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INFLUENCE OF KIND AND ADDED TIMING OF ORGANIC ADMIXTURE ON THE COMPOSITION, STRUCTURE AND PROPERTY OF FRESH CEMENT PASTE

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ABSTRACT

It is well known that the fluidity and the setting time of fresh concrete are affected by kind and added timing of organic admixture including fluidizing agent, air entraining agent and water reducing agent. The fluidity, setting time and time dependency of fluidity are measured using fresh cement paste prepared with four kinds of organic admixtures, polycarboxylic acid-based, aminosulfonic acid-based, β–naphthalenesulfonic acid-based and lignin sulfonic acid-based admixture, by two different methods of addition, that is, together with mixing water (simultaneous addition) and specified time after mixing with water (later addition). Hydration of cement, adsorptive behavior of organic admixture to clinker minerals, formation of calcium complex with organic admixture and flocculation structure of cement paste are also estimated with the state-of-the-art method such as Auger electron spectroscopy, X-ray photoelectron spectroscopy and environmental scanning electron microscopy in order to clarify the influence of kind and added timing of admixture on the properties of fresh cement paste and concrete and elucidate the mechanism of the improvement of fluidity of cement paste and concrete in later addition of admixture.

Introduction

It is well known that the fluidity and the setting time of concrete are affected by kind and added timing of organic admixture including fluidizing agent, air entraining agent and water-reducing agent. Recently, many researches and developments on high-strength concrete with superior workability prepared at low water cement ratio are made. In order to make such a concrete, it is important to realize high workability, decrease the slump loss and decrease the variation of workability according to the kind of admixture. Later addition of admixture is regarded as a useful measure to improve the workability and decrease the water cement ratio of concrete, and thereby realize high-strength concrete.

In this study, the fluidity, setting time and time dependency of fluidity are measured using fresh cement paste prepared with four kinds of organic admixtures, polycarboxylic acid-based, aminosulfonic acid-based, β–naphthalenesulfonic acid-based and lignin sulfonic acid-based admixture, by two different methods of addition, that is, together with mixing water (simultaneous addition) and specified time after mixing with water (later addition). Hydration of cement, adsorptive behavior of organic admixture to clinker minerals, formation of calcium complex with organic admixture and flocculation structure of cement paste are also estimated with the state-of-the-art method such as Auger electron spectroscopy, X-ray photoelectron spectroscopy and environmental scanning electron microscopy in order to clarify the influence of kind and added timing of admixture on the properties of fresh cement paste and concrete and elucidate the mechanism of the improvement of fluidity of cement paste and concrete in later addition of admixture.

Sample and Experimental Method

Sample

Ordinary portland cement and synthesized C_3S and C_3A were used. C_3S and C_3A were synthesized with pure reagent by burning at specified temperature in an electric furnace. Assuming the hydration in cement, anhydrite was added to C_3A so that the molar ratio of SO_3/Al_2O_3 would be 1. Four kinds of admixtures, they are polycarboxylic acid-based air entraining superplasticizer (PC), aminosulfonic acid-based air entraining superplasticizer (AS), ß-naphthalenesulfonic acid-based superplasticizer (NS) and lignin sulfonic acid-based air entraining water reducing agent (LS) were used. These are standard organic admixtures well used. The chemical composition and fineness of cement compounds and ordinary portland cement are shown in **TABLE 1** and the characters of the organic admixtures are shown in **TABLE 2**. Polished sample of ordinary portland cement clinker was used for the surface analysis to examine the adsorptive behavior of organic admixture to clinker minerals and the bonding state of admixture molecule with calcium ion.

TABLE 1

Chemical Composition and Fineness of Cement Compounds and Cement

Sample	Chemical composition (%)								f.CaO*2 (%)	Bl' *3 (cm^2/g)
	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	Na_2O	K_2O		
C_3S	26.2	0.6	0.5	73.6	1.0	—	0.4	—	—	3450
C_3A	—	37.5	—	62.0	0.5	0.5	0.4	—	—	3500
OPC*1	21.6	5.2	3.1	64.6	1.2	2.1	0.29	0.42	0.4	3300

*1: Ordinary portland cement, *2: Free lime, *3: Blaine's specific surface area

TABLE 2

Character of Organic Admixture

Kind	Type	Main constituent	Hydrophobic part	Functional group	pH	Carbon content (%) *1
PC	AE super-plasticizer	Polyether-carboxylate	Alkane	Carboxyl group	9	8.2
AS	AE super-plasticizer	Aromatic aminosulfonate	Alkylbenzene, Aminobenzene	Sulfonic group, Hydroxyl group	11	19.4
NS	Super-plasticizer	Condensate of β-naphthalene sulfonate and formalin	Naphthalene	Sulfonic group	10	25.1
LS	AE water reducing agent	Ligno sulfonate, Polyol	Alkylbenzene	Sulfonic group, Methoxyl group, Hydroxyl group	11	24.2

*1: Concentration of organic carbon in liquid organic admixture measured by total organic carbon analyzer

Experimental method

Determination of adsorption of admixture

The amount of admixture adsorbed was determined according to the method described in the previous report (**1**). Cement compound or cement was dispersed in aqueous solution of admixture of specified concentration at constant ratio of solid and solution. The suspension was stirred with a constant temperature shaking apparatus at 20°C for 5 minutes and the sample solution was separated by suction filter. The amount of organic carbon remaining in the sample solution was measured with a total organic carbon analyzer, and the amount of admixture adsorbed was calculated by deducting it from the amount of admixture added. In case of later addition, cement compound or cement was dispersed in distilled water and admixture was added to it after shaking for 30 seconds so that specified concentration would be attained. The weight ratio of admixture added to cement or C_3S was 1 % of PC, 2% of AS, 1% of NS and 0.25% of LS which are the standards of the manufactures and the solid/solution ratio by weight was 1/5. Weight ratio of admixtures added to C_3A were fixed to ten-times that to cement considering the amount of equilibrium adsorption to C_3A.

Follow-up of hydration of cement

The heat evolution curve in the hydration was determined with a conduction calorimeter in such a way that aqueous solution of admixture of a specified concentration was added to the sample set in adiabatic vessel so as to make the water cement ratio 0.5 and the heat generated by the hydration since the addition of solution was determined. In case of later addition, sample was mixed at first with distilled water and the measurement was started simultaneously, and admixture was added to the sample after the mixing for 30 seconds so that a specified concentration would be attained.

Observation of coagulation structure of paste and analysis of surface composition and structure of sample

The coagulation structure of fresh cement paste was observed by environmental scanning electron microscope (ESEM) which is an instrument for observing the secondary electron image and back scattered electron image under the low vacuum as low as 20 Torr (mmHg) (**2**).

The thickness of adsorbed layer of admixture on the polished surface of clinker was determined by Auger electron spectroscope (AES). Sample clinker was dipped in aqueous solution of admixture of the same concentration as that in the determination of the amount of admixture adsorbed for 10 minutes and then dipped in methyl alcohol to stop hydration. In case of later addition, sample clinker was dipped in distilled water for 1 minute and then dipped in aqueous solution of admixture described before. The bonding state of molecule of admixture with calcium ion was determined with X-ray photoelectron spectroscopy (ESCA) by measuring the bond energy of calcium on the polished surface of clinker dipped in aqueous solution of admixture described before.

Fluidity and setting tests of cement

The flow of cement paste was measured using apparatus specified in JIS R 5201. When the flow of cement paste was larger than the diameter of the table of apparatus, the flow was measured on an acrylic square plate of 600 mm side-length set on the table. Cement paste was prepared at water cement ratio of 0.27 at 20°C by mixing with water which contains specified amount of admixture which the manufactures offers and its flow was measured at 5, 30 and 60 minutes after the mixing. Mixing was started 20 seconds after the addition of water and continued for 90 seconds. Scraping off the paste scaled on the wall of vessel, the mixing was continued for 90 seconds again. In case of later addition, cement paste was mixed with distilled water at first for 30 seconds and then the specified amount of admixture was added. The setting test was made with an automatic tester using cement paste prepared in the same manner as the determination of flow.

Results and Discussion

Properties of fresh cement paste

Fluidity and time dependency of fluidity

Flow of cement paste prepared with four types of admixtures added by simultaneous addition and later addition are shown in **FIG. 1**. The flow of cement paste prepared without admixture is 150 mm 5 minutes after the mixing, and it decreases with time and the paste showed little fluidity 60 minutes after the mixing. The flows of cement paste just after mixing increase and the variations of them with time decrease by addition of admixtures depending upon the kinds and added timing of admixtures. In case of simultaneous addition, flow of cement paste prepared by adding AS which has the largest amount of addition shows the largest value of 300 mm just after mixing, and the flow is low in the order of the paste prepared by adding NS, PC and LS. The flow of cement paste prepared with LS is 150 mm which is almost the same as that prepared without admixture. The variation with time of flow of cement paste prepared by adding the slump loss-reducing type admixture PC and AS is smaller than those prepared by adding NS and LS.

The differences of flow of cement paste prepared with NS and AS between simultaneous addition and later addition are larger than those prepared by PC and LS. Particularly, the flow of cement paste prepared with NS added by later addition is 150 mm larger than that added by simultaneous addition, and it keeps 300 mm even 60 minutes after the mixing. The flow of cement paste prepared with PC added by later addition is slightly larger than that prepared by simultaneous addition, while those prepared by adding LS by both methods of addition are almost the same as each other on and after 30 minutes. The variations with time of flow of cement paste prepared by later addition of PC and AS are smaller than those prepared by later addition of NS and LS as well as in the simultaneous addition.

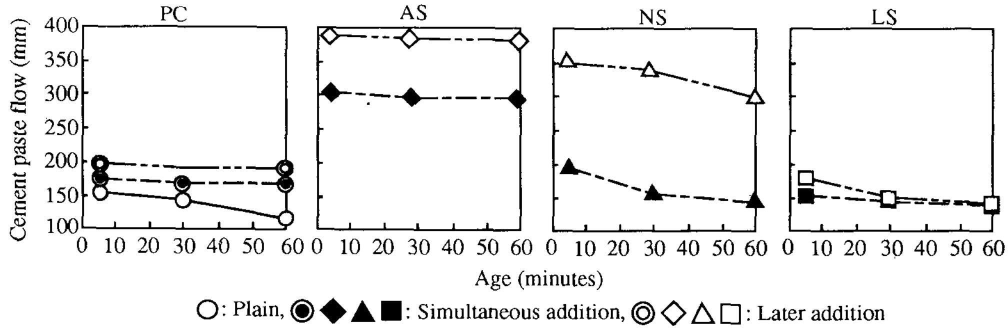
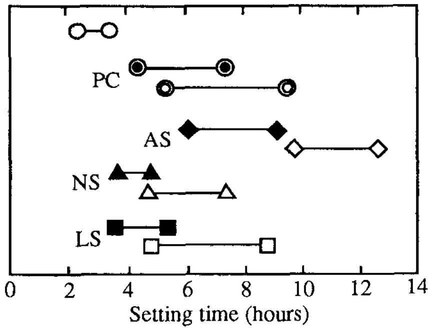


FIG. 1
Influence of Kind and Method of Addition of Organic Admixture on the Time Dependency of Fluidity of Fresh Cement Paste (20°C, W/C=0.27)

Setting time

The setting time of ordinary portland cement paste prepared with admixtures added by simultaneous addition and later addition are shown in **FIG. 2**. Setting time is delayed by addition of admixture. In case of simultaneous addition, the initial and final setting time of cement paste prepared by adding NS are 3.5 hours and 4.5 hours, respectively, and the delay of them to the cement paste prepared without admixture is about 1 hour, smallest among the four admixtures. Initial and final setting time of cement paste prepared by adding LS are 3.5 hours and 5.5 hours and the delays of them are about 1 hour and 2 hours, respectively. Initial setting time of cement paste prepared by adding PC and AS, slump loss-reducing type admixture, are 4 and 6 hours and final setting time of them are 7 and 9 hours, respectively. The setting of them are more delayed and the difference between initial setting time and final setting time are larger than those of the cement paste prepared by adding NS and LS.

The setting of cement paste prepared by adding any admixture by later addition are more delayed and the difference between the initial setting time and final setting time are larger than those by simultaneous addition. The difference between the initial setting time and final setting time of the cement paste prepared by adding LS by later addition is twice of that added by simultaneous addition, while the former of cement paste prepared by adding NS is third of the latter. The influence of the method of addition of admixture on the delay of setting is large with regard to NS and AS as well as the fluidity.



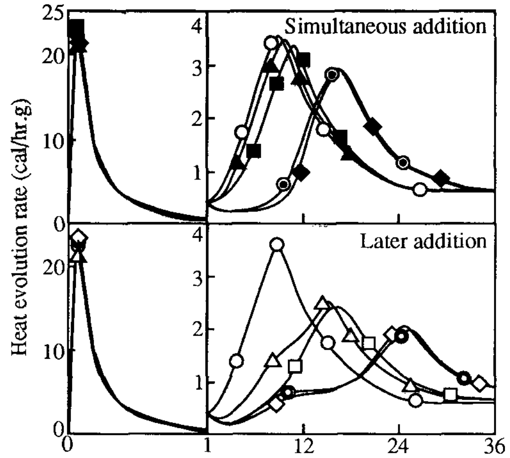
○ : Plain , ◉ ◆ ▲ ■ : Simultaneous addition ,
◎ ◇ △ □ : Later addition

FIG. 2
Influence of Kind and Method of Addition of Organic Admixture on the Setting Time of Ordinary Portland Cement (20°C,W/C=0.27)

Heat evolution curve in the hydration of cement

Heat evolution curves in the hydration of cement added admixtures by simultaneous and later addition are shown in **FIG. 3**. The second peak observed 1 hour after the mixing is delayed by the addition of any admixture depending upon the kinds and methods of addition of admixture. The second peak is caused by the starting of the active hydration of alite after the induction period and the times of the start and summit of the second peak correspond well to initial and final setting times of cement, respectively (**3**). In case of simultaneous addition, the delay of second peak to that without admixture is 1 hour in the addition of NS, the least among the four kinds of admixtures, while that in the addition of LS is 3 hours. The second peak in the addition of PC and AS is further delayed than that in the addition of LS.

In case of later addition, the second peak is more delayed than simultaneous addition in any



○: Plain , ◉◎: PC, ◆◇: AS,
▲△: NS, ■□: LS

FIG. 3
Influence of Kind and Method of Addition of Organic Admixture on the Heat Evolution of Ordinary Portland Cement Paste at Early Stage of Hydration (20°C, W/C=0.5)

admixture. The delays in the addition of NS and LS and these in the addition of AS and PC are equal to each other, and the difference between these two groups are large as well as simultaneous addition. The setting time dose not coincide well with the second peak in the heat evolution curve in the addition of PC and AS by later addition. The reason of this phenomena is not clarified and further investigation is needed.

Interaction between organic admixture and cement

Amount of organic admixture adsorbed

Amounts of organic admixtures adsorbed to ordinary portland cement added by simultaneous and later addition are shown in **TABLE 3**. The amount of admixture adsorbed to cement is correlated with the required amount of it for obtaining a specified fluidity. The larger the amount of admixture adsorbed, the larger the required amount of it is.

The amount of admixture adsorbed in later addition is smaller than that in simultaneous addition in any admixture. The differences of adsorbed amounts between simultaneous addition and later addition of PC and LS are small and those of NS and AS are large. In NS and AS, adsorbed amount in later addition are 80% or less of those in simultaneous addition.

Adsorbed amounts of admixtures to the cement compounds are shown in **TABLE 4**. In case of simultaneous addition, the difference of the adsorbed amounts of NS between to C_3S and C_3A is the largest among four kinds of admixtures and that of AS is the second largest. Those of PC and LS are nearly equal to each other and smaller than those of NS and AS. The difference of adsorbed amount of admixture to C_3S between simultaneous addition and later addition is small in any admixture, while that to C_3A differs by the kinds of admixture. There is a large difference between AS and NS, while there is a little difference between PC and LS. The differences of adsorbed amounts of admixture between to C_3S and C_3A in later addition of AS and NS are decreased five-seventh and one-fifth of those in simultaneous addition, respectively.

It is considered with the result shown in **TABLE 3** and **TABLE 4** that one of the reason why the fluidity is much improved by later addition of AS and NS is the reduction of adsorbed amount of them especially to interstitial phase which enable the reduction of required amount of them for obtaining specified fluidity.

The reason is described in previous report (4) why there is a large difference of adsorbed amounts of admixture by the kinds of cement compounds and consequential uneven adsorption to the

TABLE 3

Amount of Organic Admixture Adsorbed to Ordinary Portland Cement

Kind of organic admixture		PC	AS	NS	LS
Amount of addition (mg/g-cement)		10.0	20.0	10.0	2.5
Amount of organic admixture adsorbed (mg/g-cement)	Simultaneous addition	6.6	12.0	7.0	1.0
	Later addition	6.1	7.7	5.5	0.9

TABLE 4

Amount of Organic Admixture Adsorbed to Cement Compounds

Kind of organic admixture		PC		AS		NS		LS	
Amount of addition (mg/g-cement)		100	10.0	200	20.0	100	10	25	2.5
Cement compound		C_3A	C_3S	C_3A	C_3S	C_3A	C_3S	C_3A	C_3S
Amount of organic admixture adsorbed (mg/g-cement)	Simultaneous addition	25.4	3.9	43.4	5.1	94.3	2.6	23.4	1.8
	Later addition	25.6	4.6	23.7	4.0	20.1	2.7	21.4	1.6

surface of cement particle. Two reasons is considered why the adsorbed amount and unevenness of adsorbed amount of admixture by the kinds of cement compound are reduced by later addition. One reason is that the adsorbed amount of admixture to the network former of SiO_4^{4-} and AlO_3^{3-} exposed to the surface of clinker particles by dissolution of calcium ion to the aqueous solution is smaller than that to unhydrated cement compound, and the other reason is that the difference of adsorbed amount between silicate chain and aluminate chain is smaller than that between C_3S and C_3A.

Adsorption of admixture to the surface of cement particle

It is known that the thicknesses of the adsorbed layers of NS and LS on the surface of cement particles are quite different between alite and interstitial phase (1). For investigating the influence of the method of addition of admixtures on the adsorptive behavior of them, the changes of concentrations of C, S and Ca in the direction of depth from the surface on alite and interstitial phase were determined by AES with regard to a clinker dipped in an aqueous solution of NS which is particularly effective for improving the fluidity in the later addition. The sample corresponds to later addition of admixture was dipped in distilled water for the first 1 minutes followed by dipping in aqueous solution of admixture. The result is shown in **FIG. 4**.

In case of simultaneous addition, the carbon concentration in the adsorbed layer of the admixture on alite rapidly decreases with the increase of the depth and reaches the constant value of the background level at a depth of 50 to 100 nm, and the calcium concentration in it increases with the increase of depth and reaches the constant value at a depth of 50 nm. The carbon concentration in the adsorbed layer of the admixture on the interstitial phase decreases approximately 1/2 at a depth of 40 nm from the surface and then slowly decreases and reaches the background level at a depth of approximately 300 nm, and the calcium concentration in it slowly increases from the surface and reaches the constant value at a depth of approximately 300 nm. This value coincides with the value obtained in the addition of 2% of NS reported in the previous paper (**1**) and it indicates that the concentration of NS hardly affects the thickness of the adsorbed layer of it in the range of practical amount of addition.

In case of later addition, the carbon concentration on both alite and interstitial phase rapidly decreases from the surface of adsorbed layer and reaches the background level at a depth of 20 nm. The calcium concentration also reaches the constant value at a depth of 20 to 40 nm. These results indicate that the thickness of the adsorbed layer of NS in later addition is thinner than that in simultaneous addition and that the difference of the thicknesses of adsorbed layer between on alite and on interstitial phase in later addition is smaller than that in simultaneous addition.

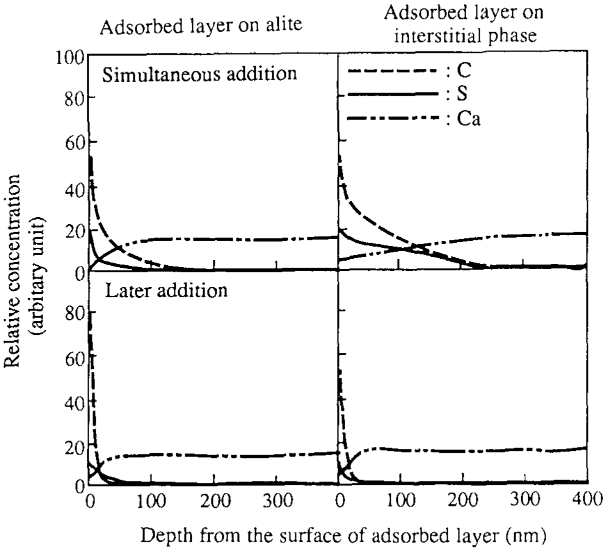


FIG. 4
Change of Carbon, Sulfur and Calcium Concentration in the Adsorbed Layer on the Polished Surface of Clinker in the Direction toward Clinker Surface Dipped in Aqueous Solution of NS Determined by AES

The relative concentration of carbon on the surface of adsorbed layer on alite in later addition is approximately 80 which is higher than that on interstitial phase and than those on alite and interstitial phase in simultaneous addition. The reason is deduced that NS is more densely absorbed on the surface of adsorbed layer though the amount of adsorption of it is reduced in later addition. Considering that approximately a half of the total surface area of cement clinker particle is composed of alite, increase of the electric charge density by the formation of dense adsorption layer on alite surface would be one of the reason of the improvement of fluidity of cement paste by later addition of admixture.

Formation of calcium complex of admixture

It is necessary to know how the admixture added reacts with elements dissolved from cement in an aqueous solution and what compounds are produced in this reaction for clarifying the influence of admixture on the hydration of cement. As an initial step to solve the problem, the bond energy spectrum of calcium on the polished surface of clinker dipped in aqueous solution of admixture was determined by ESCA to investigate the interaction of the admixture with calcium ion which plays an important role in the hydration of cement. Same measuring was done for unhydrated clinker, clinker dipped in distilled water, calcium citrate and calcium methyl sulfonate as references. The results are shown in **FIG. 5.**

The bond energy profiles of unhydrated clinker and clinker dipped in distilled water are similar to each other. This fact indicates that the bonding state of calcium of clinker exists in the region from the surface to approximately 10nm depth which can be measured by ESCA is not changed by dipping in distilled water. These spectrum are considered to correspond to the bonding state of calcium in unhydrated clinker minerals exist in the region from the surface to approximately 10nm depth. On the other hand, the Ca/Si ratio of clinker in the region from the surface to several nm depth after dipping in distilled water measured by AES is approximately 1 (5), and this fact indicates that calcium is selectively dissolved to the aqueous solution. The characteristic rough structure which suggests the dissolution of atom can be observed in the surface of clinker dipped in distilled water and the distance between peak and trough is determined approximately 10nm by atomic force microscope (5). Considering these facts, calcium in the surface of clinker may be dissolved to water leaving the skeletal structure of unhydrated clinker during the early hydration of 10 minutes after mixing with water. Peaks are observed at 347.5 eV in the spectrums of the clinker dipped in the solutions of NS, LS and AS, which are close to the peak of the bond energy profile of calcium methyl sulfonate, and it suggests that calcium is connected to the admixtures in the form of calcium sulfonate. Meanwhile, a peak is observed approximately 347.0 eV in the spectrum of the clinker dipped in the solution of PC, which coincides with the peak of calcium citrate, and it is considered that the calcium exists in the form of a chelate complex binding with carboxyl and hydroxyl group of the molecule of PC. The delay of setting by the addition of

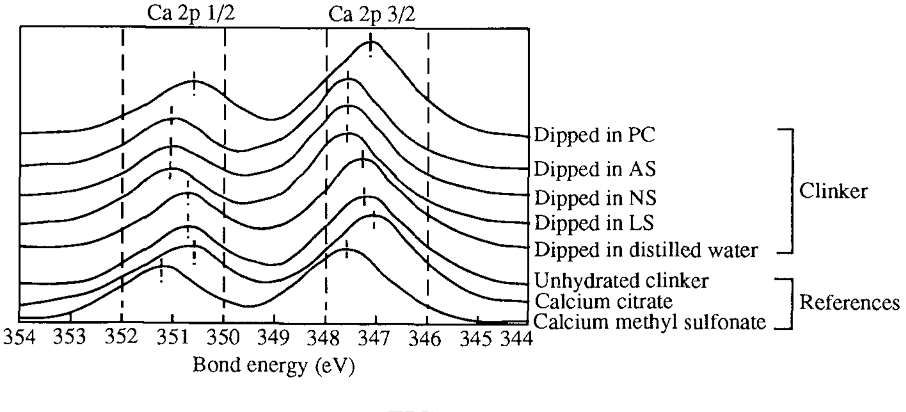


FIG. 5
Bond Energy Spectrum of Calcium on the Polished Surface of Clinker Dipped in Aqueous Solution of Organic Admixture Determined by ESCA

admixture is considered to be caused by inhibition of dissolution of calcium because of the formation of adsorbed layer of admixture on the surface of cement particles (6), and the retardation of hydration of alite (7) because of the fixation of calcium ion dissolved in aqueous solution as a complex of admixture and thereby decrease of the lime saturation ratio (8). Both of these estimations are certified by the results of measurement of thickness of adsorbed layer of admixture on cement particle by AES and detection of calcium complex of admixture by ESCA.

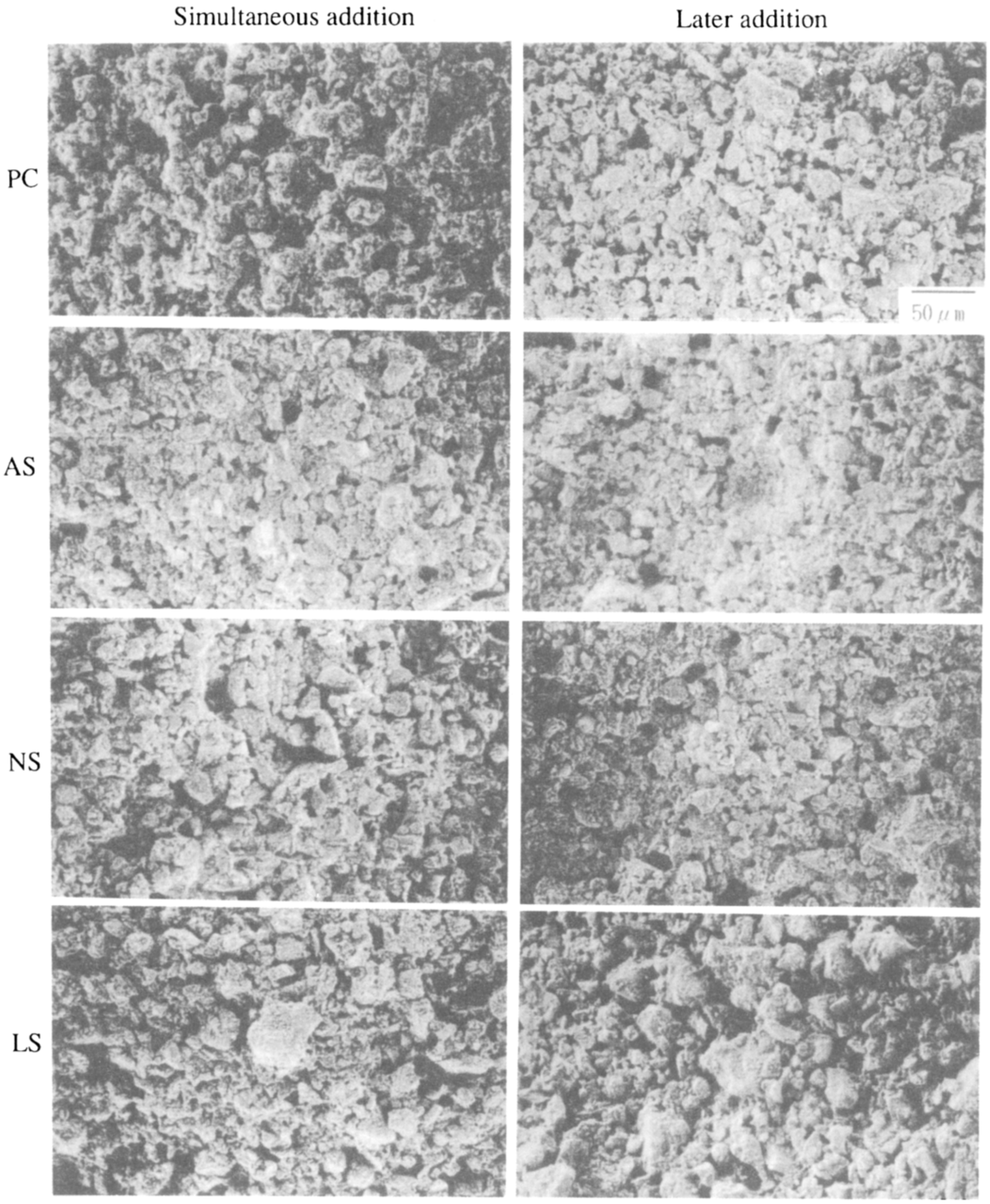


FIG. 6
Coagulation Structure of Fresh Cement Paste Observed by ESEM

Influence of method of addition of admixture on coagulation structure of fresh cement paste

Secondary electron image of fresh cement paste 10 minutes after the mixing prepared by adding various admixtures by simultaneous addition and later addition observed by ESEM are shown in **FIG. 6**. The dispersion of cement particles are different among the kind and method of addition of admixtures. In case of NS and AS, coarse coagulation structure consists of various-sized flocks of cement particles is observed in simultaneous addition, while the coagulation structure is more uniform and denser in later addition. The coagulation structures of cement paste prepared with PC by simultaneous addition and later addition is a little similar to those with NS and AS, while those with LS are independent of the method of addition and similar to that with NS by simultaneous addition. The fluidity of cement paste in later addition of NS and AS is improved probably because of the decrease of water fixed in the space inside the flocks due to the uniform dispersion of cement particles and thereby the formation of water film which have relatively uniform thickness on the surface of cement particles.

Hydrates several microns maybe ettringite are observed densely formed on the surface of cement particles and linking cement particles to each other in fresh cement paste prepared by adding PC. Cement paste prepared with PC is considered to have high yield value because it is not deformed without any vibration after releasing the flow cone from the mold. The formation of ettringite is considered to be one of the reason of the increase of the yield value of cement paste prepared by adding PC.

Summary and Conclusions

Properties of fresh cement paste such as fluidity, time dependency of fluidity and setting time are measured and heat evolution rate by hydration, amount of organic admixture adsorbed, thickness of adsorbed layer of organic admixture and bond energy profile of calcium and molecule of organic admixture are estimated using fresh cement paste prepared with four kinds of organic admixtures, mainly composed of polycarboxylic acid , aminosulfonic acid, ß-naphthalenesulfonic acid and lignin sulfonic acid, added by two different methods of addition. With these results, influence of kind and added timing of organic admixture on the fluidity and setting of fresh cement paste was clarified and the mechanism of the improvement of fluidity of cement paste in later addition of organic admixture was elucidated.

1) The flow of cement paste just after mixing is increased by use of organic admixture by simultaneous addition, while the variation with time of its flow is decreased. The variations with time of flow of cement paste prepared by adding polycarboxylic acid-based and aminosulfonic acid-based admixture are small. The flow of cement paste prepared by later addition of any admixture is higher than that of cement paste prepared by simultaneous addition of it and the difference between the former and latter is much particularly in naphthalenesulfonic acid-based and aminosulfonic acid-based admixture.

2) The setting of cement paste is delayed by adding organic admixture irrespective of the method of addition. Setting is more delayed by adding slump-loss reducing type polycarboxylic acid-based and aminosulfonic acid-based admixture containing the materials which acts as a retarder of setting than by adding naphthalenesulfonic acid-based and lignin sulfonic acid-based admixture. The retardation and the difference between the initial setting time and final setting time of cement paste prepared by later addition of admixture are larger than those by simultaneous addition. Fluidity of cement paste and the variation of it with time are improved by later addition of organic admixture than by simultaneous addition of the same amount, and thereby the amount of admixture required for obtaining the same fluidity and the variation of it with time by later addition can be reduced.

3) The position of the second peaks in the heat evolution curve of hydration which are corresponds to the final set of cement are similar in the addition of polycarboxylic acid-based and aminosulfonic acid-based admixture to each other and those in the addition of naphthalenesulfonic acid-based and lignin sulfonic acid-based admixture are also similar to each other. The former admixtures have a retarding effect of hydration of alite and the effect becomes remarkable by later addition.

4) The amount of admixture adsorbed to cement is correlated with the amount of addition of it required for obtaining a specified fluidity. The larger the amount of admixture adsorbed, the larger the amount of admixture required is. Any admixture is more adsorbed to the interstitial phase than to alite. The differences of the adsorbed amounts of naphthalenesulfonic acid-based and amino sulfonic acid-based admixture between to interstitial phase and to alite are larger than those of other admixtures, while they are reduced by later addition. The amount of naphthalenesulfonic acid-based admixture adsorbed to cement component are the largest and those of aminosulfonic acid-based admixture is the second largest in the simultaneous addition. The differences of the adsorbed amounts of admixture between to C_3S and C_3A are also in the same order as before and they are reduced by later addition. The amounts of aminosulfonic acid-based and naphthalenesulfonic acid-based admixture adsorbed to C_3A are significantly reduced by later addition, while those of polycarboxylic acid-based and lignin sulfonic acid-based admixture are hardly changed. The improvement of fluidity of cement paste by later addition of the former two admixtures is considered to be caused by the significant reduction of amount of admixture adsorbed to tricalcium aluminate phase.

5) Thicknesses of the adsorbed layer of the naphthalenesulfonic acid-based admixture on the clinker minerals including alite and interstitial phase determined by Auger electron spectroscopy are not changed by changing the amounts of addition of admixture within a practical range in simultaneous addition. The thickness of the adsorbed layer of naphthalenesulfonic acid-based admixture in later addition is approximately 20 nm both on alite and interstitial phase which is significantly thinner than those in simultaneous addition approximately 50 nm on alite and 300 nm on interstitial phase, and the difference of the thickness of adsorbed layer between on alite and on interstitial phase is reduced. The density of admixture adsorbed on the uppermost surface of the adsorbed layer in later addition is higher than that in simultaneous addition.

6) It is clarified with the result of the measurement of bond energy profile of the calcium near the polished surface of clinker dipped in aqueous solution of admixture by ESCA that calcium near the surface of clinker is dissolved in water without destroying the skeletal structure of clinker mineral at the beginning of hydration, and that the calcium ion dissolved in water is connected to the molecule of aminosulfonic acid-based, naphthalenesulfonic acid-based and lignin sulfonic acid-based admixture in the form of calcium sulfonate and it is connected to the molecule of polycarboxylic acid-based admixture in the form of calcium complex producing a chelate compound with the carboxyl and hydroxyl groups.

7) It is observed by environmental scanning electron spectroscope that cement particles are more dispersed and the coagulation structure are more uniform and denser in fresh cement paste in later addition of aminosulfonic acid-based and naphthalenesulfonic acid-based admixture which are effective for improving the fluidity by later addition. The fluidity of fresh cement paste prepared by later addition of these admixtures is improved for the reason that water fixed in the spaces inside the flocks of cement particles is decreased due to the uniform dispersion of them, and thereby water film which has relatively uniform thickness is formed on the surface of cement particles. Hydrates several microns maybe ettringite are densely formed on the surface of cement particles and link the cement particles to each other in cement paste prepared by adding the polycarboxylic acid-based admixture. This is considered to be one of the reason for the increase of yield value of cement paste and concrete prepared by adding this kind of admixture.

8) The reasons why the fluidity is improved by later addition of aminosulfonic acid-based and naphthalenesulfonic acid-based admixture are considered as follows. The amount of admixture adsorbed to the skeletal chain including SiO_4^{4-} and $Al_2O_3^{3-}(Al_6O_{18}^{18-})$ which are exposed to the surface of clinker particles by the dissolution of calcium in water after the mixing is less than that to the original surface of the clinker mineral which contains the calcium, and thereby un-adsorbed admixture remaining in the mixing water prevents the coagulation of cement particles and the formation of the coagulation structure. Considerable amount of admixture still remains in the mixing water even after the hydration of cement proceeds with the passage of time and the admixture is consumed as the calcium complex and it fixes the calcium ion successively dissolved to water, and thereby much increase of the concentration of calcium ion in the mixing water is inhibited and the active hydration of alite is prevented and the high fluidity of cement paste is kept.

9) Setting of cement is further delayed by later addition of admixture according to the same mechanism as described in 8). The admixture still remaining in the mixing water after initial setting consumes calcium ion and decreases the concentration of calcium ion in the mixing water, and thereby final setting time is prolonged and the difference between initial and final setting time is increased. This effect is remarkable in the addition of aminosulfonic acid-based and naphthalene sulfonic acid-based admixture which are effective for considerably reducing the amount of admixture absorbed by later addition.

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