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Influence of superplasticizers on the hydration of cement and the pore structure of hardened cement

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Abstract

This paper describes the influence of various types of superplasticizers such as naphthalene type (β-NS), refined lignin sulfonate type (LS) and polycarboxylate types (P34, S34) on the hydration of cement and the pore structure of hardened cement. Other superplasticizers except β-NS delayed the initial hydration of cement. In any case, it hardly influences the hydration reaction at late stage of cement. The retardation by the addition of superplasticizers is not observed after 28 days of curing. Large pores of 0.1 μm or more for hardened cement with LS or β-NS are larger than those of hardened samples with P34 or S34 cured for 28, 56 and 91 days. This is related to the coagulated structures of fresh cement pastes with various types of superplasticizers. It was presumed that the size of the cluster of aggregated particles became small when S34 or P34 that has a high dispersing ability was added compared to LS or β-NS that has a lower dispersing ability.

Keywords: Dispersion; Mercury porosimetry; Pore size distribution; Admixture; X-ray diffraction

1. Introduction

In the hydration model of cement and the texture formation of hardening samples, there is a necessity to consider the aggregate structure of cement particles. Moreover, it is reported that the coagulated structure of such particles in a suspension influences the pore structure of the cement hardening body that has chemical admixtures added [1]. The hydration of cement is delayed by addition of superplasticizers. In concentrated suspensions, although superplasticizers still disperse particles, individual particles may not be completely separated from each other and so may form loosely associated clusters. Therefore, the texture formation of the hardening body is related to the complexity of the coagulated structure of the cement particles and the hydration delay of the cement caused by superplasticizers.

Though investigation is necessary from the view points of the both the coagulated cement particles and the retardation of hydration, very few studies have concerned themselves with the influence of superplasticizers on the texture formation of hardening cement [2]. Moreover, the influence that differences from the dispersion mechanism of superplasticizer exert on the microstructure of the hardening body is rarely discussed. This paper discusses the influence of various types of superplasticizers on the pore size distribution and the pore structure in hardened cement paste and the degree of the hydration of the mineral phase of cement.

2. Experimental

Table 1 shows the chemical composition, physical properties and mineral phase composition of ordinary Portland cement (OPC). The mineral phase composition of OPC was calculated by Bogue's equation. Lignin sulfonate type (LS), naphthalene sulfonate type (β-NS) and polycarboxylate types (P34, S34) were used as superplasticizers. The molecular structures of P34 and S34 are shown in Fig. 1 [3]. P34 is α-allyl-ω-methoxypolyethylene-maleic anhydride copolymer with graft chains of poly(ethylene oxide) (PEO) with a degree of polymerization of 34. A small amount of styrene was incorporated within the backbone of the polymer. In S34, the replacement ratio of methoxypolyethylene by allyl sulfonate was 0.44. LS involves

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Table 1
Chemical composition, physical properties and mineral phase composition of OPC

Density (g/cm^3)	Fineness (cm^2/g)	Chemical composition (%)										
		SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	Na_2O	K_2O	TiO_2	P_2O_5	MnO
3.15	3160	21.6	5.3	2.3	64.5	2.1	1.8	0.22	0.59	0.31	0.23	0.09

Mineral phase composition

C_3S	C_2S	C_3A	C_4AF	$CaSO_4$
54.4	21.1	10.2	7.0	3.1

the removal of sugar with a large delayed action with the enzyme, and is a special type that is different from that usually used as an air-entraining (AE) water reducing agent.

All experiments were carried out at 20 °C. Water to cement ratio is 0.32. Using a control stress type rheometer (rotational cylinder viscometer), the viscosities of suspensions, under a 5 min shear stress cycle of 0–200–0 Pa, were measured to estimate the apparent viscosities at the shear stress of 200 Pa. Dosage of superplasticizers was changed as follows: LS 0.1 to 0.5 mass%, β-NS 0.2 to 0.45 mass%, P34 0.03 to 0.15 mass%, S34 0.06 to 0.25 mass%.

The rate of heat liberation for cement hydration was measured with a 12 points sandwich type conduction calorimeter (Tokyo Riko Co., Ltd.) [4]. The influence of superplasticizers on the main cement hydration was examined by using time (t_1) to show the maximum heat generation rate (k_1) in the main hydration. When the hydration of cement was retarded by the addition of superplasticizers, t_1 was increased and k_1 was decreased.

Mixed cement paste was put into a poly(styrene) bottle, sealed and cured for 1, 3, 7, 28, 56, and 91 days. The hydration of samples was stopped by using a large amount of acetone and the samples were then D-dried.

The loss on ignition was measured from the loss in weight at 950 °C. The unreacted amounts of C_3S, C_3A and C_4AF were measured by XRD. The peak areas were numerically integrated; MgO (prime class reagent) was used as the internal standard material. A sample was dried at 200 °C for 6 h to exclude the influence of AFm. The pore size distribution of the hardened samples was measured by Hg-porosimetry. We have performed two cycles of intrusion–extrusion and calculate the retention factor R as follows:

$$R\ (\%) = \{(\mathrm{TPV}_{\mathrm{first}} - \mathrm{TPV}_{\mathrm{second}})/\mathrm{TPV}_{\mathrm{first}}\} \times 100 \qquad (1)$$

where $\mathrm{TPV}_{\mathrm{first}}$ is the volume of mercury intruded during the first cycle and $\mathrm{TPV}_{\mathrm{second}}$ is the volume of mercury intruded during the second cycle. Retention factor R is almost the same as trapped Hg explained by Winslow [5].

3. Results and discussion

Fig. 2 shows the relationship between the apparent viscosity of the cement paste and the dosage of superplasticizer. The apparent viscosity of paste was found to significantly decrease with increasing dosage of superplasticizers; though, almost the same value is indicated from a certain dosage. When the pastes exhibit almost the same apparent viscosity, the dosage of LS, β-NS, P34, and S34 are 0.5, 0.45, 0.15 and 0.13 mass%, respectively.

Fig. 3 shows the t_1 of cement hydration with various types of superplasticizers. t_1 measured on the rate of heat liberation curve of cement without superplasticizer is 10.9 h. t_1 increases with dosage when various types of superplasticizers are added, except in the case of β-NS. When β-NS, LS, P34, and S34 are added, for almost the same apparent viscosity, t_1 is 10.7, 20.0, 19.9, and 14.5 h, respectively. The value of k_1 in the case of the additions of β-NS, LS, P34, and S34 is 11.9, 6.5, 10.7, and 9.7, respectively. A particular small value is observed for LS. Even though it is a lignin sulfonate without sugar, the delayed actions of LS are larger than those of the other superplasticizers at dosages which minimize the apparent viscosity of the paste. The early hydration of cement was retarded by addition of LS, P34 and S34.

We have investigated the degree of hydration of alite, C_3A and C_4AF in cement at dosages of different superplasticizers giving similar apparent viscosities of the paste. Fig. 4 shows the degree of hydration of alite in OPC with various types of superplasticizers. When LS is added, the degree of hydration at 3 days is smaller in the other cases. Though the delayed action of LS is larger than that of other superplasticizers, the degree of hydration of alite cured for 28 days is almost the same as with the other superplasticizers. The late stage of cement hydration is not influenced by the type of added superplasticizers.

The degree of hydration of C_3A with various types of superplasticizers is shown in Fig. 5. When P34 and S34 are added, the hydration of C_3A is accelerated compared to other

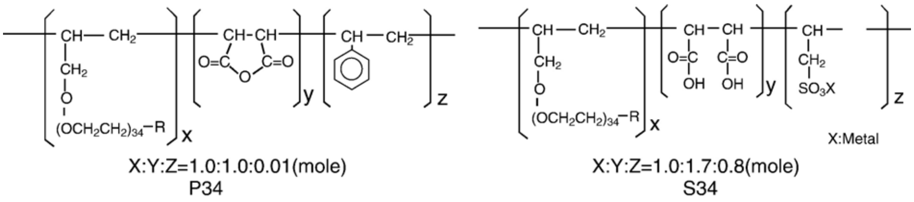

Fig. 1. Molecular structure of superplasticizers.

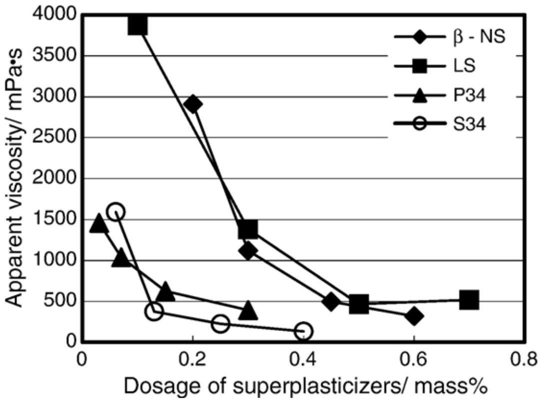

Fig. 2. Apparent viscosity of cement pastes with various types of superplasticizers.

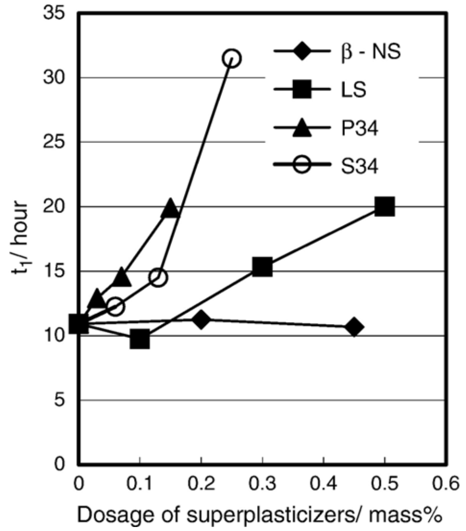

Fig. 3. Influence of various types of superplasticizers on the early hydration of cement.

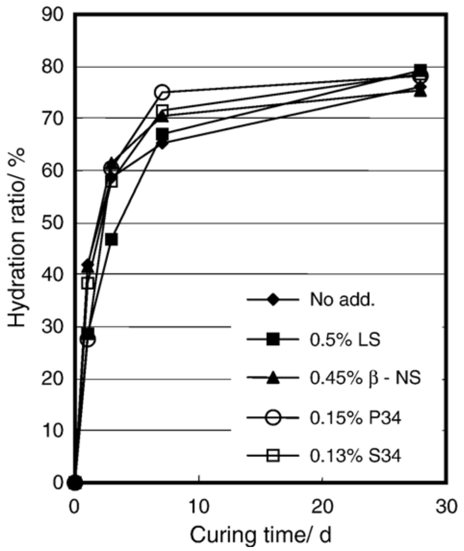

Fig. 4. Degree of hydration of alite in OPC with various types of superplasticizers.

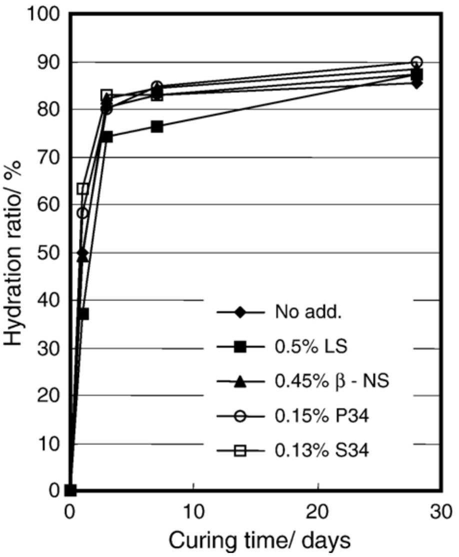

Fig. 5. Degree of hydration of C_3A in OPC.

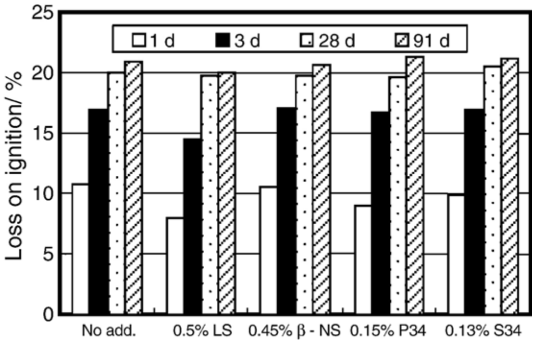

Fig. 6. Loss on ignition of hardened cement with various types of superplasticizers.

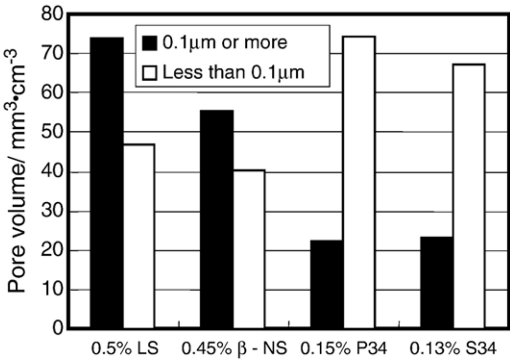

Fig. 7. Pore volume of hardened samples with various types of superplasticizers (curing time: 28 days).

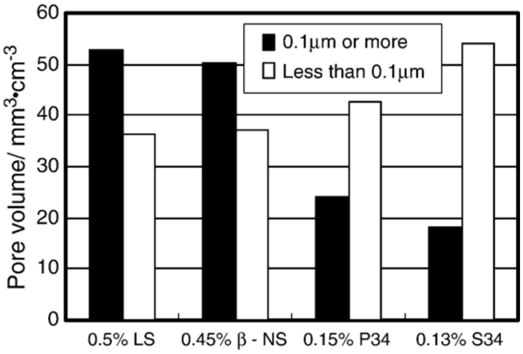

Fig. 8. Pore volume of hardened samples with various types of superplasticizers (curing time: 91 days).

cases cured for 1 day. The reason for the acceleration of the very early hydration of C_3A is thought to be that the supply of SO_4^{2-} to the surface of C_3A is prevented by the interaction of the polymer and SO_4^{2-} in the solution when P34 or S34 is added [6]. At 28 days, the degree of hydration of C_3A is practically similar when the superplasticizers are added. The hydration of C_4AF is delayed up to 7 days when LS is added. However, it reacts rapidly afterwards, and has a degree of reaction almost similar when there is no addition after 28 days of curing.

Fig. 6 shows the ignition losses of hardened samples with various superplasticizers. The value for LS is small, and it corresponds well to the results of the rate of the hydration of the compounds after 1 and 3 days. The ignition loss of hardened samples cured for 28 days or more are similar without influence of the type of superplasticizers. These results correspond well to the degree of hydration of the various compounds. The hydration of cement was retarded by the addition of superplasticizers until 3 days. However, retardation by the addition of superplasticizers is not observed after 28 days of curing.

The pores of hardened bodies were classified into pores of 0.1 µm and into pores <0.1 µm. Figs. 7 and 8 shows the distribution of pore volumes of hardened samples with various types of superplasticizers at 28 and 91 days; the hardened samples cured for 56 days also shows a similar trend, though the pore volume decreases with curing time. During these stages, hydration of cement was not retarded by adding the superplasticizers. The volume of 0.1 µm pores of hardened cement with LS or β-NS is larger than that of hardened samples with P34 or S34. When S34 or P34 was added, the volume of 0.1 µm pores decreases, and the volume of <0.1 µm pores increases. Cook and Hover suggested that the volumes of 0.1 µm pores correspond to the pore size of pore necks connecting a continuous capillary pore network [7]. And it was also reported that because the macroporosity peak was present on the mercury intrusion porosimetry results, macropores do form a connected cluster [8]. The above-mentioned reports also support that the volume of 0.1 µm pores is related to the coagulation structures of particles.

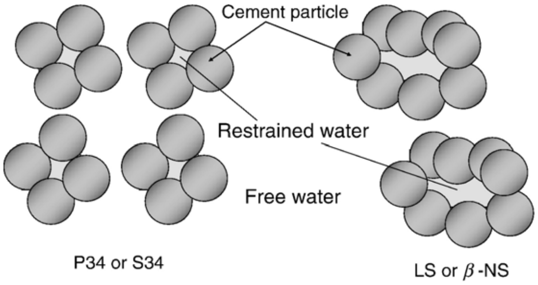

Fig. 9. Schematic illustration for aggregate structure of fresh paste with superplasticizers.

Table 2
Pore volume of hardened cement paste cured for 91 days

Samples with various superplasticizers	Retention factor *R* (%)
0.5% LS	75.6
0.45% β-NS	74.3
0.15% P34	78.3
0.13% S34	83.5

Table 2 shows retention factor calculated according Eq. (1). The retention factor of hardened samples with P34 or S34 is larger than that of samples with β-NS or LS. The retention factor indicates a big value when there a lot of 0.1 µm pores. Retention factor *R* is the amount of trapped Hg in hardened samples explained by Winslow [5]. This value may be related to the ratio of the inkbottle pores in hardened samples [9].

These are thought to be related to the coagulated structure of the fresh paste and to the dispersion mechanisms of cement grains by superplasticizers. The apparent viscosities of the cement pastes with the various superplasticizers are similar. The flow model assumes the presence of both free and retained water within the concentrated suspension, and water retention associated with the coagulated particles (particle clusters) is believed to have a significant effect on the fluidity of the concentrated suspension [10]. Therefore, it is thought that there are equal amounts of free water in the fresh pastes with various types of superplasticizers. There are few large clusters when LS and β-NS are added, but there are a lot of small clusters when S34 and P34 are added as shown in Fig. 9. When β-NS, having no retardation effect, or LS, having a retardation effect, is added, almost similar pore structures are formed in the hardened cement paste. Therefore, it is thought that the difference in the pore structures of the hardened samples with various types of superplasticizers is not related to the texture changes of the hydrates caused by the retardation of the hydration, but is related to the dispersion of the particles. It is presumed that the coagulated structure of the particles comes from the large pores formed when LS and β-NS are added; whereas the size of the clusters becomes smaller in pastes to which S34 or P34, which have high dispersion ability, are added.

4. Conclusion

The influence of various types of superplasticizers on the hydration of cement and on the pore structure of hardened cement paste has been investigated. Large pores of 0.1 µm or more for hardened cement pastes with LS or β-NS is higher than those of hardened samples with P34 or S34. When S34 or P34 is added, the volume of 0.1 µm pores decreases, and the volume of <0.1 µm pores increases. Hydration of OPC was not retarded by adding the superplasticizers at late stage. This is assumed to be related to the dispersion of cement particles, and consequently the pore structures of hardened samples reflect the coagulated structure of the particles in fresh cement paste with various types of superplasticizers.

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References

[1] T. Sugiyama, T. Uomoto, A study on microstructure of hardened cement composite using chemical admixture (in Japanese), Cement Science and Concrete Technology 56 (2002) 121–126.

[2] T. Sugiyama, A. Ohta, T. Uomoto, Effect of chemical admixture on microstructure of hardened cement composite (in Japanese), Cement and Concrete Technology 55 (2001) 49–53.

[3] E. Sakai, D. Atarashi, A. Kawakami, M. Daimon, Influence of molecular structure of comb-type superplasticizers and inorganic electrolytes on the dispersion mechanisms of limestone powder, in: V.M. Malhotora (Ed.), 7th CANMET/ACI International Conference on Superplasticizers and other Chemical Admixtures in Concrete, American Concrete Institute, Farmington Hills, Mi, USA, 2003, pp. 381–392, ACI SP-217.

[4] S. Hagiwara, E. Sakai, H. Imoto, K. Asaga, A new version of multichannel twin conduction type of calorimeter (in Japanese), Netsu Sokutei 27 (5) (2000) 226–232.

[5] D. Winslow, Some experimental possibilities with mercury intrusion porosimetry, in: L.R. Roberts, J.P. Skalny (Eds.), Pore Structure and Permeability of Cementitious Materials, MRS Symposium Proceeding, vol. 137, Materials Research Society, Pittsburgh, Pennsylvania, USA, 1988, pp. 93–103.

[6] E. Sakai, J.K. Kang, M. Daimon, Influence of superplasticizers on the very early hydration of $Ca_3Al_2O_6$ in the presence of gypsum, $CaSO_4 \cdot 0.5H_2O$ and CaO, Cement Science and Concrete Technology 56 (2002) 36–41.

[7] R.A. Cook, K.C. Hover, Mercury porosimetry of hardened cement pastes, Cement and Concrete Research 29 (1999) 33–943.

[8] R. Vocka, C. Galle, M. Dubois, P. Lovera, Mercury intrusion porosimetry and hierarchical structure of cement pastes. Theory and experiment, Cement and Concrete Research 30 (2000) 521–527.

[9] S. Diamond, Mercury porosimetry—an inappropriate method for the measurement of pore size distributions in cement-based materials, Cement and Concrete Research 30 (2000) 1517–1525.

[10] E. Sakai, K. Yamada, A. Ohta, Molecular structure and dispersion–adsorption mechanisms of comb-type superplasticizers used in Japan, Journal Advanced Concrete Technology 1 (1) (2003) 16–25.