

## Influence of $3\text{CaO} \cdot \text{Al}_2\text{O}_3$ Content on the Fluidity of Cement Increased with Interstitial Phase

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Increasing interstitial phase content in cement clinker is an effective measure to enlarge the use of industrial waste or by-products. However, it is well known that interstitial phase or  $3\text{CaO} \cdot \text{Al}_2\text{O}_3$  influences on the concrete fluidity. In this paper, we investigated the influence of  $3\text{CaO} \cdot \text{Al}_2\text{O}_3$  content and other characters of cement on the fluidity of the cement paste, when interstitial phase content was more than that in ordinary Portland cement. Cement clinkers used in this study were synthesized from industrial raw materials and reagents by using an electric furnace in laboratory. The amount of  $3\text{CaO} \cdot \text{Al}_2\text{O}_3$  and  $4\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{Fe}_2\text{O}_3$  in the clinkers were varied. Cement pastes were prepared by adding a superplasticizer. Then, its apparent viscosity was measured with a rotational viscometer. The fluidity of the cement paste depended on the amount of  $3\text{CaO} \cdot \text{Al}_2\text{O}_3$  rather than the interstitial phase of the cement. This trend was different according to the kind of superplasticizer.

Key words: Fluidity, Interstitial phase,  $3\text{CaO} \cdot \text{Al}_2\text{O}_3$ , Superplasticizer

### 1. INTRODUCTION

The cement industry contributes to the recycling of resources by utilizing various industrial waste and byproducts as raw materials and fuels. However, demand for cement in Japan is now decreasing, so it is necessary to increase the amount of waste consuming in order to secure a specified processing volume of waste. Various types of incinerated garbage ash, sewage sludge, and coal ash, commonly used as materials for cement contain a relatively large amount of  $\text{Al}_2\text{O}_3$ , suggesting the possibility of enlarging the use of waste by increasing the  $3\text{CaO} \cdot \text{Al}_2\text{O}_3$  content or the interstitial phase content (the total amount of  $3\text{CaO} \cdot \text{Al}_2\text{O}_3$  and  $4\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{Fe}_2\text{O}_3$ ) in clinker [1,2].

It is worried that the fluidity of fresh concrete may decline as the interstitial phase content in clinker is increased [3,4]. Moreover, there have been few studies of the relationship between the fluidity and composition of the interstitial phase in cement in which the interstitial phase content is larger than in ordinary Portland cement. Therefore, the basic data on the fluidity of such cement must be collected.

Furthermore, various types of superplasticizer are usually used for concrete, and it is expected that the effect of the  $3\text{CaO} \cdot \text{Al}_2\text{O}_3$  content or the interstitial phase content, on the fluidity also varies due to the type of superplasticizer used. Therefore, it is important to determine the characteristics of each type of superplasticizer in order to create guidelines for materials design.

In this study, we investigate the influence of the interstitial phase content and its composition on the fluidity of cement paste for the cases involving lignosulfonate superplasticizer and polycarboxylic acid type superplasticizer, which are often used for

ready-mixed concrete.

### 2. EXPERIMENTAL

#### 2.1 Materials

Samples of clinker were prepared using industrial materials including limestone, silicestone, coal ash, blast-furnace slag, and ferrous slag, as well as special grade reagents including  $\text{Al}_2\text{O}_3$ ,  $\text{Na}_2\text{CO}_3$ ,  $\text{K}_2\text{CO}_3$ , and  $\text{CaSO}_4$ , used to adjust the amount of  $\text{Al}_2\text{O}_3$ ,  $\text{Na}_2\text{O}$ ,  $\text{K}_2\text{O}$ , and  $\text{SO}_3$ . These materials and reagents were mixed at specified mixing ratios. The mixture was kneaded by adding water, and the dried mixture was molded into a cubic form. Clinkers were sintered in an electric furnace for 30 min at a maximum temperature of  $1550^\circ\text{C}$ , and then taken out of the furnace at a temperature of  $1350^\circ\text{C}$ . It was then rapidly quenched in the atmosphere. Table I shows the mineral composition, the amount of free lime (f.CaO), and  $\text{SO}_3$  content in samples of clinker.

Clinker samples were ground using a ball mill until the Blaine specific surface area became  $320 \pm 10 \text{ m}^2/\text{kg}$ .

Table I Character of synthesized clinker

Sample No.	Mineral composition (%)※					f.CaO (%)	$\text{SO}_3$ (%)
	$3\text{CaO} \cdot \text{SiO}_2$	$2\text{CaO} \cdot \text{SiO}_2$	$3\text{CaO} \cdot \text{Al}_2\text{O}_3$	$4\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{Fe}_2\text{O}_3$	Interstitial phase		
#1	56	22	8	10	18	0.41	0.31
#2	56	17	3	21	24	0.29	0.31
#3	57	16	6	18	24	0.14	0.36
#4	57	17	9	15	24	0.20	0.36
#5	56	16	12	12	24	0.74	0.36
#6	55	18	15	9	24	0.63	0.34
#7	54	12	15	15	30	0.95	0.31

※ Determined by Bogue's eq.

The cements were prepared by adding hemihydrate to clinker powders, adjusting the  $\text{SO}_3$  content to 2.0%. Hemihydrate prepared by heating gypsum (special grade reagent) in the atmosphere was used. Powder X-ray diffraction and TG·DTA determined the purity of the hemihydrate thus prepared to be 95% or more.

Lignosulfonate superplasticizer (LS) and polycarboxylic acid type superplasticizer (PC) were used for the superplasticizer.

## 2.2 Preparation of paste

The water-cement ratio (W/C) was fixed at 55% when adding LS and at 35% when adding PC by assuming the mixing ratios of common ready-mixed concrete. The amount of superplasticizer to be added (as determined by the ratio of solid content to cement) was set to within a practical range, i.e., 0.2 to 0.8 mass% when adding LS and 0.05 to 0.4 mass% when adding PC. Ion exchange water, in which the superplasticizer had been initially dissolved, was added to the cement and a paste was prepared in a thermostatic chamber set to 20°C. The paste was prepared using a hand mixer with a mixing time of 3 min.

## 2.3 Measurement of apparent viscosity of paste

The fluidity of paste was evaluated using a concentric-cylinder rotational viscometer (Rotovisco RV1 made by Haake Inc.; radius of the inner cylinder, 20.7 mm; clearance between the inner and outer cylinders, 1.0 mm). To minimize the effect of segregation, the time from filling to measurement was minimized. Ten minutes after adding water, the paste was stirred lightly using a spatula, subjecting it to pre-shear ( $200\text{s}^{-1}$ ) for 30 sec in the outer-cylinder vessels, and then letting it stand for 30 sec. The shear rate was increased from  $0\text{ s}^{-1}$  to  $500\text{ s}^{-1}$  over 3 min and the apparent viscosity was then measured at  $200\text{ s}^{-1}$ . The measurement program is shown in Fig.1 and flow curves of sample #7 by two types of superplasticizer (LS and PC) are shown in Fig.2, respectively.

## 2.4 Measurement of residual concentration of superplasticizer

Another paste sample prepared in the same manner was separated into solid and liquid using a centrifugal separator set to 3000 rpm (1880 G) for 10 min,

following which the supernatant was collected. The supernatant was made acidic by adding 0.1 mol/L of hydrochloric acid, diluted with distilled water, and the concentration of superplasticizer residing in the liquid phase was measured using a total organic carbon meter. During the test, the temperature in the centrifugal separator was maintained at 20°C.

## 2.5 Analysis of hydration

Another separately prepared paste sample was soaked in acetone to prevent hydration. After filtering the sample, the acetone was removed by drying in air. Specimens for analyzing hydration were prepared using a water-jet aspirator, under reduced pressure (theoretical ultimate vacuum at 20°C: 2.34 kPa) for 3 hours. After adding sufficient MgO as internal standard for analysis so that it accounted for 10 mass% of the specimen, the relative integrated intensities ( $I/I_{\text{MgO}}$ ) of ettringite, hemihydrate, and gypsum were measured by means of powder X-ray diffraction. In this case, the peak of diffraction measured was  $2\theta$  ( $\text{CuK}\alpha$ ) =  $9.1^\circ$  for ettringite,  $14.7^\circ$  for hemihydrate, and  $11.6^\circ$  for gypsum. The relative integrated intensities thus obtained were corrected by the ignition loss of the specimen.

## 3. RESULTS AND DISCUSSION

The relationship between the  $3\text{CaO}\cdot\text{Al}_2\text{O}_3$  content and the apparent viscosity for the series of pastes with LS added and the series with PC added are shown in Figs.3 and 4. The apparent viscosity of the series with LS added was constant regardless of the  $3\text{CaO}\cdot\text{Al}_2\text{O}_3$  content when the amount of superplasticizer added was 0.8 mass%. When the amount of superplasticizer added was 0.2 mass%, however, the apparent viscosity tended to increase with increasing of the  $3\text{CaO}\cdot\text{Al}_2\text{O}_3$  content. Comparing #1 and #4 (#6 and #7 as well), where the  $4\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot\text{Fe}_2\text{O}_3$  content varies while the  $3\text{CaO}\cdot\text{Al}_2\text{O}_3$  content is kept constant as shown in table 1, reveals that the apparent viscosities are almost the same. It indicates that the influence of the  $4\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot\text{Fe}_2\text{O}_3$  content is small. Therefore, the important factor in determining the initial fluidity is not the amount of the interstitial phase in the cement but its mineral composition.

Also, in the series of pastes with PC added, the

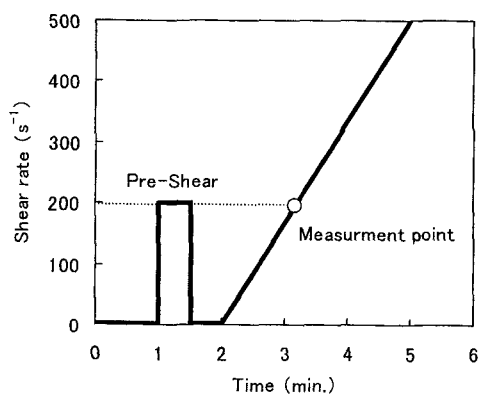


Fig.1 Viscometer test program.

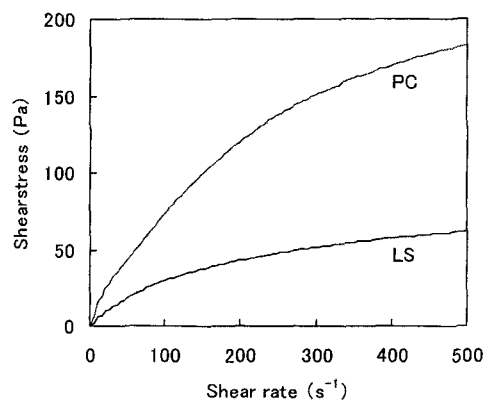


Fig.2 Flow curves of cement paste (sample #7).

difference in the apparent viscosity tended to increase with decreasing of amount of PC, as in the case of the series with LS added. However, the apparent viscosities are dispersing in this series, so factors other than the mineral composition of the interstitial phase may produce large effects.

The relationship between the residual concentration of superplasticizer in the liquid phase after 10 min of adding water and the apparent viscosity of the paste is shown in Figs.5 and 6. The fluidity of paste is often evaluated by the adsorptivity of the superplasticizer. But the amount of adsorption calculated from the residual concentration also contains the amount of superplasticizer incorporated into hydrates, so it does not represent the true amount of adsorption on the surface. Therefore, we examined the correlation between the residual concentration of superplasticizer in the liquid phase governing the adsorption equilibrium and the apparent viscosity.

In the series with LS added, the residual concentration decreased in those specimens for which the  $3CaO \cdot Al_2O_3$  content was larger when the amount of the superplasticizer added was kept constant. In the series with PC added, however, no clear differences were observed between any specimens within the range of testing.

Fig.5 indicates that the apparent viscosity of the paste generally decreases as the residual concentration of

superplasticizer increases, roughly converging to a specific value. When the residual concentration of superplasticizer is sufficiently high, the superplasticizer will be in a state of saturated adsorption on the surface of the cement particles. In this case, the apparent viscosity of the paste depends solely on the volume concentration of solid particles, with a small effect produced by the mineral composition of the cement.

The relationship between the  $3CaO \cdot Al_2O_3$  content and the relative integrated intensity of ettringite obtained by X-ray diffraction when the amount of each superplasticizer added was kept constant at 0.2 mass% is shown in Figs.7 and 8. In this test, though precipitation of gypsum in connection with hydration of the hemihydrate added was expected, no clear peak was detected by X-ray diffraction after 10 min of water addition.

The X-ray relative integrated intensity of ettringite increased in proportion to the increase of the  $3CaO \cdot Al_2O_3$  content in either series regardless of which superplasticizer was added. In the series with PC added, however, the dispersion of relative integrated intensity was large, with very high values for specimen #7. These trends were roughly in correspondence with the apparent viscosity of the paste (as shown in Figs.3 and 4).

Although the reason why a large amount of ettringite was formed in specimen #7, where PC was added, has

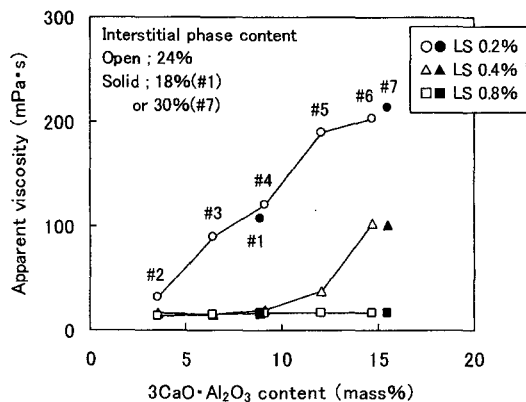


Fig.3 Relationship between  $3CaO \cdot Al_2O_3$  content and apparent viscosity (LS).

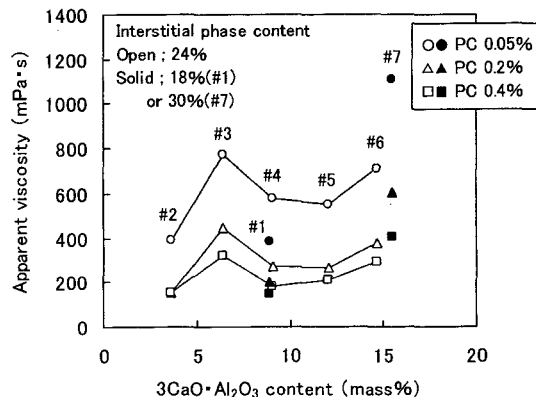


Fig.4 Relationship between  $3CaO \cdot Al_2O_3$  content and apparent viscosity (PC).

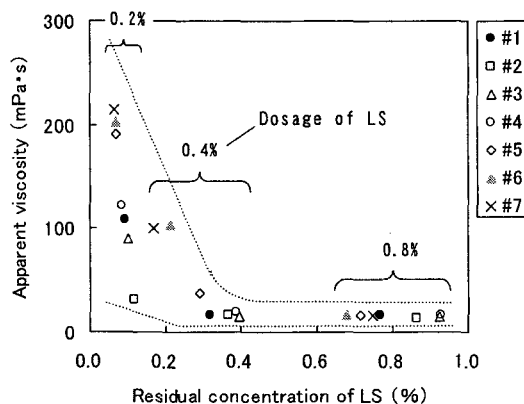


Fig.5 Relationship between residual concentration of LS in liquid phase and apparent viscosity.

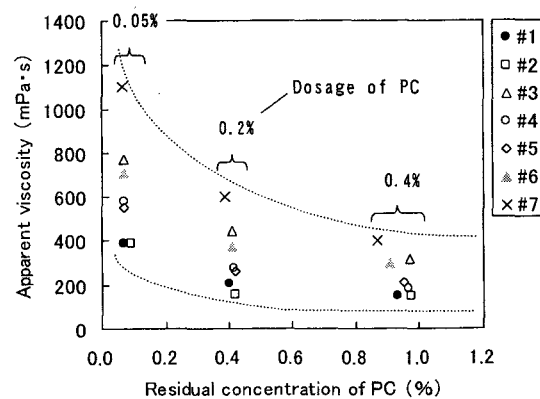


Fig.6 Relationship between residual concentration of PC in liquid phase and apparent viscosity.

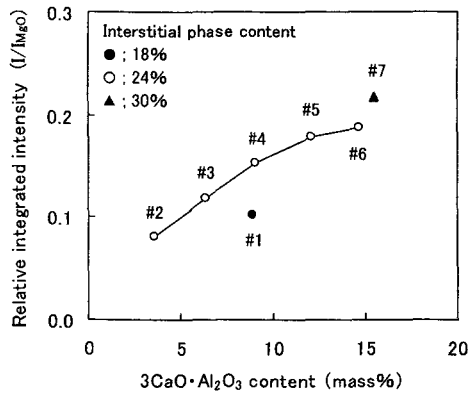


Fig.7 Relative integrated intensity of ettringite (LS dosage; 0.2%).

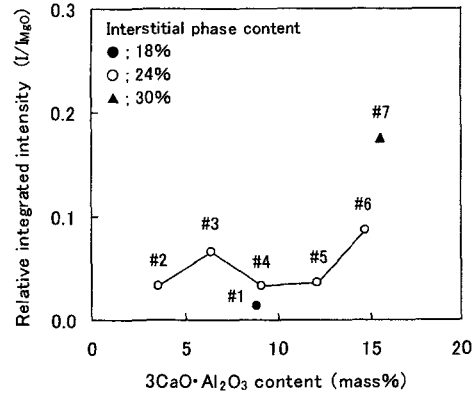


Fig.8 Relative integrated intensity of ettringite (PC dosage; 0.2%).

not been clarified, it is possible that a large quantity of  $4\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot\text{Fe}_2\text{O}_3$  has affected initial hydration. For specimens from #1 to #6, the dispersion of relative integrated intensity may have been influenced by orientation of ettringite crystals. When LS is added, the amount of ettringite and the  $3\text{CaO}\cdot\text{Al}_2\text{O}_3$  content are in good accordance with each other, so the hydration may differ from one type of superplasticizer to another.

The influence of the interstitial phase content and the composition of the interstitial phase for both the initial fluidity and the amount of hydrates may vary depending on the type of superplasticizer used. Generally, the  $3\text{CaO}\cdot\text{Al}_2\text{O}_3$  content significantly affects fluidity. For the series with PC added, however, the fluidity cannot be controlled solely with the  $3\text{CaO}\cdot\text{Al}_2\text{O}_3$  content. The hydration of  $3\text{CaO}\cdot\text{Al}_2\text{O}_3$  may be affected by the amount of free lime and gypsum in cement [5]. In the series with PC added, the influence of such minor components and the  $4\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot\text{Fe}_2\text{O}_3$  content must also be considered.

#### 4. CONCLUSIONS

Regarding the cement containing a larger amount of the interstitial phase than ordinary Portland cement, we examined the influence of the interstitial phase content and its mineral composition on the fluidity of cement paste to which lignosulfonate superplasticizer (LS) or polycarboxylic acid type superplasticizer (PC) had been added.

The main items of information obtained are as follows:

- (1) When a small amount of superplasticizer was added, the influence of the interstitial phase content and its composition on the fluidity of cement paste was significant.
- (2) When LS was added, the apparent viscosity of the paste after 10 min of water addition depended on the  $3\text{CaO}\cdot\text{Al}_2\text{O}_3$  content rather than on the interstitial phase content.
- (3) When PC was added, the apparent viscosity of the paste after 10 min of water addition and the volume of ettringite generated do not depend solely on the  $3\text{CaO}\cdot\text{Al}_2\text{O}_3$  content.

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(Received January 15, 2006; Accepted March 30, 2006)