry”, *Cem. Concr. Res.*, **10**(3), 361-366. https://doi.org/10.1016/0008-8846(80)90111-8.

Erdoğdu, S., Kandila, U. and Nayırb, S. (2019), “Effects of cement dosage and steel fiber ratio on the mechanical properties of reactive powder concrete”, *Adv. Concr. Constr.*, **8**(2), 139-144. https://doi.org/10.12989/acc.2019.8.2.139.

Felicetti, R., Gambarova, P.G. and Meda, A. (2009), “Residual behavior of steel rebars and R/C sections after a fire”, *Constr. Build. Mater.*, **23**(12), 3546-3555. https://doi.org/10.1016/j.conbuildmat.2009.06.050.

Fire insurers laboratories of korea, FILK standard (FS019-1990), Fire resistance test for building construction and materials, 1990.

Gamal, I.K., Elsayed, K.M., Makhlouf, M.H. and Alaa, M. (2019), “Properties of reactive powder concrete using local materials and various curing conditions”, *EJERS.*, **4**(6), 74-83. https://doi.org/10.24018/ejers.2019.4.6.1370.

Georgali, B. and Tsakiridis, P.E. (2005), “Microstructure of fire-damaged concrete. A case study”, *Cem. Concr. Compos.*, **27**, 255-259. https://doi.org/10.1016/j.cemconcomp.2004.02.022.

Haddad, R.H. and Shannis, L.G. (2004), “Post-fire behavior of bond between high strength pozzolanic concrete and reinforcing steel”, *Constr. Build. Mater.*, **18**(6), 425-435. https://doi.org/10.1016/j.conbuildmat.2004.03.006.

Hiremath, P.N. and Yaragal, S.C. (2018), "Performance evaluation of reactive powder concrete with polypropylene fibers at elevated temperatures", *Constr. Build. Mater.*, **169**, 499-512. https://doi.org/10.1016/j.conbuildmat.2018.03.020.

Janotk, I., Puertas, F., Palacios, M., Kuliffayova and Varga, C. (2010), "Metakaolin sand–blended-cement pastes: Rheology, hydration process and mechanical properties", *Constr. Build. Mater.*, **24**(5), 791-802. https://doi.org/10.1016/j.conbuildmat.2009.10.028.

Joshaghani, A., Moeini, M.A. and Balapour, M. (2017), "Evaluation of incorporating metakaolin to evaluate durability and mechanical properties of concrete", *Adv. Concrete Constr.*, **5**(3), 241-255. http://dx.doi.org/10.12989/acc.2017.5.3.241.

Kalifa, P., Chene, G. and Galle, C. (2001), "High temperature behavior of HPC with polypropylene fibres from spalling to microstructure", *Cem. Concr. Res.*, **31**(10), 1487-1499. https://doi.org/10.1016/S0008-8846(01)00596-8.

Korea infrastructure safety corporation (KISC) (2010), "Test method of thermogravimetry and differential thermal analysis", Korea.

Korea standard association, KS F 2257-1: Method of fire resistance test for elements building construction – General requirements, 2005.

Kushartomo, W., Bali, I. and Sulaiman, B. (2015), "Mechanical behavior of reactive powder concrete with glass powder substitute", *Procedia Eng.*, **125**, 617-622. https://doi.org/10.1016/j.proeng.2015.11.082.

Larbi, J.A., Fraay, A.L.A. and Bijen, J.M. (1990), "The chemistry of the pore fluid of silica fume-blended cement systems", *Cem. Concr. Res.*, **20**(4), 506-516. https://doi.org/10.1016/0008-8846(90)90095-F.

Lagerblad, B. (2001), "Leaching performance of concrete based on studies of samples from old concrete constructions", Technical Report TR-01-27, Swedish Cement and Concrete Research Institute.

Lee, S. (2008), "Characterization of durability and fire-resistance of metakaolin mixed high strength concrete and its field application", *Hanyang National University Master's Thesis.*

Lee, Y. (2009), "Fabrication of meta kaoline and its application", *Gyeongsang National University Master's Thesis.*

Li, Y., Tan, K.H. and Yang, E.H. (2018), "Influence of aggregate size and inclusion of polypropylene and steel fibers on the hot permeability of ultra-high performance concrete (UHPC) at elevated temperature", *Constr. Build. Mater.*, **169**, 629-637. https://doi.org/10.1016/j.conbuildmat.2018.01.105.

Lin, W., Lin, T.D. and Powers-Couche, L.J. (1996), "Microstructures of fire-damaged concrete", *ACI Mater. J.*, **93**(3), 199-205. https://doi.org/10.14359/9803.

Liu, H.B., Li, K.L. and Ju, Y. (2010), "Explosive spalling of steel fiber reinforced reactive powder concrete subject to high temperature". *Concrete*, **8**, 6-8. http://en.cnki.com.cn/Article_en/CJFDTotal-HLTF201008005.

Metakaolin, Wikipedia (2019), https://en.wikipedia.org/wiki/Metakaolin.

Mustafa, S., Metin, H.S. and Serhat Ç. (2017), "Mechanical properties of SFRHSC with metakaolin and ground pumice: Experimental and predictive study", *Steel Compos. Struct.*, **23**(5), 543-555. https://doi.org/10.12989/scs.2017.23.5.543.

Nishida, A. and Yamazaki, N. (1995), "Study on the properties high strength concrete with short polypropylene fiber for spalling resistance", *Proceedings of the International Conference on Concrete Under Severe Conditions, CONSEC'95*, Sapporo, Japan.

Parveen, P., Mehta, A. and Saloni, S. (2019), "Effect of ultra-fine slag on mechanical and permeability properties of Metakaolin-based sustainable geopolymer concrete", *Adv. Concr. Constr.*, **7**(4), 231-239. https://doi.org/10.12989/acc.2019.7.4.231.

Peng, Y., Zhang, J., Liu, J., Ke, J. and Wang, F. (2015), "Properties and microstructure of reactive powder concrete having a high content of phosphorous slag powder and silica fume", *Constr. Build. Mater.*, **101**(1), 482-487. https://doi.org/10.1016/j.conbuildmat.2015.10.046.

Poon, C.S., Azhar, S., Anson, M. and Wong, Y.L. (2001), "Comparison of the strength and durability performance of normal- and high-strength pozzolanic concretes at elevated temperatures", *Cem. Concr. Res.*, **31**(9), 1291-1300. https://doi.org/10.1016/S0008-8846(01)00580-4.

Rix, H. (2009), Fire safety of concrete buildings, in, Cement Concrete & Aggregates, Australia, ISBN 978-1-877023-27-9.

Sarika, S. and John, E. (2015), "A study on properties of reactive powder concrete", *Int. J. Eng. Res. Tech.*, **4**(11), 110-113. https://doi.org/10.17577/IJERTV4IS110170.

Seitllari, A. and Maser, M.Z. (2019), "Leveraging artificial intelligence to assess explosive spalling in fire-exposed RC columns", *Comput. Concr*. **24**(3), 271-282. https://doi.org/10.12989/cac.2019.24.3.271.

Šerelis, E., Vaitkevičius, V. and Kerševičius, V. (2016), "Influence of silica fume on the workability and hydration process of ultra-high performance concrete", *Cheminė Technologija.*, **67**(1), 58-65. http://dx.doi.org/10.5755/j01.ct.67.1.15825.

Shi, C., Wu, Z., Xiao, J., Wang, D., Huang, Z. and Fang, Z. (2015), "A review on ultra high performance concrete: Part I. Raw materials and mixture design", *Constr. Build. Mater.*, **101**, 741-751. https://doi.org/10.1016/j.conbuildmat.2015.10.088.

So, H., Yi, J., Khulgadai, J. and So, S. (2014), "Properties of strength and pore structure of rpc exposed to high temperatures", *ACI Mater. J.*, **11**(3), 335-346. https://doi.org/10.14359/51686580.

Sperinck, S., Raiteri, P., Marks, N. and Wright, K. (2011), "Dehydroxylation of kaolinite to metakaolin—a molecular dynamics study", *J. Mater. Chem.*, **7**, 2118-2125. https://doi.org/10.1039/c0jm01748e.

Tafraoui, A., Escadeillas. G., Lebaili. S. and Vidal. T. (2009), "Metakaolin in the formulation of UHPC", *Constr Build Mater.*, **23**(2), 669-674. https://doi.org/10.1016/j.conbuildmat.2008.02.018.

Tang, C.W. (2018), "Fire resistance of high strength concrete filled steel tubular columns under combined temperature and loading", *Steel Compos. Struct.*, **27**(2), 243-253. https://doi.org/10.12989/scs.2018.27.2.243.

Tang, C. W. (2017), "Fire resistance of high strength fiber reinforced concrete filled box columns", *Steel Compos. Struct.*, **23**(5), 611-621. https://doi.org/10.12989/scs.2017.23.5.611.

Yamamoto, T. (2006), "Pozzolanic reactivity of fly ash – API method and K-value", *Fuel.*, **85**(16), 2345-2351. https://doi.org/10.1016/j.fuel.2006.01.034.

Yang, H., Qin, Y., Liao, Y. and Chen, W. (2016), "Shear behavior of recycled aggregate concrete after exposure to high temperatures", *Constr. Build. Mater.*, **106**, 374-381. https://doi.org/10.1016/j.conbuildmat.2015.12.103.

Yang, Y., Feng, S., Xue, Y., Yu, Y., Wang, H. and Chen, Y. (2019), "Experimental study on shear behavior of fire-damaged reinforced concrete T-beams retrofitted with prestressed steel straps", *Constr. Build. Mater.*, **209**, 644-654. https://doi.org/10.1016/j.conbuildmat.2019.03.054.

Wild, S., Khatib, J.M. and Jones, A. (1996), "Relative strength, pozzolanic activity and cement hydration in superplasticized metakaolin concrete", *Cem. Concr. Res.*, **26**(10), 1537-1544. https://doi.org/10.1016/0008-8846(96)00148-2.

Zheng, W., Li H. and Wang Y. (2012). "Compressive Behaviour Hybrid Fiber-Reinforced Reactive Powder Concrete after High Temperature", *Mater. Des.*, **41**, 403-409. http://dx.doi.org/10.1016/j.matdes.2012.05.026.

Zhang, H.Y., Qiu, G.H., Kodur, V., Yuan, Z.S. (2020). "Spalling behavior of metakaolin-fly ash based geopolymer concrete under elevated temperature exposure", *Cem. Concr. Compos.*, **106**, 10343. https://doi.org/10.1016/j.cemconcomp.2019.103483

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