

Relationship between Composition of Cement Increased Interstitial Phase Content and the Fluidity of Fresh Cement Paste

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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 Al_2O_3 . Therefore, 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 cement clinker is an effective measure to expand their use [1, 2, 3].

There is a concern that the fluidity of fresh concrete may decline as the interstitial phase content in clinker is increased [4, 5]. 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. In order to collect basic data on the fluidity of such cement, the influence of the composition of the interstitial phase on the fluidity of cement paste was studied [6, 7].

On the other hand, minor components in cement clinker usually differ from one plant to another depending on the nature of the raw materials used, and it is expected that the effect of $3\text{CaO}\cdot\text{Al}_2\text{O}_3$ content or interstitial phase content on the fluidity varies due to the amount of these minor components. Among the minor components, alkalis and SO_3 change the amount of water-soluble alkalis existing as alkali sulfates. When a polycarboxylate type superplasticizer is added, alkali sulfates are known to be the predominant factor in the fluidity as well as the interstitial phase [8, 9, 10]. The independent effects of these factors are well researched but the interaction has not been thoroughly investigated. From a practical viewpoint, it is important to clarify the interaction and to minimize the fluidity differential between plants by whatever means possible.

In light of this situation, this study investigated the effects of interstitial phase composition on the fluidity of the fresh cement pastes involving

lignosulfonate or polycarboxylate type superplasticizers, for cements with different amounts of water-soluble alkalies.

2. Methods

2.1 Materials

Clinker samples were prepared using industrial materials including limestone, silicestone, coal ash, blast-furnace slag, and ferrous slag, as well as special grade reagents including Al_2O_3 , Na_2CO_3 , K_2CO_3 , and CaSO_4 , used to adjust the amount of Al_2O_3 , Na_2O , K_2O , and 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°C , then removed from the furnace at a temperature of 1350°C . Three types of samples were then synthesized corresponding to plants with different amounts of MgO and water-soluble alkalies. Table 1 lists the mineral composition and the amount of minor components in the clinker samples. For each series, control samples with interstitial phase content of about 18% (determined by Bogue's eq.), high $3\text{CaO}\cdot\text{Al}_2\text{O}_3$ samples, and high $4\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot\text{Fe}_2\text{O}_3$ samples were synthesized. Moreover, additional samples varied the interstitial phase content, and the amounts of MgO and alkalies were synthesized as indicated in Table 2, for additional testing to be described.

Cement samples were prepared by adding gypsum and hemihydrate to clinker adjusting the SO_3 content to 2.0%. Hemihydrate prepared by heating gypsum (special grade reagent) in the atmosphere was used. Powder X-ray diffraction (XRD) and TG-DTA determined the purity of the hemihydrate thus prepared to be 95% or more. These samples were

Table 1. Character of synthesized clinker.

Series	Sample Type	Mineral composition (by Bogue's eq., mass%)				Chemical composition (mass%)		Water soluble alkalies (mass%) ^{*2}
		C_3S	C_2S	C_3A	C_4AF	MgO	$\text{Na}_2\text{Oeq.}^{\text{*1}}$	
A	Control	57.6	21.2	8.7	9.3	0.96	0.49	0.29
	$\text{C}_4\text{AF} + 1.5\%$	59.1	18.2	8.8	10.7	0.97	0.43	0.27
	$\text{C}_3\text{A} + 1.5\%$	58.6	18.5	10.3	9.3	0.98	0.44	0.25
B	Control	57.7	21.0	8.8	9.4	0.97	0.55	0.30
	$\text{C}_4\text{AF} + 1.5\%$	59.1	17.8	9.0	10.9	0.98	0.52	0.29
	$\text{C}_3\text{A} + 1.5\%$	58.8	18.6	10.4	9.2	0.97	0.51	0.32
C	Control	56.8	20.6	8.7	9.3	1.48	0.60	0.40
	$\text{C}_4\text{AF} + 1.5\%$	56.7	19.0	8.7	10.6	1.48	0.63	0.43
	$\text{C}_3\text{A} + 1.5\%$	57.2	18.4	10.3	9.5	1.51	0.58	0.38

*1 $\text{Na}_2\text{Oeq.} = \text{Na}_2\text{O} + 0.658\text{K}_2\text{O}$

*2 Determined by ASTM C 114

(Standard test methods for chemical analysis of hydraulic cement)

Table 2. Character of synthesized clinker (for additional testing).

Sample	Mineral composition (by Bogue's eq., mass%)				Chemical composition (mass%)		Water soluble alkalies (mass%)
	Series	C ₃ S	C ₂ S	C ₃ A	C ₄ AF	MgO	
A, B (low amount of water-soluble alkalies)	58.5	20.2	9.0	9.3	0.98	0.38	0.21
	57.0	21.5	8.7	9.4	0.97	0.44	0.23
	58.0	19.5	9.0	10.7	0.98	0.37	0.20
	58.3	19.6	8.9	10.7	0.97	0.41	0.17
	58.6	19.1	10.3	9.2	0.98	0.37	0.18
	57.3	20.5	10.3	9.3	0.98	0.44	0.20
	59.1	17.7	10.2	9.3	1.48	0.53	0.28
	59.0	16.3	10.4	10.9	0.98	0.49	0.31
	57.6	18.8	8.7	11.0	0.98	0.59	0.39
C (high amount of water-soluble alkalies)	55.1	21.2	8.5	10.2	1.44	0.57	0.41
	56.1	20.0	10.3	9.3	1.51	0.54	0.36
	57.8	16.5	10.1	10.7	1.48	0.59	0.43
	58.5	16.1	10.1	10.6	1.48	0.61	0.41
	59.2	14.0	11.2	10.5	1.98	0.59	0.40
	57.9	14.0	11.2	10.5	3.00	0.60	0.43

ground using a ball mill until the Blaine specific surface area became $320 \pm 5 \text{ m}^2/\text{kg}$. For all cements, the hemihydrate contents in calcium sulfate were $80 \pm 10\%$. Lignosulfonate (LS) and polycarboxylate (PC) were used for the superplasticizer.

2.2 Experimental procedures

2.2.1 Preparation of paste

To prepare the paste, the water-cement ratio (W/C) was fixed at 0.55 when adding LS and at 0.35 when adding PC, by assuming the mixing ratios of common ready-mixed concrete. The amount of superplasticizer added to cement was 0.25 mass% when adding LS and 0.6 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 for a mixing time of 90 sec when adding LS and with a high-shear mixer at a mixing time of 2 min when adding PC.

2.2.2 Rheological measurements

After 2 min (LS) or 7 min (PC) of mixing, the fluidity of the paste was evaluated using a parallel-plate rotational viscometer (Rotovisco RV1 made by Haake Inc.; radius of the plate: 30.0 mm; clearance between the upper and lower plates: 0.5 mm; with smooth surface) [11]. To minimize the effect of segregation, the time from filling to measurement was minimized. The paste was stirred lightly using a spatula, subjected to pre-shear (200 s^{-1}) for 30 s in the plates, and then left for 30 s. The shear rate

was increased from 0 s^{-1} to 500 s^{-1} over 2 min, and the shear stress was measured. The measurement program is illustrated in Figure 1 and samples of flow curve by two types of superplasticizer (LS and PC) are displayed in Figure 2. The range of the straight section (from 200 s^{-1} to 400 s^{-1} when adding LS; from 100 s^{-1} to 400 s^{-1} when adding PC) in the flow curve was fitted to a linear equation. The yield value of the cement paste was then determined from an intercept of the axis for shear stress.

2.2.3 Analysis of paste with PC added

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 PC 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 . For the pastes, the amount of adsorption of PC was calculated using the following equation.

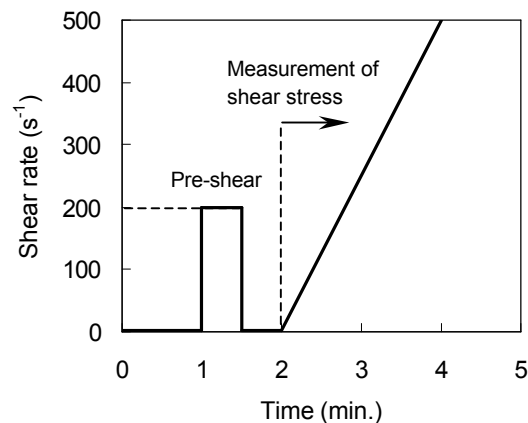


Figure 1. Viscometer test program.

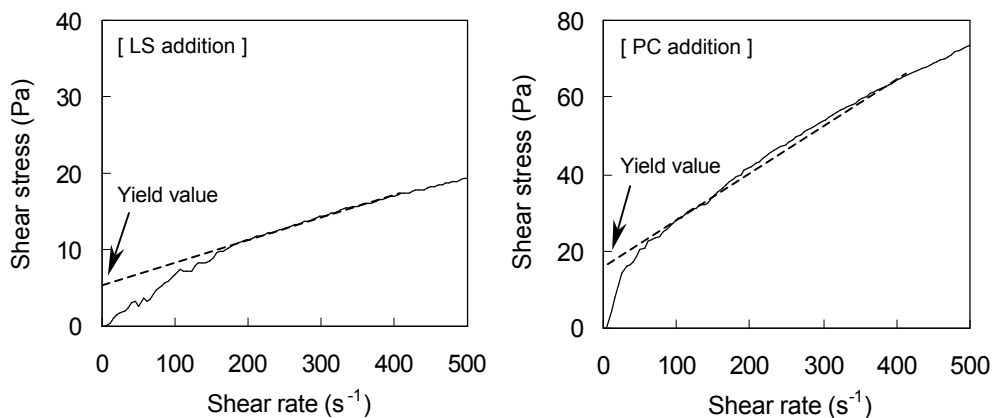


Figure 2. Samples of flow curve of cement paste.

$$AD = \left[\left(\frac{C \times SP}{100} \right) - \left(\frac{W \times C_{pc}}{100} \right) \right] \times \frac{1000}{C} \quad (\text{Eq.1})$$

where AD = adsorption of PC per unit mass of cement [mg/g], C = mass of cement [g], W = mass of water [g], SP = ratio of PC added to cement [mass%], and C_{pc} = concentration of PC residing in the liquid phase [mass%].

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 5 hours. For these specimens, the BET specific surface area was measured by means of nitrogen gas absorption method.

3. Results and discussion

3.1 Yield value of paste

The yield value for the series of pastes with LS added and the series with PC added are given in Figures 3 and 4. The yield value of the series with LS added was generally constant. No clear differences were observed between any samples, even though the interstitial phase content was increased. The flocculation of particles plays a major role in the rheology of cement paste [12]. When the water-cement ratio is sufficiently high, the yield value of cement paste will be less subject to the condensed state of cement particles. In this case, the mineral composition of the cement had a small effect on the yield value of the paste.

In the series of pastes with PC added, the effect of the interstitial phase content on the fluidity differed between the series of samples. Moreover, the difference in the yield values between the series of samples tended to increase with increasing $3\text{CaO} \cdot \text{Al}_2\text{O}_3$ content, in contrast to the series with LS added. In series C containing large amounts of MgO and water-soluble alkalis, the yield value of paste grew with increasing $3\text{CaO} \cdot \text{Al}_2\text{O}_3$ content. This indicates that the fluidity differential between plants could be expanded by increasing the use of industrial wastes and by-products.

The yield value for series C, with increasing $3\text{CaO} \cdot \text{Al}_2\text{O}_3$ content, varied amounts of water-soluble alkalis, and constant MgO content, is also included in Figure 4. When the amount of water-soluble alkalis was small, the yield value of paste was about the same magnitude as that of the control sample. This result indicates that water-soluble alkalis may produce significant effects, and that reduction of water-soluble alkalis can effectively prevent expansion of the fluidity differential between plants when the interstitial phase content is increased.

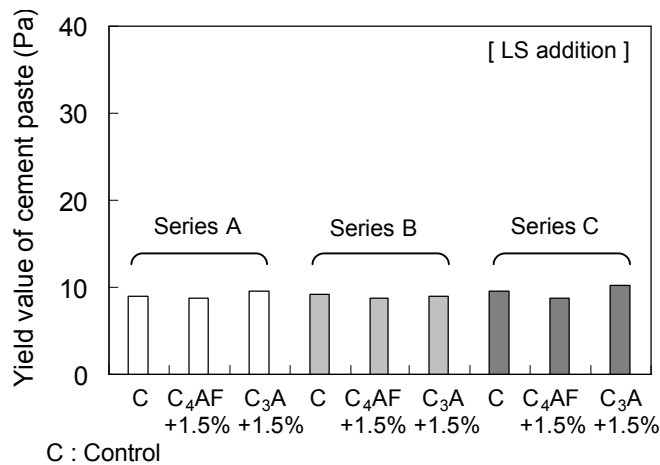


Figure 3. The yield value of pastes with LS added.

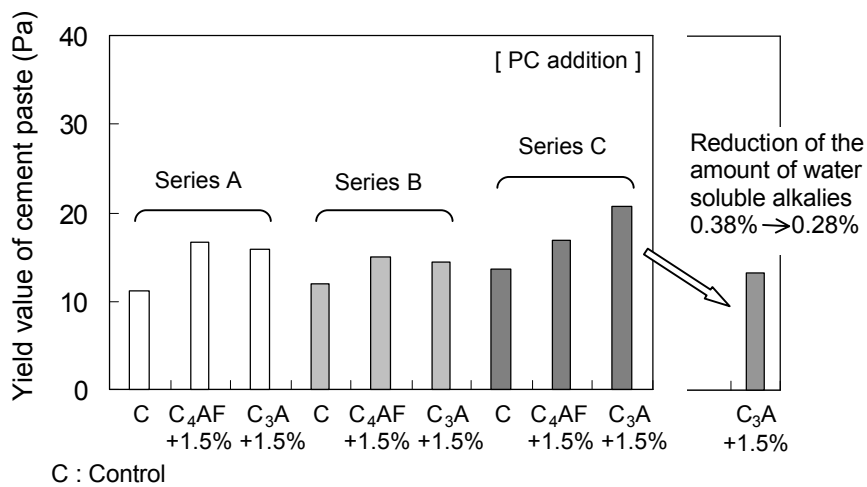


Figure 4. The yield value of pastes with PC added.

3.2 Analysis of paste

The amount of adsorption of superplasticizer and the specific surface area of hydrated cement are displayed in Figures 5 and 6. Although clear differences between samples were not observed, the amount of adsorption of superplasticizer in series C was slightly less than that in the other series, while the specific surface area of hydrated cement in series C was the same or greater than in the other series. The small amount of adsorption of superplasticizer in series C appeared to be caused by a large quantity of the water-soluble alkalis existing as alkali sulfates [9, 10].

The relationship between the amounts of adsorption of superplasticizer per unit surface area of hydrated cement and the yield value of paste is illustrated in Figure 7. The fluidity of paste is known to be dependent on the amounts of adsorption of superplasticizer per unit surface area of hydrated cement [13]. The yield value of paste in this test generally

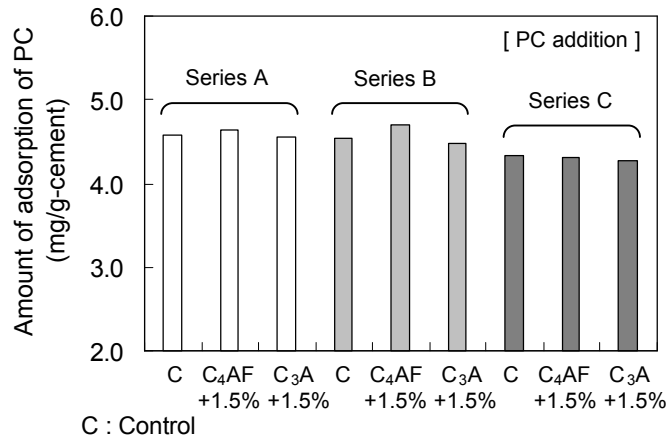


Figure 5. The amount of adsorption of superplasticizer.

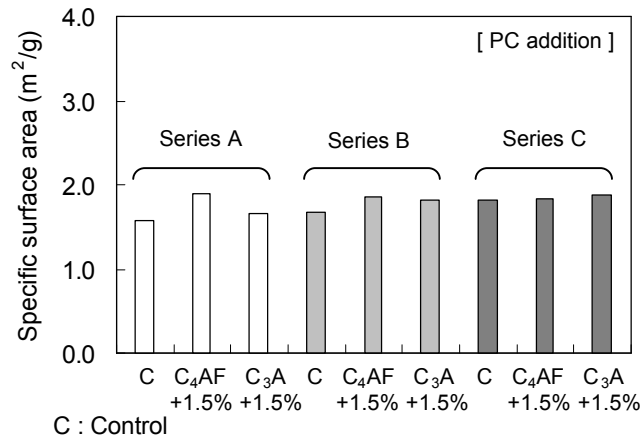


Figure 6. The specific surface area of hydrated cement.

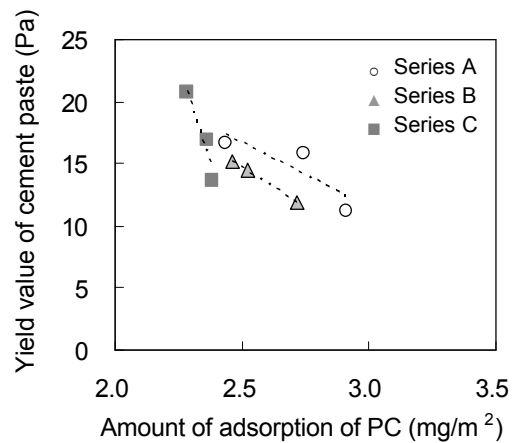


Figure 7. Relationship between the amounts of adsorption of PC per unit surface area of hydrated cement and the yield value of paste.

correlated with that index, and the relationship in series C had the largest slope. The fluidity of paste in series C may be susceptible to the specific surface area of hydrated cement because of the low amounts of adsorption of superplasticizer. Although the reason for the large slope of the relation line observed in series C has not been clarified, it is possible that a large quantity of water-soluble alkalis had affected the dispersive power of the superplasticizer.

3.3 Effect of aluminate phase

MgO in cement changes the amount of the aluminate phase determined by XRD [14]. An examination of the relationship between the amount of the aluminate phase determined by XRD and the yield value of paste, for cements with different amounts of MgO and interstitial phase (determined by Bogue's eq.), is detailed in Figure 8 (including the samples listed in Table 1). The aluminate phase of the cement clinkers was measured with the Rietveld method (Rietan2000 [15]). Experiment conditions of XRD are listed in Table 3. It should be noted that these calculations did not

Table 3. Experimental conditions of XRD and Rietveld method.

Item		Condition
Powder X-ray Diffraction	Characteristic X-ray	CuK α ($\lambda = 1.554 \text{ \AA}$)
	Tube voltage	40 kV
	Tube current	130 mA
	Measurement range	$2\theta = 10 - 60^\circ$
	Scanning step	0.02°
	Scanning rate	$0.6^\circ/\text{min.}$
Rietveld Analysis	Clinker minerals ^{*1}	Alite, Belite, Aluminate (Cubic and Orthorhombic), Ferrite (Total 100 mass%)

*1 The lattice parameters of belite and orthorhombic aluminate were fixed.

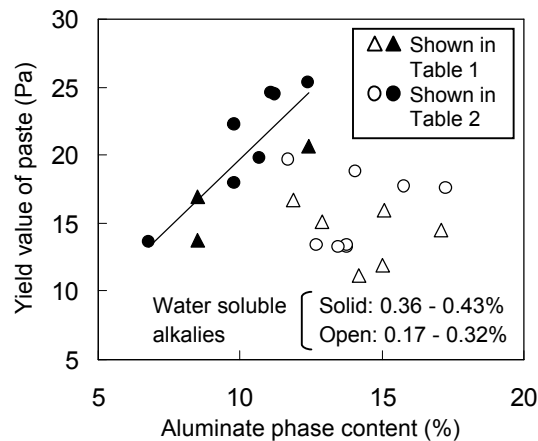


Figure 8. Relationship between the amount of an aluminate phase determined by XRD and the yield value of paste.

consider minor compounds such as free lime and periclase. Therefore, the quantitative value obtained from this test is considered a relative index.

The influence of an aluminate phase on the initial fluidity was clearly recognizable in series C containing the water-soluble alkalis over 0.36 mass%. In series A and B, however, the yield value of paste was not great, even when the aluminate phase content was relatively high. This result indicates that reduction of water-soluble alkalis could be an effective way to control the fluidity of cement with increased interstitial phase content. Although the factors affecting the fluidity in the series A and B has not been identified, it is possible that $4\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot\text{Fe}_2\text{O}_3$ has affected initial hydration. The influence of other conditions, for example the type of superplasticizer, must be examined in a future work.

4. Conclusion

This study investigated the influence of the compositions of cement increased interstitial phase content on the fluidity of the fresh cement pastes. Within the range of this study, the influence of interstitial phase composition on fluidity when polycarboxylate type superplasticizer was added varied depending on the amount of water-soluble alkalis. When the amount of water-soluble alkalis in cement exceeded 0.36 mass%, the fluidity of the cement paste depended on the amount of aluminate phase determined by XRD. These results suggest that the fluidity of cement paste increased interstitial phase could be improved by control of the minor components.

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