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Feasibility study of korean metakaolin as a mineral admixture for cementitious materials

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The use of high-performance concrete (HPC) that incorporates various mineral admixtures has been increasing worldwide. Metakaolin (MK), one of these mineral admixtures, is the most recent mineral admixture to be commercially introduced to the concrete construction industry. However, MK has not been used well in the construction field in Korea because it is fabricated only at the laboratory scale to test its use. Moreover, its use in commercial products fabricated in real plants in Korea has not been clearly verified yet. Therefore, in this study, the properties of mortar, that includes various mineral admixtures such as silica fume and MK, as a partial cement replacement were investigated in terms of workability and compressive strength to estimate the feasibility of MK fabricated in a real plant, by using Korean kaolin.

Key words: Metakaolin, Mineral admixtures, Workability, Compressive strength.

Introduction

Pozzolanic materials have contributed significantly to the improvement of the performance of concrete in terms of its fluidity, long-term compressive strength, and durability. Moreover, when fly ash and slag are used to make concrete, the construction cost can significantly drop [1]. Figure 1 shows the chemical composition of cement and various mineral admixtures such as fly ash (FA), slag (SL), silica fume (SF), and clay on a CaO-Al_2O_3-SiO_2 ternary composition system. The chemical composition of clay is very similar to that of FA and natural pozzolan.

Kaolin, a species of clay, has been used to manufacture porcelain and is supposed to be scattered widely in Korea. When heated between 650 °C and 800 °C and then cooled at ambient temperature, it can be used as a pozzolanic material, beter known as *metakaolin* [2-4]. The use of SF in concrete also has many advantages such as higher compressive strength and improved durability [5-6]. However, SF has been used only in limited cases in Korea because of its high import cost.

Recently, MK has been reported as an alternative to SF [7-8]. Especially, MK has economic advantages over SF in Korea, because of the nationwide availability of its raw materials, as mentioned earlier. Many researchers have established the theoretical and practical basis for the use of MK in concrete. However, most researches on MK have focused on the development of compressive strength and durability [9-10]. From the practical viewpoint, the workability of mortar and concrete that contains MK (hereinafter referred to as "MK mortar") is an important aspect to consider seriously, but the influence of MK fabricated in a real plant in Korea on the workability of concrete has hardly been studied. Therefore, this study experiments on the properties of MK manufactured in Korea in mortar and concrete in terms of fluidity and compressive strength, and projects the performance of MK in comparison to that of SF.

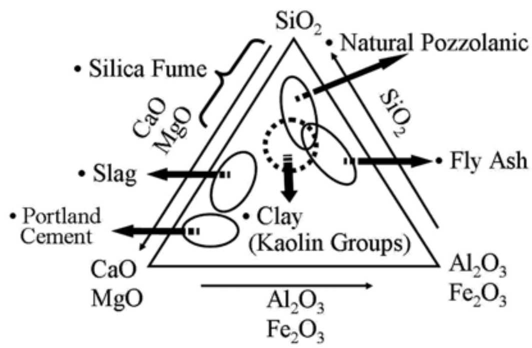

Fig. 1. General chemical compositions of cement and mineral admixtures.

Experimental Procedure

Type I Portland cement was used in all the mortar and concrete mixtures. MK was fabricated in a real plant, as shown in Figure 2. This manufacturing process is similar to the fabrication process of refractory

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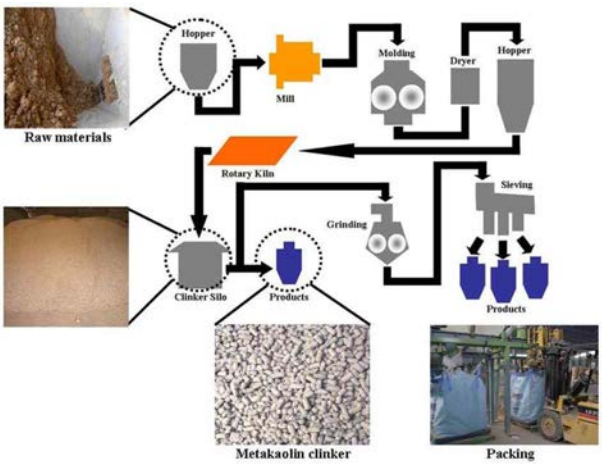

Fig. 2. Manufacturing process of metakalin.

materials using kaolin. However, it is specialized for the meta-stabile formation of kaolin through the special control of a rotary kiln.

It seems that Korean MK has the same potential as geopolymer material due to its sufficient SiO_2 content, unlike that of OPC [11]. To compare MK with OPC with respect to their fluidity and compressive strength, mineral admixtures such as MK and SF were used. They were commercial products produced in Korea, and SF was imported from Czechoslovakia. The chemical composition of each mineral admixture is shown in Table 1.

Figure 3 shows the XRD patterns of MK and SF, which reveal their basically low crystallinity. However, MK has the same crystallinity as quartz and mica. Therefore, it seems that both a slightly modified manufacturing process and the addition of additives are needed to accelerate the diffusion of aluminate and silicate ions from the crystallinity of MK.

Both mortar and concrete tests were carried out on the fluidity and compressive strength to determine the basic properties of MK and confirm its performance by applying it in high-strength concrete. Table 2 shows the mixing proportions of the mortar. For all the mortar specimens, a W/B ratio of 0.4 and an S/B ratio of 2.14 were applied, and each mineral admixture replaced ordinary Portland cement by 10%. The dosage of the polynaphthalene sulfonate (PNS) superplasticizer was set within the range of 1.25-2.50% to achieve the initial target flow of 170-180 mm [12]. The mortar flow was measured for up to 90 min., with an interval of 30 min. Mortar molds were prepared using ASTM C 109, and the compressive strength was measured after 1, 3, 7, and 28 days of hydration. The hydrate specimens of cement paste that incorporated MK or SF were also analyzed via XRD and SEM to observe their hydrated phases.

Table 1. Chemical composition of cementitious materials.

Content	OPC (%)	MK (%)	SF (%)
SiO_2	21.0	56	94.0
Al_2O_3	5.4	37	0.6
Fe_2O_3	3.13	2.4	1.3
MgO	3.06	0.3	0.1
CaO	62.11	2.4	0.3
TiO_2	–	0.2	–
K_2O+Na_2O	1.2	0.9	2.2
Blaine (cm^2/g)	3,386	12,000	150,000
Appearance	Gray	Light pink	Gray

*OPC: Ordinary Portland Cement, MK: Metkaolin, SF: Silica Fume.

Table 2. Mixture proportion of mortar.

W/B	B	S	W	PNS
40%	900 g	1926 g	360 g	1.25-2.50%

*Binder (B): When MK was used, 10% of normal portland cement wasreplaced with MK or SF.
*Liquid type superplasticizers (solid content 40%) were used.

Results and Discussion

Figure 4 shows the mortar flow of various mortars that contain each mineral admixture. When 1.25% PNS was dosed in the OPC, the initial mortar flow was measured to have been close to the target mortar flow (180 mm). However, in the cases of the MK and SF at the same PNS dosage, the initial mortar flow was much smaller than that of the OPC. The initial target mortar

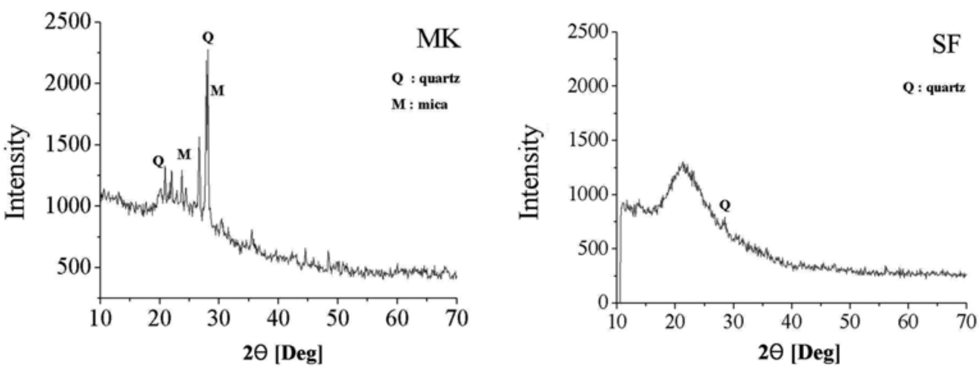

Fig. 3. XRD patterns of MK and SF.

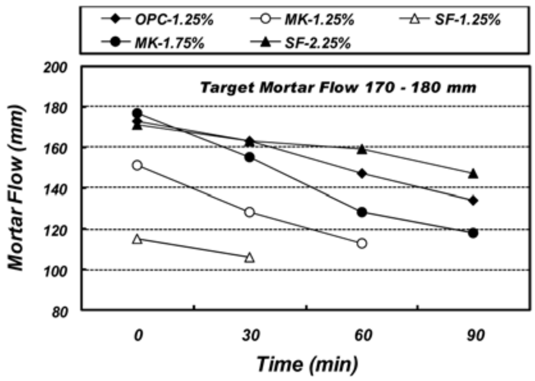

Fig. 4. Effect of PNS dosage on the fluidity of MK mortar and SF mortar.

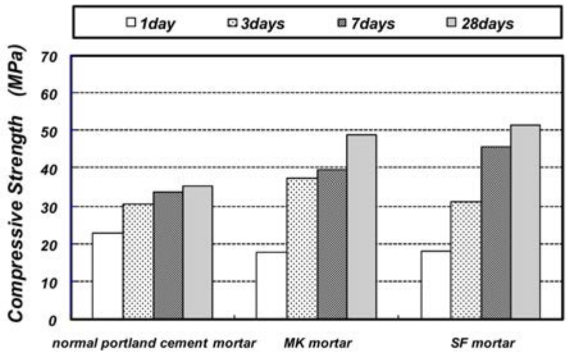

Fig. 5. Compressive strength of mortars with hydration time.

flow for the MK and SF was achieved at PNS dosages of 1.75% and 2.25%, respectively. It was revealed that the larger PNS dosage for the MK and SF was due to their extremely large Blaine (MK: 12,000 cm^2/g and SF: 200,000 cm^2/g). Moreover, the Blaine of the OPC was 3,386 cm^2/g. However, although the initial flows of the MK or SF mortar at the aforementioned dosages were very similar, their fluidity behavior appeared to have significantly differed. However, the SF mortar showed high fluidity behavior retention, but the MK mortar rapidly lost its fluidity.

Figure 5 shows the development of the compressive strength of the mortars that contained OPC, MK, and SF. The mortars that contained MK and SF exhibited lower compressive strength than normal Portland cement mortar on Day 1. However, the compressive strengths of the MK and SF mortars were much higher than those of the mortars that contained OPC after three days, because of the higher reactivity of MK and SF. In the case of the SF mortar, the compressive strength after seven days was much higher than that of normal Portland cement mortar. On Day 28, the compressive strengths of the MK and SF mortars improved by 40% and 46%, respectively, unlike the compressive strength of normal Portland cement mortar. These results show that the MK produced in Korea appears to be an effective pozzolanic material, similar to SF, in the development of strength. MK also requires a lower PNS dosage to achieve the same initial flow as that of SF, but its rapid flow loss needs to be improved to allow its use in ready-mixed concrete. Therefore, XRD and SEM analyses were performed to clarify this problem of MK on workability.

Figure 6 and Figure 7 show the SEM morphologies

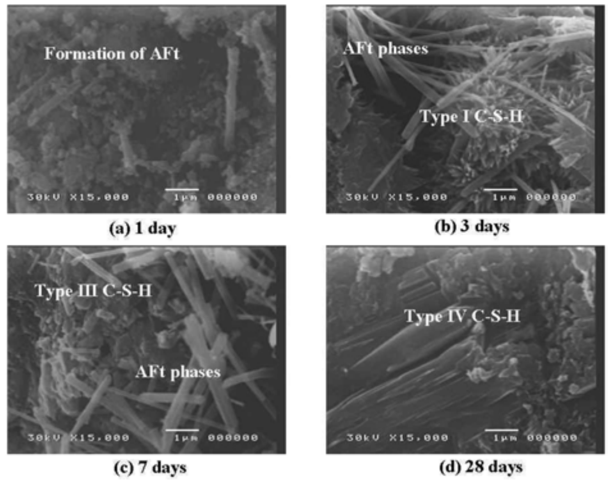

Fig. 6. SEM analysis of cement paste incorporating MK.

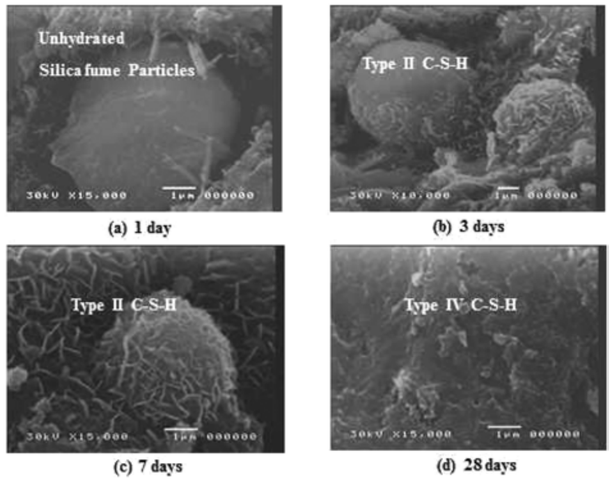

Fig. 7. SEM analysis of cement paste incorporating SF.

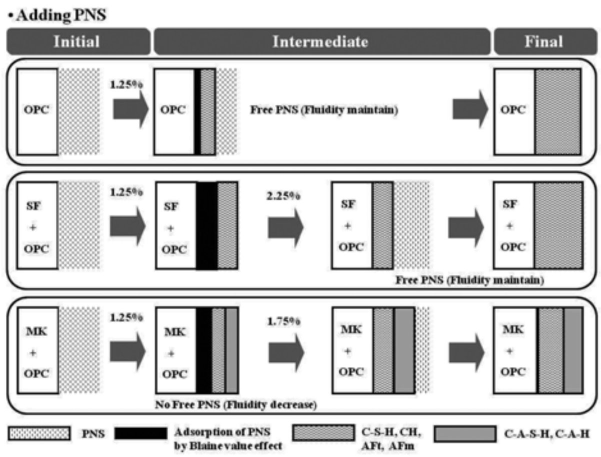

Fig. 8. Schematic representation of the adsorption state of PNS.

of the cement paste with 10 wt% of MK or SF, respectively. In the case of MK, small 3-5 μm-long AFt phases were formed on the surface on Day 1. Then small amounts of AFt phases and type I C-S-H were formed in three days, followed by the formation of large amounts of AFt phases and type III C-S-H in seven days. Finally, a hydrate of cement paste with MK formed type IV C-S-H with an AFt or AFm phase. On the other hand, particles of SF were hydrated partially for three days and then formed type II C-S-H and type IV C-S-H after seven days. This means that the MK more significantly affected the formation of the AFt and AFm phases than did the SF in its early stage [13-14]. In other words, although they affected the rapid flow loss in the early stage by fine particle size, the mechanisms of the rapid flow loss differed, as shown in Figure 6(b). It especially seemed that the rapid flow loss in the MK case was related to the formation of the AFt and AFm phases via the adsorption of sulfate ions from the PNS superplasticizer [15-16].

Figure 8 shows a schematic representation of the adsorption state of the PNS in the cases of the OPC, MK, and SF [17]. In the case of the OPC and SF, when the PNS dosage reached the saturation point after the addition of the PNS superplasticizer, the free PNS remained in the system and then worked for slump retention between the cement particles and the mineral admixtures. However, the MK reacted with the sulfate ions from the free PNS to fabricate the AFt, AFm, and C-A-S-H phases after reaching the saturation point. Therefore, if the AFt or AFm phase of the MK can be controlled by other superplasticizers that have good compatibility with the AFt or AFm phase, it seems that this problem could be overcome in the early stage.

Figure 9 shows the XRD patterns of the MK and SF pastes with the hydration time. The amount of $Ca(OH)_2$ in the cement paste with MK and SF decreased noticeably after three days, unlike with ordinary Portland cement paste. $Ca(OH)_2$ seems to be consumed to form the AFt, AFm, C-A-S-H, and C-S-H phases with the hydration time. These results also showed that the differential reduction ratio of the CH between the MK and SF pastes. In the case of the SF, it decreased continuously with the hydration time due to the pozzolanic reaction. Especially, the pozzolanic reaction was accelerated after seven days, and therefore, the CH also decreased significantly. In the case of MK, the CH seemed to have been consumed mainly to form the AFt, AFm, and C-A-H phases in Stage I. The formation of these phases was also faster than in the SF case, which is attributed to the increment of the compressive strength in the early stage compared to the SF case. Then the reduction ratio of the CH after Stage II showed a tendency similar to that in the SF case. It seems that CH consumes to rapidly format C-A-S-H and C-S-H as a pozzolanic reaction [18-19].

Therefore, the results could be interpreted as follows: silica fume contributes to compressive strength in the long term due to the formation of C-S-H with a high silicate concentration ratio, and metakaolin increases the compressive strength due to the formation of AFt, AFm, C-A-S-H [$Ca_2Al_2SiO_7H_2O$],[5] and C-S-H [20], although its particle size is much larger than that of silica fume. In other words, if the dissolution of silicate ions from MK ions can be accelerated by catalysis, the compressive strength of MK will be compensated for,

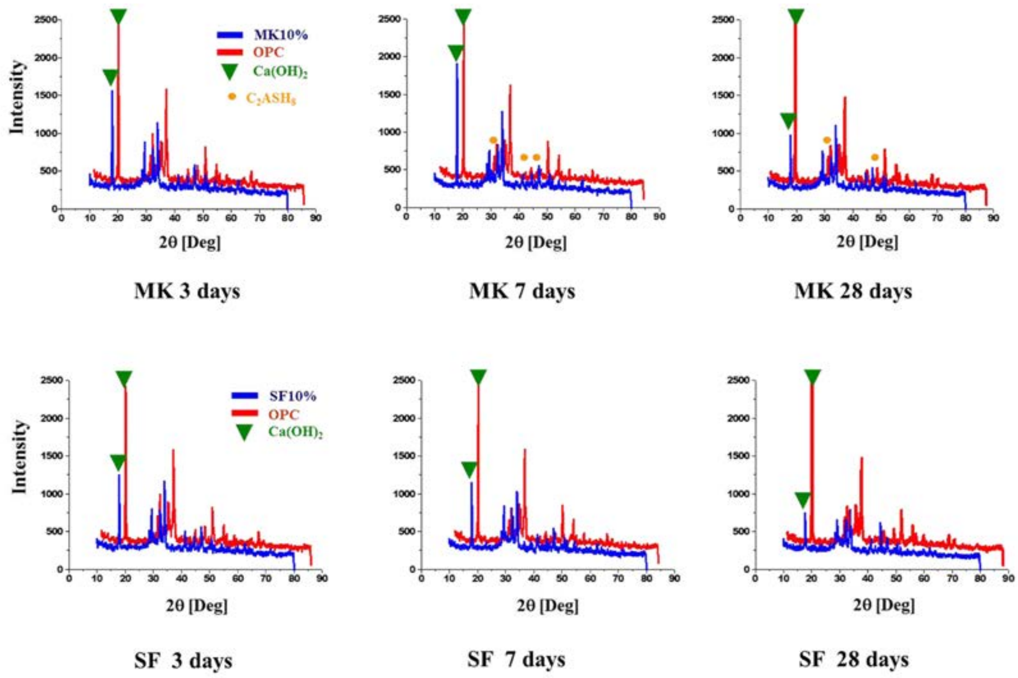

Fig. 9. Relationship between Ca(OH)2 and pozzolanic reaction of MK and SF.

compared to SF in Stage II.

Conclusions

The properties of MK manufactured in Korea in mortar were investigated to develop high-performance concretes.

(1) The replacement of ordinary Portland cement with 10 wt% MK significantly improved the compressive strength, as does silica fume in mortar.

(2) The different types of PNS superplasticizer considerably affected the fluidity and compressive strength of the metakaolin mortar and concrete. The low workability of concrete that contains MK, a common disadvantage of MK, could be improved by using a PNS superplasticizer. Therefore, a PNS superplasticizer is desirable for use in making high-strength concrete that contains MK.

(3) The addition of a PNS superplasticizer to MK-blended cement improved the fluidity and early compressive strength, which is attributed to the formation of the C-A-H and Stratling (C-A-S-H), AFt, and AFm phases. Especially, additives of the PNS superplasticizer accelerated the diffusion of MK in the cement system.

(4) It was found that high-performance concretes with high fluidity and compressive strength can be manufactured by using Korean MK as a mineral admixture in replacement of SF. MK manufactured in Korea also has a high potential for use in cement and concrete, as well as in other construction materials.

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