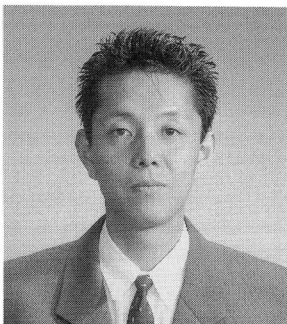


EFFECT OF FINENESS OF CEMENT ON THE FLUIDITY
OF CEMENT PASTE AND MORTAR

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SYNOPSIS

The influence of fineness of cement, namely surface area and particle size distribution, on the fluidity of mortar and cement paste was studied in the systems both with and without superplasticizer. The early hydration of cement and the adsorption of superplasticizer were also examined. The rheological study shows that cement fineness markedly influences the fluidity of mortar and cement paste and that the effect of fineness of cement on the fluidity depends on the existence of superplasticizer. In the absence of superplasticizer, the fluidity of mortar and cement paste was related to the amount of medium sized fraction, while in the presence of superplasticizer, their fluidity increased with an increase in fraction finer than $11\mu\text{m}$. The interpretation of the results is discussed in terms of heteroflocculation of cement particles.

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1. INTRODUCTION

An admixture such as superplasticizer improves the workability of concrete and brings about a given degree of workability at a lower water/cement ratio. It leads to high strength concrete at a lower water/cement ratio. The action and effect of the admixture, however, is affected by the composition and fineness of the cement. The problem of compatibility between cement and admixture has become significant with the rapid increase in the use of high strength concrete.

Whiting[1] reported that the amount of C_3A and alkali in cement as well as the fineness of cement affected the fluidizing effect of a superplasticizer. Similar results were obtained by Hattori et al.[2] who also pointed out that the amount of SO_3 in cement contributed to improving the effect of the superplasticizer. The authors investigated the mechanism of the effect of chemical composition, gypsum and alkali sulfate, and concluded that this effect could be explained by reference to the heteroflocculation of cement particles[3], [4].

On the other hand, the effect of fineness of cement on the fluidity of cement mixtures has been studied by a number of investigators. Kokubu et al.[5] reported that the particle size distribution of cement has a greater influence on the fluidity of cement paste than the specific surface area. Ozawa et al.[6] and Uchida et al.[7] reported that the controlling of particle size distribution of cement particles resulted in a higher fluidity of cement mixtures, such as paste, mortar and concrete, in the presence of a superplasticizer. Although the effect of fineness of cement on the fluidity of cement mixtures with superplasticizer has received a lot of attention, there have been only a few reports discussing this mechanism from the physicochemistry viewpoint. Several points concerning the mechanism of their effect are yet to be identified.

In the present work, the effect of cement fineness on the fluidity of paste and mortar containing superplasticizer was investigated in order to clarify the mechanism of compatibility between the cement and admixture. In addition, the role of cement fineness and the effect on the fluidity of cement mixtures are discussed with respect to the hydration of cement, the adsorption of admixture on cement and heteroflocculation between cement particles.

2. EXPERIMENTAL

2.1 Materials

Seven kinds of ordinary portland cement marketed in Japan which were either of different brands or the same brands but produced at different plants were used in this study. Their clinker compositions are shown in Table 1. The type of gypsum and amount of alkali sulfates as well as the clinker phases were different among the cements. In order to eliminate the effect of the chemical compositions of cement, six kinds of cement were prepared in the laboratory according to the following procedures: a clinker, of which the chemical and mineral phase compositions are shown in Table 2, was ground with gypsum in a small size ball mill to the Blaine specific surface area of 2,980, 3,390 and 3,930 cm^2/g . The powder obtained was mixed

Table 1 Phase composition, amount of SO_3 , and amount of water soluble alkali in commercial cement.

Kind of cement	Mineral phase composition				SO_3 (%)	Water soluble alkali (eq. Na_2O)
	C_3S	C_2S	C_3A	C_4AF		
C 1	46.7	28.8	9.0	9.1	2.1	0.40
C 2	48.8	25.8	8.7	9.1	2.1	0.46
C 3	46.7	28.6	9.4	8.8	2.1	0.41
C 4	47.2	27.0	10.0	8.1	2.0	0.27
C 5	48.7	27.0	9.4	7.9	2.1	0.61
C 6	43.1	32.4	9.3	8.5	2.1	0.47
C 7	41.6	33.2	9.2	9.1	1.8	0.35

Table 2 Chemical and mineral phase compositions of clinker.

Chemical composition (%)											Mineral phase composition (%)				Water soluble
ig. loss	insol.	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	SO ₃	Na ₂ O	K ₂ O	Total	C ₃ S	C ₂ S	C ₃ A	C ₄ AF	alkali (eq. Na ₂ O%)
0.4	0.0	22.2	5.2	3.4	65.1	1.9	0.5	0.34	0.49	99.5	55.0	22.2	8.0	10.3	0.41

to prepare six kinds of cement of different finenesses. The amount of gypsum added was 1.5% as converted to the amount of SO₃.

For fine aggregate, crushed sand produced from sand stone at Ryougami in Chichibu was used. The superplasticizer used was a commercial one (hereinafter referred to as NSF) with a major component being the salts of sulfonated naphthalene formaldehyde codensate.

2.2 Preparation of Cement Paste and Mortar

Mortar was prepared using a Hobert type mixer according to JIS R 5201. The proportion of mortar was the water/cement (W/C) ratio of 0.4 and the sand/cement (S/C) ratio of 2.2.

Cement paste with W/C ratio of 0.4 was prepared by mixing at low velocity (141rpm) for 3 minutes in a Hobert type mixer. NSF was added to the mixing water. The dosage of NSF showed the percentage of solid by weight of cement.

2.3 Measurement and Methods

Fineness Characteristics of Cement

As for the fineness characteristics of the cement, specific surface area, particle size distribution and fineness modulus of cement were determined. Specific surface area was measured by the Blaine air permeability method. Particle size distribution was measured by the laser light scattering spectroscopic method. According to the definition proposed by Kokubu et al.[5], the fineness modulus of cement (C.F.M.) was calculated by the following formula.

$$\text{C.M.F.} = [(\% \text{ residue on } 88 \mu\text{m}) + (\% \text{ residue on } 62 \mu\text{m}) + (\% \text{ residue on } 44 \mu\text{m}) + (\% \text{ residue on } 31 \mu\text{m})] / 100 \quad (1)$$

Measurement of the Fluidity of Cement Mixtures

The flow of mortar was measured according to JIS R 5201. The fluidity of cement paste was evaluated from a flow curve of cement paste measured using a rotational viscometer. Shear stress during cycles, in which the shear rate was first increased up to the maximum of 360s⁻¹ at a rate of increase of 120s⁻¹/minute and then decreased at the same rate, was measured. In the first cycle, the adhesion between cement paste and the wall of the viscometer was not uniform. The apparent viscosity was thus calculated from the flow curve of a second cycle at a 360 s⁻¹ shear rate. As shown in Fig.1, there was a good correlation between the flow of mortar and the apparent viscosity of the cement paste.

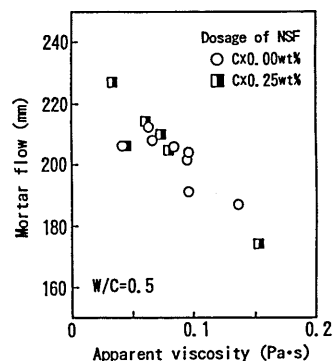


Fig.1 Relationship between apparent viscosity of cement paste and flow of mortar: S/C of mortar without and with NSF are 2.6 and 2.8, respectively.

Analysis of Early Hydration of Cement

The liquid phase of cement paste (W/C=0.4) was obtained by filtration after fixed curing time, and ionic concentration of the liquid phase was measured. Concentrations of K^+ , Na^+ , Ca^{2+} and SO_4^{2-} were determined by plasma emission spectroscopy, and OH^- ion concentrations were determined by titration. The hydrated sample was dispersed in acetone in order to stop its hydration and then dried under air with relative humidity of 15% and a temperature of 40°C. The amount of ettringite in the hydrated sample was determined by the DSC-TG method.

Measurement of Adsorption of Admixture

Cement paste with NSF and a water/cement ratio of 0.4 was prepared. The amount of adsorbed NSF was calculated by comparing the differences in the concentration of NSF in liquid phase before and after adsorption. The liquid phase was separated by vacuum filtration and was diluted to an optimum concentration. The concentration of NSF in the aqueous solution was measured by UV spectrophotometer at 270–293 nm.

Flocculation Characteristics Analysis

To examine the flocculation characteristics of cement particles, particle size distributions of cement particles in diluted suspensions were determined according to JIS A 1204.

3. RESULTS AND DISCUSSION

3.1 Fluidity of Cement Paste and Mortar

Table 3 shows the fineness characters of commercial cements. Fig.2 shows the relationship between mortar flow and Blaine specific surface area. There was no clear correlation between these factors. Table 4 shows the results of single correlation analysis between fineness of cement and flow of mortar. We also found that there was no correlation between surface area and flow of mortar. On the other hand, there was a high correlation between the fineness modulus of cement (C.F.M.) and mortar flow in the presence of NSF, of which the regression coefficient (γ) was about 0.6 or more. Therefore, when the variation of specific surface area was small, ranging from 3,280–3,470 cm^2/g , particle size distribution rather than specific surface area contributed to the fluidity of mortar. The evidence coincides with the results obtained by Kokubu et al[5].

Moreover, we found a higher correlation between the ratio of each particle fraction and the flow of mortar than between C.F.M. and flow of mortar. In the absence of NSF, there was a relatively high negative correlation of medium fractions ranging from 16–31 μm to flow of mortar. In the presence of NSF, on the other hand, there was a high negative correlation between fractions finer than 11 μm and flow of mortar, while there was high positive correlation for coarse fractions ranging from 31–62 μm .

Table 3 Specific surface area and particle size distribution of commercial cement.

Kind of cement	Blaine specific surface area (cm^2/g)	Fraction (vol%)								C. F. M
		0~5.5 μm	5.5~11 μm	11~16 μm	16~22 μm	22~31 μm	31~44 μm	44~62 μm	62~88 μm	
C 1	3360	21.5	13.7	11.7	14.1	14.8	13.5	7.7	3.0	1.15
C 2	3330	21.0	13.4	11.6	13.2	14.2	13.2	9.4	3.9	1.20
C 3	3470	21.0	15.3	12.6	15.4	13.9	11.4	7.7	2.7	1.10
C 4	3300	21.7	15.1	11.7	15.0	13.9	11.4	7.5	3.7	1.11
C 5	3280	21.6	15.0	12.1	14.0	13.4	12.9	8.1	2.9	1.12
C 6	3320	21.9	15.7	12.7	15.1	14.2	12.0	6.7	1.5	1.05
C 7	3330	22.3	14.7	10.7	12.5	13.8	12.2	7.9	5.5	1.17

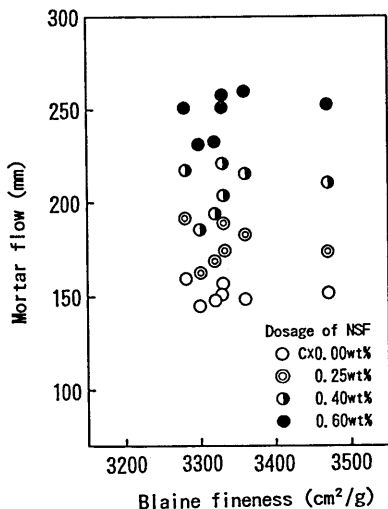


Fig.2 Relation of Blaine specific surface area to flow of mortar:W/C is 0.4, S/C is 2.2, hydration time is 7 min.

Table 4 Correlation coefficients for statistical analysis of fineness of cement and flow of mortar.

Factors		Amount of NSF added (% by wt. of cement)			
		0.0	0.25	0.40	0.60
Blaine Fineness(cm^2/g)		-0.117	-0.132	0.204	0.356
C. F. M		0.335	0.685*	0.581	0.725*
Fraction (%)	0~5.5 μm	0.128	-0.161	-0.581	-0.421
	5.5~11 μm	-0.053	-0.615	-0.647*	-0.737*
	11~16 μm	-0.265	-0.366	-0.056	-0.320
	16~22 μm	-0.570	-0.727*	-0.425	-0.535
	22~31 μm	-0.609	-0.103	0.100	0.237
	31~44 μm	0.313	0.787**	0.748*	0.676*
	44~62 μm	0.384	0.703*	0.703*	0.664*
	62~88 μm	0.339	0.332	0.062	0.326

Significant level: *10%, ** 5%

Table 5 Specific surface area and particle size distribution of cement prepared in laboratory.

distribution of cement prepared in laboratory.							
Kind of sample		S 1	S 2	S 3	S 4	S 5	S 6
Fraction (%)	0-5.5 μm	22.2	22.5	23.6	23.8	25.2	28.4
	5.5-11 μm	15.5	15.9	16.4	16.3	16.9	18.1
	11-16 μm	9.1	9.9	9.6	10.7	10.7	10.6
	16-22 μm	12.7	12.4	10.4	12.1	12.3	12.6
	22-31 μm	13.9	14.1	14.0	14.3	13.9	13.0
	31-44 μm	13.3	13.6	14.2	13.8	12.7	10.4
	44-62 μm	9.1	7.7	7.9	6.4	6.1	5.5
	62-88 μm	5.2	3.9	3.9	2.8	2.3	1.4
Blaine specific surface area(cm^2/g)		2970	3180	3290	3390	3570	3930

Based on the above results, which were obtained from experiments using commercial cements, it can be said that particle size distribution largely contributed to the fluidity of mortar but that this effect was altered by the addition of NSF. As shown in Table 1, however, commercial cements differed not only in fineness but also in chemical compositions, thus making it difficult to analyse the effect of fineness of cement alone. The effect of fineness of cement using cements manufactured in the laboratory was therefore examined.

Table 5 shows the particle size distribution and Blaine specific surface area of cements prepared in the laboratory. Fig.3 shows the apparent viscosity of cement paste after 15 minutes of hydration at shear rate of 360 s^{-1} as functions of particle fraction ranging from 0~11 μm and 31~88 μm . Decreasing with

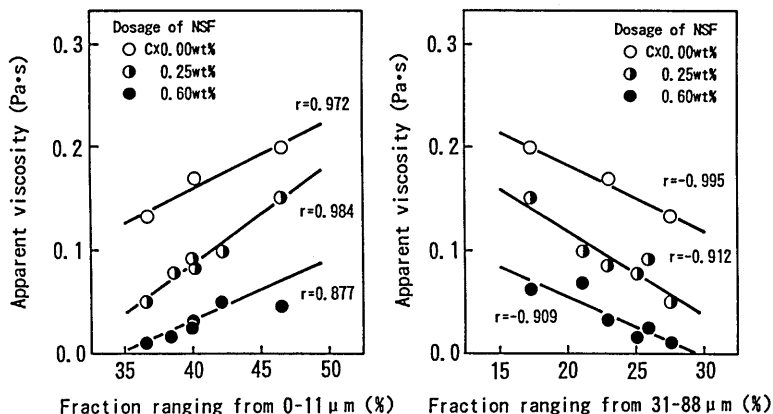


Fig.3 Effect of particle size distribution on apparent viscosity of cement paste at 15 minutes of hydration where W/C=0.4.

fractions finer than $11\mu\text{m}$ or increasing with fractions above $31\mu\text{m}$ reduced the apparent viscosity of cement paste and resulted in an improved fluidity of the cement paste. The results coincided with those obtained using mortar. For the laboratory manufactured cements, however, there was a high positive correlation (with a correlation coefficient (γ) of over 0.9) between Blaine specific surface area and apparent viscosity. An explanation for this is given below. The variation of specific surface area of laboratory manufactured cements was large ranging from 2,970–3,930 cm^2/g and their chemical compositions were constant.

The results from a rheological study of mortar and cement paste clearly indicated that the fluidity of cement paste and mortar was influenced by fineness of cement, that is surface area and particle size distribution.

3.2 Early Hydration

Ono et al.[9] and Uchikawa et al.[10] reported that the fluidity of cement paste largely depended on the amount and form of hydration products of the aluminate phase. The amount of ettringite produced was increased in line with the surface area of cement[11]. This suggested that the effect of fineness of cement on the fluidity was derived from the early hydration of the cement concerned.

Fig.4 shows the relation of the amount of ettringite produced to the Blaine specific surface area at 15 minutes of hydration for cements prepared in the laboratory. The amount of ettringite was increased in proportion to the specific surface area. Fig.5 shows the apparent viscosity of cement paste at 15 minutes of hydration as a function of the amount of ettringite produced. The apparent viscosity increased linearly with increased production of ettringite. Thus it seems that the effect of fineness of cement on the fluidity of cement paste could be explained by deposition of hydrates. However, the relationship between them differed depending on the amount of NSF added. Although the amount of ettringite was the same, the viscosity of the paste decreased with increase in the added amount of NSF.

According to the above there seems to be factors other than the deposition of hydrate contributing to the change of fluidity of paste with fineness of cement.

The authors[3],[4] reported that the dissolving rate of SO_4^{2-} ion significantly influenced the fluidity of cement paste. The dissolving rate of SO_4^{2-} ion from gypsum may be expected to increase with specific surface area of

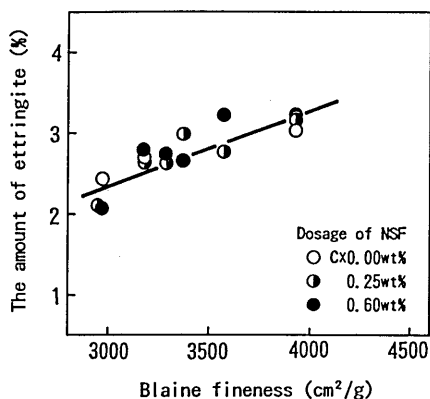


Fig.4 Effect of specific surface on amount of ettringite produced in paste at 15 minutes of hydration where $W/C=0.4$.

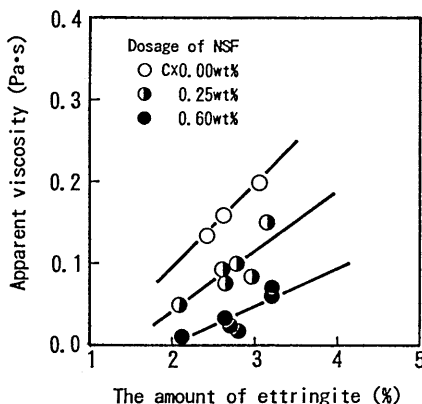


Fig.5 Correlation of amount of ettringite produced to apparent viscosity: $W/C=0.4$, hydration time is 15 min.

cement. Therefore, the change of the fluidity of paste due to the fineness of cement may be considered to be induced by the difference in the dissolving rate of SO_4^{2-} ions. To confirm this, the ionic concentration in the liquid phase of the paste was studied. The results of the study at 5 minutes of hydration is shown in Fig.6. Similar results were also obtained at 1 and 15 minutes of hydration. Thus, the effect of fineness on the dissolving rate of gypsum was determined to be negligible.

From these results, it is concluded that the differences in fluidity due to fineness of cement cannot be explained by early hydration properties alone.

3.3 Adsorption

The dispersing action of NSF is induced essentially by an increase in electrostatic repulsion force among cement particles adsorbed by admixture molecules on their surfaces. The differences in the relation of viscosity of paste and the amount of ettringite, which are shown in Fig 5, are thus thought to be attributed to the difference in the amount of adsorbed NSF on cement particle due to the amount of NSF added. Moreover, Hattori et al.[2] pointed out that the fineness of cement influenced the adsorption of the admixture. Therefore we examined here the effect of fineness of cement on the adsorption of NSF.

Fig.7 shows the effects of specific surface area on the amount of NSF adsorbed onto cements prepared in laboratory. It was found that the amount of adsorbed admixture increased linearly with an increased Blaine specific surface area. This result was consistent with that obtained by Hattori et al.[2]. Fig.8 shows the relationship between the amount of adsorbed NSF and the apparent viscosity of the paste. The authors previously obtained similar results to that shown in Fig.8 in the earlier experiments[3] [4] and gave an explanation as follows: NSF was preferentially adsorbed onto C_3A and C_4AF and the adsorption rate here was

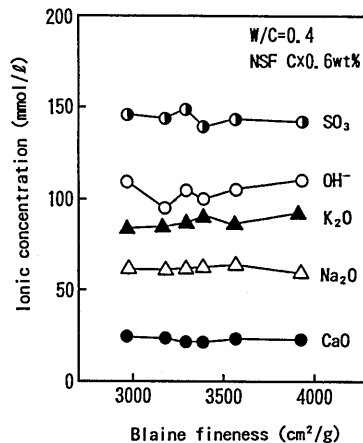


Fig.6 Ionic concentration in liquid phase in paste prepared from cement with different fineness at 5 minutes of hydration.

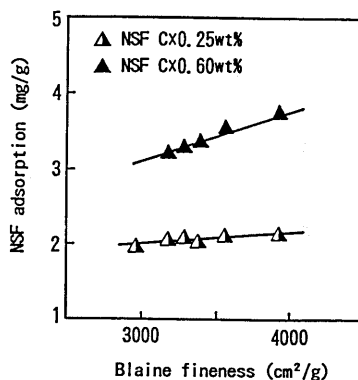


Fig.7 Effect of specific surface of cement on amount of NSF adsorbed onto cement in paste where $W/C=0.4$.

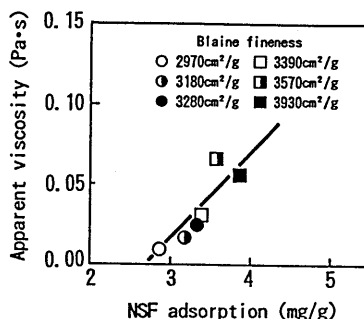


Fig.8 Relationship between amount of NSF adsorbed and apparent viscosity of cement paste at 15 minutes of hydration where $W/C=0.4$: the dosage of NSF is 0.6% by weight of cement.

markedly high. The residue of admixture was then adsorbed on C_3S which attributed significantly to the fluidity of the paste. Increasing the adsorption on C_3A and C_4AF therefore decreased the adsorption on C_3S and then cement particles flocculated, resulting in lowering fluidity of cement mixtures.

Fig.9 shows the amount of adsorbed NSF onto cements prepared in the laboratory as a function of time. The amount of adsorption within 1 minute of hydration time increased greatly as the specific surface area of cement was raised and the difference between the cements remained thereafter. The amount of adsorption within 1 minute of hydration time corresponded to that on C_3A [12]. On the

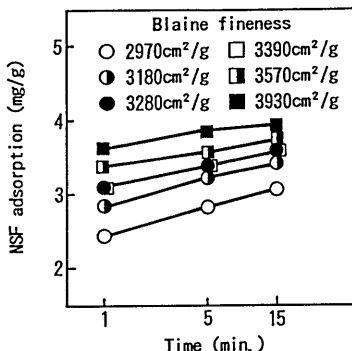


Fig.9 Change in amount of NSF adsorbed with hydration time: W/C is 0.4, the dosage of NSF is 0.6% by weight of cement.

basis of these results, therefore, it was suggested that increase in specific surface area promoted the adsorption on C_3A and reduced the amount of adsorption on C_3S resulting in the lower fluidity of cement paste.

As can be seen in Fig.9, however, when the amount of NSF added was 0.6% by weight of cement, namely 6 mg NSF in 1 g cement, 2-3 mg NSF/1g cement remained in the liquid phase even after 15 minutes of hydration time. This corresponded to 0.5-0.75 wt% as the solution concentration. Hattori et al.[13] reported that adsorption of NSF to cement saturated at about 0.75 wt% of solution concentration where a surface potential, namely zeta potential, reached a maximum. Thus, when a large amount of NSF such as 0.6 wt% was added, there was no noteworthy change of the adsorption onto C_3S in cements, especially in cements with low Blaine fineness. It is suggested therefore that a factor other than the adsorption of admixture, namely, surface potential of cement particles played a role in the effect of fineness on the fluidity.

4. GENERAL DISCUSSION

From the results in this study, it is evident that the effect of fineness of cement upon the fluidity of cement paste is closely related to the early hydration and adsorption of admixture, but this effect cannot be fully explained by both of them. The authors[3] pointed out that the fluidity of cement paste containing admixture was closely affected by dispersion/flocculation properties of cement particles, and that the flocculation of cement particles should be treated as a heteroflocculation because the cement paste consisted of particles with different surface potentials. The heteroflocculation of particles took place not only by the difference in surface potential of cement particles but also by the difference in their radius[14]. The radius of particles in cements differs depending on fineness, that is specific surface area or particle size distribution. Thus the discussion presented here shows an attempt to obtain a theoretical understanding of the effect and role of cement fineness on fluidity from a point of view of heteroflocculation of cement particles.

4.1 Heteroflocculation of cement particles

With heteroflocculation, the electric repulsion potential (V_A) and van der Waals attraction potential (V_R) between two spherical particles, of radii a_1 and a_2 and surface potential ϕ_1 and ϕ_2 , is given by[14]:

$$V_R = \frac{\varepsilon a_1 a_2 (\phi_1^2 + \phi_2^2)}{4(a_1 + a_2)} \left[\frac{2\phi_1 \phi_2}{(\phi_1^2 + \phi_2^2)} \ln \frac{1 + \exp(-\kappa H_0)}{1 - \exp(-\kappa H_0)} + \ln(1 - \exp(-2\kappa H_0)) \right] \quad (2)$$

$$V_A = - A a_1 a_2 / 6(a_1 + a_2) H_0 \quad (3)$$

where ε is the dielectric constant of the dispersion medium, κ is the Debye-Hückel reciprocal length, A is the Hamaker constant, and H_0 is the distance between the surfaces.

The flocculation/dispersion of particles is determined by the extent of the potential energy barrier (V_{\max}) on the total potential energy (V_t), namely the sum of V_R and V_A . The V_{\max} determined the flocculation/dispersion of particles at equilibrium. For a cement mixture with NSF, however, it is generally agreed that there is a progressive loss of fluidity with time. This evidence indicates that the flocculation of cement particles did not reach equilibrium within 1-2 hours after mixing where the cement paste was still workable. Under such condition, therefore, the flocculation of cement particles in paste has to be investigated from the point of view of the kinetics of flocculation.

In the absence of any repulsive barrier, all collisions between particles give rise to flocculation and the rate of flocculation is given by:

$$K = 4 kT / 3 \eta \quad (4)$$

where η is viscosity of dispersion medium.

When there are energy barriers between particles, the rate of flocculation is decreased by a factor W . This is a slow coagulation and a factor W is called the stability ratio. The stability ratio W_{ij} between two particles of type i and j is given by [14]:

$$W_{ij} = 2 \int_2^{\infty} \exp \left(\frac{V_t^{(ij)}}{kT} \right) \frac{dS}{S^2} \quad (5)$$

This integral can be approximated as follows [15].

$$W_{ij} = 1/2 \kappa a \exp(V_{\max}/kT) \quad (6)$$

From the above equation, the rate of flocculation was determined almost entirely by the value of the height and extent of the potential energy barrier V_{\max} . It is thus considered that the V_{\max} is closely related to the kinetic of flocculation, namely the fluidity of paste. Hattori et al. [16] investigated the correlation between the viscosity of paste and V_{\max} and identified its relationship as follows:

$$\log \eta = A - 2/3 \log(B + \exp(V_{\max}/kT)) \quad (7)$$

where $A = 2/3 \log(2K\kappa a t n^2) + C_1$, $B = 2K\kappa a t n$, C_1 is constant, a is radius of particle, n is a number of particles, and t is elapsed time.

From the above equation, as the height and extent of energy barrier increased, the cement particles in paste dispersed well and the viscosity of the paste decreased, so that the fluidity of the paste improved. Moreover, as mentioned previously, there was a good correlation between the mortar flow and the apparent viscosity of paste. Hence it should be possible to predict the fluidity of mortar by the energy barrier V_{\max} between cement particles.

The curve of total interaction energy V_t between particles having the same surface potential and dissimilar size has been calculated. The curve shown in Fig. 10 corresponds to the situation in C_3S particles, which contributed

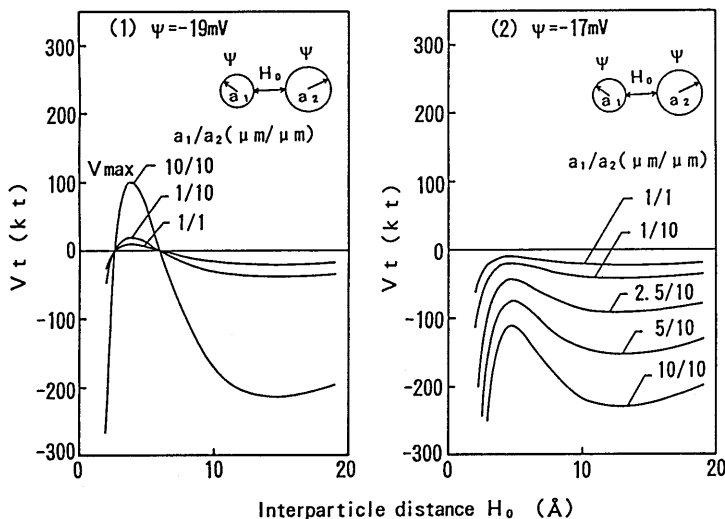


Fig. 10 Total potential energy of interaction
between particles having different radii :
 $I=0.35\text{mol/l}$, $A=2\times 10^{-21}\text{J}$, $T=20^\circ\text{C}$.

largely to the fluidity of cement paste. The Hamaker constant of cement had 2×10^{-21} joules according to the data by Hattori[17]. The zeta potential values are representative of C_3S in the presence of NSF and are -17 and -19 mV [3]. When the value of the surface potential was -19 mV, the V_{max} between particles of $1\mu\text{m}$ was larger than that between particles of $10\mu\text{m}$. The V_{max} between two dissimilar particles, of $1\mu\text{m}$ and $10\mu\text{m}$, was no different from that between two particles of $1\mu\text{m}$. Under this condition therefore it also seems that smaller particles flocculated easily compared to larger particles, so that flocculation of this system is governed by smaller particle size.

On the other hand, when the value of surface potential decreased from -19 mV to -17 mV, where the difference is just 2 mV in absolute value, the V_{max} showed a negative value and the stability ratio W became smaller than 1. Under such condition, there was an attraction between particles and the rate of flocculation was accelerated as the value of V_{max} decreased. In this system, the value of V_{max} between large particles was more negative than that between small particles and thus the large particles flocculated easily with one another compared to flocculation between small particles. The V_{max} between particles with dissimilar sizes decreased as the size of smaller particles increased. This means that larger particles also tend to flocculate easily in the case of flocculation of dissimilar size particles. This is entirely contrary to what occurred when surface potential was -19 mV. It is clear therefore that the height and extent of potential barrier V_{max} was influenced by the particle size and that the effect of particle size on the heteroflocculation was different depending on the values of surface potential.

Similar results were obtained in cement particles having a different surface potential. In Fig.11, the change of V_{max} as against particle size is indicated when the values of surface potential have the experimentally measured values of C_3A and C_3S in a system to which NSF is added. The surface potential of C_3S was -35 mV[3]. As can be seen in the diagram, the value of V_{max} was governed by the particle size as well as by the smaller surface potential in absolute value. Particularly when $\phi_2=-12\text{mV}$, one can see the marked effect of difference in particle size: the V_{max} between particles of $1\mu\text{m}$ were small and the particles

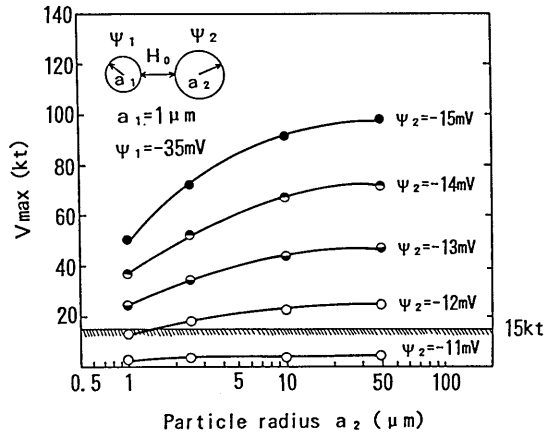


Fig. 11 Effects of particle radius and surface potential on the potential energy barrier between particles: $l=0.35\text{mol/l}$, $A=2 \times 10^{-2}\text{J}$, $T=20^\circ\text{C}$.

flocculated with one another. For combination of particles of $1\mu\text{m}$ and $2\mu\text{m}$, however, V_{max} exceeded 15 kT , the critical value to achieve stable dispersion of particles above $1\mu\text{m}$ to prevent flocculation.

From these results, it is confirmed that the flocculation of cement particles in paste was influenced by the particle size as well as by the surface potential.

4.2 Role of Cement Fineness on Fluidity of Cement Mixture

As mentioned in the last section, flocculation can advance as far as the coarser particles when the surface potential is small in a system without NSF, while the flocculation is limited in finer particles when the surface potential is large in a system including NSF. This coincides with the data shown in table 4. It is thus considered that the effect of cement fineness on the fluidity of paste and mortar can be related to the influence of particle size on flocculation of cement particles. However, the overall rate of flocculation of particles in suspension depends on the possibility of encounter between particles as well as the possibility of flocculation between two particles overcoming the V_{max} . In a system of particles having different sizes, such as cement paste, there were various types of combination of encounter between like and unlike particles. To discuss the effect of cement fineness, therefore, it is necessary to consider the possibility of encounter between cement particles.

The overall stability ratio of a system consisting of different sized particles was calculated by summing up multipliers of reciprocal stability ratio and the possibility of encounter for individual combinations of particle size. As an example, in a heterogeneous system consisting of two kinds of particles (1 and 2), there are three possible interactions which can occur between the particles. For each of these three possibilities, separate stability ratios W_{11} , W_{22} and W_{12} will be given by eqn.(5). In such system the probabilities of a given encounter between like or unlike particles are given by[14]:

$$\begin{aligned} P_{11} &= n^2 \\ P_{22} &= (1-n)^2 \\ P_{12} &= 2n(1-n) \end{aligned} \quad (8)$$

where n is the overall proportion in terms of numbers of particles of component 1 in the system.

It is now possible to define an overall stability ratio W_t of a dispersion containing two dispersed species as the following equation:

$$\frac{1}{W_t} = \frac{n^2}{W_{11}} + \frac{(1-n)^2}{W_{22}} + \frac{2n(1-n)}{W_{12}} \quad (9)$$

Fig.12 shows the particle number distribution which was calculated by the mean particle size assuming that the cement particles were spherical. Particles smaller than $11\mu\text{m}$ amounted to about 99% of the cement. It suggested that the collision probability between coarse particles was very low.

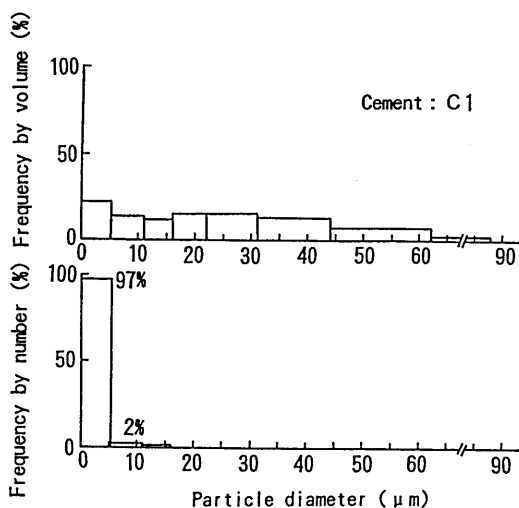


Fig.12 Particle size distribution of commercial cement.

In view of this, even if the surface potential of cement particles was small in absolute value, the probability of flocculation between smaller particles was higher than that between larger particles due to an increase in collision probability. Fine particles were thus flocculated easily and then increased the apparent number of coarser particles, so that new flocculation of coarser particles developed and so on. The progressive flocculation of particles continued until the flocculation rate was equal to the dispersion rate which occurred at the particle size governed by the potential energy barrier V_{max} .

The particle size distribution of cement in suspension using ethyl alcohol, 0.05% NSF solution, or pure water as a solution is shown in Fig.13. In ethyl alcohol, cement particles almost perfectly dispersed and became primary particles. In both NSF solution and pure water, a fine fraction of cement particles flocculated and became flocs, so that particle size distribution showed a marked shift to a larger size. As expected from the above,

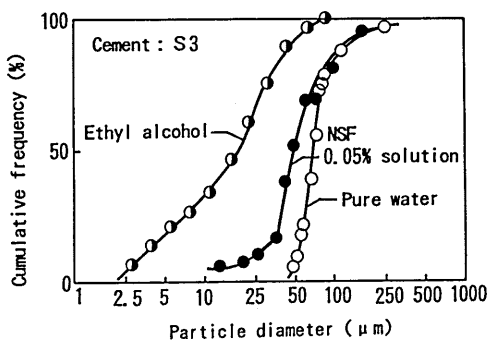


Fig.13 Flocculation/dispersion of cement particles in diluted suspension.

the extent of shift was affected by surface potential. In water, where the surface potential of cement was small, there were no flocs smaller than $65\ \mu\text{m}$, while in NSF solution the cement suspension contained many particles smaller than $65\ \mu\text{m}$ owing to an increase in the absolute value of surface potential. These results indicate that flocculation of cement particles advanced progressively from smaller particles to larger ones and it seems that the maximum diameter of flocs was determined by the energy barrier (V_{max}) which can be expressed as a function of surface potential and particle size.

Such a mechanism has interesting consequences; the fluidity of the paste was more favorable when there were fewer small particles in the cement because the possibility of an encounter between particles was decreased. This tendency was deduced to be more significant when the absolute value of the surface potential was large, such as a system to which NSF had been added, where flocculation of the cement particles was governed by the smaller size of the particles. This deduction was in good agreement with the fact that the fluidity of the cement paste was improved by cutting particles fractions smaller than $3\ \mu\text{m}$ and the effect was significant in a system to which an admixture had been added[7]. Furthermore, this deduction could explain the results shown in Fig. 3. The fluidity of the cement paste was improved with both a decrease in fine particles smaller than $11\ \mu\text{m}$ and an increase in large sized particles of $31\text{--}88\ \mu\text{m}$. On the other hand, cement with the same fraction smaller than $10\ \mu\text{m}$ and an abundant medium sized fraction of $10\text{--}30\ \mu\text{m}$, such as those ground by a roller mill, required a high water content to obtain standard consistency[18],[19]. This fact was also well explained by the previously mentioned mechanism: In a system without an admixture, the surface potential of the cement particles was small and thus, V_{max} was low so that the flocculation advanced as far as the large sized particles. It seems that the overall flocculation of cement particles is governed by those of medium sized particles. In the absence of an admixture, therefore, flocculation of cement with the same small sized fraction, that is, its fluidity, was related to the number of medium sized particles present in the sample.

For a cement paste, since the ionic concentration in the liquid phase was high, the electrical double layer was compressed and did not act over distances of less than 20 Å. It has already been pointed out that ettringite produced in the early stage of hydration was $0.1\text{--}1\ \mu\text{m}$ [20] which is much more than the double layer thickness. This means that the precipitation of ettringite increased the apparent number of particles smaller than $1\ \mu\text{m}$. It may be deduced that increasing the amount of ettringite produced resulted in further flocculation of the cement particles and then increased the viscosity of the cement paste. This explained well the results shown in Fig.5. It was also deduced that slump loss increased when the amount of small particles or hydration products became larger which was in good agreement with the experimental results of Nagataki et al.[8]. It can be concluded that the fluidity of cement mixtures was affected by early hydration because of the influence of particle size on the heteroflocculation of cement particles.

When the surface potential was the same, small particles tended to flocculate due to an increase in the possibility of collision. Blaine surface areas were proportional to the amount of small particles when their size variation was large. Thus, it explained well why the apparent viscosity of cement paste increased as did the Blaine surface area in laboratory manufactured cements.

The previous discussion indicated that the effect of cement fineness on fluidity was determined by the balance between the possibility of collision between two particles and the energy barrier (V_{max}) which is a function of the surface potential and particle size.

5. CONCLUSIONS

The results of this study show the effect of fineness of cement on the fluidity of cement paste and mortar arising from heteroflocculation due to differences in particle size. In cement paste and mortar, which consist of heterogeneous particles having different surface potentials and sizes, flocculation of particles is affected by particle size as well as surface potential. The fluidity of cement paste and mortar is thus determined by a balance of surface potential and particle size. Small sized particles govern the flocculation when the absolute value of the surface potential is large, while large sized particles accelerate the flocculation when the absolute value of the surface potential is small.

In cement, the fine fraction occupies as much as about 90% in number. Considering the possibility of collision, the flocculation of cement particles basically advances from smaller ones to larger ones. Therefore, when the surface potential is the same, cement with a large amount of small particles shows a lower fluidity.

Hydrates deposited due to the hydration of cement are considered to be fine particles when compared with the extent of interaction between particles. This might suggest that the effect of hydration on the fluidity of cement paste and mortar can be explained as a function of the effect of particle size on heteroflocculation.

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