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Adsorption characteristics of superplasticizers on cement component minerals

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Abstract

Adsorption characteristics of various superplasticizers on portland cement component minerals were investigated. Adsorption isotherms of various types of superplasticizers and ζ-potentials of cement component minerals at the maximum adsorption of the superplasticizers were measured. The value of the adsorption isotherm was calculated from the amount of the superplasticizer adsorbed on a cement component mineral in an equilibrated solution. The maximum amounts of adsorption and the adsorption isotherms varied with types of component mineral and superplasticizer. For all types of superplasticizers, a larger amount of superplasticizer was adsorbed on C_3A and C_4AF than C_3S and C_2S. However, the equilibrated concentration of each superplasticizer at the maximum adsorption was not influenced by types of superplasticizer. Without superplasticizer, C_3S and C_2S had negative ζ-potential. On the contrary, C_3A and C_4AF had positive ζ-potential. Therefore, accelerated coagulation of cement particles might occur due to their electrostatic potentials that are opposite each other. However, all component minerals of cement had negative ζ-potential when they were mixed with any superplasticizer. Fluidity of fresh cement paste is improved due to electrostatic repulsion acting between particles.

Keywords: Admixture; Adsorption; Dispersion; Cement; Cement paste

1. Introduction

Superplasticizer improves fluidity of concrete by dispersing cement particles in paste. High-performance concrete that includes the high-strength concrete and the high-fluidity concrete can be produced with superplasticizer [1]. Sodium salts of formaldehyde condenses of β-naphthalene sulfate (BNS) disperse cement particles by electrostatic repulsion that results from the adsorption on cement surfaces. Polycarboxylic acid (PC) with graft chains disperses cement particles with the help of the steric hindrance effect that results from the extension of their graft chains away from the surface of cement particles. Recently, a new type of superplasticizer has been developed. This superplasticizer is contrived so as to activate both of the preceding two effects. These dispersing mechanisms are also predicted from interparticle forces theoretically calculated from potential energy [2–5].

It is reported that the type of superplasticizer and the mixing method varied the fluidity of cement paste [6–8]. Portland cement mainly consists of four minerals, namely Ca_3SiO_5, Ca_2SiO_4, $Ca_3Al_2O_6$ and $Ca_4Al_2Fe_2O_{10}$, which are abbreviated to C_3S, C_2S, C_3A, C_4AF and gypsum. For these cement component minerals, superplasticizers are not expected to adsorb uniformly. Some component minerals might adsorb much larger amount than the others.

Therefore, it is important to understand how superplasticizers are adsorbed on each cement component mineral for controlling fluidity of cement paste and concrete. In this paper, the adsorption characteristic of superplasticizers (BNS, PC and the new type) was studied by measuring adsorption isotherms to these component minerals. Furthermore, the relationship between the ζ-potential of each cement component mineral and the fluidity of cement paste was investigated at a dosage of the maximum adsorption.

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2. Experimental methods

2.1. Materials

Commercial ordinary portland cement was used, and cement component minerals were synthesized in laboratory. Tricalcium silicate (C_3S), dicalcium silicate (C_2S), tricalcium aluminate (C_3A) and tetracalcium ferroaluminate (C_4AF) were used. The composition of these component minerals was $Ca_{105}Mg_2Al(AlSi_{35})O_{180}$, $Ca_{85}MgAl_2Fe(Na_{0.5}K_{0.5})(Al_3Si_{42})O_{180}$, $Ca_3Al_2O_6$ and $Ca_4Al_2Fe_2O_{10}$, respectively. These samples were synthesized by rapid cooling after reacting raw materials at 1550, 1450, 1350 and 1350 °C, respectively, and mineralogical components of these materials were identified with an X-ray diffractometer.

Four types of commercial superplasticizers used in this study are shown in Table 1, together with their dispersing mechanisms and solid contents. The presumed chemical structure of the main component in each superplasticizer is also shown in Fig. 1. All cement component minerals were pulverized in a mortar by hands just before each experiment.

2.2. Measurements

2.2.1. Fluidity of cement paste

Cement paste was prepared with a water/cement ratio of 0.26. A certain amount of superplasticizer was added to mixing water in advance. A flow cone specified in JIS R5201 was filled with a sample. After the cone was removed from the sample, the maximum diameter of the spread sample and the maximum width perpendicular to that diameter were measured. The average of these two values was defined as the flow value.

2.2.2. Adsorption measurements

The mass of superplasticizers adsorbed on a cement component mineral was measured with a TOC in case of C and an ultraviolet and visible spectrophotometer in the other cases. In the latter case, the wavelength of 500 nm was used for quantitative analysis. In this study, it was confirmed that the calibration curves were not influenced by OH^- concentration in cement paste. This OH^- concentration would be varied with the kind of cement component mineral and the water/cement ratio.

Ten grams of solution containing various amount of superplasticizer and 0.5 g of each component mineral of cement were mixed by a magnetic stirrer for 10 min. In this study, the water/component mineral ratio was 2000%. The paste sample was filtrated with a 0.22-μm membrane filter using a suction pump. The concentration of the superplasticizer remaining in the resultant solution was measured. The amount of superplasticizer adsorbed on the component mineral was calculated from the difference between the amount of the superplasticizer in liquid before and after mixing. The equilibrated concentration of adsorption was determined by this concentration of superplasticizer after mixing. These concentrations were represented as weight percent of solids in the superplasticizer. The adsorption isotherms were drawn with the value of adsorption and the equilibrated concentration. In addition, the amount of superplasticizers adsorbed on C_3A and C_4AF in saturated gypsum solution was measured. The saturated gypsum solution was prepared with $CaSO_4{\cdot}2H_2O$ of qualified reagent. All operations were made at 20 °C.

Table 1
Classification of superplasticizer

Repulsion mechanism					
Electrostatic	Steric hindrance	Symbol	Type	Composition	Solid content (wt.%)
◎	–	MT	BNS	Maleic acid derivatives	42.0
○	○	C	Polysulfonic acid	Methacrylic acid	28.3
–	○	HP	PC	Ether chain	27.0
–	◎	MH	PC	Long ether chain	25.0

C is a new type of superplasticizer.

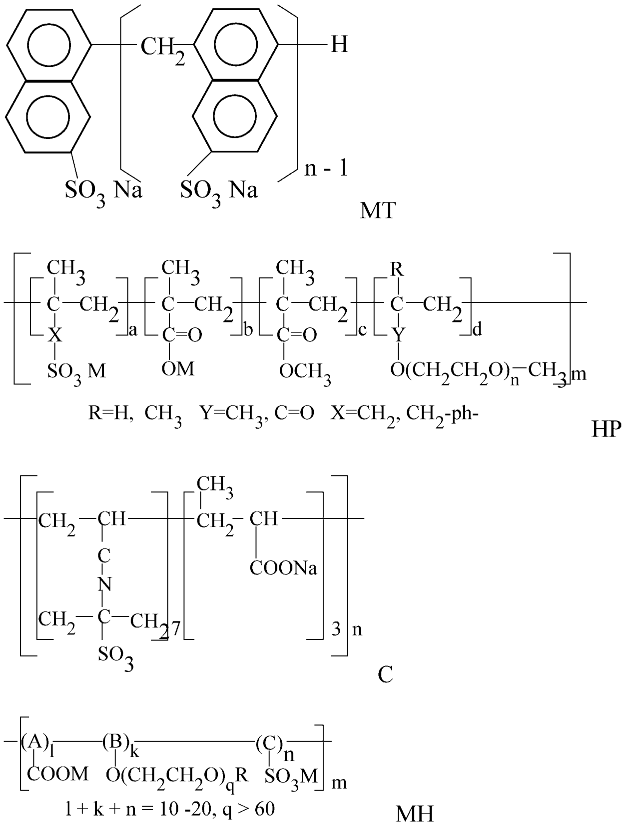

Fig. 1. Chemical structure of main component in each superplasticizer.

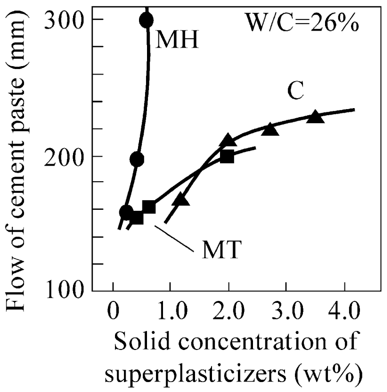

Fig. 2. Flow curve for cement paste.

2.3. ζ-potential measurement

The component sample and the solution containing the superplasticizer were mixed by hands for 5 min. The concentration of the superplasticizer in this solution was the maximum concentration of adsorption. The samples for ζ-potential measurement were prepared by diluting the above paste with deionized water up to 1500 times and mixed for 3 min. A ζ-potential meter using electrophoresis of a colloid particle (made by Rank Brothers) was used for the ζ-potential measurements of each component particle. In addition, for C_3A and C_4AF particles, their ζ-potential in saturated gypsum solution was also measured.

3. Results and discussions

3.1. Fluidity of cement paste

Flow values of cement pastes as a function of solid concentrations of superplasticizer are shown in Fig. 2. The value of paste flow increases with the increased concentration. The increment varied with the types of superplasticizer. The paste flow value increases with much smaller dosage of MH than that of the other superplasticizers. The paste mixed with MH at a dosage of 0.4 wt.% was segregated into cement and solution. In the cases of MT and C, the paste flow value increases gently with the increased dosage of superplasticizer. Then, the value reached to a constant value for more than 2 wt.% of their dosage.

3.2. Adsorption isotherm

The adsorption isotherms on each component mineral of cement are shown in Figs. 3–6, respectively, for MT, C, HP and MH. The value of maximum adsorption and the equilibrated concentration of superplasticizer corresponding to the maximum adsorption are presented in Table 2. The shape of adsorption isotherm varied with the type of superplasticizers. The value of adsorption of MT and C increased gradually with the increase of the equilibrated concentration of superplasticizer and then the value approached to a constant value. These adsorption isotherms showed a typical Langmuir curve. The value of maximum adsorption varied with the type of superplasti-

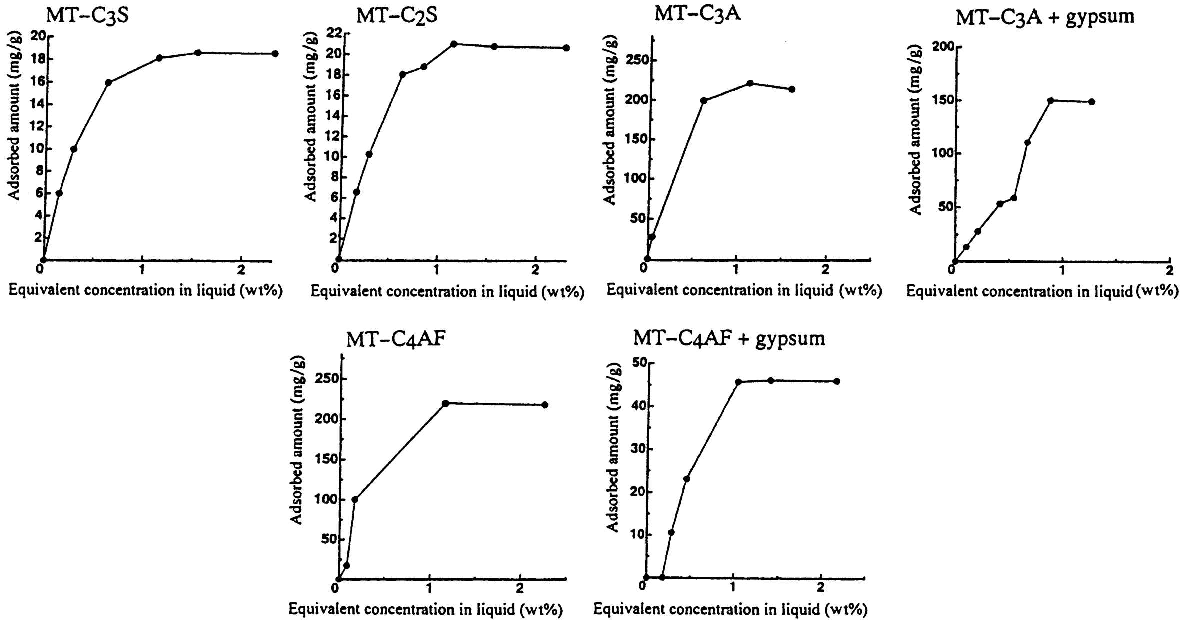

Fig. 3. The adsorption isotherms on each component of cement for MT.

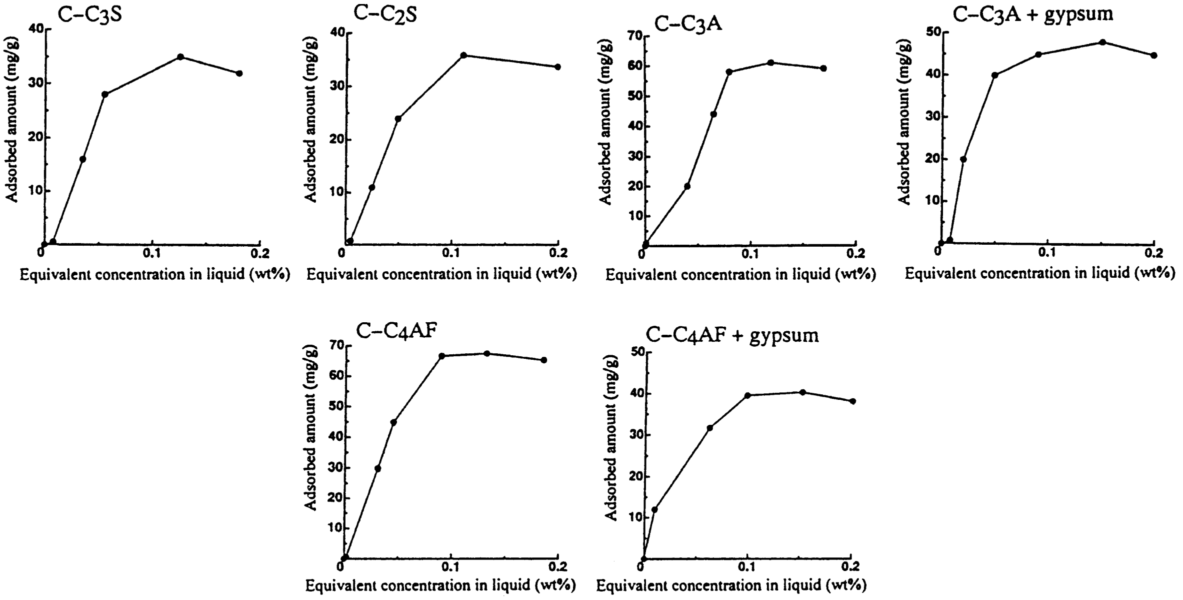

Fig. 4. The adsorption isotherms on each component of cement for C.

cizer used. This value of HP and MH was larger than that of the others.

It was reported that the maximum value of adsorption of the polycarboxylic-type superplasticizer was approximately 1 mg/1 g of cement, in which using a lower water/cement ratio than the ratio in this study [7]. The maximum values of adsorption in this study were larger than that reported in the previous studies.

The value of adsorption of HP and MH increased by two steps with increasing equilibrated concentration of superplasticizer and decreased again after reaching a maximum value. It was reported by Kawai et al. [8] that the adsorption isotherm of a polycarboxylic-type superplasticizer on each component minerals showed a similar behavior.

With regarded to this observation, the following reasons could be considered. Micelles of the superplasticizer might be formed due to higher concentration of the superplasticizer in solution and higher water/component minerals ratio in this study. The adsorption behaviors observed for HP and MH in this study might be explained by the same mechanism. There is an opinion, however, that some of the adsorbed superplasticizer might have separated from par-

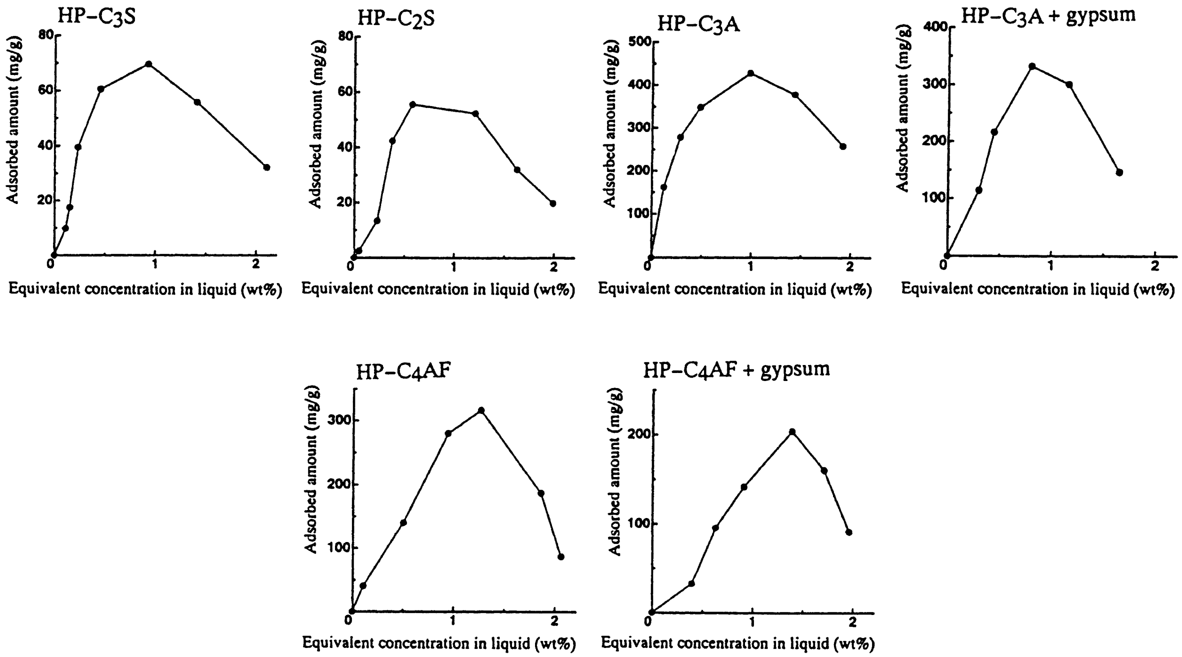

Fig. 5. The adsorption isotherms on each component of cement for HP.

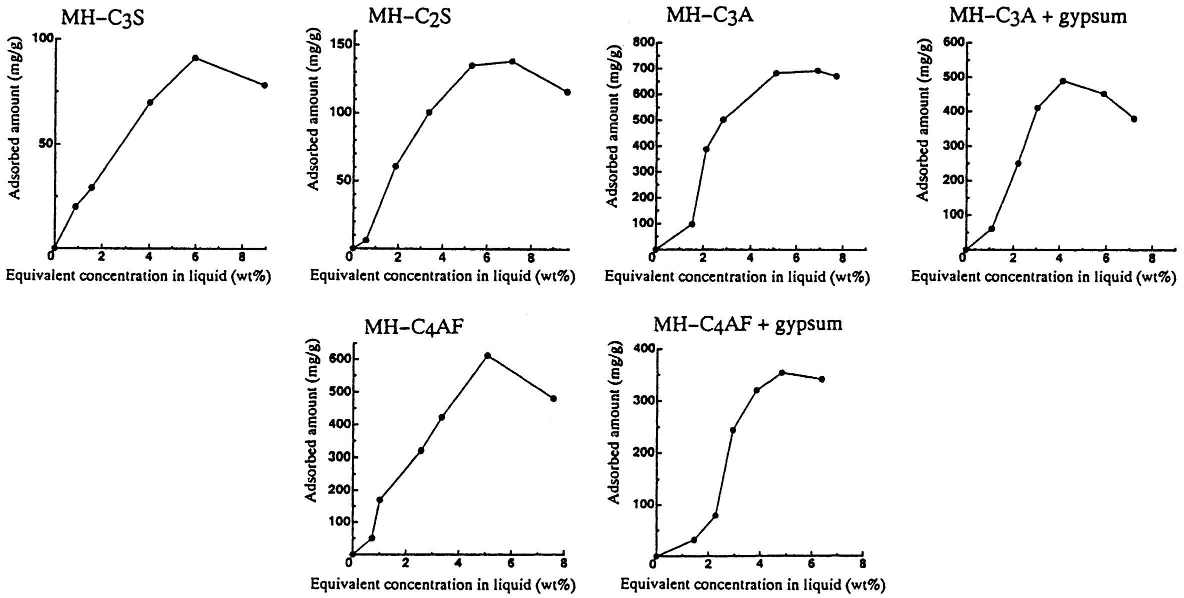

Fig. 6. The adsorption isotherms on each component of cement for MH.

ticles during filtering process [8]. Therefore, the value of adsorption in this study was the value of ‘‘apparent’’ adsorption in the strict sense of the word.

The maximum value of adsorption varied with mineralogical compositions of cement particles and the type of superplasticizer. Compared with calcium silicate particles, C_3A and C_4AF adsorbed much more superplasticizer. The ratio of the maximum value of adsorption on C_3A to that on C_3S is shown in Table 3. A larger amount of the superplasticizer MT was adsorbed on C_3A and C_4A in particular, while the superplasticizer C was adsorbed on all component minerals without great difference.

The shape of adsorption isotherm in deionized water resembled with that in gypsum-saturated water for all types of superplasticizers. The maximum value of adsorption of superplasticizer in saturated gypsum water, however, was smaller than that in deionized water. Especially, the maximum value for MT in gypsum-saturated water decreased to 1/5 of that in deionized water. It was reported that (a) some type of superplasticizer was adsorbed on the specific component mineral more than on the others and (b) the value of adsorption of superplasticizer decreased when sulfate ion was supplied from gypsum to a higher concentration [9–12]. These experimental behaviors reported were in good agreement with the results of this study.

The equilibrated concentration of superplasticizer varied with the type of superplasticizer when adsorption was saturated. On the contrary, the concentration was not changed with the type of mineralogical composition of cement. The equilibrated concentrations of superplasticizer were the same regardless of the presence of gypsum in solution. The reason might be presumed that the cement particles have some site, which could combine with the superplasticizer, and the number of the sites were changed with the type of component mineral. The site might decrease with increasing concentration of SO_4^{2-} supplied from gypsum. On the contrary, the adsorption equilibrium

Table 2
The maximum (apparent) adsorption on cement composition (upper in cell) and equilibrated concentration of superplasticizer in solution (lower in cell)

Mineralogical composition	Type of water	Maximum (apparent) adsorption (mg/g) equilibrated concentration (wt.%) MT	C	HP	MH
C_3S	Deionized	19	35	70	90
	water	1.5	0.13	0.9	6.0
C_2S	Deionized	21	36	55	138
	water	1.0	0.11	0.6	7.0
C_3A	Deionized	225	61	425	692
	water	1.1	0.12	1.0	5.0
	Gypsum	150	48	330	490
	saturated	0.9	0.15	0.8	4.0
C_4AF	Deionized	220	68	320	600
	water	1.1	0.12	1.3	6.0
	Gypsum	45	41	200	350
	saturated	1.0	0.15	1.4	4.9

Table 3
The ratio of maximum value of (apparent) adsorption on C_3A to that of C_3S and the ratio in deionized water to that in gypsum saturated water

Mineralogical composition	Type of water	Ratio of maximum value of (apparent) adsorption (−) MT	C	HP	MH
C_3A/C_3S	Deionized water	11.8	1.7	6.1	7.7
C_3A	Deionized water/ gypsum-saturated water	1.5	1.3	1.3	1.4
C_4AF	Deionized water/ gypsum-saturated water	4.9	1.7	1.6	1.7

of each site was not influenced by the presence of gypsum in solution.

3.3. ζ-potential

ζ-potentials of each mineralogical composition of cement in a solution with and without superplasticizer are shown in Fig. 7. For C_3A and C_4AF particles, their ζ-potential in gypsum-saturated water is also shown in Fig. 7. Without superplasticizer, the ζ-potentials of C_3S and C_2S were negative (− 5 mV). However, those of C_3A and C_4AF were positive from + 5 to + 10 mV. Therefore, accelerated coagulation of cement particles in a plain paste might occur due to their electrostatic potentials that are opposite each other.

With superplasticizer, ζ-potentials of component minerals varied with the type of superplasticizer. The ζ-potential of C_3S with superplasticizers was approximately − 10 mV immediately after mixing. The others were approximately − 15 mV. With superplasticizer, all component minerals were negative in their potential. With the aid of the Derjaguin–Landau–Verway–Overbeek (DLVO) theory, the ζ-potential of cement must be less than − 15 or less than − 25 mV for stable dispersion, with some discrepancy depending on the authors [13–15]. According to this theory, C_3S, which composes approximately 60% of cement, could not be stably dispersed because the absolute value of its charge is less than 10 mV. In fact, the paste with MT showed higher fluidity than that without superplasticizer. This means that we cannot explain this improvement in fluidity only by electric repulsion. It was observed that superplasticizer made all component particles into electrostatically homoparticles, thereby significantly improving the fluidity of paste immediately after mixing. It was reported that the superplasticizers MH and HP dispersed cement particles mainly by steric hindrance effect [1]. It has been shown, however, that component particles are charged into a homosystem even with these superplasticizers.

For any superplasticizer, the ζ-potential increases with time elapsed. Especially, the ζ-potential of C_3S with MT and that of C_4AF with C increased remarkably. It is known that the flow value of paste with MT greatly

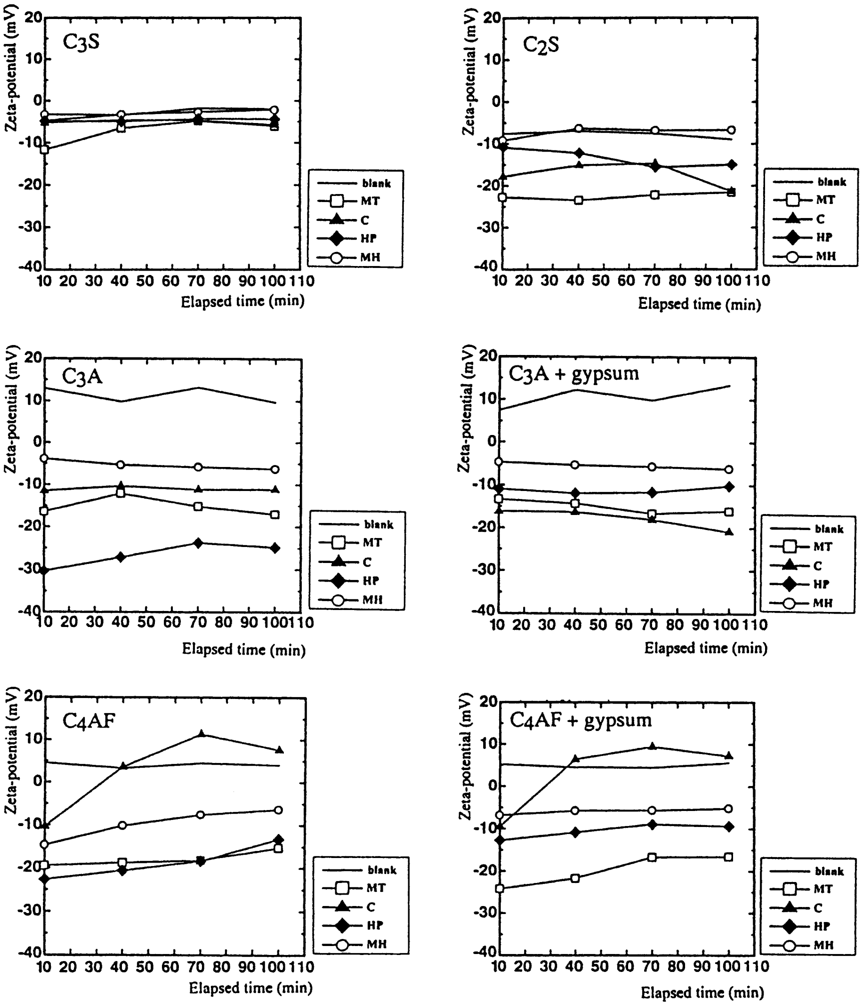

Fig. 7. The ζ-potentials of each mineralogical composition of cement in a solution with and without superplasticizer.

decreases with time, corresponding to "the slump-loss of concrete." It was explained that the paste flow decreased due to the increase in the ζ-potential [14]. In this study, ζ-potential of MT-adsorbed C_3S particles has changed from -12 mV at 10 min after mixing to -5 mV after 70 min. This increase in ζ-potentials of C_3S particle could be the main cause of "the slump-loss of concrete," because the ζ-potential of the other mineralogical compositions remained almost unchanged.

The maximum adsorption of C_3A and C_4AF decreased significantly in saturated gypsum solution, but the ζ-potential of C_3A and C_4AF was not varied with and without gypsum. Therefore, the adsorbed amount of adsorption of superplasticizer on C_3A and C_4AF did not have direct influence on the ζ-potential of these particles at the maximum adsorption.

4. Conclusions

Adsorption characteristics of various types of superplasticizers on mineralogical compositions of portland cement were investigated. As a result, the following conclusions were obtained.

1. A larger amount of superplasticizers was adsorbed on C_3A and C_4AF particles than on C_3S and C_2S for all types of superplasticizers. However, the equilibrated concentration of superplasticizer was much the same value at the maximum adsorption.
2. Without superplasticizer, C_3S and C_2S had negative ζ-potential. On the contrary, C_3A and C_4AF had positive ζ-potential. Therefore, accelerated coagulation of cement particles in a plain paste might occur due to this opposite charge in particles.
3. All mineralogical components of cement showed negative ζ-potential when they are dispersed in a solution with superplasticizer. Therefore, it is expected that fluidity of cement paste in early age is improved by hindering accelerated coagulation described in the above.

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