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FLUIDITY OF SPHERICAL CEMENT AND MECHANISM FOR CREATING HIGH FLUIDITY

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ABSTRACT

The water/cementitious binder ratio of spherical cement concrete was decreased by 6–8%, and its unit weight of water was decreased by 14–30% in the same level of fluidity as that of normal Portland cement concrete. The superplasticizer dosage could be reduced to a maximum 2/3. The mechanism for the creation of high fluidity was considered as below. 1) The spherical shape is highly effective in increasing fluidity. 2) The particle size distribution, which is distributed in 3–40 μm, contributes to the creation of high fluidity. 3) The adsorption of superplasticizer to spherical cement particle surface decreases by 40% because of a decrease of the specific surface area and localization of the interstitial phase with gypsum. 4) The initial heat evolution amount of spherical cement is smaller by 25% than that of normal Portland cement. This low activity at initial hydration contributes to the creation of high fluidity. *© 1998 Elsevier Science Ltd*

Introduction

Spherical cement is cement in which the particle shape is round. We have previously reported the fundamental properties of spherical cement prepared by the dry-impact blending method and the possibility of utilizing the concept of spherical cement to produce high-fluidity concrete, high-strength concrete, and high-durability concrete (1–5).

In this paper, the fluidity of spherical cement concrete was reviewed on the basis of the previous paper (4). Furthermore, a mechanism for creating the high fluidity of spherical cement was considered through examining the difference between spherical cement and normal Portland cement in the properties of particle shape, size distribution, chemical surface properties, and initial hydration. In particular, the affect of chemical surface properties to fluidity was considered in detail by some new data.

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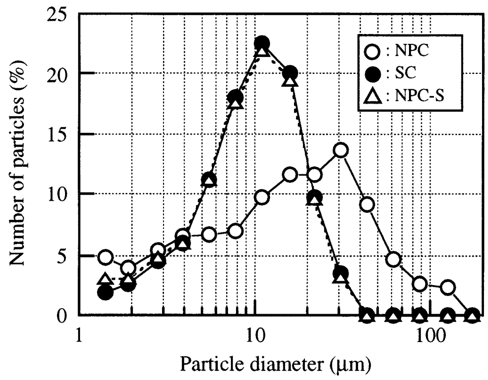

FIG. 1.
Particle size distributions of cement.

Experiment

Material

Spherical cement, commercial normal Portland cement, and size-controlled cement were used. Spherical cement was prepared by the same method used in the previous paper, (1) using normal Portland cement as the raw material. Then it was treated by a dry-impact blending method. This method required 20 min for treatment. Size-controlled cement was cement with a particle size distribution controlled to be as narrow as that of spherical cement by using air classifiers from normal Portland cement. Though size-controlled cement had the same particle size distribution as spherical cement, the degree of roundness differed from that of spherical cement. Figure 1 shows the particle size distributions of the three kinds of cement, and their powder properties are shown in Table 1. In this paper, spherical cement is hereafter indicated as SC, normal Portland cement is indicated as NPC, and size-controlled cement is indicated as NPC-S.

Toyoura standard sand or Ogasa land sand was used for mortar preparation. Oigawa river sand, Fujigawa river sand, Ome crushed stone, Fujigawa river gravel, or Iwase crushed stone was used for the concrete preparation. Their properties are shown in Table 2.

Lignin sulfonic acid-based or naphthalene sulfonic acid-based superplasticizer was used as

TABLE 1
Powder properties of cement.

Properties＼cement	SC	NPC	NPC-S
Degree of roundness (Perfect sphere: 1)	0.85	0.67	0.67
Mean diameter (μm)	11.3	13.5	11.0
Specific surface area (cm^2/g)	2700	3360	2900
N value from Rosin-Rammler	1.18	0.97	1.16

TABLE 2
Aggregate characteristics.

	Test sample	Kind of aggregate	Maximum size (mm)	Specific gravity	Fineness modulus	Water absorption (%)	Solid volume (%)
Fine aggregate	Mortar	Toyoura standard sand	0.3	2.63	—	0.29	58.0
		Ogasa land sand	5.0	2.60	2.78	1.50	68.2
	Concrete	Oigawa river sand	5.0	2.60	2.91	1.37	70.5
		Fujigawa river sand	5.0	2.63	2.49	2.00	67.1
Coarse aggregate	Concrete	Ome crushed stone	20.0	2.65	6.78	0.63	60.8
		Fujigawa river gravel	20.0	2.65	6.57	0.78	65.4
		Iwase crushed stone	20.0	2.65	6.70	0.70	58.9

a chemical admixture. Silica fume, which is an ultra-fine particle of SiO_2, was used as a mineral admixture for the concrete preparation in mixproportion condition with a water/cementitious binder ratio of under 20%.

Apparatus and Technique

Estimation of Fluidity. Flows of fresh cement mortar were measured by the procedure specified in JIS R 5201. The water/cement ratio (w/c) was 0.55, whereas cement/Toyoura standard sand mixture ratio was 0.5, and cement/Ogasa land sand mixture ratio was 0.33. In the case of paste, the w/c ratio was 0.45, and a flow corn of ϕ 5 cm $\times$ h 5 cm was used.

Table 3 presents mixproportions of fresh concrete. The slump value of concrete was measured by the procedure specified in JIS A 1101.

Packing Property. The packing property was evaluated by apparent density measured using a 100-mL vessel in tight packing. The vessel was tapped 180 times. The mixing weight ratios were as follows: cement/Toyoura standard sand mixture ratio 0.5; cement/Ogasa land sand mixture ratio 0.33.

Element Distribution of Sectional View. The element distribution of the sectional view of the cement particle was analyzed using an electron-probe X-ray microanalyzer (EPMA, Model JXA-8600S, JEOL Ltd., Tokyo, Japan).

Chemical Composition. The chemical composition of the cement was analyzed by the procedure specified in JIS R 5202.

TABLE 3
Mix proportions of concrete.

Mix No.	Cement	Unit weight of cement (kg/m^3)	W/C (+SF)* (%)	s/a (%)	Admixture (Wt. % vs. cement) Sp.	SF*	Air (%)	Aggregate
1		517	12–16	37	4.4**	11.2	1.0	F:Ogasa C:Fujigawa
2		512	22–28	39	1.6**	—	1.0	F:Oigawa
3	SC	305	50–53	40	0.25***	—	3.0 ± 1	C:Ome
4		400	36.2	43	0–1.0**	—	3.0 ± 1	F:Ogasa
5		450	32.2	42	0–1.0**	—	3.0 ± 1	C:Iwase
6		500	29.0	41	0–1.0**	—	3.0 ± 1	
7		517	14–20	37	4.4**	11.2	1.0	F:Ogasa C:Fujigawa
8		512	22–28	39	1.6**	—	1.0	F:Oigawa
9	NPC	305	53–58	40	0.25***	—	3.0 ± 1	C:Ome
10		400	36.2	43	0.5–2.5**	—	3.0 ± 1	
11		450	32.2	42	1.5–2.5**	—	3.0 ± 1	F:Ogasa
12		500	29.0	41	0.5–3.0**	—	3.0 ± 1	C:Iwase

*Silica-fume; **Naphthalene sulfonic acid-based superplasticizer; ***Lignin sulfonic acid-based superplasticizer

Zeta Potential. The zeta potential was measured using a Zeta-Meter microelectrophoresis apparatus under 1 g/L at 20°C condition (Model ELS-800, Otsuka Electronics Co. Ltd., Tokyo, Japan).

Adsorption Amount of Superplasticizer. Solutions of several concentrations of naphthalene-type superplasticizer were mixed with cement (w/c ratio=5) for 10 min at 20°C. After mixing, the supernatant solution was separated from the slurry by centrifugation and filtration. The saturated adsorption amount of superplasticizer was evaluated by the final superplasticizer amount of the supernatant solution by use of an ultraviolet spectrum analyzer (293 nm) (6).

Initial Heat Evolution Rate and Heat Evolution Amount of Hydration. The initial heat evolution rate and the heat evolution amount of the cement paste mixed at a w/c ratio = 0.5 at 20°C were measured by conduction calorimetry.

Results and Discussion

Fluidity of Concrete

Figure 2 shows the relationship between the w/c ratio or water/cementitious binder ratio (including silica-fume) and the slump value in fresh concrete

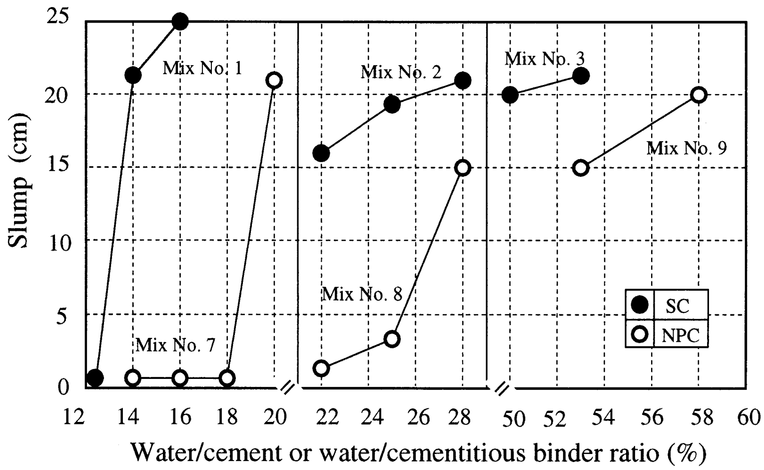

FIG. 2
Relationship between water/cement (+S.F.) ratio and slump in fresh concrete.

SC concrete was more fluid than NPC concrete, similar to mortar (1). The slump value of concrete using SC was larger than that of NPC with the same water/cementitious binder ratio. As a result, the water/cementitious binder ratio of concrete using SC was decreased by 6–8%, and its unit weight of water was decreased by 14–30% in the same level of slump as that of NPC. The reduction of water weight was clearly evident in the low water/cementitious binder ratio. A decrease in the water weight is also effective at increasing the strength of hardened concrete

Figure 3 shows the relationship between the superplasticizer dosage and the slump value in fresh concrete. The slump value increased in proportion to the increases of superplasticizer concentration in both SC and NPC, regardless of their unit weight of cement. Superplasticizer

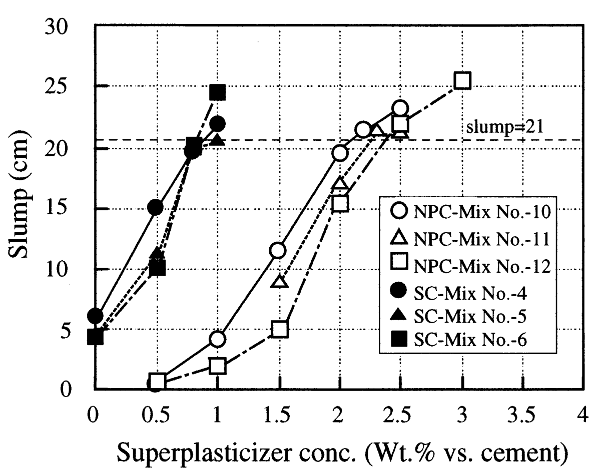

FIG. 3
Relationship between superplasticizer (naphthalene type) concentration and slump.

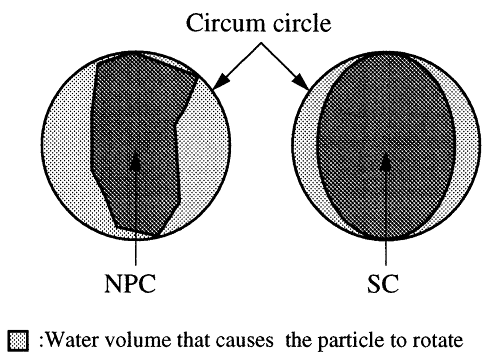

FIG. 4
Scheme of the difference in water volume that causes the particle to rotate.

dosage in SC concrete could decrease as compared with NPC concrete in the same level of slump value. For example, though NPC concrete needed a 2.0–2.5% superplasticizer concentration vs. cement for a slump value of 21 cm, SC concrete needed only 0.8–1.0% superplasticizer. It was recognized that the dosage in SC concrete was about a third as much as that in NPC concrete at the same level of fluidity.

Mechanism for Recognition of High Fluidity

It is said that fluidity of concrete relates to the shape of the cement and the aggregate, particle size distribution of the cement and the aggregate, adhesion and cohesion of cement particles, the level of activity in cement hydration, and the adsorption of superplasticizer to cement particles, etc. (7). In this paragraph, a mechanism for high fluidity of SC was considered through examining the difference between SC and NPC in the properties of particle shape, size distribution, chemical surface properties, adsorption of superplasticizer, and initial hydration property.

Shape. Examination was made of the water volume necessary to cause the cement particle to rotate in water by evaluation, using Eqs. 1 and 2 in conjunction with the scheme shown in Figure 4. The water amount was calculated for the two-dimensional level by scanning electron microscopySEM observing standard SC (degree of roundness was about 0.8) and NPC (degree of roundness was about 0.7). The mean value of NPC was about 1.07, and that of SC was about 0.41. These values indicate that NPC needs an amount of water having a similar area to cause the particles to roll, whereas SC needs only half its area of water. To sum up, the spherical shape of SC is highly effective in increasing the fluidity.

$$S_N = (S\text{-}S_1)/S_1 \tag{1}$$

$$S_S = (S\text{-}S_2)/S_2 \tag{2}$$

where S_N = area of water needed to make NPC particles rotate in water/cross-sectional area of NPC; S_S = area of water needed to make SC particles rotate in water/cross-sectional area of SC; S = area of circum circle; S_1 = cross-sectional area of NPC; and S_2 = cross-sectional area of SC.

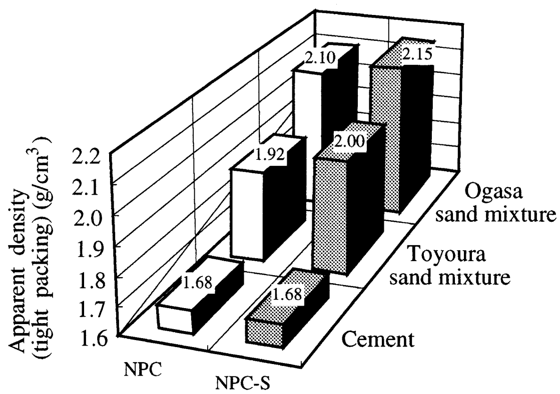

FIG. 5
Apparent densities of NPC and NPC-S.

Particle Size Distribution. The particle size of SC is distributed in a narrow range. In order to clarify the effect of particle size distribution and fine cement particles on fluidity, the packing ratio and fluidity of NPC-S were compared with those of NPC. NPC-S had the same particle size distribution as SC. Specifically, NPC-S had a narrow-range particle size distribution as compared with NPC because NPC-S was prepared by removing fine particles under 3 μm and large particles over 40 μm of NPC

Figure 5 presents the apparent densities of cement and the cement-aggregate mixture of NPC and NPC-S. The apparent density of NPC-S was nearly as large as that of NPC, whereas the apparent density of the NPC-S-aggregate mixture increased 2–4% over that of the NPC mixture. Generally, it has been reported that the packing ratio of powder particles increases in proportion to the increase in the range of size distribution, in other words, the packing ratio increases with the decrease in N value in the 1–2 range (7). Though the N value of NPC-S was about 1.2 and that of NPC was about 1.0, the packing ratio of the NPC-S-aggregate mixture increased 2–4% over that of NPC. This suggests that fine particles influence the packing ratio. Generally speaking, fine particles are highly adhesive and condensable, and it has been reported that fine particles under 3 μm significantly affect the decrease in the packing ratio in the case of cement (8). Because the volume of fine NPC-S particles was less than that of NPC, the decrease in the volume of fine particles is concluded to have contributed to the decrease in adhesion and condensation and to the increase in the packing ratio

Figure 6 indicates the flow values of NPC and NPC-S paste and mortar. The flow value of NPC-S paste increased about 20% over that of NPC, and the flow value of NPC-S mortar increased about 10–20% over that of NPC. These results demonstrate that the decrease in the volume of fine particles under 3 μm also affects the increase in fluidity. In addition, it has been reported that fine particles under 3 μm are very easily hydrated (9). Therefore, in the case of SC, it was expected that the decrease in initial hydration would also contribute to the increase in fluidity

From these findings, it is concluded that the decrease in the volume of fine particles under 3 μm is more effective in increasing the packing ratio and fluidity than widening the range of particle size distribution for cement that is highly adhesive, condensable, and hydrated. Therefore, particle size distribution of SC, which is distributed in a narrow range, contributed to the creation of high fluidity.

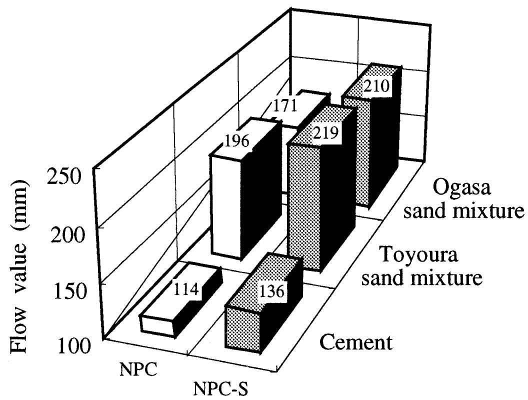

FIG. 6
Flow values of NPC and NPC-S.

Chemical Surface Properties. The elements Al, Fe, and S were found surrounding the surface of the SC particle shown in Figure 7. In the case of NPC, a random distribution of elements was observed. This indicates that the cement interstitial phase and gypsum were made into fine particles which then adhered to the surface of the larger core particles in the process of SC formation. The cement interstitial phase is namely C_3A and C_4AF, consisting primarily of the elements Al, Fe, and Ca. Gypsum consists primarily of the elements S and

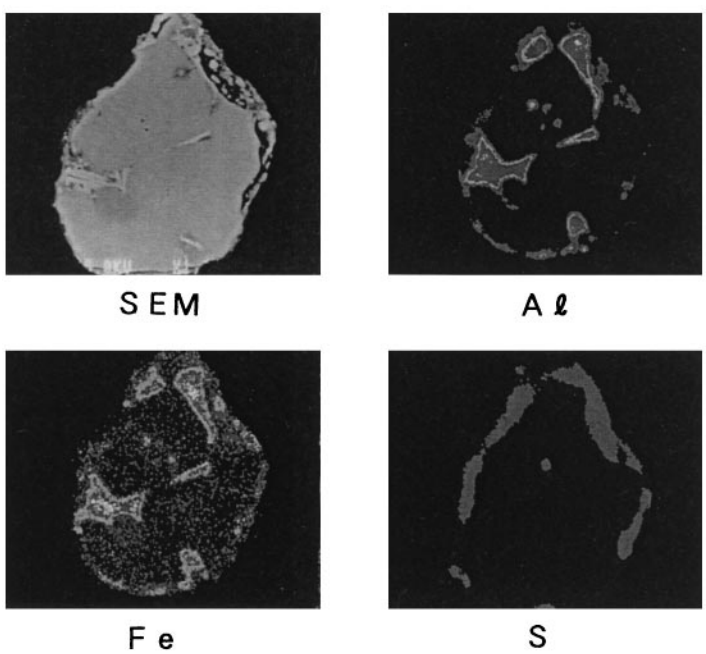

FIG. 7
Scanning electron microphotograph and X-ray image map of Al, Fe, and S on SC sectional view.

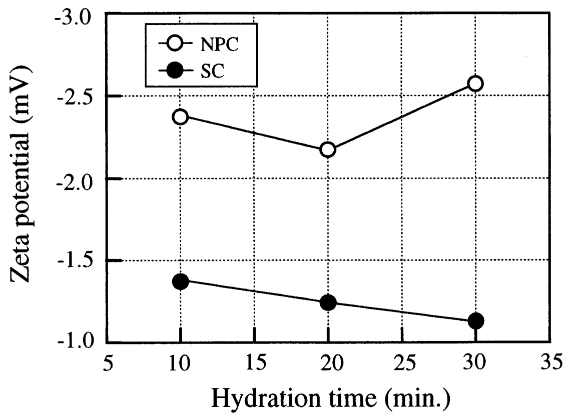

FIG. 8
Zeta potential of cement after mixed with water.

Ca. The cement interstitial phase and gypsum are easily ground components. It was expected that a change in the distribution of the elements in a cement particle surface affects the zeta potential. Figure 8shows the zeta potential for SC and NPC up until 30 min after it was mixed with water. The zeta potential value of SC charged in the positive side, as compared with that of NPC. The zeta potential of the interstitial phase particles has previously been reported to have a positive charge (10). The value of SC supported the fact that fine particles, which mainly consisted of interstitial phase particles, adhered and embedded to the surface of the SC particle, surrounding it like a microcapsule

In contrast, Table 4 gives the chemical composition of whole cement powder. There is hardly any difference between SC and NPC. Therefore, the change in the element composition of SC occurred only at the surface

Figure 9 shows the adsorption isotherm of superplasticizer to the cement particle surface. The shape of the curve was similar to the Langmuir type based on a classification by Giles (11). Single layer adsorption was observed until 1.5% in equilibrium concentrations of superplasticizer in both SC and NPC. The saturated adsorption amount of superplasticizer at 1.5% concentration for NPC was about 8.5 mg/g, whereas that of SC was 5 mg/g. Therefore, the saturated adsorption amount of superplasticizer for SC was about 3/5 as much as that for NPC. The specific surface area of SC was about 4/5 as much as that of NPC. Even if the difference of the specific surface area is taken into consideration, the adsorption amount of superplasticizer on a unit surface area of SC was smaller by 20% than that of NPC. A possible explanation for this phenomenon is shown below

It was reported that, although the cement interstitial phase easily adsorbs large amounts of

TABLE 4
Chemical composition.

	Ignition loss	Insoluble residue	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	Na_2O	K_2O	Total (%)
SC	2.4	0.1	21.1	5.0	2.9	64.4	1.4	1.9	0.22	0.42	99.84
NPC	1.6	0.6	21.2	5.1	3.1	63.5	2.0	2.0	0.30	0.45	99.85

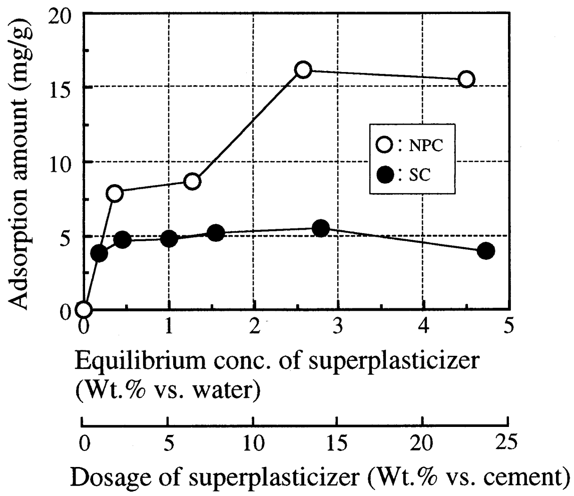

FIG. 9
Adsorption isotherm of superplasticizer to cement surface.

superplasticizer, the adsorption amount of superplasticizer decreases by 1/6–1/7 when superplasticizer coexists with gypsum because of adsorption competition between superplasticizer and gypsum to the interstitial phase (12,13). The interstitial phase and gypsum were attached to the surface of SC particles, as previously mentioned. Therefore, it was thought that this surface condition affected the decrease in the adsorption amount of superplasticizer on SC particles

These findings support the fact that SC concrete is highly fluid with small doses of superplasticizer as compared to NPC as shown in Figure 3.

Initial Hydration Property. Figures 10 and 11 give the heat evolution rate curve and the integral heat evolution amount curve for cement paste. The height of the first and second

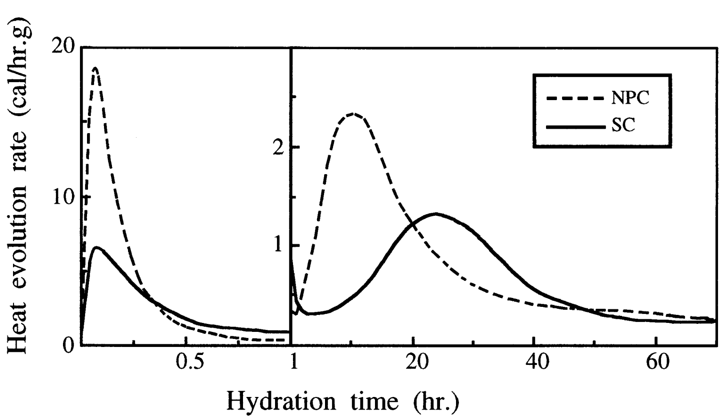

FIG. 10
Heat evolution rate curve of cement paste.

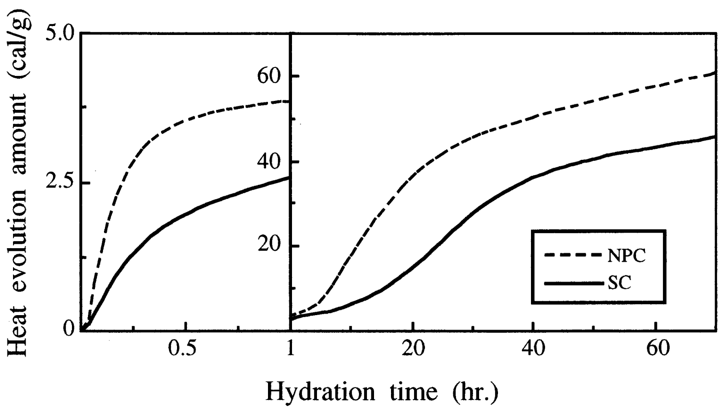

FIG. 11
Integral heat evolution curve of cement paste.

peaks of the heat evolution rate curve of SC were lower than those of NPC, and the heat evolution amount of SC up to 72 h was smaller by 25% than that of NPC. From these results, the initial hydration of SC decreased as compared to NPC. It was considered that this was due to the decrease of specific surface area, which was caused by the increase of the degree of particle roundness and the decrease in the volume of fine particles under 3 μm. It was also theorized that the decrease of the apparent specific surface area of the interstitial phase, which was active in initial hydration and was fixed to the surface of the SC particles, affects the lowering of the initial hydration of SC. Therefore, the decrease of initial hydration activity was contributed to the creation of high fluidity in SC

This low activity at initial hydration suggests a decrease in the strength of SC concrete. However, it is expected that there is no problem in the creation of strength over a long range of time because there is hardly any difference between SC and NPC in chemical composition of the whole cement powder.

Conclusion

1) The fresh concrete using SC was more fluid than that of NPC with the same water/cementitious binder ratio. The water/cementitious binder ratio of concrete using SC was decreased by 6–8%, and its unit weight of water was decreased by 14–30%, in the same level of fluidity as that of NPC. Moreover, the superplasticizer dosage in SC concrete could be reduced to a maximum 2/3 as compared with NPC concrete, in the same level of fluidity
2) The mechanism for the creation of high fluidity in SC was considered as follows. The spherical shape of SC is highly effective in increasing fluidity. It was calculated that NPC needed an amount of water having a similar area to cause the particles to roll, whereas SC needed only half its area in water at the two-dimensional level. The particle size distribution of SC, which is distributed in 3–40 μm, contributes to the creation of high fluidity. This is because a reduction of fine particles under 3 μm is more effective in increasing the fluidity than widening the range of particle size distribution for cement that is highly adhesive, condensable, and hydrated. The cement interstitial phase and

gypsum surrounded the surface of the SC particle. The adsorption of superplasticizer to SC particle surface decreased by 40% because of a decrease of the specific surface area and localization of the interstitial phase with gypsum. These support the fact that SC concrete was highly fluid with a small dosage of superplasticizer compared to NPC. The heat evolution amount of SC up to 72 h was smaller by 25% than that of NPC. This low activity at initial hydration contributes to the creation of high fluidity of SC.

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