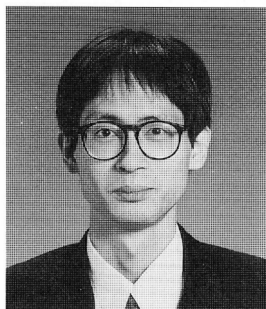# A Fundamental Study on Set-Retardation of Concrete Due to Superplasticizers

(Translation from Concrete Research and Technology, Japan, Vol.5, No.1 Jan. 1994)

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SYNOPSIS

It has been a practice in recent years to use mineral admixtures and superplasticizers to improve the properties of concrete. However, the interaction between cement, mineral-admixture, and super-plasticizer retards the setting and hardening of concrete. The mechanism of this retardation has not been clarified, and it is difficult at present to estimate setting time and to predict its effects on hydration. In this paper, a model to explain the concrete setting mechanism due to water-cement ratio and superplasticizer is proposed to estimate the setting time. The effect of blast-furnace slag and fly ash is also considered.

Keywords: mineral-admixture, superplasticizer, set-retardation

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1. Introduction

Due to the deterioration characteristics of aggregate, superplasticizers have become essential in recent years for reducing the unit water content in order to produce high durability concrete, and are being applied in an increasing number of ways. The main compounds of these superplasticizers are various types of surfactant, which produce a water-reducing effect by being adsorbed to cement and other particles, thereby causing electrical repulsion between the particles. The factors of chemical structures that cause the water-reducing capability of superplasticizers are their molecular weights, molecular weight distribution, and the balance between hydrophilic and hydrophobic groups[1]. In this regard, superplasticizers are chemically composed in such a way that they possess a high water-reducing capability. Meanwhile, retardation of setting by superplasticizers is assumed to be negligible, causing no problems when applying normal test methods[2]. Thus, within a certain range of ratio of a super-plasticizer to portland cement, concrete can be produced where the water content is reduced to a considerable extent with no appreciable retardation of setting.

However, in many instances, superplasticizers have been used recently with concretes containing various mineral admixtures to improve the properties of the concrete. In special concretes such as superworkable concrete, for example, a superplasticizer is added to a ternary system consisting of large amounts of blast-furnace slag and fly ash mixed with portland cement. Reports have shown that this can lead to abnormally retarded setting compared with normal concretes. Retardation of setting, which is negligible in normal use, becomes significant in these cases[3]. The mechanism of this retardation has not been clarified, and it is difficult at present to estimate setting time and to predict its effects on hydration. Such adverse effects of superplasticizers on various mineral admixtures have normally been explained qualitatively in terms of "compatibility", with hardly any discussion the interactions between the materials.

In this study the authors intend to explain the mechanism of retardation of setting by superplasticizers, and to clarify the interactions between superplasticizers and cementitious materials, which is significant when proportioning concrete. This will be done using experimental data and the results of past studies. Model equations for obtaining the setting time will also be presented.

2. Factors affecting the setting time of concrete

The setting phenomenon of concrete is the passage from the fresh state to the hardened state, and is a critical factor in the progress of work after hardening. The setting time depends on the following parameters:

1) Water-cement ratio
2) Cement
3) Aggregate
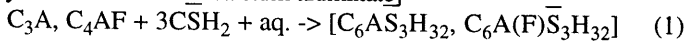4) Chemical and mineral admixtures
5) Ambient temperature and humidity

Except for ambient temperature and humidity, all these parameters are related to proportioning; hence a change in one parameter affects the others. In other words, it is a matter of balance, and is difficult to evaluate quantitatively. When comparing the magnitudes of effects, however, the effects of the water-cement ratio and chemical admixtures, which affect the hydration of cement, are considered to be predominant. Thus the authors considered that the setting time can be estimated, albeit under limited conditions, by investigating their effects on the hydration and setting of portland cement, with the type of chemical admixtures limited to superplasticizers and the fixed ambient temperature of 20°C.

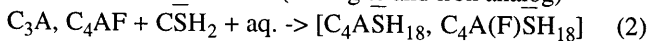# 3. Early hydration of portland cement

Since setting is a state in the process of hydration of portland cement, the hydration of the cement must be explained first. Portland cement consists of various compounds, such as C_3A, C_4AF, C_3S, C_2S, and gypsum, whose contributions to setting differ. The chemical equations for the hydration of
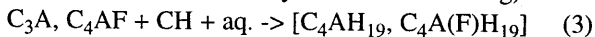
portland cement are simplified as follows[4]:

[Hydration reaction of calcium aluminate]

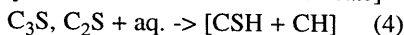$$C_3A, C_4AF + 3C\bar{S}H_2 + aq. \rightarrow [C_6AS_3H_{32}, C_6A(F)\bar{S}_3H_{32}] \quad (1)$$
$$\text{(Ettringite and iron analog)}$$

$$C_3A, C_4AF + C\bar{S}H_2 + aq. \rightarrow [C_4A\bar{S}H_{18}, C_4A(F)\bar{S}H_{18}] \quad (2)$$
$$\text{(Monosulfate hydrate and iron analog)}$$

$$C_3A, C_4AF + CH + aq. \rightarrow [C_4AH_{19}, C_4A(F)H_{19}] \quad (3)$$
$$\text{(Calcium aluminate hydrate and iron analog)}$$

[Hydration reaction of calcium silicate]

$$C_3S, C_2S + aq. \rightarrow [CSH + CH] \quad (4)$$
$$\text{(Calcium silicate hydrate has about 1.5 lime-silica ratio)}$$

where, $C = CaO$, $A = Al_2O_3$, $F = Fe_2O_3$, $S = SiO_2$, $H = H_2O$, and $\bar{S} = SO_3$

The hydration of calcium aluminate shown in equation 3 proceeds very quickly and is called flash-setting. This is why gypsum is used in portland cement; and as such, the reaction expressed by equation 1 inhibits the reaction of equation 3. For this reason the reactions of calcium aluminate do not constitute the principal reaction of setting. Uchikawa et al. investigated the effects of various superplasticizers on the rate of heat evolution due to hydration using a conduction calorimeter[5]. According to their report, the first peak corresponding mainly to hydration of calcium aluminate is scarcely affected by the superplasticizers, and only the second peak corresponding to the reactions of C_3S, or alite, tends to be delayed, as shown in figure 1. This is true regardless of the type of superplasticizer,i.e., naphthalenesulfonate, aminosulfonate, or polycarboxilate derivatives. It follows that the set-retarding property of a superplasticizer can be understood in terms of the hydration of C_3S.
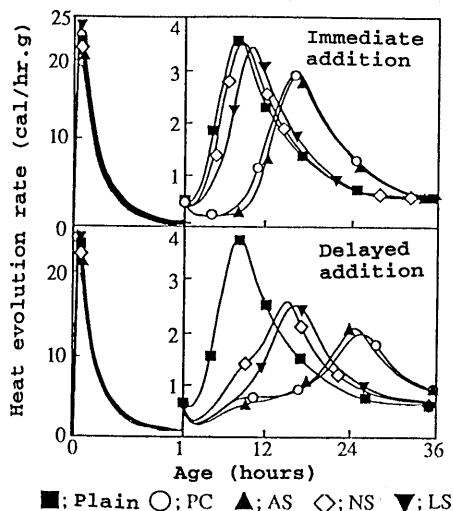

■; Plain ○; PC ▲; AS ◇; NS ▼; LS

Fig.1 Influence of Organic Admixture and
the Method of Addition on the Heat
Evolution of Ordinary Portland Cement
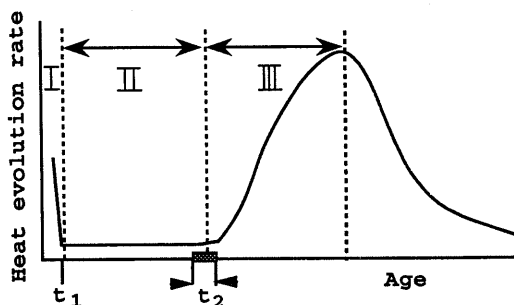Paste (20℃,W/C=0.5) (Uchikawa et al.) 5)

Fig.2 Hydration Process of C_3S

According to the hydration process of C_3S explained by Kondo et al.[6], the heat evolution curve is illustrated, as shown in figure 2, and the reactions up to setting are divided into the following three stages:

<u>Stage I</u>: Formation of CSH on the surfaces of C_3S by intense hydration.

<u>Stage II</u>: Also called the "dormant stage". The reactions make little progress, but the dissolution of C_3S into the liquid phase occurs. The very slow progress of the reactions is due to the films formed on the surfaces of the C_3S particles, which substantially reduce the rate of material transfer between C_3S and the exterior liquid. At the end of stage II the concentration of calcium ions temporarily decreases because of the formation of $Ca(OH)_2$ crystal nuclei.

<u>Stage III</u>: A stage of active reactions. Hydration becomes increasingly active.

JIS defines setting as the moment when the concrete attains a specified hardness[7], and this corresponds to a point in time in stage III, shortly after the transition from stage II[8]. In other words, the transition from stage II to stage III is important for retardation of setting.

Accordingly, each reaction stage is explained in terms of reaction kinetics as presented below. This explanation forms the basis of the concept of the setting mechanism in this paper. Arabic numbers are used to distinguish our stage numbers from those of Kondo et al.

<u>Stage 1</u>: In general the rate of solid reactions is controlled mostly by the diffusion of water inwards from the surfaces of particles. The same is true for the rate of reactions of C_3S in stage 1. The process of CSH formation on the surfaces of particles is the formation of crystals by oversaturation near the surfaces due to extremely rapid reactions. The reaction rate is in the negative first order, and if the reaction rate is denoted by α, then

$$d\alpha/dt = k/\alpha. \quad (5)$$

<u>Stage 2</u>: According to a report by Uomoto, Goto, et al.[9], no particular equation for the reaction rate is defined for stage 2, the dormant stage. They assume this stage to be one where the reactions that started immediately after contact with water. Here we consider the simple concept shown below to approximate the equation for the rate of reaction in stage 2. When the films reach a certain thickness, the rate of outward diffusion from the surfaces of particles increases. The CSH near the surfaces is no longer oversaturated, and the thickness of the films then no longer increases. stage 2 is therefore defined as one where the resistance to material transfer through a film of constant thickness controls the reaction rate. Here the reaction rate is constant, and is in the zero order.

$$d\alpha/dt = Const. \quad (6)$$

<u>Stage 3</u>: When the reactions in stage 2 progress, the products in the liquid phase become oversaturated, forming crystal nuclei. This triggers the active reactions of stage 3. Since actual cement is a composite material, consisting of various components with multiple reactions, it is impossible to pinpoint the transition period from stage 2 to stage 3. However, stage 2, the dormant stage, can be assumed to be the step that determines the rate, because in actual reactions setting occurs at the beginning of stage 3, in which the reactions progress very quickly up to setting. Consequently, setting, i.e., the period between the initial and final setting times, is assumed here to be related to the transition period from stage 2 to stage 3.

These are the assumptions from the standpoint of the hydration of cement. Actual penetration resistance measurements can be affected by factors other than water and cement, such as the fine aggregate content. In the case of mortars with the same water-cement ratio but different sand-cement ratios, for example, the penetration resistance is affected by the sand-cement ratio[10]. This may be attributed to the physical effects of fine aggregate and the effects of water segregation on the results of the Japanese Industrial Standards (JIS) test, in which measurements are made on the upper side of specimens. Here, the physical effects of factors other than water and cement are assumed to be negligible, because the hydration of cement is predominant in its effects on setting. However, water segregation is considered to have a significant influence on the water-cement ratio of the parts to be measured. The setting times defined here are not intended to cover proportions that cause significant water segregation.

4. Effects of water-cement ratio on setting time

4.1 Concept of water-cement ratio

The proportioning of concrete is expressed differently in the civil engineering and architectural fields in Japan. In civil engineering, the standard specifications require the aggregate to be saturated surface-dry, the water absorbed into the aggregate not being included in the unit water content[11]. In architecture, the standard specifications require the aggregate to be either oven-dry or saturated surface-dry, provided the state is reported. If the aggregate is oven-dry, the unit water content will include the water to be absorbed into the aggregate[12]. This means the unit water content and water-cement ratio of concrete depend on the method of expressing proportioning. The authors have assumed the case where oven-dry aggregate is used, in order to eliminate the influence of aggregate on the unit water content. In other words, aggregate is regarded simply as a filler, while the water-cement ratio can be defined as the ratio of actual water content to cement content equally for cement paste, mortar, and concrete. To distinguish between the two types of water content, that with oven-dry aggregate will be denoted by W^*, and that with saturated surface-dry aggregate by W.

On the basis of the concept of hydration of cement mentioned in the previous chapter, the beginning of stage 2 and the transition period to stage 3 (setting time) shown in figure 2 are denoted by t_1 and t_2, respectively, when considering the effects of the water-cement ratio.

The reactions during stage 1 are mostly those within the particles. If the diffusing medium is water, and if the particles are in perfect contact with the water, the reactions are not affected by the water-cement ratio. In other words, t_1 is constant.

The reactions in stage 2 are affected by the water-cement ratio, because they form products, which lead to oversaturation in the liquid phase, causing crystals to precipitate. In other words, t_2 is delayed as the water-cement ratio increases. In actual portland cement, the effects of the water-cement ratio should be investigated considering the amount of water consumed up to time t_1 by reactions such as hydration of calcium aluminate immediately after contact with water. However, the amount of water consumed by such reactions is assumed to be small, and their effects are assumed to be negligible here, because these reactions up to t_1 are not the main reactions leading to setting. Since the rate of hydration is assumed to be constant in equation 6, the initial and final setting times are proportional to the water-cement ratio.

The physical properties of cement vary within a certain range from one product to another. In order to express the effects of the water-cement ratio in an equation, the basic value of setting time is necessary for each type of cement used. If t_1 and t_2 for a basic paste with a water-cement ratio of W^*_B/C_B are known, the setting time, T, affected by the water-cement ratio can be expressed as follows:

$$T = t_1 + ((W^*/C)/(W^*_B/C_B)) \cdot (t_2 - t_1). \qquad (7)$$

where, T is the initial or final setting time in hours, W^*/C is the water-cement ratio, W^*_B/C_B is the water-cement ratio of basic portland cement paste, t_1 is the time of completion of reactions in stage 1 in hours, and t_2 is the initial or final setting time of basic portland cement paste in hours.

The above equation is based on the paste in an ideal condition, with no segregation of water and cement. Since the JIS setting test is carried out on the top surface of a specimen, the water-cement ratio changes when the cement and water clearly segregate or when there is an appreciable amount of bleeding water. The effects of water segregation are significantly small in actual concrete with a high water-cement ratio because of the water-retaining effect of fine aggregate. For this reason, an inert water retainer is used to inhibit water segregation where its effects are appreciable. The physical effects of the water retainer are assumed to be negligible, because the chemical effects of the hydration of the cement are predominant in setting.

4.2 Outline of experiment

Experiment as explained below were carried out to verify the concept regarding the effects of the water-cement ratio, as follows:

Ordinary portland cement was used with water-cement ratios, W^*/C, of 25%, 50%, and 100%. The specimens in which W^*/C equalled 25% were prepared as paste so there would be little water segregation. Those in which W^*/C equalled 50% and 100% were prepared as mortars containing oven-dry fine aggregate as a mere water retainer. This was because segregation was clearly observed when they were prepared as paste. It was in which W^*/C equalled 25% and adding twice as much sand by weight as reduced cement, to proportion mortars in which W^*/C equalled 50% and 100%. The sand-cement ratios of the mortars in which W^*/C equalled 50% and 100% were 2 and 6, respectively. The mortar and concretes were mixed for 5 minutes with a Hobert type mixer. The physical properties of the materials are given in table 1.

Setting tests were carried out in accordance with the JIS method of testing the setting of concrete[7]. The initial and final setting times were defined as the times taken to achieve penetration resistances of 35 and 280 kgf/cm^2, respectively.

Table 1 Chemical and Physical Properties of Materials

Ordinary portland cement	Chemical (%)	SiO_2 21.5	Al_2O_3 5.3	Fe_2O_3 3.0	CaO 64.8	MgO 1.6	SO_3 2.0
	Physical	Specific gravity 3.15	Specific surface (cm^2/g) 3300	Water (%) 28.2	Setting time (hr.-min.) Initial 2-49		Final 4-10
Fine aggregate	Pit sand from KISARAZU	Specific gravity under oven-dry 2.56	Adsorption (%) 1.42	Fineness modulus 2.71			

4.3 Results

The results are shown in figure 3. The calculated values shown in the figure are obtained with equation 7 by the following substitutions: $t_1 = 1.0$ hours when the reaction rate of stage 1 becomes sufficiently low in the tests for the exotherm rate on ordinary portland cements using a conduction calorimeter[13]; $t_2 = 2.5$ hours (initial) or 3.5 hours (final), because the initial and final setting times of ordinary portland cement with W^*/C at 25% obtained from manufacturers' test reports of cements are normally 2.0-3.0 hours and 3.0-4.0 hours, respectively. The experimental values match well with calculated values for both initial and final setting times, suggesting the validity of the explanation of hydration of portland cement.
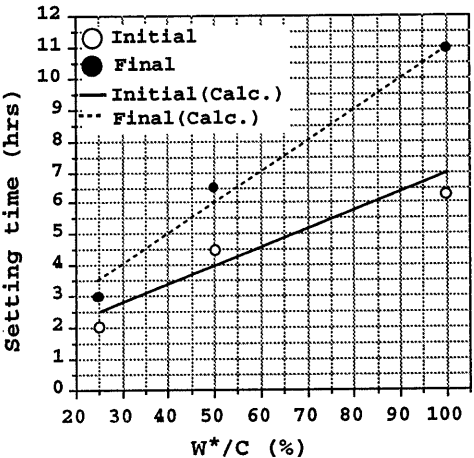

Fig.3 Influence of Water-cement Ratio on Setting Time

5. Mechanism of retardation by superplasticizers

Commercial superplasticizers have a variety of main components, suggesting a variety of effects on retardation. The effects may also depend on the various supplementary components included to deal with various factors, such as reducing the slump loss. Accordingly, the authors decided to investigate experimentally the effects of the type and dosage of superplasticizers and then investigate the retardation mechanism considering conventional hypotheses.

5.1 Outline of experiment

To investigate the relationship between the dosage and the setting time, two types of commercial superplasticizer were selected: a naphthalene type, the main components of which were polyalkyl aryl sulfonate and a reactive polymer; and an aminosulfonate type, the main components of which were polyaromatic aminosulfonate derivatives. The manufacturers recommended dosages for both types are 1.0-2.0% by weight of cement. It is normally sufficient to investigate the retardation mechanism in this range, but the authors covered a range up to 3.0%, which is twice the standard dosage against cement weight, to include the cases where superplasticizers are used excessively. The experiment was conducted on concrete in which W/C equalled 55%. The concrete for the experiment was proportioned to lead to a slump of 18 ± 1 cm when the aminosulfonate superplasticizer is added at a dosage of 1.5% against cement. The air content was adjusted to 4.5 ± 1.5% using an air-entraining agent. The physical properties of the materials and the mix proportions of the concrete are given in tables 2 and 3, respectively. The mixing procedure was as shown in figure 4. The items tested are as follows:

> Freshly mixed: Slump (JIS A 1101)
> Slump flow spread (JSCE-1990)
> Air content (JIS A 1128, waterless method)
> During setting: Setting time (JIS A 6204, Appendix I)
> After setting: Compressive strength (JIS A 1108, standard water curing)

Table 2 Properties of Materials

Ordinary portland cement	Brand name	Specific gravity	Specific surface (cm^2/g)	Water (%)	Setting time (hr.-min.) Initial	Setting time (hr.-min.) Final	Stability	Compressive strength (kgf/cm^2) 3d	7d	28d	Chloride (%)	R_2O (%)
	A	3.16	3190	27.8	2-30	3-52	Good	139	239	420	0.006	0.61
	B	3.16	3370	27.3	2-21	3-22	Good	156	253	414	0.004	0.64
	C	3.16	3350	27.4	2-23	3-24	Good	157	252	416	0.003	0.63

*Mix proportion of three brand OPC; A:B:C = 1:1:1

	Type	Specific gravity	Adsorption (%)	Fineness modulus		Type	Specific gravity	Adsorption (%)	Fineness modulus
Fine aggregate	Sea sand from MUROKI-OKI	2.54	2.06	2.58	Coarse aggregate	Crushed stone from KASAMA	2.65	0.87	6.70
	Crushed sand from AKOU	2.54	2.13	2.81					
	7:3 Mixture	2.54	2.08	2.63					

*Mix propotion of fine aggregate; sea sand: crushed sand = 7:3

Table 3 Mix Proportion of Concrete

Ambient temperature	W/C (%)	s/a (%)	Mix proportion (kg/m^3) W	C	S	G
20	55.0	48.0	175	318	834	943

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┌─────────────────────────────────────────────┐
│ Pan-type mixer with a capacity of 50 liters  │
└─────────────────────────────────────────────┘
1/2 fine aggregate │Mixing│ Water  │Mixing│Coarse   │Mixing│
       Cement      ├─────►│   +    ├─────►│aggregate├─────►│Stop
1/2 fine aggregate │5sec. │Admixture│30sec.│         │60sec.│
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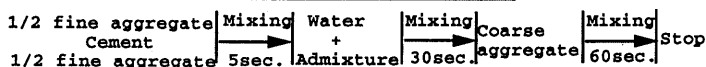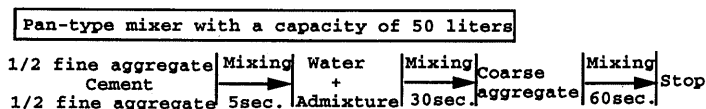
Fig.4 Mixing Method

5.2 Results

The slump, slump flow spread, and air content of freshly mixed concrete are shown in figures 5, 6 and 7, respectively. The dosages required to obtain the same slump depend on the type of super-plasticizer, but the slump and slump flow spread increased similarly as the dosage increased.

Figure 8 shows the results of the compression test. Though both superplasticizers produced a lower one day strength as the dosage increased, the strength was restored with aging.

Figure 9 shows the results of the setting test. For both types of superplasticizer, in the dosage ranges recommended by the manufacturers, both the initial and final setting times were extended in proportion to the increase in superplasticizer dosage. This suggests that a similar mechanism operated to cause retardation. With the naphthalene type, however, the dosage of 3.0% relative to the amount of cement, which is twice the standard dosage, led to a significant retardation of setting, suggesting that there can be a different mechanism of set retardation for each type of superplasticizer.

Detailed investigations are required to clarify this. Nevertheless, the dosage and the setting time are found to be proportional up to a certain dosage, regardless of the type of superplasticizer.
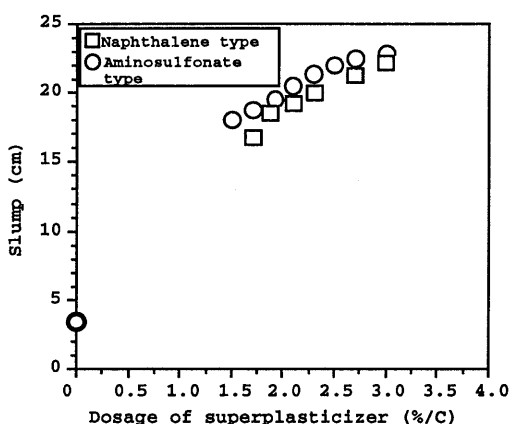
Fig.5 Influence of Dosage of
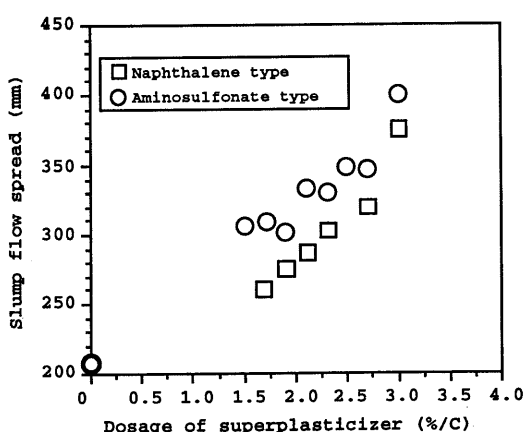Superplasticizer on Slump

Fig.6 Influence of Dosage of Superplasticizer
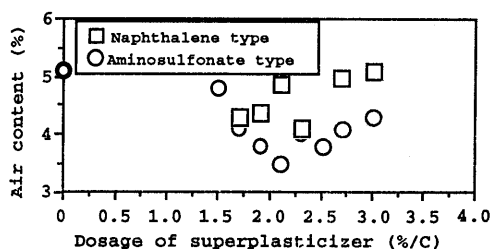on Slump Flow Spread

Fig.7 Influence of Dosage of
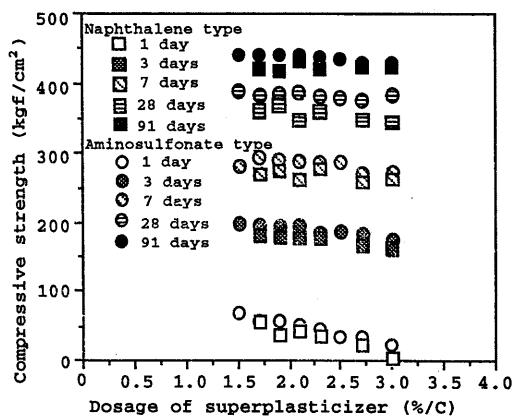Superplasticizer on Air Content

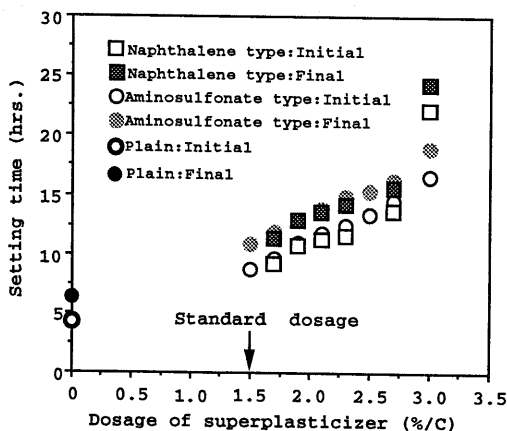Fig.8 Influence of Dosage of Superplasticizer on Compressive Strength

Fig.9 Influence of Dosage of Superplasticizer on Setting Time

5.3 Examination of conventional hypotheses

Though there have been no detailed reports on the mechanism of retardation of seting by super-plasticizers, two hypotheses have been proposed for the qualitative mechanism of setretarding agents[14].

(1) Interruption of hydration by adsorption films or precipitation films in the solid phase.
(2) Inhibition of crystallization or inhibition of crystal nucleus formation in the liquid phase.

Though these mechanisms could operate in combination, the main mechanism to be examined in this study is based on the assumption that there is no combined mechanism.

In the solid phase, the adsorption of various proprietary superplasticizers by the surfaces of cement particles takes the form of Langmuir's monolayer adsorption, in which the adsorption approaches saturation as the dosage of the superplasticizer increases. In the case of the naphthalene type, for example, the adsorption is approximately 80% of saturation with W/C at 65% and the solid dosage at 0.5%/C (equivalent to an undiluted solution at 1.0-1.5%/C), whereas the saturated adsorption is attained with the solid dosage at 1.0% of cement[15]. If the retardation of setting depended on the adsorption amount in the solid phase, the degree of retardation would have become smaller as the dosage increased, and the setting time would have approached a constant value. In the test results shown in figure 9, however, the setting time extends in proportion to the dosage, which is unexplainable simply due to the interruption of hydration that occurs in the solid phase.

In contrast to the solid phase, the amount of the superplasticizer in the liquid phase is nearly proportional to the dosage, in the range above the standard dosage, because at the standard dosage the surfaces of the cement particles are fairly close to saturated adsorption[16].   The set-retarding process in the liquid phase is considered to be as follows: the functional groups in the superplasticizer that contribute to the dispersion, e.g., sulfonic groups, react with Ca^{2+} produced by the hydration of the cement, resulting in calcium salts and consuming the superplasticizer. This is evidenced in a report by Uchikawa et al., in which they measured the binding energy of calcium on polished surfaces of clinker immersed in solutions of naphthalene-sulfonate-type and amino-sulfonate-type superplasticizers and suggested the existence of calcium sulfonate in both cases[5]. Daimon et al. also demonstrated that a precipitate is formed by mixing a saturated $Ca(OH)_2$ solution with a superplasticizer solution[17].   In other words, the formation of $Ca(OH)_2$ crystal nuclei is retarded and the rate of crystallization is reduced by the consumption of Ca^{2+} resulting from the hydration of cement. If the commencement of stage 3 is assumed to be the formation of $Ca(OH)_2$ crystal nuclei, the inhibition of the crystal nuclei is included in stage 2, whereas the inhibition of crystallization is included in stage 3.

It follows that the inhibition of crystal nucleus formation is the main cause of retardation of setting, since the setting time is understood as the transit period from stage 2 to stage 3 in this study.

6. Effects of superplasticizers on setting time

6.1 Concept of effects of superplasticizers

In this study each stage of hydration is understood as given below, according to the concept described as stages 1-3 under Section 3, "Early hydration of portland cement". The model is shown in figure 10.
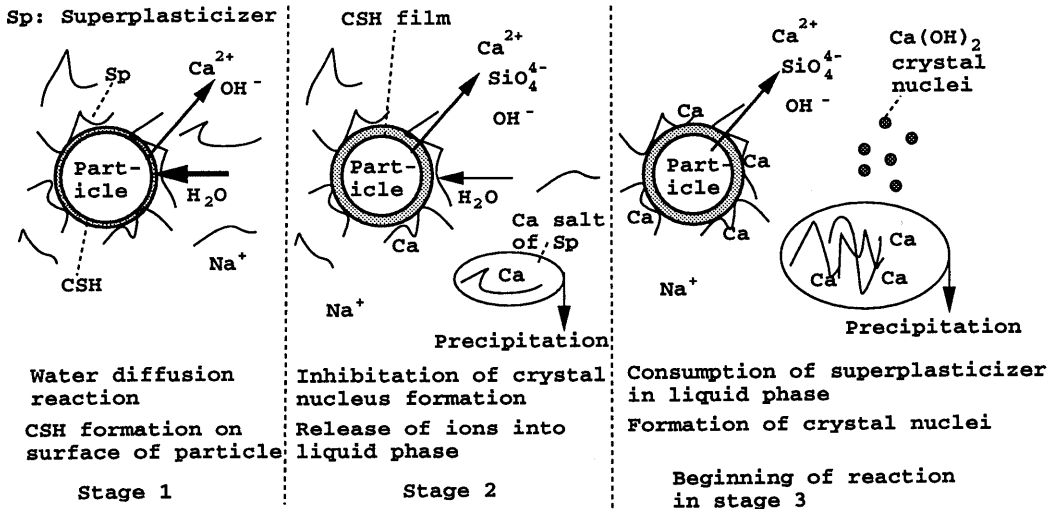

Fig.10 Model of Mechanism on Set-retardation due to Superplasticizer

Stage 1: The reactions occur mostly on the surfaces of the cement particles. The effects of the superplasticizer are small, because the hydration of the cement is quick and rapidly precipitates the hydrates on the surfaces of the particles. In other words, t_1 is constant. Part of the superplasticizer is considered to be consumed independently of the retardation by being incorporated in the hydration products of interstitial substances, such as C_3A, which go through rapid hydration in this period. The amount consumed is constant if the dosage exceeds the consumption.

Stage 2: This is the period during which various ions are released into the liquid phase. Ca^{2+}, released into the liquid phase by the hydration of the cement, reacts with the superplasticizer, forming calcium salts. In other words, the functional groups contributing to the dispersion in the superplasticizer are consumed by the reactions with Ca^{2+}. As a result, Ca^{2+} in the liquid phase is reduced and is prevented from oversaturating, retarding the formation of crystal nuclei. This inhibits the hydration of cement from proceeding to stage 3. Since the rate of hydration is constant in stage 2, the setting of the cement is retarded in proportion to the dosage of superplasticizer.

Stage 3: When the superplasticizer has been used up and $Ca(OH)_2$ crystal nuclei are formed, the reactions in stage 3 are triggered.

The amount of the superplasticizer consumed independently of the retardation in stage 1 depends on the type of superplasticizer, as does the degree of retardation. Therefore, these have to be determined experimentally from the relationship between dosage and setting time. Equation 7 for initial and final setting times is modified as below, to include the effects of superplasticizer:

$$T = t_1 + ((W^*/C)/(W^*_B/C_B)) \cdot (t_2 - t_1) + k \cdot (Sp - A). \qquad (8)$$

where, Sp $\geqq$ A, T is the initial or final setting time, in hours, W^*/C is the water-cement ratio, W^*_B/C_B is the water-cement ratio of basic portland cement paste, t_1 is the time until the end of reactions in stage 1, in hours, t_2 is the initial or final setting time of basic portland cement paste, in hours, k is the retardation time per 1.0%/C superplasticizer, in hours, Sp is the dosage of superplasticizer, in %/C, and A is the superplasticizer content consumed independent of retardation, in %/C.

6.2 Outline of experiments

Experiments were conducted as described below, to verify the above-mentioned concept of the effects of superplasticizers: The same ordinary portland cement as in the experiment regarding the effects of the water-cement ratio under Section 4.2 was used in the form of a paste with the water-cement ratio, W^*/C, at 25%. Only an aminosulfonate type for high strength concrete was used as the superplasticizer, in which the dry solid content is 30% by weight.

The concept of proportioning is as follows: Being a liquid, superplasticizers are normally used as part of the mixing water. By such a method of batching, the percentage of superplasticizer solid in the mixing water increases, and the actual water-cement ratio decreases, as the dosage increases. Using superplasticizers as part of the mixing water poses no problem in normal proportions with a high water-cement ratio, because the influence of the superplasticizer is greater than that of the water where the percentage of water is high relative to cement. In the range of very low water-cement ratios, however, the influence of the water becomes so high that a higher dosage of superplasticizer can lead to a lower flowability by the normal method of batching. In this experiment, therefore, the actual water-cement ratios of all dosages were adjusted to the same level (24.4%) as that of the dosage of 2.0%/C. The superplasticizer dosages ranged from 1.0% to 30.0%, to investigate the scope of application of the model as well. With W^*/C at 25%, the dosage of 30.0% is practically equivalent to mixing with the undiluted superplasticizer.

The mortars were mixed for 5 minutes using a Hobert type mixer. The setting test method was the same as that for the effects of the water-cement ratio in Section 4.2, in accordance with the JIS method for the setting time of concrete.

6.3 Results

The results of the experiment are shown in figure 11. Since the superplasticizer is intended for use at 1.0-3.0%/C, the results for this range are exaggerated. The straight lines in the figures are obtained by linear regression of the setting time (initial and final) and the dosages of 1.0-3.0%. If the basic W^*/C and the W^*/C of the target proportions are the same at 25% in equation 8, $(W^*/C)/(W^*_B/C_B)$ equals 1, and the equation can be transformed to:

$$T = (t_2 - k \cdot A) + k \cdot Sp. \qquad (9)$$

By substituting the setting time of basic portland cement with W^*/C at 25% into t_2, the retardation time per dosage of 1.0%/C, k, and the superplasticizer content consumed independently of retardation of setting, A, are obtained from the regression equation for the dosages of 1.0-3.0%/C. The experimentally obtained initial and final setting times of mortar containing no superplasticizer were 2.02 hours and 3.03 hours, respectively. By substituting these values into t_2, k and A were determined as follows:

Initial k = 6.15 (hr), A = 0.81 (%/C)
Final k = 7.29 (hr), A = 0.81 (%/C)

It was confirmed from the results of the experiment that the dosage of the superplasticizer used here is proportional to the setting time, and that part of the superplasticizer is consumed independently of the retardation of setting. Consequently, the setting time is considered to be predictable in a dosage range up to around 10%/C. Very high dosages of over 20%/C led to extreme retardation. At a dosage of

30%/C, the mortars still did not attain the initial setting at 22 days after placing. This may be attributed to the action of another mechanism, other conceivable mechanisms of retardation being:
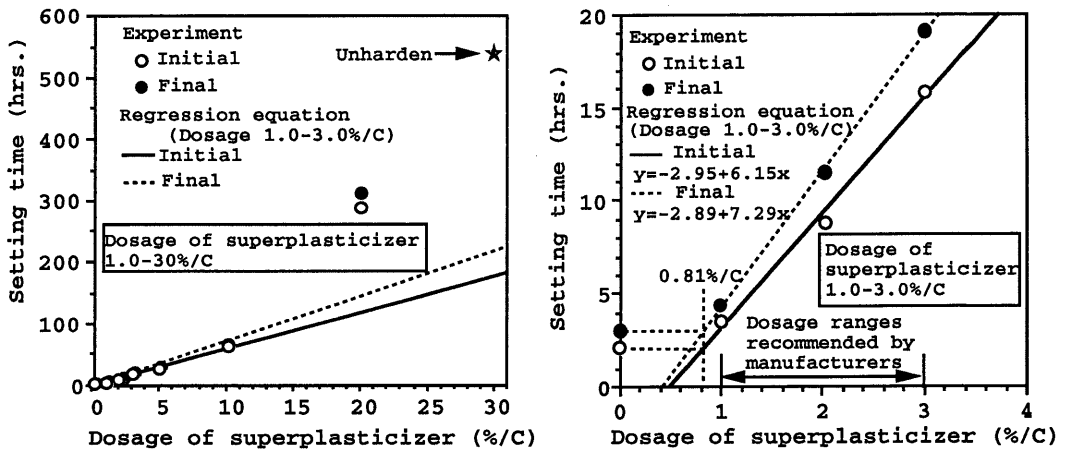

Fig.11 Influence of Dosage of Superplasticizer on Setting Time

1) The water-retaining action of the superplasticizer is so strong that it inhibits the transfer of water, thereby inhibiting the hydration of cement.

2) The existence of a large amount of superplasticizer between hydration products prevents the cement particles from forming crosslinking structures.

3) The reaction required for finishing stage II increases. In other words, the reactions of the cement particles proceed deeper from the surfaces inwards, reducing the rate of reaction in stage II.

If these do affect retardation of setting, they may be closely related to the problems of set retardation due to incompatibility between superplasticizers and segregation-inhibiting agents used for antiwashout underwater concrete, etc. This poses a key subject for the future.

7. Application to cements used with multiple mineral admixtures

Such mineral admixtures as blast-furnace slag and fly ash have been used recently to improve the properties of concrete. In such cases as ternary-system cement used in superworkable concrete, high mineral admixture contents are used in combination, to which a superplasticizer may be added. When such high mineral admixture contents are used, the setting properties are quite different from those of normal concretes, in which ordinary portland cement is the only binder[18][19]. Thus an investigation was carried out on the applicability of these model equations to ternary systems of cement with different mix proportions of mineral admixtures.

7.1 Outline of experiment

An experiment was conducted using paste with a water-binder ratio of 25% to investigate how hardening is affected by the dosage of superplasticizer and the mix proportions of ternary systems of cement. The method of proportioning was the same as that of the experiment on the effects of superplasticizers in Section 6.2. The actual water-binder ratio was adjusted to 24.4% in all cases. The dosage of the superplasticizer ranged up to 6.0% of the total binders. The paste was mixed for 5 minutes using a Hobert type mixer. The dosage of the superplasticizer was adjusted to produce a flow range of 350 ±30 mm by paste flow tests using a cone 70 mm in diameter at the top and 100 mm in diameter at the bottom, and 60 mm in height. In the case where the mixture did not become a paste

even when the maximum 6.0% was added, the mixing time was extended. The ordinary portland cement used was the same as that used in the experiment on the effects of the water-cement ratio in Section 4.2. The chemical composition of the mineral admixtures is presented in table 4. The mix proportions of the ternary-system cement and dosage of superplasticizer against binder are shown in figure 12. The superplasticizer was the same as that used in the experiment on the effects of superplasticizers in Section 6.2. In order to simplify the experiment, measurements were made up to the time when a strength of over 20 kgf/cm^2 was attained.

Table 4 Chemical Compositions of Mineral Admixtures

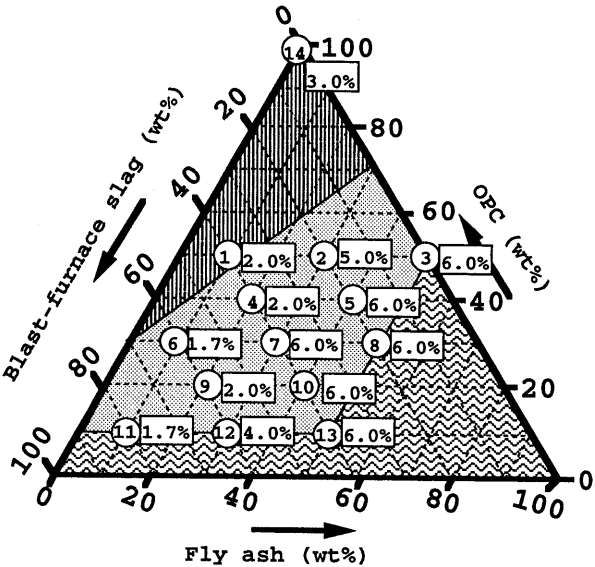| Chemical, Type	Specific gravity	Specific surface (cm^2/g)	SiO$_2$ (%)	Al$_2$O$_3$ (%)	Fe$_2$O$_3$ (%)	CaO (%)	MgO (%)	SO$_3$ (%)
Blast-furnace slag	2.89	6260	30.6	13.2	0.3	43.1	6.1	2.1
Fly ash	2.24	3060	56.7	27.9	2.8	5.1	1.2	1.0

Fig.12 Mix Proportions Ternary-system and
Dosage of Superplasticizer against Binder

7.2   Results and setting time estimation

The results of the experiment are shown in figure 13.   Blast-furnace slag and fly ash are both materials that react with the calcium hydroxide resulting from the hydration of the cement. The release of Ca^{2+} by these materials into the liquid phase is therefore considered to be much smaller, and thus the consumption of the superplasticizer by these materials is much lower than by ordinary portland cement. This led to the assumption here that blast -furnace slag and fly ash are inactive until setting time, and are mere fillers. The calculated values in figure 13 are the final setting times obtained from equation 8.   A value assumed from the exotherm rate was used as t$_1$.   Other values are obtained experimentally from the initial and final setting times of ordinary portland cement paste with a water-cement ratio of 25%. The substituted values are as follows:

W$^*_B$/C$_B$ = 25%

$t_1 = 1.00$ hr (assumed from exotherm rate)
$t_2 = 3.03$ hr (experimental)
$k = 7.29$ hr (experimental)
$A = 0.81$ %/C (experimental)

The results shown in figure 13 are the numbers of days up to hardening, and so do not always coincide with the estimated final setting time. However, they do suggest a tendency. Consequently, the setting time it may be possible predict to a certain extent by the above method, and the above-mentioned mechanism of retardation of setting is considered to be valid.

When the proportion of ordinary portland cement is small and the superplasticizer dosage is high relative to the combined binder, the superplasticizer content is very high relative to the ordinary portland cement. Figure 14 shows the results of the same experiment in the form of the relationship between the number of days required for hardening and the superplasticizer content against ordinary portland cement. The experimental values reveal a correlation indicating a strong influence by the superplasticizer on the number of days required for hardening. The calculated setting times under the effects of water-cement ratios indicated in equation 7 are 3.03 hours and 21.30 hours with ordinary portland cement at 100% and 10%, respectively. It follows that the first and second terms of equation 8 produce a difference of no more than one day, suggesting that the number of days required for hardening is practically governed by the effects of the third term, i.e., the superplasticizer. The calculated values in figure 14 are obtained by using only the third term. The slope of the straight line obtained by regression of the experimental value, k (the retardation time per 1.0%/C superplasticizer), is 8.33 hours. The value of k increases as the process proceeds from initial setting through final setting to hardening.
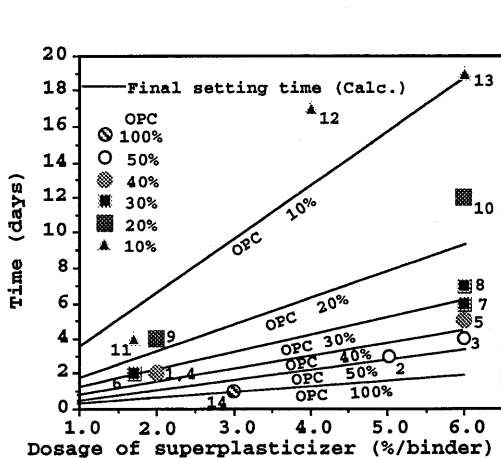

Fig.13 Relationship between Numbers of Days Required for Hardening and Dosage of Superplasticizer against Binder (Numbers on Fig. indicated mix proportionson Fig.12)
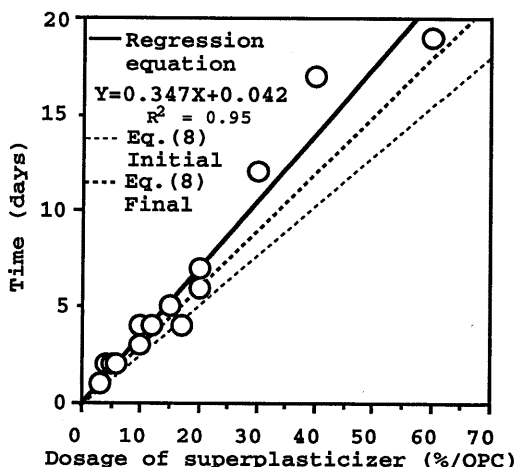
Fig.14 Relationship between Numbers of Days Required for Hardening and Dosage of Superplasticizer against OPC

8. Conclusions

The results of this study are summarized as follows:

(1) Among the hydration reactions of compounds of portland cement, C_3S has a major influence on setting time. Retardation of setting is mainly due to the extension of stage 2, or the dormant stage in the hardening process.

(2) The rate of hydration of C_3S, which greatly affects the setting time, is controlled by the diffusion of water in stage 1 and by the material transfer in the CSH film of constant thickness in stage 2. Since the changes in the reaction rate are small in stage 2, the reaction rate can be assumed to be constant in stage 2 when calculating the setting time.

(3) Retardation of setting due to the effects of superplasticizers is considered to be due more to the consumption of calcium ions by the superplasticizer, and the consequent inhibition of crystal nucleus formation of $Ca(OH)_2$ in the liquid phase, than to the interference of hydration by the adsorption films and precipitation films of the superplasticizer in the solid phase.

(4) The authors have proposed equations for estimating the setting time of concrete at an the ambient temperature of 20°C when using ordinary portland cement only. These equations include the effects of the water-cement ratio and superplasticizers.

(5) Setting time is proportional to the superplasticizer dosage in the normally used range, provided that the ambient temperature is 20°C, the water-cement ratio is 25%, and that only ordinary portland cement is used. However, when the dosage of the superplasticizer is 5 times the normally used level, retardation of setting becomes significant.

(6) When ternary systems of cement containing blast-furnace slag and fly ash are used at an ambient temperature of 20 °C and a water-binder ratio of 25%, the setting time can be predicted to a certain extent if the slag and ash are assumed to be inactive fillers until the setting time.

(7) The results of this study suggest that it is even possible to estimate the setting time of concretes with complicated mix proportions, provided various properties deriving from such materials as cement, mineral admixtures, and chemical admixtures are determined in advance. This estimation can therefore provide a key information on the interactions between materials and admixtures, which have so far been explained by the qualitative term "compatibility".

These results suggest that the use of such mineral admixtures as blast-furnace slag and fly ash in combination with portland cement should not be dealt with as the normal case of using portland cement alone. Instead, such use requires special consideration.

This investigation was basically limited to the results of using ordinary portland cement and an amino-sulfonate type superplasticizer. Retardation of setting due to other factors may arise, though the fundamental mechanism may be as explained here. Investigation will therefore be required on the effects of type of the cement, mineral admixture, and aggregate, in order to further clarify the set retardation mechanism. Environmental factors such as temperature are also considered to be important.

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