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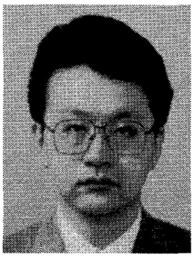
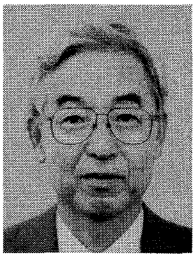
EFFECTS OF MOLECULAR STRUCTURE OF POLYCARBOXYLATE POLYMERS ON CEMENT PARTICLE DISPERSIBILITY

(Translation from Proceedings of JSCE, No.662/V-49, November 2000)



Takumi SUGAMATA   Makoto HIBINO   Masahiro OUCHI   Hajime OKAMURA

The particle-dispersing effect of various superplasticizers (SP) containing polycarboxylate polymers with different molecular structures is examined under conditions of extended mixing time. The particle-dispersing effect of an SP, represented by the ratio of the relative flow area ratio of the mortar to the relative funnel speed ratio of the mortar, increases in a straight line as the dosage of SP increases. Although dependent on the molecular structure of the SP, the apparent adsorption onto cement particles scarcely increases as dosage is increased; in other words, only the amount remaining in the liquid phase increases. The decrease in particle-dispersing effect of an SP as a result of mixing can be divided into two contributions: 1) a decrease corresponding to the amount remaining in the liquid phase when the dosage of SP is reduced; and 2) a larger decrease in particle-dispersing effect than expected given the decrease in the amount remaining in the liquid phase. The main factor responsible for this behavior is the molecular structure of the SP and its effect on the adsorption rate of the SP onto the cement particles.

Keywords: *mixing time, flow, funnel, molecule structure of polycarboxylate-based superplasticizer*

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1. INTRODUCTION

Concrete is an excellent material for use in the development of social infrastructure because structures of any strength, shape, and size can be constructed using relatively cheap, domestically available materials. Chemical admixtures are widely used in concrete to improve its placement characteristics and durability after hardening. In many respects, the role of such admixtures is crucial, since they enable larger structures to be built and work time to be reduced. The self-compacting concrete developed by Professors Okamura and Ozawa [1] depends on the fresh concrete retaining two basic properties from the time of mixing to placement: high fluidity and high material segregation resistance. Superplasticizers are essential to the design of concrete that exhibits these properties in suitable balance.

Superplasticizers first came onto the market in the latter 1980s, and have been improving year by year since then. Presently, they can be divided into four types in terms of their main component: naphthalene sulfonate, melamine sulfonate, polycarboxylate, and amino sulfonate.

Years ago, when superplasticizers first came into use, naphthalene-based ones were widely used. However, the number of polycarboxylate-based products is growing, because these superplasticizers achieve the required fluidity at lower dosages than naphthalene-based and melamine-based ones. Moreover, their molecular structure can easily be modified to improve their dispersing effect on powder particles (the "particle dispersion effect") and the retention of this effect [2], [3]. It has been noted that the fluidity and fluidity retention of self-compacting concrete containing superplasticizers depends on the type of powder used [4], differences in ambient temperature [5], and mixing method [6]. In future, to further improve superplasticizer performance, it will be crucial to elucidate the mechanism of their particle-dispersing action.

The authors have previously selected a polycarboxylate-based superplasticizer for study, and have discussed the main reasons for the observed decrease in mortar fluidity when mixing time is extended [7]. These are a decrease in dispersing effect of the superplasticizer, an increase in cement hydride content (due to mixing) which causes an increase in relative surface area, and a decrease in the amount of superplasticizer adsorbed per unit surface area of cement particles.

In this study, a quantitative evaluation of the change in particle-dispersing effect with extended mixing time is carried out for polycarboxylate-based superplasticizers with various molecular structures. In addition, to clarify the reason for the varying reduction in particle-dispersing effect even with the same extended mixing time, the authors study the increase in the amount of superplasticizer adsorbed as the relative surface area of the cement particles increases. This allows the effect of adsorption speed to be expressed in terms of molecular structure.

2. PARTICLE-DISPERSING EFFECT OF POLYCARBOXYLATE-BASED POLYMERS

The polycarboxylate-based polymer used in this study (**Fig. 1**) consists of a polyacrylic acid main chain and polyethylene oxide graft chains (or side chains). In this text, the acrylic acid component is referred to as the "acid," while the esterized part of the ethylene oxide is referred to as the "ester". When this type of polymer dissolves in water, an anion appears due to the dissociation of a carboxyl group, and this bonds to a cation on the surface of a cement particle to give the cement surface a negative charge. However, this zeta potential is quite a lot smaller than in the case of naphthalene-based superplasticizers [2], and little particle dispersion can be expected as a result of static electrical repulsive forces. On the other hand, the ethylene oxide side chains are thought to spread into the liquid phase and can prevent agglomeration of the cement due to steric hindrance repulsive forces , which can be represented by an osmotic pressure effect and an entropy effect. This repulsion is affected by the thickness of the layer of adsorbed molecules, so it can be understood that the longer the side chains and the larger the value of coefficient "a" (see **Fig. 1**), the more effective the steric hindrance repulsion [2]. Further, the molecular structure of polycarboxylate-based polymers is more easily altered than that of other dispersing agents. If the ratio of acid to ester (that is, the ratio of coefficients "n" to "m" in **Fig. 1**) is altered, the characteristics of the polymer change [3]. If the ratio of acid is high, due to the presence of more carboxyl groups, it is easy for the polymer to adsorb onto cement particles, and good dispersibility is obtained at smaller doses. On the contrary, if the ratio of esters is high because there are many side chains, the carboxyl groups account for a smaller proportion of the polymer and adsorption becomes difficult. This leaves more of the polymer in the liquid phase. Therefore, polycarboxylate-based superplasticizers exhibit less dispersibility at the same dosage than materials having a greater proportion of acid. However, the polymer remaining in the liquid phase slowly adsorbs onto the cement as time passes, resulting in improved dispersion retention.

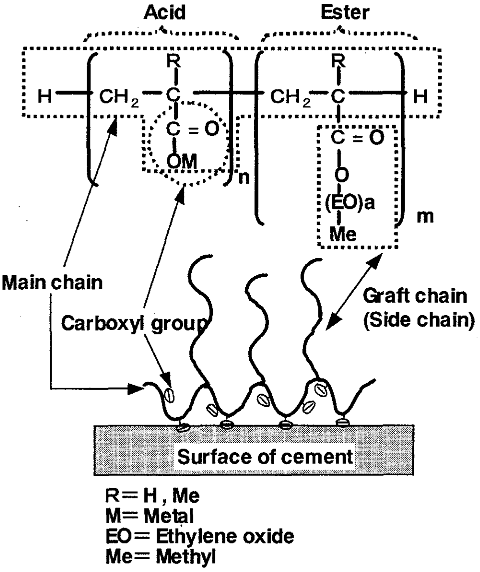


Fig. 1 Basic molecular structure of polycarboxylate-based polymer and mechanism diagram

Table 1 shows the relationship between molecular structure and dispersion/dispersion retention. According to this table, high dispersibility is obtained if the molecular weight of the main chain is low and the side chains are long but spaced widely apart. Polymers that have long side chains spaced more closely together exhibit improved dispersion retention [3].

Table 1 Relationship between molecular structure and dispersibility, retention ability

Characteristics of polymer	Length of main chain	Length of side chain	Density of side chain
Low-dispersibility and low retention ability	Long	Short	High
High dispersibility	Short	Long	Small
High retention ability	More short	Long	High

As the repulsion depends on the amount adsorbed as well as the thickness of the adsorbing layer, it is worthwhile focusing on the properties of adsorption onto cement particles as an index of the dispersing effects of a superplasticizer. The fact that an increase in adsorption corresponds to an increase in dosage of the superplasticizer is a good explanation for the static repulsive forces and steric hindrance repulsion. The authors note a recent depression-effect theory by which even a superplasticizer that does not adsorb onto the surface of particles has a dispersing and agglomeration effect. Depressive-dispersion is deemed to occur when particles come close to each other, the free (not adsorbed) superplasticizer between them is excluded, and a repulsion force is set up to unify the difference in concentration between the space of particles and the liquid phase [8]. This depression-effect theory has not yet been fully established, but Nawa et al. reported that the fluidity of a cement paste containing a naphthalene-based superplasticizer gains temperature reliability due to the depression effect of the non-adsorbed polymer [9].

3. OUTLINE OF EXPERIMENT

The powders used in this experiment were low-heat Portland cement and fine limestone powder. The fine aggregate was crushed sand, and the chemical admixture was a polycarboxylate-based superplasticizer. Since this study targets the mortar component of a highly self-compacting concrete, the authors selected low-heat Portland cement because it is easier to impart higher fluidity at lower water-cement ratios than ordinary Portland cement. The polymers "a" to "c" in **Table 2** were used as the polycarboxylate-based superplasticizers. Looking at the polymers listed in **Table 2** according to the relationship given in **Table 1**, polymer "b" has a shorter main chain, a greater ratio of acid, and longer side chains than polymer "a", and results in better dispersion. In the same manner, polymer "c" has the same ratio of acid and ester as polymer "a"; however, since it has side chains with the same length as those of polymer "b" yet a shorter main chain than polymer "b", it exhibits good dispersibility retention.

Table 2 Synthetic conditions for polycarboxylate-based polymers

Polymer	Relative length of graft	Molar ratio of acid and ester	Mw[*)]
a	Short	2 : 1	36000
b	Long	3 : 1	28500
c	Long	2 : 1	23000

[*)] GPC method, polyethylene oxide standard

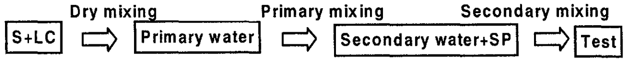
Three types of experiment were conducted to elucidate the influence of the molecular structure of the polycarboxylate-based superplasticizer. The superplasticizers used for these three experiments were as follows:

(1) SP1: Using polymer "a"
(2) SP2: Using a mixture of polymer "b" and polymer "c" to obtain the required fluidity at the same dosage as SP1.
(3) SP3: Using polymer "c"

The ratio of the two polymers in SP2 was designed such that the dosage was equal to SP1, because the authors hoped to measure the retention of dispersibility in terms of the influence on adsorption rate of different molecular structures, rather than in terms of SP dosage.

To yield concrete with adequate self-compaction ability once the appropriate amount of coarse aggregate was added, the water-cement volumetric ratio was set at 0.84 in the case of SP1. For SP2 and SP3, the water-cement ratio was 0.87. The volumetric ratio of fine aggregate for all mortars was 0.40. The dosage of superplasticizer for mortars containing SP1 and SP2 was 1.4% (abbreviated as C x 1.4%), while for SP3 it was C x 1.7%.

A mixing method involving the staged addition of water was adopted, as shown in **Fig. 2**. This method ("standard mixing") consisted of 30 seconds of dry mixing, and then primary and secondary mixing periods of 2 minutes each. To extend the mixing time, primary mixing was increased to 11 minutes and secondary mixing was increased to 30 minutes. The authors hoped to be able to clarify differences in the particle-dispersing effects of a superplasticizer by adopting the following two extremes of mixing: 1) extended mixing of the stiffened mortar before adding the admixture, and 2)



Mixing method	Dry mixing	Primary mixing	Secondary mixing
Standard mixing	0.5 min.	2 min.	2 min.
Extension of primary mixing		X_1 min.	2 min.
Extension of secondary mixing		2 min.	X_2 min.

where X_1=2~11, X_2=2~30
LC : Low-heat Portland cement
S : Crushed sand
SP : superplasticizer

SP1 was measured 5 minutes after mixing
SP2 and SP3 was measured 15 minutes after mixing

Fig. 2 Mortar mixing method

extended mixing of very soft mortar after the superplasticizer is added.

The mixed mortar was allowed to settle for a while to stabilize deformability and viscosity. Mortar containing SP1 was measured 5 minutes after mixing, and mortar samples containing SP2 and SP3 were measured 15 minute after mixing. Referring to a report by Ozawa [10], the primary water content was fixed at 64.2%, i.e., the water-cement volumetric ratio required to attain a relative flow area ratio (***Γp***), as obtained from the paste flow value of low-heat Portland cement, of -3.

The following 4 measurements were taken:
- Mortar flow
- V-funnel discharge time
- Amount of superplasticizer remaining in the liquid phase
- Relative surface area of the cement particles

The flow value was converted into a relative flow area ratio (***Γm***) for use as an index of mortar deformability. The V-funnel discharge time was converted into a relative funnel speed ratio (***Rm***) as an index of mortar viscosity [1].

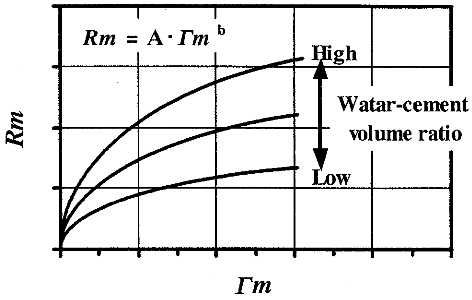


Fig. 3 Relationship between ***Γm*** and ***Rm*** when SP dosage is varied

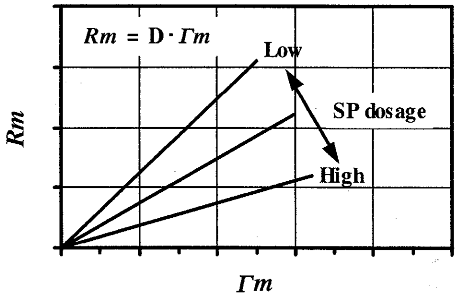


Fig. 4 Relationship between ***Γm*** and ***Rm*** when water-powder ratio is varied

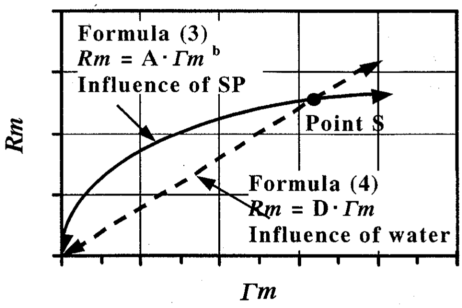


Fig. 5 Difference in the effect of SP and free water

The authors have previously found that the relationship between ***Γm*** and ***Rm***, (shown in **Figs. 3** and **4**), which independently identifies the roles of water and superplasticizer and is closely related to mortar deformability and viscosity in the case of self-compacting concrete, remains applicable when the mixing time is extended. They also found that the particle dispersion effect of the superplasticizer can be expressed quantitatively using the ratio of ***Γm*** to ***Rm*** (***Γm/Rm***) [7]. That is, as shown in **Fig. 5**, it was demonstrated that when the mixing time is extended, if the plots of ***Γm*** and ***Rm*** for a particular mortar having a certain deformability and viscosity (point “S” on the graph) follows the line made by Equation 1, then this is due to a difference in the particle-dispersing effect of the superplasticizer. On the other hand, if they follow the line made by Equation 2 (passing through the origin), then this is due to a difference in water content.

The authors make use of the same understanding in this work. The materials and experimental methods were as shown in **Table 3**.

4. TEST RESULTS AND CONSIDERATION

Table 3 Lists the materials used and test method

Fine aggregate	Type	Density in saturated surface-dried condition	Adsorption	Fineness modulus	Under 0.15mm	Surface moisture	Fine aggregate volume ratio in mortar
	Crushed sand	2.60(g/cm^3)	1.94%	3.04	8%	0.5% to 1.0%	0.40
Cement	Type	Density	Blain specific surface area	C_3S	C_2S	C_3A	C_4AF
	Low-heat	3.24(g/cm^3)	3410(cm^2/g)	25%	56%	2%	12%
Mix proportion of mortar	Water-cement volume ratio	Mixing volume					
	SP1:0.84, SP2 and SP3:0.87	1.5 liter					
Apparent adsorption volume of SP	Liquid was extracted from mortar samples by centrifugal separation (10,000 rpm, 10 min., minimum rotating radius of 6.7 cm, maximum rotating radius of 11.3cm). The total organic carbon content of the liquid was measured by a whole organic carbon measuring device. This mass, subtracted from the total added mass and calculated in terms of mass per gram of cement was taken to be the amount of adsorbed SP per unit weight of cement (expressed as mg/g). This value, divided by the relative surface area of the cement particles obtained using the BET method, was taken to be the amount of adsorbed SP per unit surface area of cement particle (expressed as mg/m^2).						
BET specific surface area of cement particles	The mortar was mixed with acetone to stop hydration, then dried at a temperature of 40℃ and R.H. of 30%, then forced through a 75 micrometer sieve to prepare the samples. The samples were measured using a gas flow relative surface area device (N_2 and He as the mixing gases, BET 1 point method). Drying before the measurements was in air at a temperature of 40℃ for one hour.						

4.1 Influence of molecular structure on particle-dispersing effect and adsorption characteristics of superplasticizers

a) Changes in particle-dispersing effect and adsorption when superplasticizer dosage is varied

Dosages of superplasticizers SP1 to SP3 were varied and both mortar flow values and V-funnel discharge times were measured. Flow values were converted into relative flow area ratios (***Γm***), while V-funnel discharge times were converted into relative funnel speed ratios (***Rm***). This made it possible to obtain the relationship with superplasticizer particle-dispersing effect as expressed by the ratio ***Γm/Rm***. The amount of superplasticizer remaining in the liquid phase was measured in concrete samples containing various dosages of superplasticizers, and this amount subtracted from the initial dosage was deemed to be the apparent adsorbed amount. The ratio of apparent adsorbed amount to cement content was then determined. The relationship between dosage or adsorbed amount of superplasticizer and ***Γm/Rm*** is shown in **Fig. 6**.

With increasing dosage of SP1, a bi-linear relationship develops. The rate of increase in ***Γm/Rm*** as the dosage of superplasticizer increases from 1.4% to 2.2% is quite small as compared with dosages below 1.2%. In the same manner, the gradient of the SP2 line tapers off beyond a dosage of C x 1.6%. This

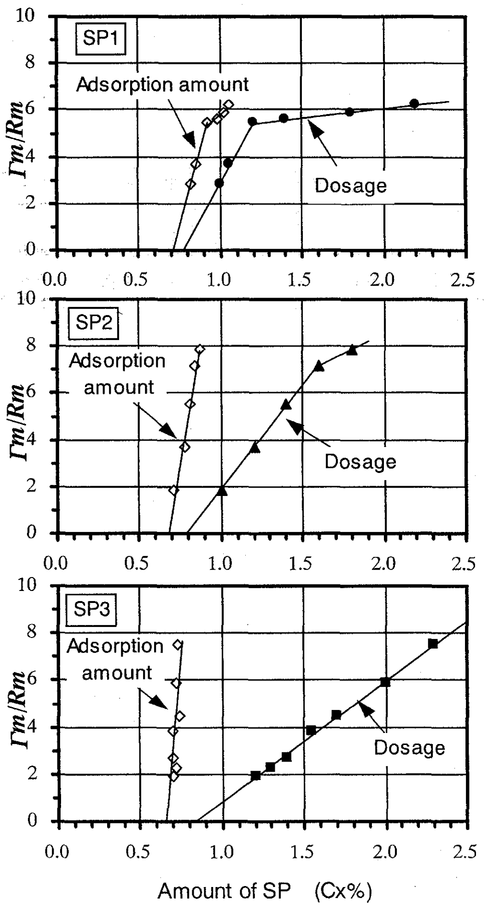


Fig.6 Relationship between amount of SP and ***Γm/Rm***

means that the dispersion effect varies with dose. The absolute value of ***Γm/Rm*** in this case is 7, it is larger than the 5.5 of SP1. Further, in the case of SP3, no rate change was seen in ***Γm/Rm*** over the dosage range of C x 1.2% to 2.3%, so the relationship is linear.

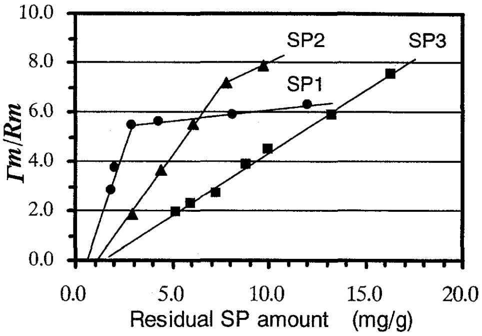


Fig.7 Relationship between residual SP amount and ***Γm/Rm***

All superplasticizers exhibited a slight increase in adsorption compared with the increase in dosage. The higher the dosage, the greater the difference between the amount of superplasticizer added and the additional amount adsorbed; i.e. the amount of superplasticizer remaining in the liquid phase increased greatly. In particular, in the dosage range C x 1.2% to 2.3% in the case of SP3, the absolute value of adsorbed amount hardly changed, indicating that adsorption had reached saturation. Considering this finding and the observation that particle dispersion increases linearly, it is suggested that steric hindrance caused by the adsorption of polymer onto cement particles and the influence of other effects, such as the depression effect, contribute to the particle-dispersing effect of a superplasticizer. **Figure 7** shows the same data as **Fig. 6**, but the X-axis (dosage) has been replaced with the amount of superplasticizer remaining in the liquid phase. It is clear that, as dosage increases, the amount remaining in solution also increases, so ***Γm/Rm*** can be expressed as a positive function. While ***Γm/Rm*** increases linearly, the amount of liquid-phase SP3 required to obtain a particular ***Γm/Rm*** is greater than other types, while SP1 is the least of the three types. The amount of superplasticizer remaining in the liquid phase of SP1 steadily increases even if the increase of ***Γm/Rm*** does not increase. The value ***Γm/Rm*** obtained when the liquid-phase amount of SP1 and SP3 is 12 to 13 mg/g is approximately 6, and the two relationships are very similar.

b) Change in mortar flow value and funnel discharge time in terms of mixing time

Based on the mixing method shown in **Fig. 2**, the primary mixing time only was varied, from 2 to 11 minutes, while the secondary mixing time was fixed. Then, in the second part of the experiment, the primary mixing time was fixed at 2 minutes and the secondary mixing time was varied from 2 to 30 minutes. Changes in ***Γm/Rm*** were determined, as shown in **Figs. 8** and **9**. Here, the mixing time on the x-axis is not the total mixing time but the only primary or secondary mixing time (depending on which was varied). The results afterward are expressed in the same manner.

In the relationship between primary mixing time and ***Γm***, ***Γm*** rapidly decreased after a certain mixing time when a superplasticizer was present. However, when the secondary mixing time was extended to 30 min, ***Γm*** did not greatly decrease.

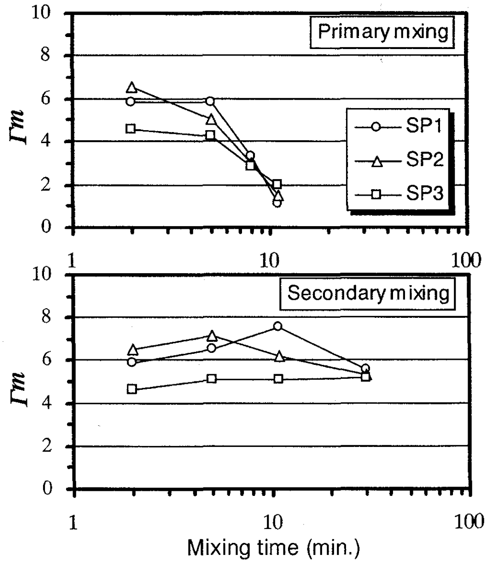


Fig.8 Relationship between mixing time and ***Γm***

In the same manner, in the relationship

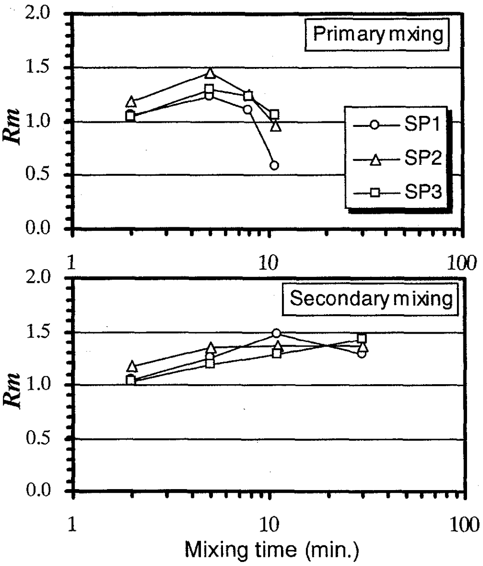


Fig.9 Relationship between mixing time and ***Rm***

between the mixing time and ***Rm***, mixtures containing superplasticizers attained a maximum value after 5 minutes when primary mixing time was extended, falling away rapidly with longer mixing. When the secondary mixing time was extended, all mixtures containing superplasticizers and being mixed for 30 minutes yielded a larger ***Rm*** than those mixed for 2 minutes.

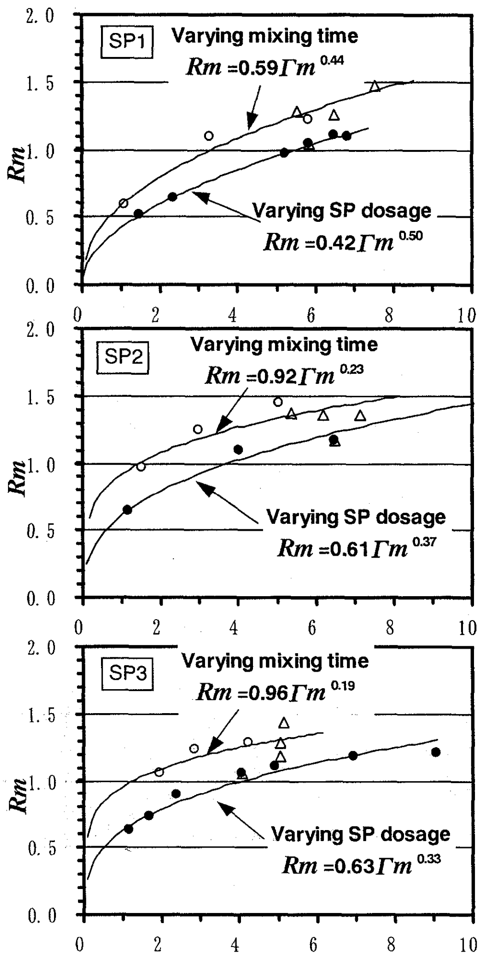


Fig. 10 Relationship between ***Γm*** and ***Rm***

c) Difference in particle-dispersing effect of superplasticizers in terms of mixing time

Based on the results shown in **Figs. 8** and **9**, the relationships of ***Γm*** and ***Rm*** for mortars containing SP1 to SP3 are shown in **Fig. 10**. Compared with changing the dosage of the superplasticizer in the standard mixture, when the mixing time is extended, the relationship between ***Γm*** and ***Rm*** appears on the line of Equation 1 that has a larger coefficient A. This appears to match the observations made when the dosage of superplasticizer is varied in a mixture with a larger water-powder volumetric ratio than the standard mixture. Thus it indicates that the change in fluidity of mortar with extended mixing time is mainly due to a change in particle-dispersing effect.

As shown in **Fig. 11**, the relationship between the mixing time and particle-dispersing effect of a superplasticizer (***Γm/Rm***) rapidly decreases with increased primary mixing time, regardless of which superplasticizer is added. Yet when secondary mixing time is extended, the degree of decrease in ***Γm/Rm*** for all superplasticizers is of a lesser degree. These decreases in ***Γm/Rm*** were compared with those obtained using the standard mixture but with varying mixing times. When primary mixing was extended to 11 minutes, the ***Γm/Rm*** of mixtures containing SP1 to SP3 were 67.3%, 72.0%, and 57.9% lower, respectively. When secondary mixing was extended to 30 minutes, the figures were 22.6%, 29.5%, and 18.3%,

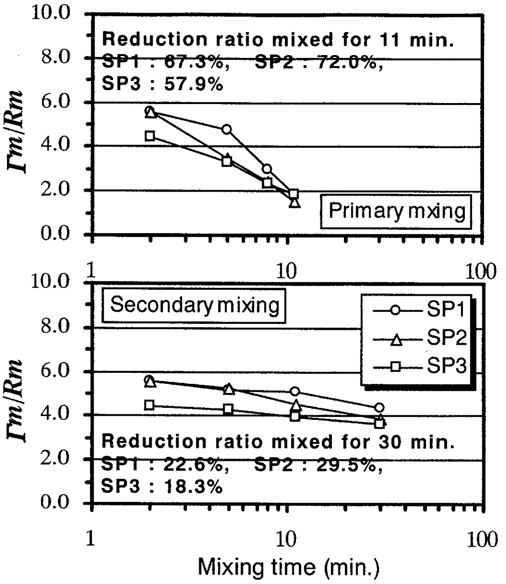


Fig. 11 Relationship between total mixing time and *Γm/Rm*

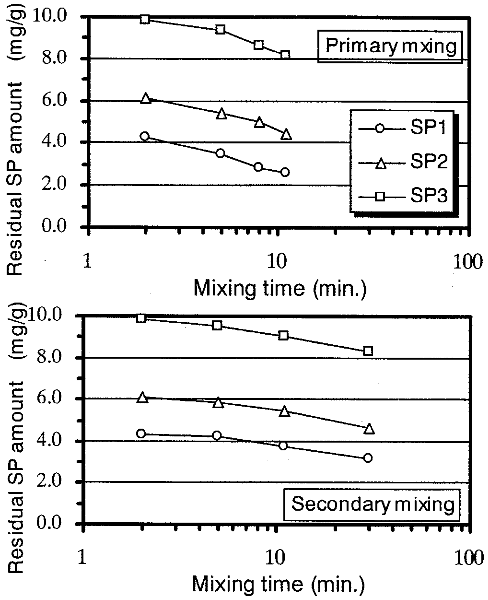


Fig. 12 Relationship between total mixing time and residual SP

respectively. The decrease in *Γm/Rm* with SP3 was the least with extension of both primary and secondary mixing time.

d) Differences in adsorption characteristics with mixing time

In considering the differences in particle-dispersing effect of superplasticizers with extended mixing times, the following is thought to explain the observations.

When dispersion is promoted by mixing, the relative surface area of the cement particles increases as the layers of hydride thicken. Initially, the amount of superplasticizer adsorbed per unit cement mass is equal to that of the standard mixture, so adsorption per unit surface area is reduced compared to that of the standard mixture. Consequently, the particle-dispersing effect decreases. To maintain an equal particle-dispersing effect in the SP case, longer mixing is required. Therefore, a polymer with a molecular structure that promotes retention in the liquid phase is desirable.

As seen in **Fig. 12**, the amount of superplasticizers SP1 to SP3 remaining in the liquid phase decreases as mixing time is extended. The absolute value of the amount remaining was largest in the case of SP3. When SP1 is compared with SP2 at equal dosages, the amount of SP1 remaining is lower. The amount of SP remaining in the liquid phase thus varies with molecular structure. Looking at this result in light of the results for the dispersing effects of superplasticizers (*Γm/Rm*) with various mixing times (**Fig. 11**), it is clear that the molecular structure of SP3 gives it the lowest adsorption onto cement particles so the proportion remaining in the liquid is greater than for the other superplasticizers. The authors consider that the decrease in the particle dispersion effect of SP3 due to mixing is smaller than that of the other superplasticizers.

e) Relationship between remaining superplasticizer and particle-dispersing effect

The relationships between the amount of superplasticizer remaining in the liquid phase and particle-dispersing effect when the mixing time is extended are shown in **Fig. 13**. The numbers given by the points on the graph indicate the primary or secondary mixing times. Regardless of primary and secondary mixing, SP1 exhibits a constant relationship between remaining superplasticizer and particle-dispersing effect; the greater the remaining amount, the greater ***Γm/Rm***. On the other hand, SP2 and SP3 exhibit generally the same tendency as SP1 in that the greater the remaining amount, the greater ***Γm/Rm***; however, when primary and secondary mixing time are extended, ***Γm/Rm*** differs for a given remaining amount. That is, ***Γm/Rm*** values of SP2 and SP3 mixtures with the same amount of superplasticizer in the liquid phase are higher when secondary mixing is extended as compared with when primary mixing is extended.

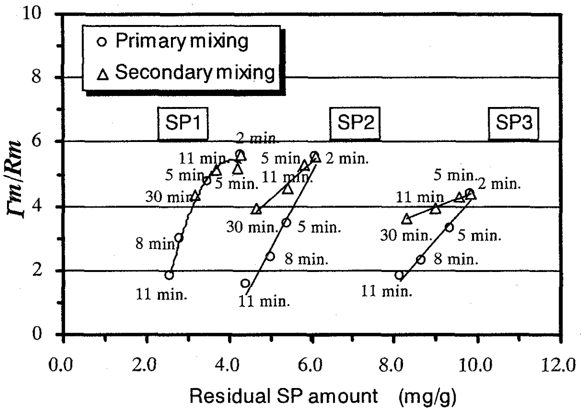


Fig. 13 Relationship between residual SP and ***Γm /Rm***

Next, the authors studied the main factor responsible for differences between amount of remaining superplasticizer and ***Γm/Rm*** ratio when the mixing time was varied. When variations in the amount of remaining superplasticizer with mixing time and ***Γm/Rm***, as in **Fig. 13**, are plotted into the relationship between remaining superplasticizer with various dosages and ***Γm/Rm*** in **Fig. 7**, the result are as shown in **Fig. 14**.

In the case of SP1, when primary and secondary mixing are extended, the relationship between remaining superplasticizer and ***Γm/Rm*** gradually deviates from the line obtained by varying the dosage with standard mixing. This indicates that the dose of SP1 needed to obtain a required particle-dispersing effect has to be increased when mixing time is longer. Similarly, when the primary mixing time of mixtures containing SP2 and SP3 is extended, the relationship deviates from the line obtained by varying the dosage under standard mixing conditions. However, when the secondary mixing time is extended, the two relationships follow roughly the same line. Even if the secondary mixing time of SP2 and SP3 is extended, the relationship between remaining superplasticizer and ***Γm/Rm*** is similar to that when the dosage of superplasticizer is varied in standard

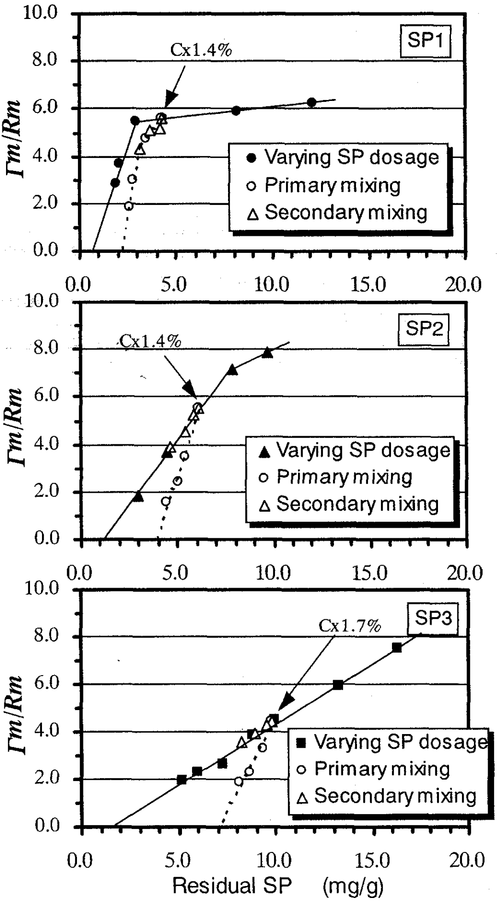


Fig. 14 Relationship between residual SP and ***Γm/Rm***
(Compared to varying SP dosage and mixing time)

mixing. This means that the expected **$\Gamma m/Rm$** is consistent with the decrease in remaining amount. To determine whether this relationship is consistent when the mixing time is varied in the same manner, the dosage of SP1 was fixed at C x 1.2% and C x 1.8%, and the dosage of SP2 was fixed at C x 1.2%. The relationship between remaining superplasticizer and **$\Gamma m/Rm$** was determined, as shown in **Fig. 15**.

Fig. 15 displays the results of the following tests: 1) SP1 at a dosage of C x 1.2%; standard mixing, primary mixing time extended to 8 minutes, and secondary mixing time extended to 15 minutes; 2) SP1 at a dosage of Cx1.8%; standard mixing, primary mixing time extended to 8 and 11 minutes, secondary mixing time extended to 11 and 30 minutes, 3) SP2 at a dosage of Cx1.2%; standard mixing, primary mixing time extended up to 8 minutes, and the secondary mixing time extended up to 11 and 30 minutes.

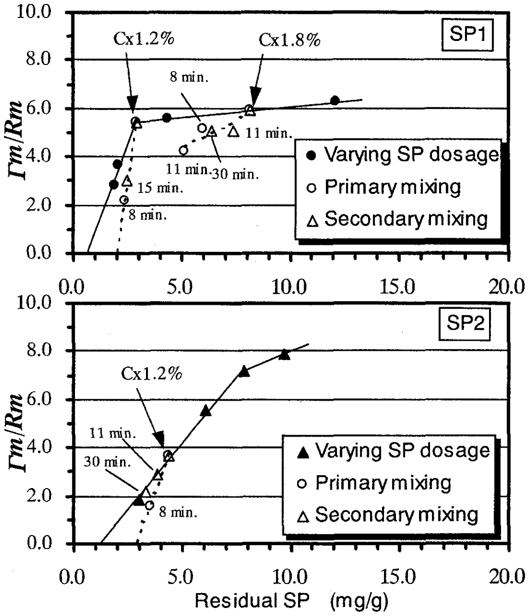


Fig. 15 Relationship between residual SP and **$\Gamma m/Rm$**
(Compared to another SP dosage)

When SP1 was added at dosages of either C x 1.2% or C x 1.8%, as mixing time was extended, the relationship between remaining amount and **$\Gamma m/Rm$** gradually deviated from the line obtained with standard mixing. On the other hand, with SP2 at a dosage of C x 1.2%, when primary mixing time was extended, the relationship deviated in the same way from the line with standard mixing; however, when the secondary mixing time was extended, the relationship fell on same line as in the case of C x 1.4%. Therefore, when mixing time is extended and SP1 is used, the relationship between the remaining superplasticizer and **$\Gamma m/Rm$** falls near the line obtained by changing the dosage with short primary and secondary mixing times. However, as the mixing time is extended, this relationship gradually deviates from the standard mixing line. When the dosage of SP1 is high, i.e. C x 1.8%, the mixing times at which deviation from the standard line occur tend to be longer ones. It is determined that when the primary mixing of SP2 and SP3 was extended, the relationship deviated from the line that is obtained by varying the dosage of superplasticizer. However, when the secondary mixing is extended, the relationship locates on the same line and forms the **$\Gamma m/Rm$** that is presumed to be based on the decrease in the remaining amount.

4.2 Change in relative surface area of cement particles during mixing and its influence on particle-dispersing effect

The difference in amount adsorbed per unit surface area as mixing time is extended is described by a factor representing the relationship between remaining amount of superplasticizer and **$\Gamma m/Rm$**. The authors also looked at the relationship between increase in relative surface area of the cement particles and the increase in amount of superplasticizer adsorbed.

a) Degree of increase in relative surface area of cement particles

Using SP1 and SP2, the relative surface areas of cement particles was measured with primary mixing extended to 11 minutes, secondary mixing only extended to 30 minutes, and standard mixing. The results are shown in **Fig. 16**. The relative surface area of cement particles in samples containing SP1 was measured 5 minutes after mixing, and that of SP2 measured 15 minutes after mixing. It was found that with identical mixing methods, the effect of the additional 10 minutes of standing time was small, and there is no significant difference in the relative surface area of cement particles when SP1 and SP2 are used. The reason for the increase in relative surface area with 11 minutes of primary mixing, despite the short mixing time after contact with water, is a synergetic increase in relative surface area (after the physical dispersion of particles), which is affected by the stiffness of the mortar and the accelerating hydration of the cement. Based on these results, the authors deemed that the superplasticizers used in this test, even with varying dosages, all yield an almost equal increase in relative surface area of the cement particles due to hydration. Using the average values of the relative surface area of cement particles in specimens containing SP1 and SP2 with 11-minute primary mixing or 30-minute secondary mixing, the authors compared the change in the relative surface area of the cement particles and the amount of superplasticizer adsorbed for different dosages.

b) Particle-dispersing effects of superplasticizers when mixing time is extended

Figure 17 shows the relationship between increase in relative surface area of cement particles under standard mixing, with primary mixing for 11 minutes, and with secondary mixing of 30 minutes and the increase in superplasticizer adsorption. In the event that SP1 is added at a dosage of C x 1.4% and when a) primary mixing only is extended to 11 minutes and b) secondary mixing only is extended to 30 minutes, the increase in adsorption falls below the line drawn to represent a 1:1 relationship between increase in relative surface area and adsorption. This means that the adsorption amount per unit surface area decreases.

When SP is added at a dosage of C x 1.8%, the adsorption when a) primary mixing only is extended to 11 minutes and b)

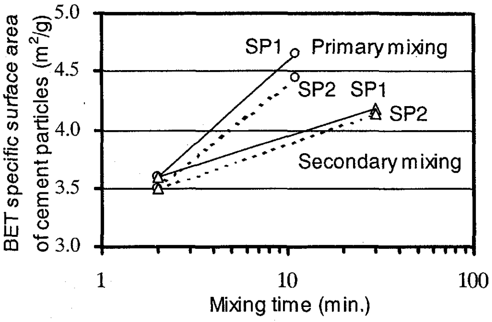


Fig. 16 Relationship between mixing time and BET specific surface area of cement particles

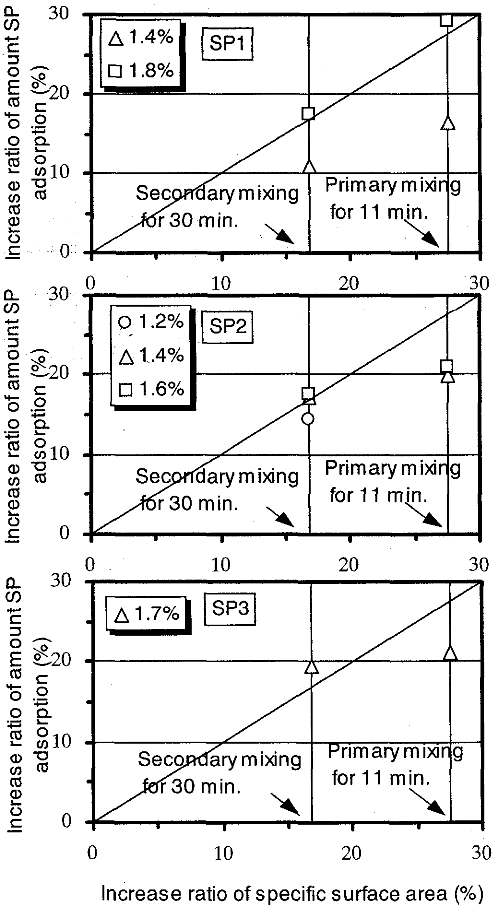


Fig. 17 Relationship between increase ratio of specific surface area and SP adsorption

Table 4 Comparison of phenomena in **Fig.17** and **Fig.14-15**

Type of SP	SP dosage	Mixing	Varying of amount SP adsorption per unit surface area of cement (Fig.-17)	Comparison	Relationship between residual SP and $\Gamma m/Rm$ (Fig.-14, 15)
			(Comparison to varying SP dosage in standard mixing)	⟺	(Compared to varing SP dosage in standard mixing)
SP1	Cx1.2% and Cx1.4%	Primary mixing for 11 min. Secondary mixing for 30 min.	× (Decrease in SP adsorption per unit surface area)	Equal	× (Less than varying SP dosage in standard mixing)
	Cx1.8%	Primary mixing for 11 min. Secondary mixing for 30 min.	○ (Almost the same as SP adsorption per unit surface area of cement)	Not equal	× (Less than varying SP dosage in standard mixing)
SP2	Cx1.2% and Cx1.4%	Primary mixing for 11 min.	× (Decrease in SP adsorption per unit surface area)	Equal	× (Less than varying SP dosage in standard mixing)
		Secondary mixing for 30 min.	○ (Almost the same as SP adsorption per unit surface area of cement)	Equal	○ (Agree to varying SP dosage in standard mixing)
SP3	Cx1.7%	Primary mixing for 11 min. Secondary mixing for 30 min.	○ (Almost the same as SP adsorption per unit surface area of cement)	Equal	○ (Agree to varying SP dosage in standard mixing)

secondary mixing only is extended to 30 minutes increases in proportion to the increase in relative surface area. The adsorption per unit surface area does not change.

Similarly, with any dosage of SP 2 and SP3, when primary mixing is for 11 minutes, the adsorption does not increase very much despite the increase in relative surface area, and the adsorption per unit surface area decreases. However, with secondary mixing of 30 minutes, the adsorption at any dosage increases in proportion to the increase in relative surface area, and the adsorption per unit surface area is constant.

Table 4 compares these results with the phenomenon that the relationship between remaining SP and $\Gamma m/Rm$ with extended mixing time depends on the type of SP, as previously shown in **Figures 14** and **15**. Except at the SP dosage of C x 1.8%, when the adsorption volume per unit surface area is less than that in standard mixing, $\Gamma m/Rm$ decreased more than the decrease in remaining volume obtained by varying the dosage. Further, when the adsorption per unit surface area was almost the same as in the standard mixture, the decrease in $\Gamma m/Rm$ obtained by varying the dosage corresponded with the decrease in remaining SP. The authors consider that differences in particle-dispersing effects of superplasticizers with mixing depend on the ability of superplasticizer in the liquid phase to adsorb onto the surface of cement particles that has increased in area due to hydration. To ensure greater adsorption, a molecular structure that yields a slow adsorption rate and thus a greater amount of SP in the liquid phase is preferable.

However, comparing to varied the dosage of the SP in the standard mixing regime, despite the same adsorption volume per unit surface area, $\Gamma m/Rm$ decreased in proportion to the decrease in remaining amount of SP. The authors therefore consider that even superplasticizer still in the liquid phase exhibits some particle-dispersing effect. Further, it is supposed that for a given amount of superplasticizer adsorbed per unit surface area, when mixing time is extended, the adsorbed superplasticizer may become covered with cement hydride crystals, thus reducing the particle-dispersing effect. This hypothesis appears to be consistent with the decrease in remaining amount. Since polymer “a” in SP1 has shorter side chains than polymer “b” or polymer “c”, it is presumably to have a greater influence. Even when the dosage is C x 1.8%, the adsorption per unit surface area is constant, and the authors assume that this is the main factor responsible for the greater reduction in $\Gamma m/Rm$ rather than the decrease in remaining SP caused by varying the dosage. Sakai et al. estimated that the adsorption layer thins due to the influence of early alite hydration on the potential between particles. Their results showed that the dispersion distance with hydration [2]. It is difficult to measure the thickness of crystallized hydrides on cement particles or the thickness of the layer of superplasticizer adsorbed onto the surface of particles, so the authors were unable to clarify the mechanism of influence by remaining SP in these experiments. In the same manner, regarding the dispersing effect of remaining superplasticizer obtained with different dosages, the authors' results are based on the assumption that superplasticizer adsorbed onto the cement particles does not desorb when the filtrate is extracted.

Since polymer "c" in SP3 has a large number of side chains, the number of carboxylic groups adsorbed onto the surface of cement particles is low. This polymer exhibits dispersing effects by adsorbing to particles, but it desorbs when the filtrate is extracted, so this desorbed amount may be mistaken for un-adsorbed polymer. Future studies aiming at improving the properties of superplasticizers must include methods of directly measuring the amount of superplasticizer adsorbed onto particles so as to elucidate the mechanism of dispersion.

5. CONCLUSIONS

The particle-dispersing effect of polycarboxylate-based superplasticizers after extended mixing times is quantitatively represented by the ratio ***Γm*/*Rm*** (***Γm***: relative flow area ratio; ***Rm***: relative funnel speed ratio) in terms of molecular structure. The relationship between particle-dispersing effect and amount of remaining superplasticizer when the dosage is varied and the mixing time is varied differs with the type of superplasticizer. The authors examined the factors responsible for this observation and discussed the changes in adsorption characteristics of superplasticizers as the relative surface area increases during mixing time. The following results were obtained:

(1) When dosages of three different superplasticizers (with differing amounts of ethylene oxide in their polycarboxylic polymers and different side chain lengths) were increased, the particle-dispersing effect of the superplasticizers, as represented by ***Γm*/*Rm***, increased linearly. It was noted that, with some superplasticizers, increasing the dosage causes an increase in the amount of superplasticizer remaining in the liquid phase, but results in hardly any increase in the amount of superplasticizer adsorbed. The authors also note that the amount of remaining superplasticizer also contributes to particle dispersion.

(2) When primary mixing was of a stiff mortar prior to addition of the superplasticizer and this mixing phase was extended, the value ***Γm*** and ***Rm*** of mortar containing superplasticizers rapidly decreased. However when secondary mixing was of a soft mortar after the addition of superplasticizer and this secondary mixing phase was extended, ***Γm*** and ***Rm*** did not fall but gradually rose as the mixing time was extended.

(3) The ratio of ***Γm*** to ***Rm*** represents the particle-dispersing effect of a superplasticizer. The value of ***Γm*/*Rm*** for all superplasticizers rapidly decreased as primary mixing time was extended. When secondary mixing time (soft mortar mixing) was extended, ***Γm*/*Rm*** decreased slightly but to a much smaller degree than when primary mixing time was extended.

(4) The amount of superplasticizer remaining in the liquid phase decreased linearly with mixing time; however, absolute volumes of remaining superplasticizer were compared at the same dosage and found to be different depending on the molecular structure of the polycarboxylic polymer.

(5) The decrease in particle-dispersing effects of all superplasticizers accompanying longer primary mixing times was greater than would have been expected based on the decrease in amount remaining in the liquid phase measured by varying the dosage. However, when secondary mixing time was extended, some superplasticizers exhibited the same tendency as

when the primary mixing is extended, but others had particle-dispersing effects consistent with the expected values.

(6) When the relationship between relative surface area of cement particles in standard mixing and the increase in superplasticizer adsorption was investigated, most superplasticizers exhibited a small increase in adsorption when primary mixing was extended to 11 minutes as compared with the increase in relative surface area. When secondary mixing time was extended up to 30 minutes, the increase in relative surface area and in adsorption were almost proportional.

(7) The authors conclude that differences in adsorption per unit area of cement particles during standard mixing are the primary factor responsible for variations in the dispersing effect of superplasticizers when primary or secondary mixing is extended.

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