

# 論文 Influence of Dosing Method of Superplasticizers on Double Mixing Effect Observed for Slag or Limestone Powder Replaced Cement

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**ABSTRACT :** This paper reports the properties of fresh cement paste, fresh and hardened concrete using superplasticizers with different dispersing mechanisms for cement particles, and their compatibility with blast furnace slag and limestone powder. For the sample prepared by single mixing and double mixing and by changing sequence of addition of superplasticizers. Fluidity, loss of fluidity, setting time and strength development are influenced by types of superplasticizers, binder, mixing method and dosing sequence of superplasticizer.

**KEYWORDS:** Superplasticizer, dispersing mechanism, loss of fluidity, double mixing, dosing sequence.

## 1. INTRODUCTION

“Double mixing”(DM) was originated from “SEC”(Sand Enveloped with Cement method) in 1977 but it was first verified in 1981 after being proved by Tazawa et.al that the reduction of bleeding which is the effect of “SEC”, can be obtained only by mixing primary water with cement for a certain period of time and then mixing the rest of water. The optimum condition of mixing primary water was found to be between  $W_1/C$  of 20% and 25%[1]. The dosage of superplasticizers required to obtain a given flow of cement paste with different types of superplasticizers is different. While the difference in bleeding of cement paste with different types of superplasticizers is large when prepared by single mixing, the difference is lower for  $W_1/C$  closer to the optimum one when prepared by double mixing. The optimum  $W_1/C$  for superplasticized cement paste lies between 20% and 24%[3].

This tendency is maintained even if the temperature of cement paste is varied [3]. The effect of blast furnace slag, limestone powder, type and dosing methods of superplasticizers possessing electric repulsion, steric barrier and those possessing both dispersing mechanisms were investigated. Characteristics of cement paste, fresh and hardened concrete containing those admixtures when prepared by different mixing methods are reported.

## 2. EXPERIMENTS AND PROCEDURE

### 2.1 MATERIALS

#### (1) Superplasticizers

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Four types of superplasticizers of different functional radicals and dispersion mechanisms designated by A, B, C and D were used. The superplasticizer A is the new type of superplasticizer whose dispersion mechanism is by both electric repulsion and steric repulsion. Dispersion mechanism of B and C is by steric repulsion, while that of D is by electric repulsion. The superplasticizer A has a molecular weight of 56000 unless specified. When the effect of molecular weight is investigated, the number in the designation A-84, A-114 and A-220 corresponds to the molecular weight in thousands. Table 1 shows the type and composition of the superplasticizers used.

(2) Cementitious materials

The type of cement used was normal portland cement of 3.16 specific gravity and Blaine specific surface area of 3390cm<sup>2</sup>/g while as replacement materials blast furnace slag of Blaine specific surface area of 5930 cm<sup>2</sup>/g and 2.9 of specific gravity and limestone powder of 5030 cm<sup>2</sup>/g Blaine specific surface area and 2.7 of specific gravity were used. (These materials are referred as C, BFS and LP respectively)

(3) Aggregate

The type of fine aggregate used was crushed quartzite trachyte having 2.54 of specific

Table 1. Classification of superplasticizers

Symbol	Type	Composition	Electric repulsion	Steric repulsion
A ●	Poly-sulfonic acid	Methacrylic acid	*	*
B ◎	Poly-carboxylic acid	Long ether chain		*
C ◎	Poly-carboxylic acid	Ether chain		*
D ●	Naphthalene sulfonate	Maleic acid derivatives	*	

● High range water reducing agent

◎ Air entraining high range water reducing agent

Table.2.1 Mix. proportion of 1m<sup>3</sup> of cement paste

Binder	W(Kg)	C(Kg)	BFS(Kg)	LP(Kg)	P/(P+C)(%)	W/(P+C)(%)
C	449	1727	0	0	0	26%
C + BFS	448	1291	431	0	25	26%
C + BFS	448	776	948	0	55	26%
C + LP	441	1272	0	424	25	26%

Table.2.2 Mix. proportion of 1m<sup>3</sup> of concrete

Binder	W(Kg)	C(Kg)	BFS(Kg)	S(Kg)	A(Kg)	W/(P+C)	P/(P+C) (%)	s/a(%)
C+BFS	175	100	400	859.9	901	35	20	50
C+BFS	178	228	279	838	880	35	55	50

P: Mineral admixture

-For DM-concrete: W<sub>1</sub> of 21% is used for the SP-D and 23% for the SP A and B

-For DM-paste: W<sub>1</sub> /C of 21% is used for the SP-D 23% for the SP A and B

gravity, 1.9% of water absorption and 2.51 of fineness modulus while the type of coarse

aggregate used was trachyte quartzite of 20 mm maximum size, 0.31% of water absorption, 2.67 of specific gravity and 6.55 of fineness modulus.

## 2.2 EXPERIMENTS

For various types of superplasticizers, the dosage required to produce the flow value of  $200 \pm 15$  mm of cement paste was determined. The dosages corresponding to the flow of  $200 \pm 15$  mm of cement paste prepared by single mixing were used in cement paste prepared by double mixing.

In double mixing,  $W_1/C$  of 21% and 23% was adopted because, at this interval bleeding of cement paste is minimum and thus considered to be the interval of optimum dispersion[3]. For cement paste, superplasticizers were added in the primary water and secondary water to clarify the effect of sequence of addition of superplasticizers on fluidity and flow loss, while the effect of mixing method and dosing sequence on setting time and compressive strength of concrete were investigated. Table 2 shows the mix. proportions of cement paste and concrete.

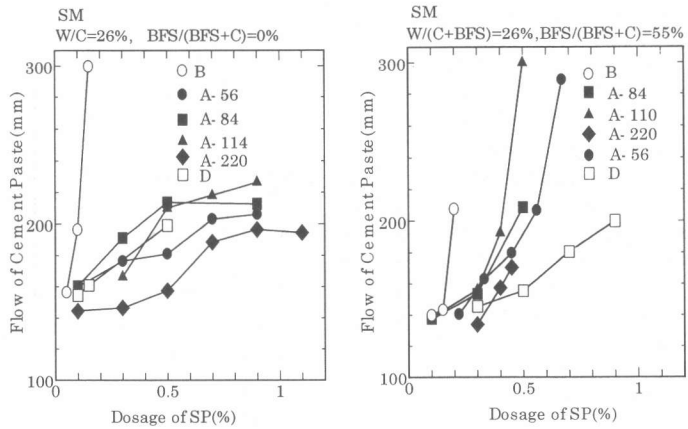


Fig.1 Relation between dosage of superplasticizers and flow

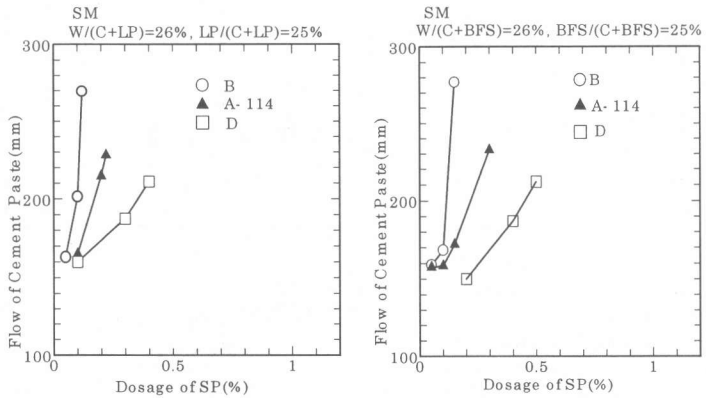


Fig.2 Effect of replacement ratio and material on fluidity

## 3. EXPERIMENTAL RESULTS AND DISCUSSION

### 3.1 CEMENT PASTE PREPARED BY SINGLE MIXING

#### (1) Flow of cement paste with different types of superplasticizers

From Fig. 1 and Fig.2 it is shown that dosage of the superplasticizer B was the lowest of all to obtain low W/C cement paste having the flow of  $200 \pm 15$  mm. It can also be noted that, fluidity was notably improved by replacing blast furnace slag or limestone powder with cement for the superplasticizer A.

#### (2). Effect of addition of superplasticizer by single mixing on fluidity of cement paste

From Fig. 3 it is shown that flow of cement paste increased with time up to at least 30 minutes and at most 60 minutes after mixing when cement paste was prepared with the superplasticizer A of various molecular weights by single mixing. For the superplasticizer B, flow loss was observed from as early as 30 minutes after mixing. There is a significant difference in flow loss between the two types of superplasticizers and even among the superplasticizers "A" of different molecular weight. When cement was replaced with blast furnace slag, the difference in values of flow between the superplasticizers was lower than

that in the case of cement without any replacement. The optimum molecular weight of A at which the maximum flow was obtained was changed with replacement of blast furnace slag. This suggests that there should be some chemical interaction such as selective adsorption which occur between superplasticizers and cementitious materials.

### 3.2 CEMENT PASTE AND CONCRETE PREPARED BY DOUBLE MIXING

(1). Effect of addition of superplasticizers at  $W_1$  on fluidity of cement paste

From Fig.3 it is shown that, the flow loss tendency of cement paste with the superplasticizer A of varied molecular weight was higher when added with  $W_1$  than that in the single mixing addition, while for the superplasticizer B no significant change in the tendency was observed. It is also noted that, the difference in flow values with elapsed time for various superplasticizers is lower than in the case of single mixing. When cement was replaced with blast furnace slag, the difference became lowest of all other cases.

(2)Effect of delayed addition of superplasticizers(at  $W_2$ ) on fluidity of cement paste

From Fig.3, it is shown that, a significant increase in the absolute value of flow for the superplasticizer A of varied molecular weight was observed when superplasticizers were added in secondary water for cement paste without replacement. While, flow just after mixing was slightly lower compared to that by using single mixing for the superplasticizer B. It is also noted that for this mixing condition, flow loss of cement paste with the superplasticizer B became small although it showed highest flow loss tendency of all other types of superplasticizers when it is mixed by single mixing or

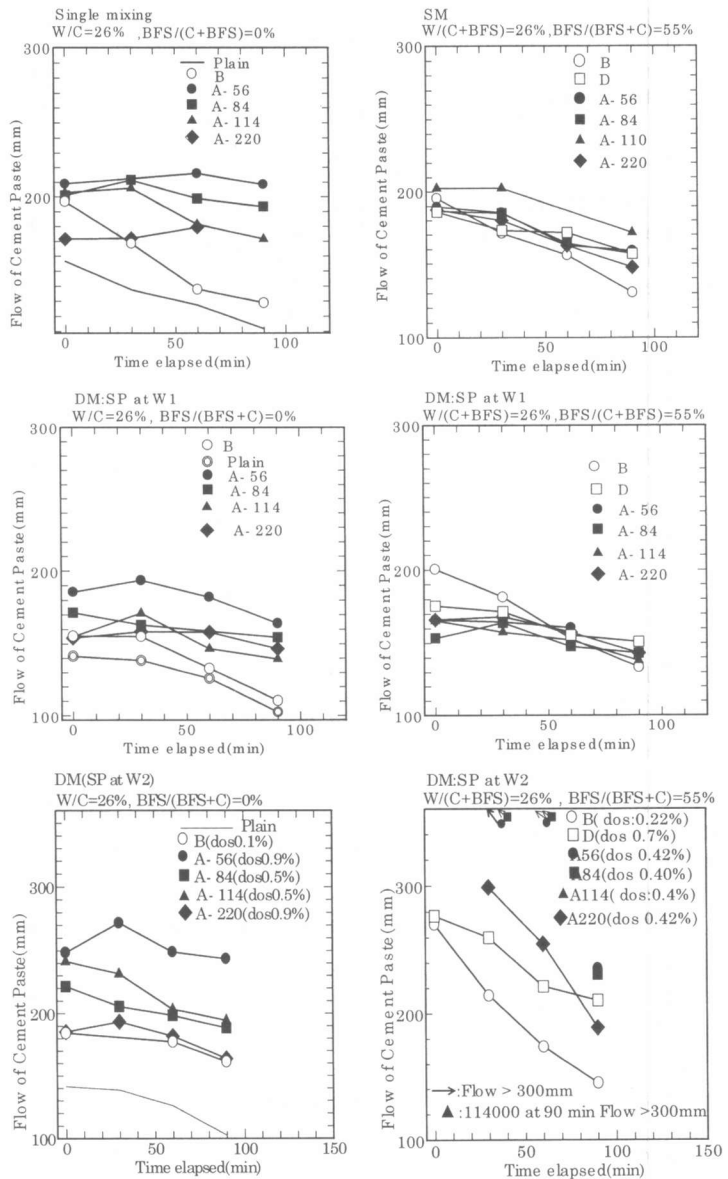


Fig.3 Effect of blast-furnace slag and dosing method of superplasticizers on fluidity of cement paste

added in primary water. Flow of paste with the superplasticizer A became more sensitive to its molecular weight and higher flow was observed for lower molecular weight. When cement was replaced with blast furnace slag, only flow of cement paste with superplasticizers B and D could be measured at zero minutes where the value of flow was about 280 mm while for the superplasticizers A-220, A-84 and A-56, flow could be measured after 30 minutes and 90 minutes and the flow of 300 mm and 240 mm respectively was obtained. It can be seen that the tendency to flow loss is highest when cement is replaced with blast furnace slag. It is understood that by using this method of dosages are needed for the superplasticizer A of various molecular weight to obtain the same consistency as that of the superplasticizer B even though B showed the highest fluidity in the other mixing condition.

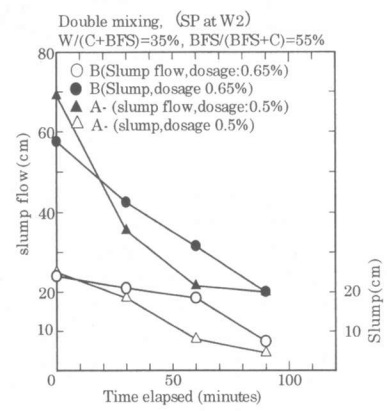
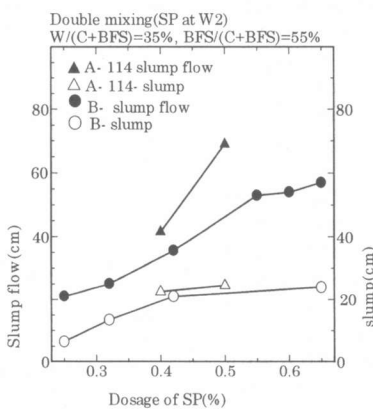


Fig.4 Fluidity of double mixed concrete with SP added in W<sub>2</sub>

(3) Fluidity of blast furnace slag replaced concrete with superplasticizers added at W<sub>2</sub>

It can be seen from fig.4 that the ratio of dosage of the superplasticizer A-114 to that of the superplasticizer B required to obtain the same flow was reduced from 2 when cement paste was prepared by single mixing to 0.77 when concrete was prepared by double mixing with addition of superplasticizers in secondary water. This shows that for this dosing method, proportion of dosages required to obtain the same fluidity varies from those in other dosing methods and that the sensitivity of fluidity to dosing method and slag replacement depend on the type of superplasticizers. It can also be seen that, flow loss of concrete with both of the superplasticizers A and B was similar when were added in W<sub>2</sub> while the superplasticizer A-114 showed lowest flow loss when prepared by other dosing methods.

(4) Effect of mixing method and dosing method of superplasticizers on setting time of concrete

From Fig. 5, it is shown that the setting time of concrete prepared by double mixing with the superplasticizers in primary water is for both of the superplasticizers lower than that prepared by single mixing. It is also noted that for concrete prepared by both single mixing and "double mixing with the superplasticizers in W<sub>1</sub>", setting time of concrete

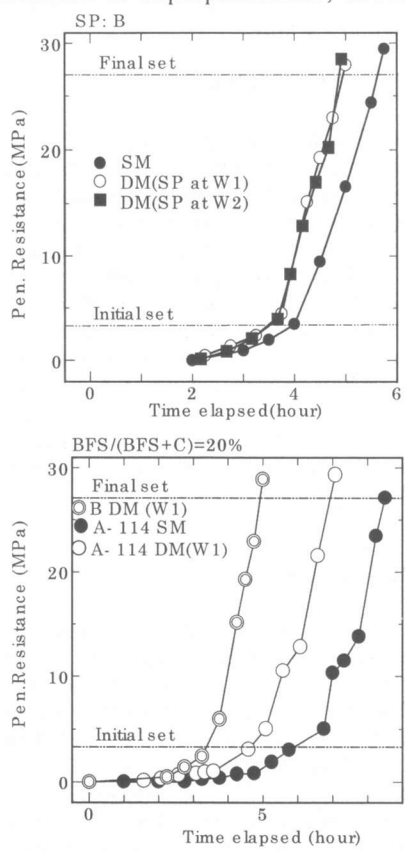


Fig. 5 Setting time of concrete

with the superplasticizer B is shorter than that with the superplasticizer A-114. While a test for the setting time of concrete with the superplasticizer A-114 in  $W_2$  was not conducted because of segregation, for the superplasticizer B, the setting time of concrete with superplasticizer at  $W_1$  and  $W_2$  were same.

(5) Effect of mixing method and dosing method of superplasticizers on compressive strength of concrete

It can be seen from fig.6 that concrete mixed with the superplasticizers A and B showed the same strength development when prepared by single mixing while when prepared by double mixing, the 7 day compressive strength of concrete with the superplasticizer B in primary water was very high and increased slightly with age. While, 7, 14 and 28 day compressive strengths of concrete with the superplasticizer A in primary water was lower than that with the superplasticizer B, strength development was more gradual than that of concrete with the superplasticizer B. When the superplasticizer B was added at  $W_2$ , the 7 day compressive strength was highest. While, the 28 day compressive strength was lower than that when it was added in primary water.

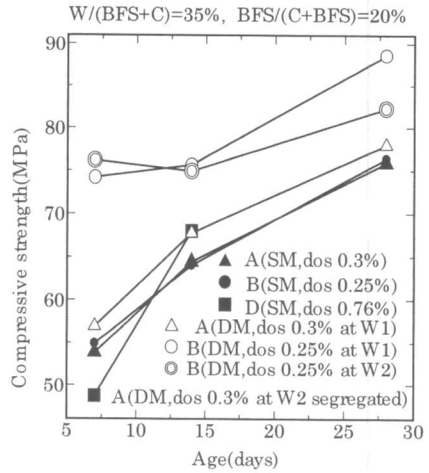


Fig.6 Strength development of concrete

#### 4. CONCLUSION

(1) Fluidity is dependent on the type of superplasticizer. The superplasticizer B requires the lowest dosage to obtain the given flow when different types of superplasticizers are used for cement paste prepared by conventional mixing method,

(2) For the superplasticizer A, fluidity of the same water binder ratio is improved by replacing cement with blast furnace slag or limestone powder but for the superplasticizers B and D, fluidity deteriorates.

(3) When superplasticizer B is added to normal portland cement without replacement, fluidity deteriorates by double mixing regardless of dosing sequence. For the superplasticizer B, flow loss is generally largest of all other types of superplasticizers.

(4) When superplasticizer A is added with the primary water on double mixing of normal portland cement, fluidity is decreased, but when added with secondary water, fluidity is increased. This tendency is further pronounced when 55% of cement is replaced with blast furnace slag where fluidity of concrete with the superplasticizer A is higher than that with the superplasticizer B.

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