Diffusion behavior of aluminate and silicate on the metakaolin concrete adding various superplasticizers

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Three different superplasticzers such as PNS(poly naphthalene sulfonate), PNS based blends(PNS+AD), and PC(polycarboxylate based superplasticizer) were used to investigate the effect of superplasticizer types on the properties of mortar and concrete incorporating metakaolin(MK). When metakaolin was hydrated, diffusion behaviors of aluminate and silicate were examined separately at 1, 3, 7 and 28 days by X-ray diffraction, SEM/EDS and for compressive strength. It was found from XRD analysis that the superplasticizer type had a considerable effect on the hydration rate and hydrates types. Notably, PNS+AD had two distinct effects on the MK paste such as the acceleration of pozzolanic reaction and formation of different types of hydrates such as type II CAH [$Ca_6Al_2O_6(OH)\cdot 2H_2O$], type III CASH [$Ca(Si_7Al_2)O_{18}\cdot H_2O$], and AFt which were not formed in MK paste including PNS, nor MK paste including PC. The results showed that PNS+A D seem to be effective in inducing the dissolution of MK. It was concluded that when metakaolin is used for the purpose of manufacturing high performance concrete, it is desirable to use PNS based blends rather than PNS and polycarboxylate based superplasticzer.

Keywords : Metakaolin, C-A-H, C-A-S-H, Superplasticizer

1. INTRODUCTION

The construction industry has made great strides especially in the construction material field over the past two or three decades. Among construction materials, pozzolanic materials such as silica fume, fly ash, slag and natural pozzolans have played an important role in improving the quality of concrete products in compressive strength and durability. This is due to the fact that the calcium hydroxide produced by the cement hydration reacts with the pozzolan and produces an additional gel which has a pore blocking effect, and therefore alters the pore structure and the strength. Moreover, reduction of calcium hydroxide (CH) leads to improved resistance against sulphate attack and alkali-silicate reactions.

Recently metakaolin (MK) is reported as showing similar properties with silica fume in cement hydration behavior and development of compressive strength. However, it also contains alumina, which upon reaction produces additional alumina containing phases, some of which are crystalline such as C_4AH_{13}, C_2ASH_8 and C_3AH_6. Therefore, it has a slightly different hydration behavior compare to silica fume. [1,2]

Many researchers have established the theoretical and practical basis like the workability of mortar and concrete using various superplasticizers for the use of MK in concrete. [1,2,3] However, no detailed examination has been reported for the interaction between ion diffusion behavior of MK and various superplasticizers during hydration.

The aim of this study is to evaluate ion diffusion behavior of MK according to various superplasticizers. In addition, the effect of superplasticizer type on the hydration acceleration of MK mortar and concrete together with compressive strength was also investigated. In order to understand the influence of superplasticizer type on the hydration of cement paste incorporating MK, XRD, and SEM/EDS analysis were also performed.

2. MATERIALS AND EXPERIMENTAL METHODS

2.1 Materials

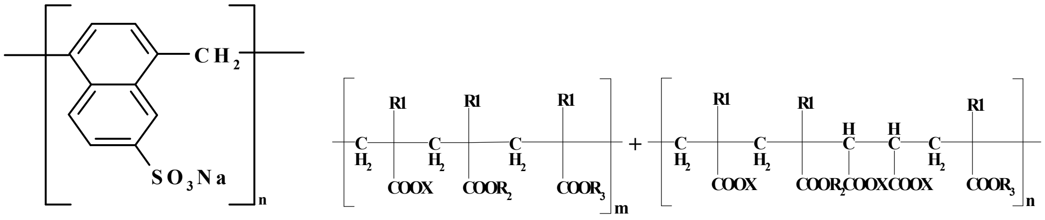
Type I normal portland cement and MK were used as binding materials. Both the normal portland cement and MK are commercial products manufactured in Korea. The chemical composition of each mineral admixture is shown in Table 1. MK consisted of 56 % of SiO_2 and 37 % of Al_2O_3. Contents of SiO_2 and Al_2O_3 of MK produced in other countries are in the range of 50 – 54 % and 40 – 45 %, respectively. The color of MK manufactured in Korea is light pink because of its relatively high content of Fe_2O_3 while the color of MK manufactured in other countries is nearly white.

Table 1. Chemical Composition of Cement and MK

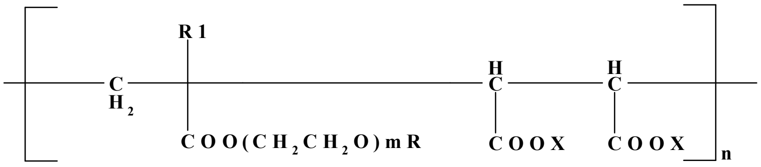
Content	Normal portland cement	MK
SiO_2	21.0 %	56 %
Al_2O_3	5.4 %	37 %
Fe_2O_3	3.13 %	2.4 %
MgO	3.06 %	0.3 %
CaO	62.11 %	2.4 %
TiO_2	-	0.2 %
K_2O+Na_2O	1.2 %	0.9 %
Blaine(cm^2/g)	3,400	12,000
Appearance	Gray	Light Pink

2.2 Superplasticizers

Three different types of commercially available superplasticizers such as PNS, PNS-based blends and a polycarboxylate(PC) type superplasticizer were used in order to investigate the effect of each superplasticizer on the fluidity and the compressive strength of MK mortar and concrete. Solid content of all superplasticizers was 40 %. PNS-based blends were prepared by mixing PNS with additives, respectively. Chemical structure of each superplasticizer is shown in Fig. 1.



(a) PNS (b) AD (Additive)



(c) PC (Polycarboxylate)

Fig. 1 Chemical Structure of PNS, AD and PC

2.3 Experimental Method

Table 2 shows the mixture proportion of mortar test. All mortars having a 0.40 W/B(B: Binder) and 2.14 S/B were tested. MK was used to replace normal portland cement by 10 wt%. Dosage of each superplasticizer was in the range of 0.65 – 1.75% to obtain the target initial fluidity (170 – 180 mm) of mortar. Mortar flow was measured up to 90 minutes, at time interval of 30 minutes. Mortar cubes were prepared according to the ASTM C 109 test method and the compressive strength was measured at 1, 3, 7 and 28 days. All concretes had 0.30 W/B and 0.42 S/A in this study. The slump flow of concrete was measured at 0, 30 and 60 minutes and the compressive strength of concrete was determined according to ASTM C 39 at 1, 3, 7 and 28 days.

Table 2. Mixture Proportion of Mortar

W/B	B	S	W	SP
40 %	900 g	1926 g	360 g	0.65 – 1.75 %

* Binder(B) : When MK was used, 10 % of normal portland cement was replaced with MK.

* Liquid type superplasticizers(solid content 40 %) were used.

2.4 XRD and SEM/EDS Analysis

The XRD analysis was carried out to investigate the effect of superplasticizer type on the hydration behavior of MK pastes. All pastes having 0.40 W/B were treated with acetone after 1, 3, 7 and 28 days to prevent further hydration and ground in order to analyze their XRD pattern. The superplasticizers were used to obtain the initial mini-slump flow(diameter of cement paste) in the range of 130 to 140 mm. All mortar specimens for SEM/EDS were cast at room temperature and cured for 24h at 20°C in a moist curing room. After demolding, the specimens for SEM/EDS were examined at different ages in order to clarify the ion diffusion behavior of MK.

3. RESULTS AND DISCUSSION

3.1 Hydration mechanism of cement paste incorporating MK and effect of superplasticizer type on the MK mortar

In previous research [1,2,3], when MK is used to make a high-performance concrete containing PNS, it is necessary to improve the rapid fluidity loss. It was hypothesized that rapid flow loss of MK on workability was related to the formation of AFt, AFm and C-A-S-H phases seen through XRD and SEM analysis of hydration products. (Fig. 2)

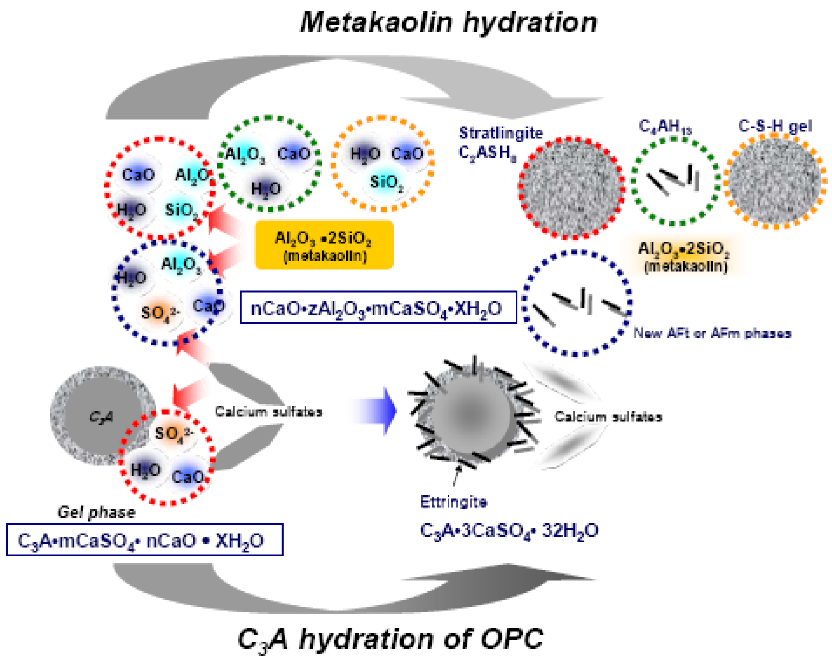


Fig. 2 Mechanism of Hydration on Cement Paste incorporating MK

In the case of cement past incorporating MK, small amounts of ettringite and type I C-S-H were observed after 3 days. In addition, large amounts of ettringite and type III C-S-H were also observed at 7 days by SEM micrographs. Finally, hydrate of cement paste incorporating MK formed type IV C-S-H with AFt or AFm phases. However, formations of these depend on the hydration conditions by acceleration or retardation of catalysis by the superplasticizer. In other words, compressive strength and workability of MK mortar and concrete will be effected by the formation of AFt, AFm, C-A-S-H $[Ca_2Al_2SiO_7H_2O]^{5)}$ as well as C-S-H. Therefore, the effectiveness of different types of superplasticizers on the fluidity of MK mortar was investigated in order to find reasonable superplasticizers for

MK. In this part, three different superplasticizers such as PNS, PNS-based blends and PC were used. As shown in Fig. 3, the effect of the superplasticizer type on the fluidity retention was considerably different, even though all the MK mortars had a similar initial fluidity by the addition of 1.75 % of PNS, 1.75 % of the PNS-based blends and 0.65 % of PC, respectively. PC appeared to be most effective in retaining the fluidity followed by the PNS-based blends and PNS. Although PC showed excellent performance in fluidity retention, it exhibited poor performance in the development of compressive strength.

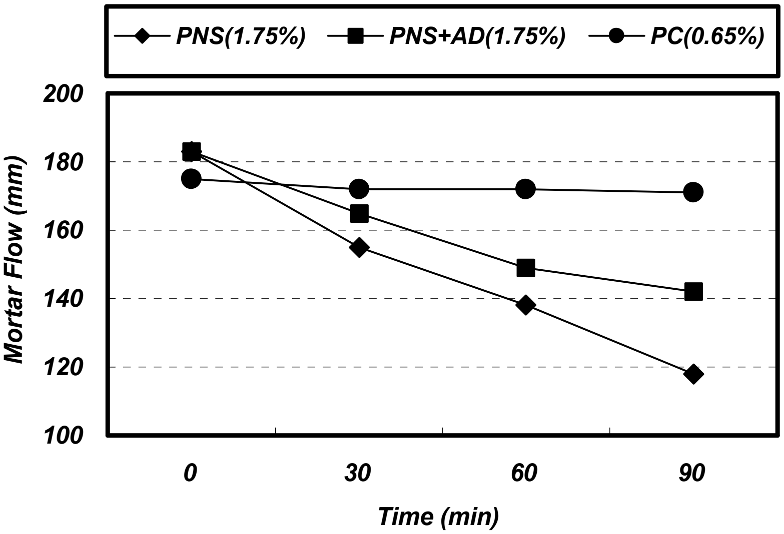


Fig. 3 Effect of superplasticizer type on the fluidity of MK mortar.

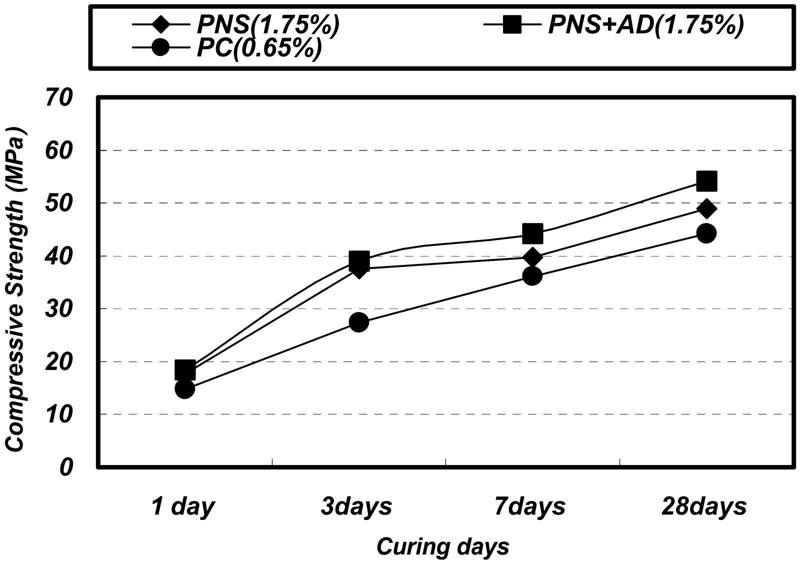


Fig. 4 Effect of superplasticizer type on the compressive strength of MK mortar.

As shown in Fig. 4, PC appeared to retard the hydration of MK mortar compared to PNS and the PNS-based blends. In contrast, the PNS- based blends seemed to accelerate the hydration of the MK mortar compared to the other superplasticizers. Considering both the fluidity and the compressive strength of MK mortar, it can be concluded that based on the limited tests, when MK is used for the purpose of manufacturing high-performance concrete, it is desirable to use the PNS-based blends rather than the PNS and PC.

3.2 Hydration mechanism of MK mortar containing various superplasticizers

As described above, MK will be affected by various superplasticizers. Therefore, to clarify these mechanisms, XRD and SEM/EDS analysis are carried out. Table 3 shows the XRD patterns of normal portland cement and MK pastes with hydration time. In the XRD analysis, PNS, PNS+AD and PC were used.

Table 3. Main hydration products of each paste sample by XRD

Time Sample	1 day	3 days	7 days	28 days
OPC (PNS)	$Ca(OH)_2$ C_3S, C_2S	$Ca(OH)_2$ C-A-H(I)	$Ca(OH)_2$	$Ca(OH)_2$ C-S-H
MK (PNS)	$Ca(OH)_2$ C_3S, C_2S	$Ca(OH)_2$ C-A-H(I) C-A-S-H(II)	$Ca(OH)_2$ C-A-H(I) C-A-S-H(II)	$Ca(OH)_2$ C-A-S-H(II) C-S-H
MK (PNS + AD)	$Ca(OH)_2$ C-A-H(I) C-A-H(II) C_3S, C_2S	$Ca(OH)_2$ C-A-H(I) C-A-S-H(I) C-A-S-H(II)	$Ca(OH)_2$ C-A-S-H(I) C-A-S-H(II) C-A-S-H(II)	$Ca(OH)_2$ C-A-S-H(II) C-A-S-H(III) C-S-H
MK (PC)	$Ca(OH)_2$ C-A-H(I) C_3S, C_2S	$Ca(OH)_2$ C-A-H(I)	$Ca(OH)_2$, C-A-S-H(II)	$Ca(OH)_2$ C-A-S-H(I) C-A-S-H(II) C-S-H

C-A-H (I) : $3CaO \cdot Al_2O_3 \cdot 6H_2O$, C-A-H (II) : $Ca_6Al_2O_6(OH) \cdot 2H_2O$
C-A-S-H (I) : $CaO \cdot Al_2O_3 \cdot 2SiO_2 \cdot XH_2O$
C-A-S-H (II) : $2CaO \cdot Al_2O_3 \cdot 2SiO_2 \cdot (Al \cdot SiO_2) \cdot XH_2O$
C-A-S-H (III) : $CaO \cdot Al_2O_3 \cdot 2SiO_2 \cdot (5SiO_2) \cdot XH_2O$

The hydration of MK pastes appeared to be retarded compared to normal portland cement paste, including the PNS at 1 day. This seems to be the result of the higher dosages of the PNS in the MK pastes than that in normal portland cement paste, and the lower content of cement. Among the three superplasticizers, PC appeared to significantly retard the cement hydration. The XRD pattern of the MK paste including PC was close to that of normal portland cement, except a $Ca(OH)_2$ peak appeared and small quantities of CSH and CAH($[Ca_3Al_2(OH)_{12}]$) were produced. [2,3]

There was no distinct difference in the hydration between MK paste including PNS and MK paste including PNS+AD. However, in case of MK paste including PNS+AD, there appeared two types of CAH such as [$Ca_3Al_2(OH)_{12}$] (type I CAH) and [$Ca_6Al_2O_6(OH)\cdot 2H_2O$](type II CAH) as well as CSH. Type II CAH, which seemed to be produced by a pozzolanic reaction, was not visible in the MK paste including PNS and MK paste including PC. Moreover, evidence of formation of AFt or AFm phases from MK was first detected in case of PNS+AD. X-ray spectra obtained from these phases revealed particular trends in their chemical composition as formation of AFt or AFm phases proceeded. It was observed that the ratio of sulfate peak height increased. (Fig. 5)

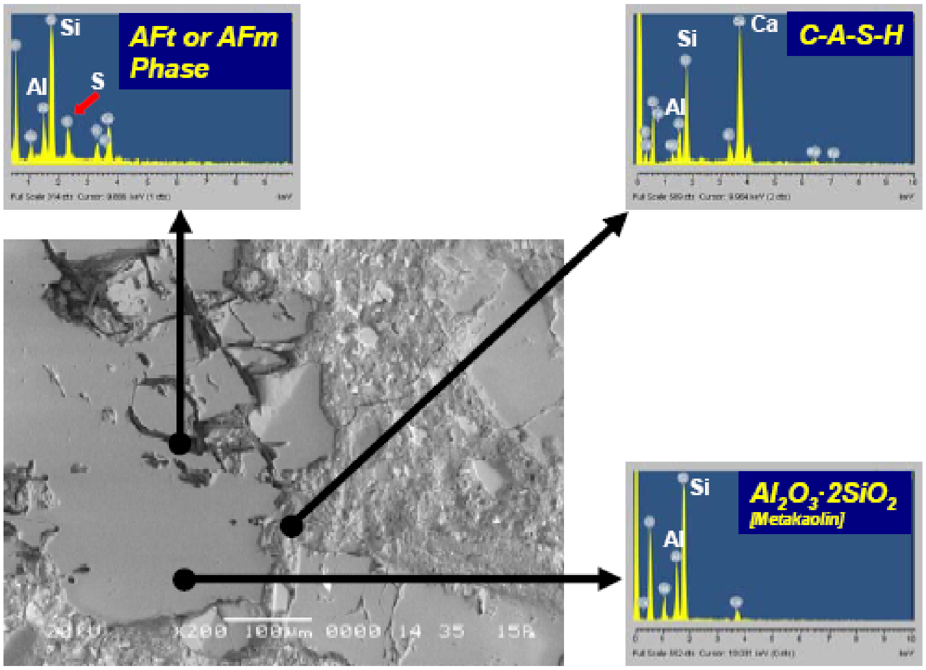


Fig. 5 X-ray spectrum from MK mortar containing PNS+AD at 1day

At 3 days, two types of CASH such as [$CaAl_2Si_2O_8\cdot H_2O$](type I CASH) and [$Ca_2Al_3(SiO_4)(Si_2O_7)\cdot(XHO)_2$](type II CASH) appeared in the MK paste including PNS+AD. However, in the MK paste including PNS, type I CASH was not found at 3 days. Moreover, there was no CASH peak in MK paste including PC at 3 days. Fig. 6, 7 and 8 show the X-ray maps and spectra taken from reacted MK particles on each specimen at 3 days. Fig. 6 shows X-ray maps of the partially diffused MK particles from MK paste including PNS, In addition, Fig. 7 shows accelerate d diffusion of MK particles in case of PNS+AD compared to PNS and PC case. Evidence of various C-A-S-H phases according to Ca ion and Al ion was detected in this specimen. However, X-ray spectra taken from MK particles including PC shows also retarded diffusion on hydration.

At 7 days, another different type of CASH([$Ca(Si_7Al_2)O_{18}\cdot H_2O$], type III) was produced at 7 days only in MK paste including PNS+AD, while type I CASH disappeared. These results seemed that type I CASH reacted with silicate to form type III CASH. It was also observed that, type II CASH began to appear in MK paste including PC.

At 28 days, the main hydrates in MK paste including PNS+AD were CSH, type II CASH and type III CASH. However, type III CASH was not found in MK paste including PNS nor in MK paste including PC. There was a considerable amount of CAH in MK paste including PC, which means that the retardation effect of PC lasted up to 28 days.

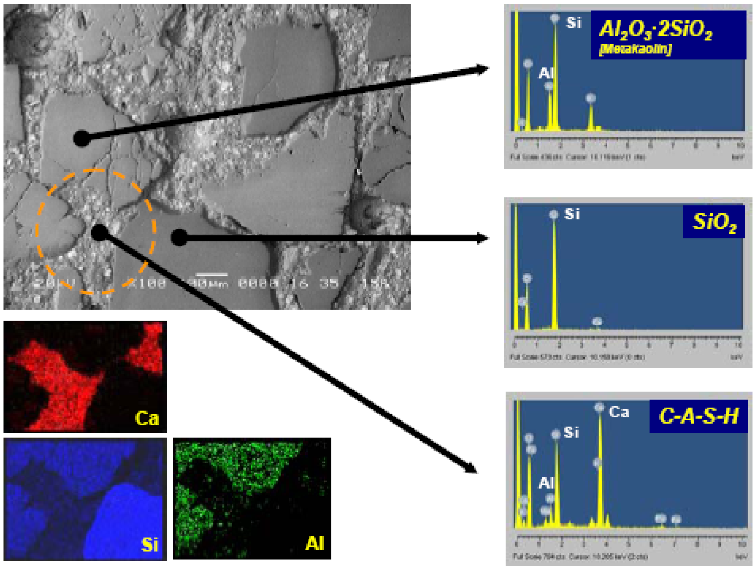


Fig. 6 X-ray spectrum from MK mortar containing PNS at 3day

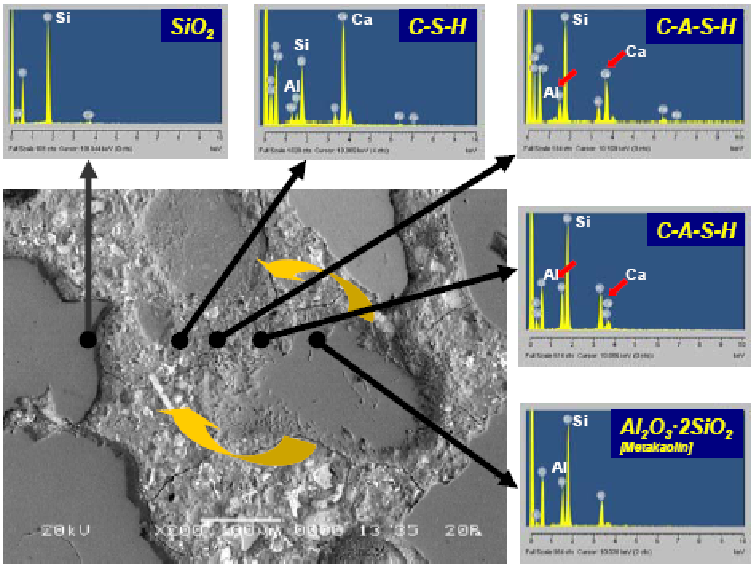


Fig. 7 X-ray spectrum from MK mortar containing PNS+AD at 3day

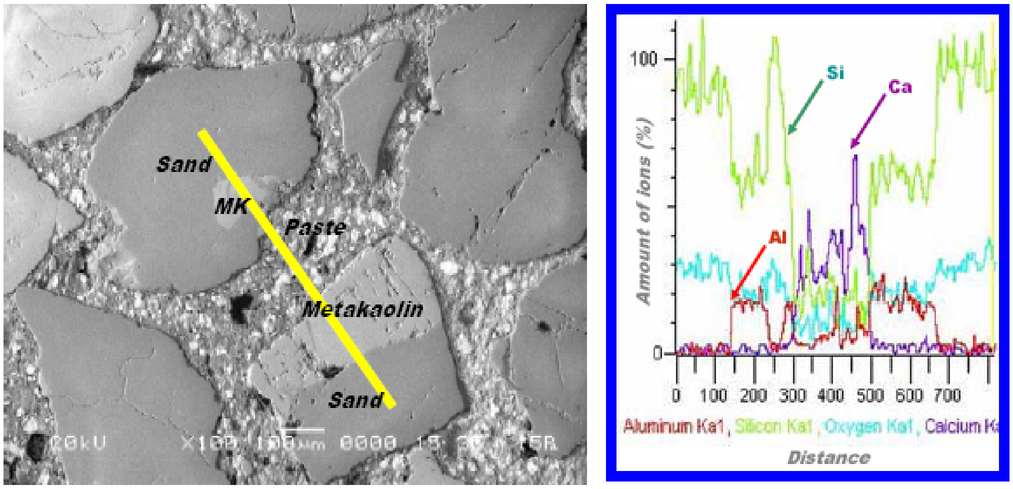
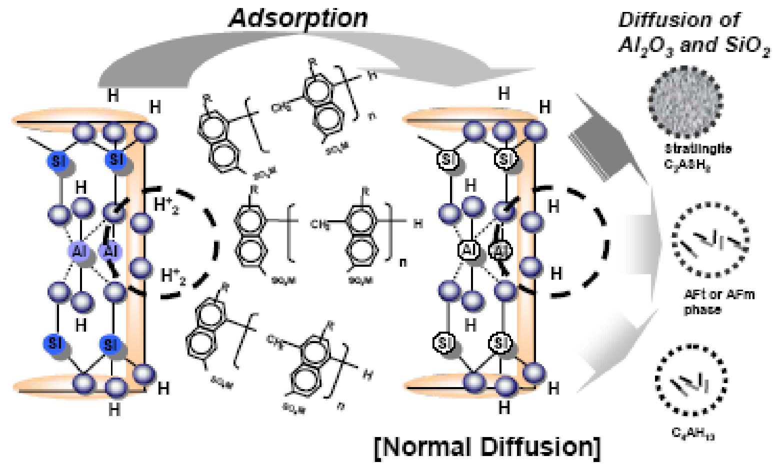


Fig. 8 X-ray spectrum from MK mortar containing PC at 3day

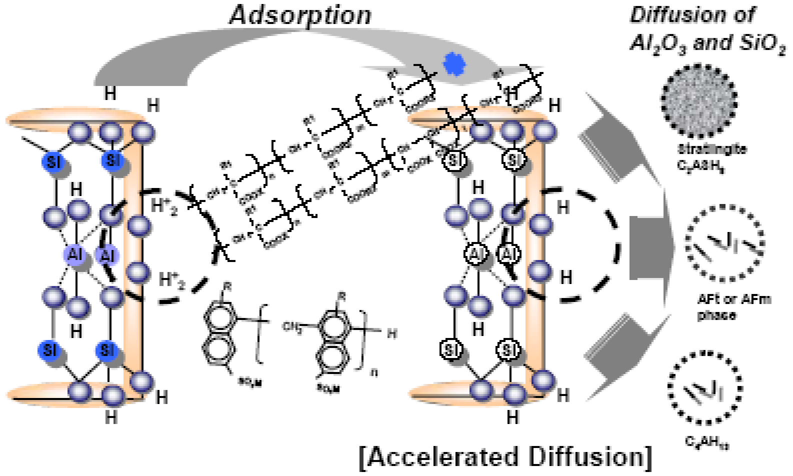
It has been reported that C_2ASH_8 and CSH gel are the most important hydrates in MK-lime system, however, the hydrates types and their stabilities with hydration time depend on the MK/lime ratio, temperature and the presence of different activators. Hydration behavior and hydrates types in a MK-cement system is more complicated than those in a MK-lime system. Nevertheless, considering the complexity of a MK-cement system, it was found from XRD and SEM/EDS analysis that the superplasticizer type considerably affected the hydration rate and hydrates types.

PNS+AD had two distinct effects on the MK paste; the acceleration of pozzolanic reactions and the formation of different types of hydrates, such as type II CAH , type III CASH and AFm, which were not formed in MK paste including PNS nor MK paste including PC at early stage. Therefore, considering the fact that type III CASH contains larger amount of Si than type I CASH and type II CASH, it can be said that PNS+AD seems to be effective in inducing the dissolution of MK.[AD will act as an accelerator for diffusion of MK] Fig. 9 shows a schematic summary of accelerated or retarded hydration of MK paste and mortar depending on various superplasticizers. It can be concluded that PNS+AD increases the compressive strength of MK mortar after 3 days because of its acceleration of both dissolution of MK and pozzolanic reactions.

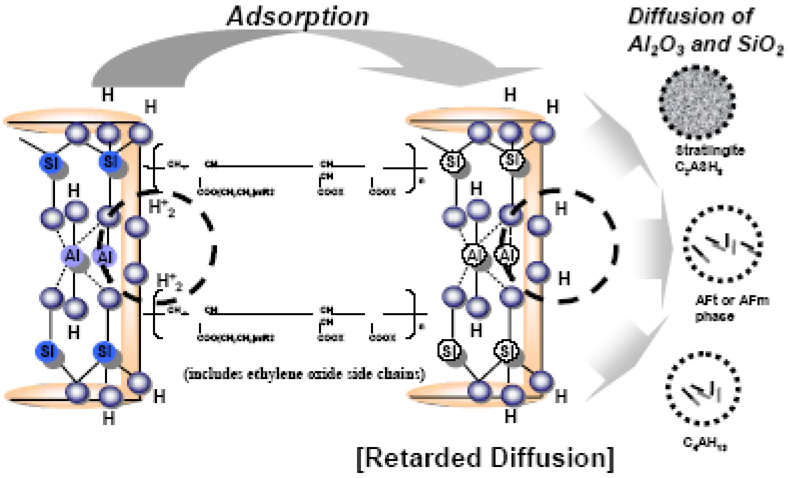
Finally, the $CaO-Al_2O_3-SiO_2-H_2O$ system at ordinary temperatures is modified by the addition of various superplasticizers to cement paste incorporating MK. Especially, CH reacted with Al or Si ions from MK at an early stage, and then it was decreased during curing. C-A-S-H[stratlingite] was also formed with hydrogarnet phases when hydration of MK was accelerated by accelerator as AD. Therefore, a phase diagram of cement incorporating MK could be predicted, as shown Fig. 10, and its phase boundary condition will be studied by thermodynamic calculation in future works.



(a) PNS type (Poly Naphthalene Sulfonate)



(b) PNS based blends type (PNS+AD)



(c) PC type (Polycarboxylate)

Fig. 9 Interaction between metakaolin and various superplasticizers

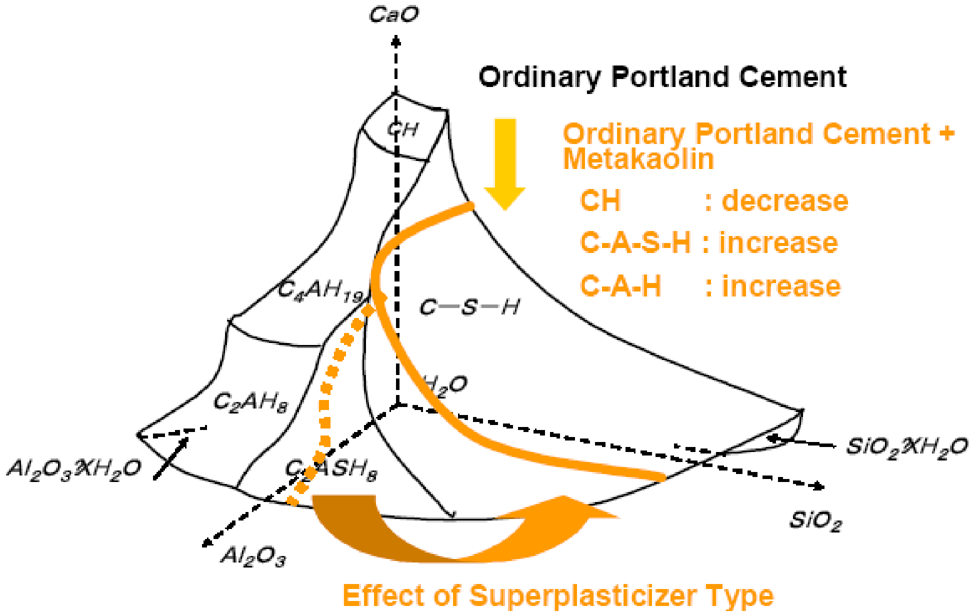


Fig. 10 Modified CaO-Al_2O_3-SiO_2-H_2O system at ordinary temperature by various superplasticizers

3.3 Effect of superplasticizer type on the strength of MK concrete

The performances of MK as pozzolanic materials in high-performance concrete were investigated. Three types of superplasticizers such as PNS, PNS-based blends and PC were used. Similar to the results of mortar tests, PC appeared to be the most effective in slump flow retention followed by PNS-based blends and PNS. However, it shows also poor performance on compressive strength. The compressive strength of the concretes are shown in Fig. 11.

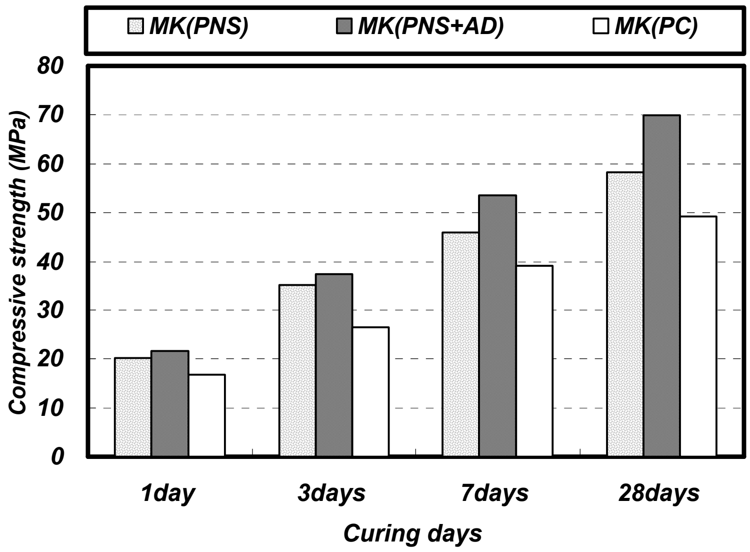


Fig. 11 Compressive strength of MK concrete according to superplasticizer

It can be seen that MK concretes exhibited high compressive strengths, which are slightly higher compressive strengths than in some conventional concrete mixtures. This confirms that the MK could be used as a mineral admixture for the production of high-performance concrete. Moreover, the PNS-based blends, similar to the result of compressive strength of mortars, seemed to accelerate the cement hydration compared to PNS while PC significantly retarded the cement hydration. From the results of the fluidity and the compressive strength of MK concrete, PNS-based blends appear to be efficient superplasticizers for MK concrete.

CONCLUSIONS

1. The superplasticizer type significantly affected the fluidity and compressive strength of the MK mortar and concrete. PNS-based blends are more desirable for the production of high-performance MK concrete because PNS-based blends increase the compressive strength as well as improve the fluidity of MK mortar and MK concrete.

2. The addition of PNS-based superplasticizer blends to the metakaolin blended cement improved the fluidity and early compressive strength , which is attributed to the formation of C-A-H and Stratling(C-A-S-H), AFt and AFm phases. Especially, additives of PNS-based blends acted as an accelerator for the diffusion of MK in the cement system.

3. The XRD and EDS/SEM analysis results revealed that the rate of pozzolanic reaction and hydrate types were largely dependent on the superplasticizer type. PNS-based blends were efficient superplasticizers in accelerating pozzolanic reaction, which seemed to contribute considerably to the higher compressive strength of the MK mortar and concrete.

ACKNOWLEDGEMENTS

The author would like to thank the INTChem.Co.Ltd. in Korea for their financial support. (www.intchem.com)

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