Effectiveness of a New Type Superplasticizer for Ultra Rapid hardening Cement

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1. Introduction

1.1 Superplasticizers

Superplasticizers (SP) are important chemical admixture widely used for improving concrete properties. Addition of a small amount of SP gives good workability of concrete by dispersing cement particles. Sulfonated naphthalene formaldehyde condensates (NS) and sulfonated melamine formaldehyde condensates (MS) are the first generation of SPs [1,2]. These are polymers which have a single repeating unit. Thus NS and MS do not have much variation of molecular structures. These PCs can disperse cement particles by electrostatic repulsions. New generation of SP based on polycarboxylate polymers (PC) has been developed [2]. PC has two or more structural units that provide for more variation in molecular structures. The typical PC is based on comb-type copolymers of acrylic acid and acrylic ester. The PC can disperse cement particles by steric hindrance effect by long graft chain of ester unit. The characteristics of PC can be varied by altering the ratio of acid unit and ester unit, changing length of graft chain and changing length of main chain. In Japan, main type of SP was NS around 1990. From 1993, PC type SP overtook NS type SP. PC occupied 80% of the entire SP products in 2004 [3]. Many researches have been devoted toward increasing the understanding of cement – PC interactions and the mechanisms behind PC perforamance [4-8].

1.2 Ultra rapid hardening cement

Ultra rapid hardening cement is usually used for urgent construction and repair construction because of early developing strength [9]. Concrete using Ultra rapid hardening cement shows enough strength for practical use in several hours. Some methods have been used to obtain Ultra rapid hardening cement. They include the use of mixture of Portland cement and calcium aluminate cements. Another approach has been the manufacture of clinkers containing either $C_{11}A_7CaF_2$ or C_4A_3S both of which hydrate rapidly under appropriate conditions with the formation of etringite [10]. Usually chemical retarders are required to control the rate of reaction and NS type SP is added to obtain adequate workability.

1.3 New SP for Ultra rapid hardening cement

PC usually shows a higher dispersibility than NS for Portland cements. But it was found that almost commercial PCs did not work well for Ultra rapid hardening cement; they did not disperse Ultra rapid hardening cement or need higher dosage to obtain adequate fluidity. In this study, a new type of polucarboxylate polymers (NPC) was evaluated. Fluidity and strength of mortar and concrete of Ultra rapid hardening cement were examined. It was found that NPC had higher dispersibility than NS for Ultra rapid hardening cement. Required dosage of NPC was very lower than that of NS to obtain same fluidity of mortar and concrete. Strength of mortar and concrete using NPC were almost same as mortar and concrete using NS. Heat of libration of Ultra rapid hardening cement paste was measured by conduction calorimeter. It was shown that NPC did not delay the hydration of Ultra rapid haradening cement.

2. Experimental details

2.1 Materials

2.1.1 Cement

The commercially available Ordinary Portland Cement and Ultra rapid hardening cement (JET cement; Sumitomo Osaka Cement CO.,LTD) were used. Chemical properties and mineral compositions of cements are shown

Table 1 Chemical and mineral composition of ordinary Portland cement

Chemical composition(%)									
ig.loss	insol.	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	Na_2O	K_2O
1.9	0.1	21.5	5.2	2.9	64.4	0.9	1.9	0.2	0.5

Mineral composition(%)					Blain(cm^2/g)
C_3S	C_2S	C_3A	C_4AF	$C_{11}A_7CaF_2$	
54.2	20.7	8.9	8.8	-	3470

Table 2 Chemical and mineral composition of ultra rapid hardening cement

Chemical composition(%)									
ig.loss	insol.	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	Na_2O	K_2O
0.8	0.1	13.8	11.4	1.5	59.1	0.9	10.2	0.7	0.3

Mineral composition(%)					Blain(cm^2/g)
C_3S	C_2S	C_3A	C_4AF	$C_{11}A_7CaF_2$	
50.7	1.7	-	4.7	20.6	5600

in Table 1 and Table 2.

2.1.2 Superplasticizers (SP)

Table 3 shows three types of SP which were used in this study. Fig. 1 shows the chemical structure of NS. PC and NPC are polycarboxylate based polymers. PC is designed for dispersing Portland cement. NPC has been developed for dispersing Ultra rapid hardening cement. Model structure of polycarboxylate type SP is shown in Fig. 2. Image of difference between PC and NPC is shown in Fig. 3. PC has many methyl group in the structure. Thus the main chain of PC is more rigid than that of NPC.

Table 3 List of superplasticizers

Symbol	Contents
NS	napthalene formaldehyde condensate
PC	polycaboxylate polymers with graft chains
NPC	polycaboxylate polymers with graft chains

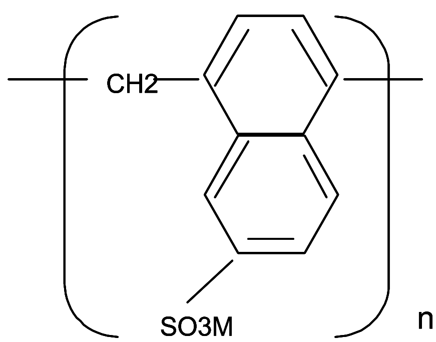

Fig.1 Molecular structure of NS

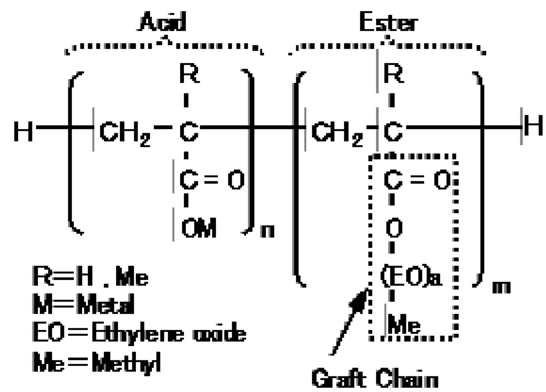

Fig. 2 Basic molecular structure of polycarboxylate-based superplasticizer

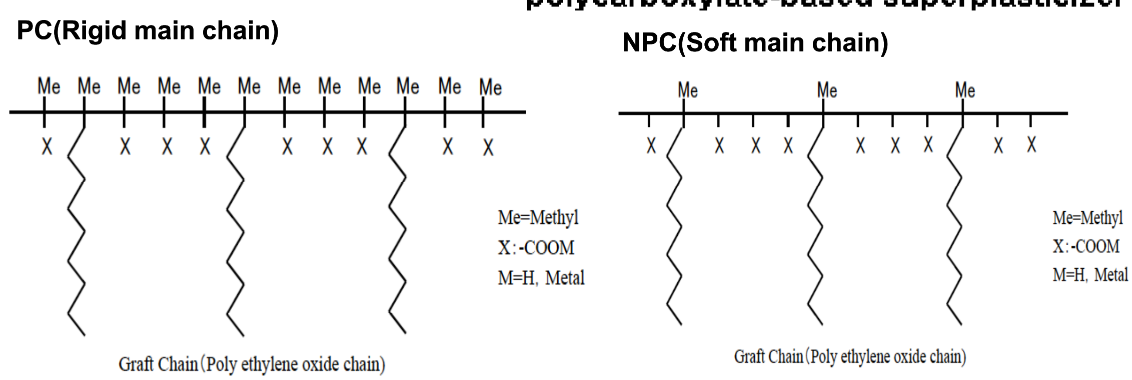

Fig.3 Image of difference between PC and NPC

2.1.3 Retarder

Oxycarboxylate type retarder (JET Setter; Sumitomo Osaka Cement CO.,LTD) was used for adjusting setting time of ultra rapid hardening cement mortar and concrete.

2.2 Mortar mixing procedure

The mortars were mixed in Japanese Industrial Standard mixer (JIS R 5201). Mixing procedure was same as Japanese Industrial Standard mixing method (JIS R 5201). Flow values and compressive strength of mortars were measured by Japanese Industrial Standard method (JIS R 5201). Table 4 shows the mix proportions of Ordinary Portland cement mortars. Mix proportions of Ultra rapid hardening cement mortars is shown in Table 5.

Table 4 Mix proportions of ordinary Portland cement mortars

W/C	S/C	C(g)	W+SP(g)	S(g)	SP type
0.3	0.85	1588	477	1350	PC,NPC

Table 5 Mix proportions of ultra rapid hardening cement mortars

W/C	S/C	C(g)	W+SP(g)	S(g)	R(g)	SP type
0.38	1.2	1000	380	1200	2.0	NS,PC,NPC
0.34	1.2	1000	340	1200	2.0	NPC
0.3	1.2	1000	300	1200	2.0	NPC

R:retarder

2.3 Concrete mixing procedure

The concretes were mixed in 50L volume forced mixing type mixer with mixing time of 120 seconds. Mix proportions of concretes is shown in Table 6. Slump, Slump loss and compressive strength of concretes were measured.

Table 6 Mix proportiopns of concretes

		Kg/m^3				R(Cx%)	SP type
W/C	S/a	W	C	S	G		
0.4	42.2	160	400	751	1074	0.2	NS,NPC
0.35	42.2	140	400	774	1108	0.25	NS,NPC
0.3	42.2	120	400	795	1140	0.25	NPC

R:retarder

2.4 Conduction calorimeter

Rate of heat liberation of cement pastes containing each SPs were measured by conduction calorimeter (TCC-23; Tokyo Riko Co.,LTD). Water cement ratio of pastes were 0.5.

3. Results and discussion

3.1 Flow values and compressive strength of mortars

Fig.4 Shows the relationship between dosage of SP and flow value of ordinary Portland cement mortars. Dispersibilities of PC and NPC were almost same for ordinary Portland cement. Relationship between dosage of SP and flow value of Ultra rapid hardening cement mortars is shown in Fig.5. In the case of NS used mortar, range in 1.5 to 2.5%, flow value of mortars did not change very much at 0.38 water cement ratio. Maximum value of mortar flow was 220mm. PC needed more dosage to get a same flow value ad NS used mortar. Usually, PC shows higher dispersibility than NS for ordinary Portland cement. These results show that PC does not work well for Ultra rapid hardening cement. In the case of NPC used mortar at 0.38 water cement ratio, it could make a same flow value with about 30% of NS dosage. Flow value of mortar increased linearly with increasing dosage. It could make a higher flow value than limit flow value of NS used mortar. In the case of 0.34 and 0.30 water cement ratio, it could make a same flow value as limit value of NS used mortar at 0.38 water cement ratio by using adequate dosage of NPC. These results mean that NPC is more effective SP than NS for Ultra rapid hardening cement. Fig.6 shows compressive strength of Ultra rapid hardening cement mortars at 3 hours after mixing. NPC used mortar showed almost same strength as NS used mortar at 0.38 water cement ratio. The higher strength was observed in lower water cement ratio. Fig.7 shows a relationship between water cement ratio and compressive strength of NPC used mortar. The compressive strength increased linearly with decreasing water cement ratio.

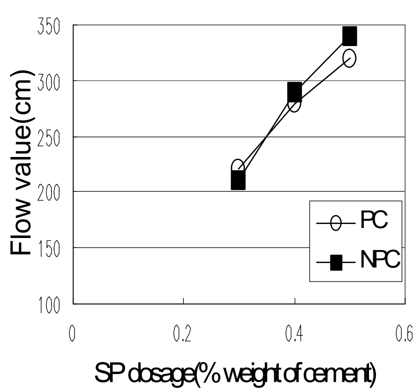

Fig.4 Relationship between SP dosage and mortar flow(ordinary portland cement)

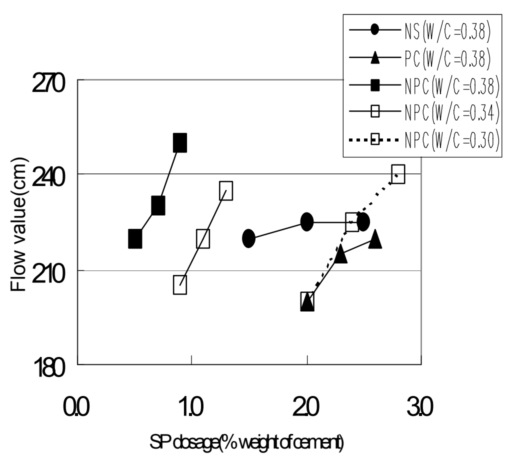

Fig.5 Relationship between SP dosage and mortar flow(ultra rapid hardening cement)

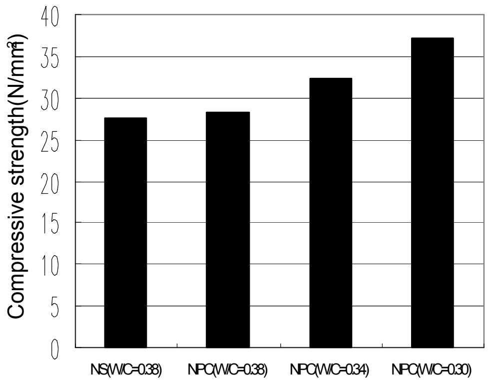

Fig.6 Compressive strength of mortar at 3hr after mixing

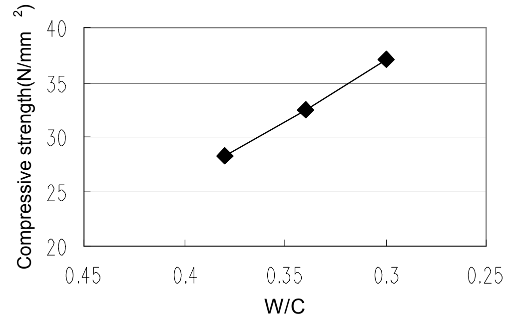

Fig.7 Relationship between W/C and compressive strength at 3hr after mixing

3.2 Slump and compressive strength of concretes

Relationship between dosage of SP and concrete slump is shown in Fig.8. In the case of NPC used concrete, it could make a same slump as NS used concrete with about 30% of NS dosage at 0.4 water cement ratio. Slump value increased with dosage of NPC. It could make a higher slump value than that of NS used concrete. When the water cement ratio was 0.35, slump of NS used concretes was only 2cm and did not change with dosage of NS. In the case of NPC used concrete, it could get a same slump at lower water cement ratio as slump at 0.4 water cement ratio with addition of adequate dosage of NPC. Fig.9 shows the slump loss of concretes. Slump loss of NPC used concrete was almost same as that of NS used concrete at 0.4 water cement ratio. Fig.10 shows the compressive strength of concretes. Compressive strength of NPC used concrete at 3 hours and 1 day curing time were almost same as that of NS used concrete at 0.4 water cement ratio. Fig.11 shows a relationship between water cement ratio and compressive strength of NPC used concrete. The compressive strength increased linearly with decreasing water cement ratio. These results suggest that it can make more workable and higher strength ultra rapid hardening concrete by use of NPC.

3.3 Rate of heat liberation of cement paste

Fig.12 shows a rate of heat liberation of Ultra rapid hardening cement paste. Usually, polycarboxylate type SP delays the hydration of cement [11]. The degree of delay increases with increase of dosage of SP. But rate of heat liberation of NPC used paste did not change with dosage of NPC. It means that NPC did not delay the hydration of ultra rapid hardening cement paste. It seems that this is why NPC used mortar and concrete showed a same strength as that of NS used concrete at early age.

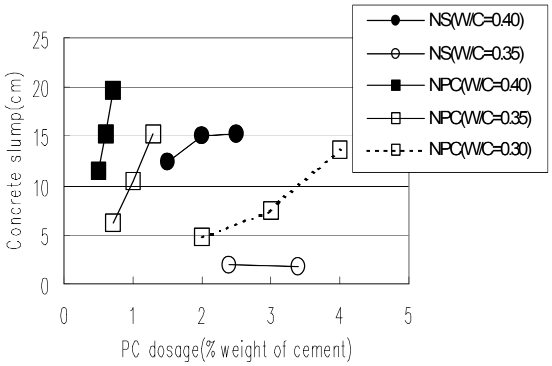

Fig.8 Relationship between PC dosage and concrete slump

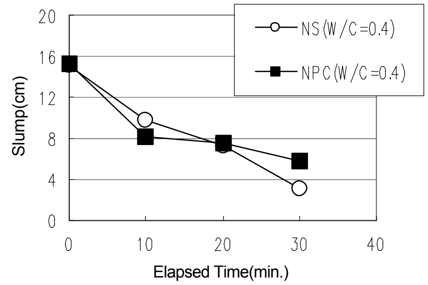

Fig.9 Slump loss of concrete

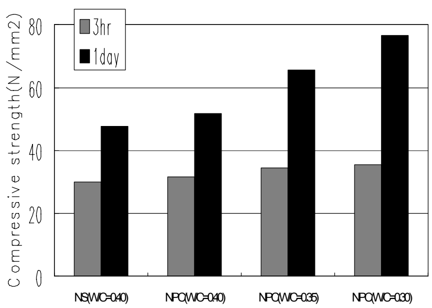

Fig.10 Compressive Strength of concrete

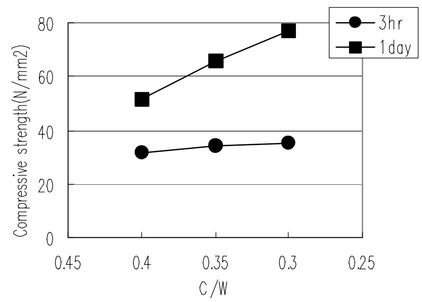

Fig.11 Relationship between W/C and compressive strength of concrete

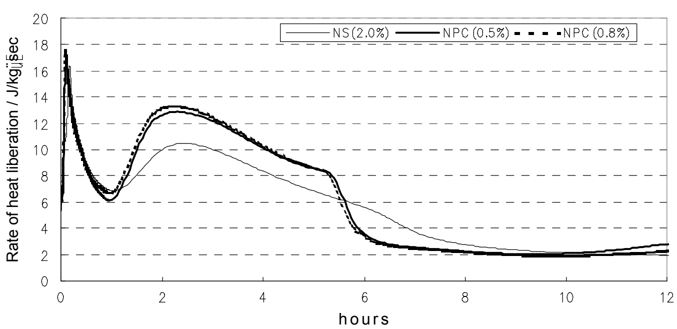

Fig.12 Rate of heat liberation from cement paste

4. Conclusions

(1) PC showed a same dispersibility as NPC for ordinary Portland cement. But it did not work well for Ultra rapid hardening cement.

(2) Adequate dosage of NS dispersed Ultra rapid hardening cement. But higher dosage of NS did not improve workability of mortar or concrete. It could not reduce the water cement ratio of concrete.

(3) NPC showed a higher dispersibility than NS for Ultra rapid hardening cement. Workability of mortar and concrete were improved with increase of NPC dosage. NPC could reduce water cement ratio of mortar and concrete under same workability.

(4) Compressive strengths of mortar and concrete using NPC were almost same as mortar and concrete using NS.
(5) Compressive strength of mortar and concrete showed a linear correlation with cement water ratio.

These results indicated that workability of mortar and concrete using Ultra rapid hardening cement would be improved by NPC and it is possible to produce higher fluidity concrete and higher strength concrete using Ultra rapid hardening cement.

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