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Effects of water/powder ratio, mixing ratio of fly ash, and curing temperature on pozzolanic reaction of fly ash in cement paste

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Abstract

The effects of the mix proportion and curing temperature on the pozzolanic reaction of fly ash in cement paste were investigated by examining the productions of calcium hydroxide and the pozzolanic reaction ratio of fly ash. It is possible to accurately determine the reaction ratio of fly ash in cement paste from the insoluble residue and the quantity of dissolved Al_2O_3. The reaction ratios of fly ash, at the curing temperature of 40°C, the water/powder ratio of 50%, and the substitution rate of fly ash of 40%, are 12% and 32% at the ages of 7 days and 1 year, respectively. The higher the curing temperature or the higher the water/powder ratio is, the higher the reaction ratio of fly ash. The starting time of the pozzolanic reaction at the curing temperature of 20°C is at the age of 28 days or more because the reaction ratio at 28 days is nearly 0%. The pozzolanic reaction of fly ash in cement paste highly depends upon the curing temperature. The reaction ratio of fly ash decreases with an increasing fly ash substitution rate.

Keywords: Fly ash; Thermal analysis; Blended cement; Cement paste; Microstructure

1. Introduction

There currently exists a great need for technology which utilizes the surplus of industrial waste of fly ash. It is very important to elucidate the details of the pozzolanic reaction of fly ash in order to increase the reliability of the development of the physical properties including the strength of fly ash concrete. Although a lot of research on the development of the strength of fly ash concrete has been published, few studies [1–3] on the analyses of the starting time of the pozzolanic reaction and its reaction ratio have been reported. Calcium hydroxide is consumed excessively by the proceeding pozzolanic reaction and it is feared that a phenomenon called self-neutralization, lowering the alkalinity of the hardened cement and concrete, occurs [4].

Results from studies hitherto made [5], show that the quantity of calcium hydroxide produced by the hydration of alite and belite, the starting time of the pozzolanic reaction of fly ash, and the reaction ratio are varied due to changing the water/powder ratio, the substitution rate of fly ash for cement, and the curing temperature.

This paper reports a method of determining the reaction ratio of fly ash using the insoluble residue and the quantity of Al_2O_3 dissolved from the cement paste, and investigates in detail the effect of the reaction ratio of fly ash with the age of hardened cement advancing.

2. Samples and experimental methods

2.1. Materials for experiment

As listed in Table 1, ordinary Portland cement and fly ash with the Blaine specific surface area of 4000 cm^2/g produced at the Hekinan Power Plant in Japan are used in this experiment.

Table 2 lists the chemical composition of the fly ash.

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Table 1
Physical properties of cement and fly ash

	Specific gravity	Blaine specific surface area (cm^2/g)
Ordinary Portland cement	3.14	3370
Fly Ash	2.33	4000

2.2. Molding of fly ash paste specimens

The mixture proportions of the fly ash cement used for this experiment are listed in Table 3. By fixing the water/powder ratios at 30% and 50%, the proportion of fly ash equivalent to the substitution rate is substituted for cement.

After putting powder and water into a 2-l Hobart mixer at the same time, both materials are mixed at low speed for 3 minutes at 20°C. Samples for each age are prepared, filled up in a 100-ml plastic vessel, and then the vessel is hermetically sealed. The samples are cured at 20°C and 40°C.

Test specimens are prepared by cutting off a 7-mm cube from each molded sample with a diamond cutter at the specified ages. The hydration is terminated by dipping the cut samples in acetone and drying them by D-drying under 5×10^{-4} mm Hg.

2.3. Experimental methods

2.3.1. Loss on ignition

The loss on ignition and combined water of the D-dried test specimen are determined at 950°C.

2.3.2. Content of calcium hydroxide

The production of calcium hydroxide is determined using the D-dried test specimen by DSC. It is indicated with the value for the sample after the loss on ignition test for eliminating the effect of the combined water.

2.3.3. Insoluble residue and quantity of dissolved Al_2O_3

The insoluble residue is determined according to JIS R 5202 using the D-dried test specimen. The quantity of Al_2O_3 dissolved in the filtrate obtained by the test for the insoluble residue is analyzed by inductively coupled plasma spectrometry.

2.3.4. BEI and SEI observation

The secondary electron image (SEI) of the broken surface of the hardened cement is observed by FE-SEM. The back scattered electron image (BEI) of the polished surface is observed by EPMA applying the accelerating voltage of 15 kV.

Table 2
Chemical composition of fly ash used in this study

Chemical composition (% by mass)											
SiO_2	Al_2O	Fe_2O	CaO	FCaO	MgO	Na_2O	K_2O	TiO_2	SO_3	C	ig. (%)
54.4	31.1	4.6	4.4	0.1	0.8	0.6	0.8	1.4	0.4	1.3	1.4

Table 3
Mixture proportions of fly ash cement paste

W/P (%)	W/C (%)	Fly ash substitution rate (% by mass)	Mixture proportions (% by mass) Water	Cement	Fly ash
30	30.0	0	23.1	76.9	0
	33.3	10	23.1	69.2	7.7
	37.5	20	23.1	61.5	15.4
	50.0	40	23.1	46.2	30.8
	75.0	60	23.1	30.8	46.2
50	50.0	0	33.3	66.7	0
	55.6	10	33.3	60.0	6.7
	62.5	20	33.3	53.3	13.3
	83.3	40	33.3	40.0	26.7
	125.0	60	33.3	26.7	40.0

3. Experimental results and discussion

3.1. Combined water in fly ash cement paste

The relationship between the amount of combined water with age is illustrated in Fig. 1. In a test conducted at the water/powder ratio of 50%, the curing temperature of 20°C and the substitution rate of fly ash of 0%, the amount of combined water increases with age. The rate of increase of

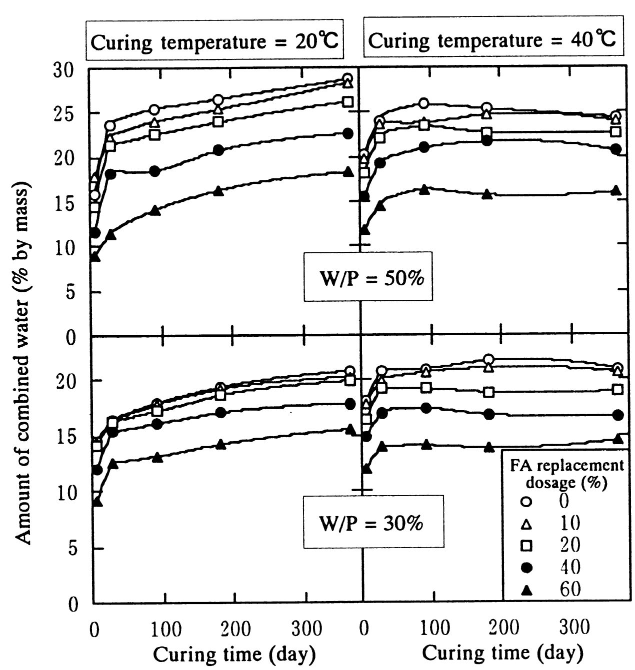

Fig. 1. Variation of the combined water of paste mixtures made with 30% and 50% water/powder and containing various fly ash substitution rates with curing time.

the percentage combined water moderates after the age of 28 days. In a test conducted at the fly ash substitution rate of 10%, the amount of combined water at the age of 7 days is higher than that at 0%. After the age of 7 days, however, the amount of combined water decreases with increases in the substitution rate of fly ash. The combined water per unit weight of cement increases with fly ash substitutions. The increase in the amount of combined water per unit weight of cement during the period of time from the age of 28 days to 1 year of the samples preparation at the fly ash substitution rate of 60% is larger than that at 0% because the pozzolanic reaction of fly ash proceeds.

In a test conducted at 30% of the water/powder ratio and 20°C of the curing temperature, the combined water increases less with age than in the test conducted at 50% of the water/powder ratio. In the range of up to 20% of the fly ash substitution rate, the trend in the amount of combined water is similar to that in cement that does not contain fly ash.

Although the amount of combined water in the hardened cement cured at 40°C is greater than that cured at 20°C in the early stage of curing, there is little increase thereafter and at the age of 1 year, a slight decrease which results in a smaller amount of combined water compared to the sample cured at 20°C.

3.2. Calcium hydroxide in fly ash cement paste

The production of calcium hydroxide at various fly ash substitution rates plotted against the curing temperature, water/powder ratio and ages is illustrated in Fig. 2.

The production of calcium hydroxide in the test specimens prepared at the fly ash substitution of 0% increases with age independent of the curing temperature and water/powder ratio.

A straight line drawn by connecting the productions of calcium hydroxide at the 0% and 100% substitution rates of fly ash in the figure indicates the quantities of calcium

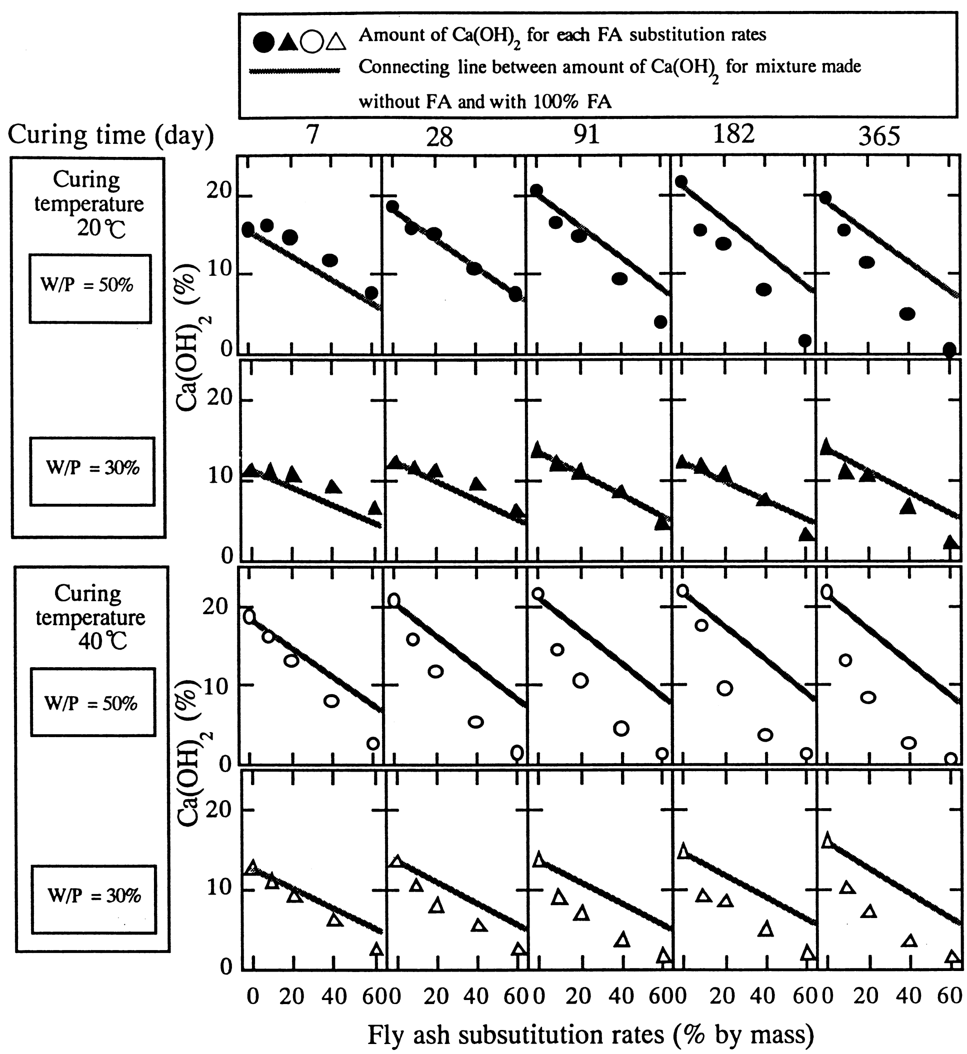

Fig. 2. Amount of produced $Ca(OH)_2$ as percentage of sample weight obtained after an ignition loss test.

hydroxide produced by the hydration of cement at various substitution rates. When the plotted data fall on the straight line, the pozzolanic reaction of fly ash does not proceed. Meanwhile, the pozzolanic reaction proceeds further with downward estranging of the plotted data from the straight line.

The productions of calcium hydroxide in the test specimen with fly ash, prepared by curing at 20°C for 7 days and at 50% of the water/powder ratio, are greater than the values indicated by the straight line. This is because the depositing sites of hydrate are increased by increasing fly ash in the paste, and the hydration of cement is accelerated by increasing the practical water/cement ratio. At the age of 28 days, every substitution rate of fly ash falls on the straight line corresponding to the production of calcium hydroxide. Accordingly, the pozzolanic reaction hardly proceeds. At 91 days and thereafter, the production of calcium hydroxide decreases with the increasing fly ash substitution rate and the plotted data are estranged from the straight line. This means that the pozzolanic reaction further proceeds.

The production of calcium hydroxide from cement using the test specimen prepared at the curing temperature of 20°C and the water/powder ratio of 30% is less than that using the test specimen prepared at the water/powder ratio of 50%. In case of water/powder ratio of 30%, the consumption of calcium hydroxide by the pozzolanic reaction at the age of 91 days is still small. At 1 year of age, however, the plotted data are estranged downward from the straight line according to the substitution rate of fly ash.

The production of calcium hydroxide from cement using the test specimen cured at 40°C is larger than that cured at 20°C. The plotted data of the test specimen prepared at the water/powder ratio of 50% are estranged further from the straight line with the increasing substitution rate at the age of 7 days and also cured at 40°C. This suggests that at 40°C, the pozzolanic reaction has begun before the age of 7 days. Calcium hydroxide is consumed up to as much as 1.6% by the age of 28 days according to the test specimen prepared at the fly ash substitution rate of 60%. Using the same test specimen, the estrangement of the plotted data from the straight line is not proportional to the substitution rate of fly ash at the age of 91 days and after. It is inferred from this that calcium hydroxide is insufficient for the proceeding of the pozzolanic reaction in fly ash cement paste.

The estrangement of the plotted data from the straight line using the test specimen prepared at the water/powder ratio of 30% is smaller than that using the test specimen prepared at 50%. This suggests that the pozzolanic reaction proceeds moderately at low water/powder ratios.

The higher the curing temperature is, the earlier the starting time of the pozzolanic reaction of fly ash. When either the water/powder ratio or the curing temperature is high, the reaction weight is large and the pozzolanic reaction of fly ash dependence on temperature is high.

When the substitution rate of fly ash is as high as 60%, calcium hydroxide is so insufficient that self-neutralization may occur. Therefore, it is desirable to not exceed 40% of the fly ash substitution rate for cement.

Table 4
Insoluble and dissolved Al_2O_3 percentages obtained on hardened mixtures containing 0% and 40% fly ash (% by mass per 1 g of D-dry sample, Curing temperature = 40°C, W/P = 50% by mass)

Curing time (day)	Insoluble residue (%)		Dissolved Al_2O_3 (%)	
	FA = 0%	FA = 40%	FA = 0%	FA = 40%
7	0.1	25.3	4.1	5.0
28	1.0	21.5	4.0	5.6
91	0.1	20.3	3.9	5.8
182	0.2	19.3	3.9	5.8
365	0.2	18.6	3.9	6.1

Table 5
Insoluble and dissolved Al_2O_3 percentages obtained on unhydrated samples (% by mass per 1 g of D-dry sample)

Unhydrated sample	Insoluble residue (%)	Dissolved Al_2O_3 (%)
Fly ash (FA)	83.9	3.4
Ordinary Portland cement	0	5.1
FA/OPC blended cement (FA = 40%)	33.2	4.4

3.3. Pozzolanic reaction ratio of fly ash in cement paste

The insoluble residue in and the amount of Al_2O_3 dissolved from various types of hardened paste, prepared at different curing temperatures, water/powder ratios and substitution rates of fly ash, were analyzed for determining the reaction ratio of fly ash. Fly ash and unhydrated cement prepared by substituting 40% fly ash were included in the analyses.

The insoluble residues and the amounts of Al_2O_3 dissolved per 1 g of D-dried cement paste samples are listed in Table 4. Although the insoluble residue of the cement paste with 0% of the substitution rate of fly ash does not vary with age, that of the sample with 40% of the fly ash substitution rate decreases with age. Moreover, although the quantity of Al_2O_3 dissolved from the sample with 0% of the substitution rate of fly ash does not change with age, that from the sample with the 40% fly ash substitution rate increases with age. The measurements of the unhydrated samples are listed in Table 5.

The decrease with age of the insoluble residue in the samples, and the increase with age of the quantity of Al_2O_3 dissolved from the samples containing fly ash suggest that since a firm network silicate or aluminate from the glass phase in each sample was gradually cut off by the basic pore solution, the glass phase is increasingly dissolved and the pozzolanic reaction then proceeded.

For example, the reaction ratio per unit weight of fly ash is determined from the insoluble residue in and the quantity

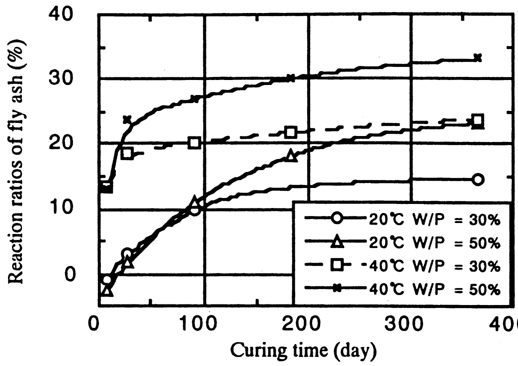

Fig. 3. Reaction ratios of fly ash determined from insoluble residue for cement paste containing 40% fly ash.

of Al_2O_3 dissolved from a sample with 40% of the fly ash substitution rate according to the following method below.

The reaction ratio per unit weight of fly ash was determined from the insoluble residue according to Eq. (1).

$$b_d = (a_0 - a_d)/(f_r \times f_i/100) \tag{1}$$

where b_d: reaction ratio determined from the insoluble residue at the age of d days (%); a_0: insoluble residue in the unhydrated blended cement ($=f_r \times f_i$) (33.2%); a_d: insoluble residue at the age of d days compensates for combined water by $/(1-\mathrm{IG}_d/100)$ (%); IG_d: loss on ignition at the age of d days (%); f_r: substitution rate of fly ash (0.4); f_i: insoluble residue in unhydrated fly ash (83.9%).

The reaction ratio of fly ash was determined from the quantity of Al_2O_3 dissolved according to Eqs. (2) and (3).

$$z_d = ((y_d - y_0)/(F_{al} - y_0)) \times 100 \tag{2}$$

$$y_d = (X_d - C_{al}(1 - f_r))/f_r \tag{3}$$

where z_d: reaction ratio determined from Al_2O_3 at the age of d days (%); y_0: amount of Al_2O_3 dissolved per unit weight of unhydrated fly ash (3.4%); y_d: amount of Al_2O_3 dissolved per unit weight of fly ash at the age of d days (%); x_d: amount of Al_2O_3 dissolved from fly ash blended cement at the age of d days $Al_2O_3/(1-\mathrm{IG_d}/100)$ (%); C_{al}: amount of Al_2O_3 dissolved from cement (5.1%); F_{al}: Al_2O_3 content in fly ash (31.1%)

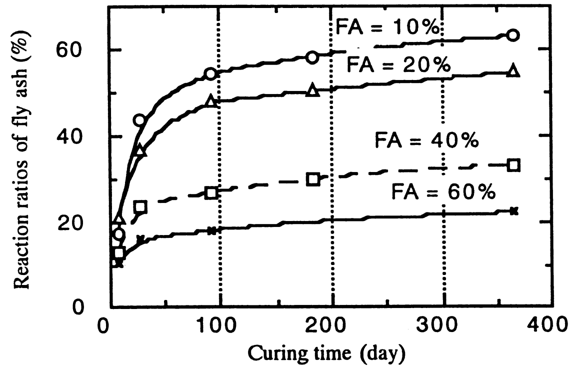

Fig. 5. Reaction ratios of fly ash determined from insoluble residue for cement paste made with 50% water/powder and containing various fly ash contents.

The reaction ratios determined from the insoluble residue of samples prepared by different curing temperatures and water/powder ratios are illustrated in Fig. 3.

The reaction ratios of fly ash in cement paste samples prepared at the curing temperature of 40°C and at the water/powder ratio of 50% at the ages of 7 and 28 days are 12% and 23%, respectively. The ratios then gently increase to 32% at the age of 1 year. The reaction ratio of the sample with the water/powder ratio of 30% at the age of 7 days is the same as that of the sample with 50% water/powder ratio. However, the reaction ratio of the former increases less with age than the latter. The reaction ratio of the samples cured at as low as 20°C are lower than that of the samples cured at 40°C, particularly during the early days. The pozzolanic reaction of fly ash proceeds during the period of time from the age of 28 to 91 days. This period of time is the same while the strength of fly ash paste increases.

The reaction ratios determined from the amounts of Al_2O_3 dissolved from the samples cured at different temperatures are illustrated in Fig. 4. The reaction ratios of fly ash from the samples, cured at 40°C with the water/powder

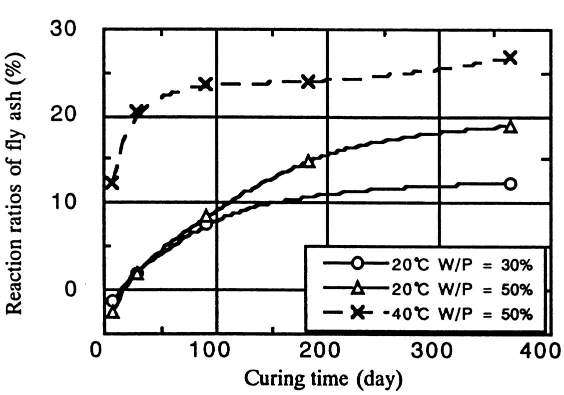

Fig. 4. Reaction ratios of fly ash determined from dissolved Al_2O_3 for cement paste containing 40% fly ash.

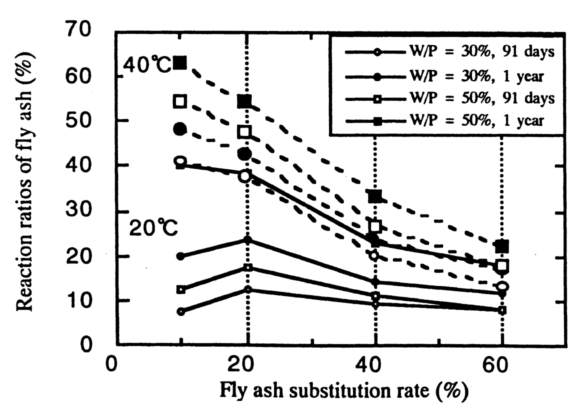

Fig. 6. Relationships between fly ash substitution rates and reaction rates of fly ash determined from the insoluble residue.

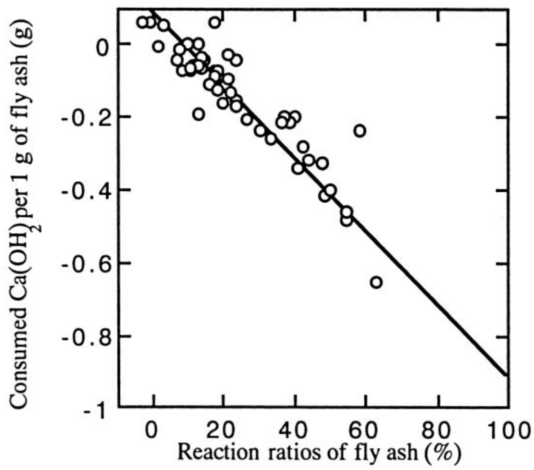

Fig. 7. Relationships between reaction ratios of fly ash determined from the insoluble residue and consumed amount of $Ca(OH)_2$ determined from DSC thermal analysis.

ratio of 50% at the ages of 7, 28, and 365 days, are 12%, 21%, and 27%, respectively. The reaction ratios of the samples cured at 20°C are lower than those cured at 40°C. The reaction ratio of the sample cured at 40°C for 7 days is almost the same as that of the sample cured at 20°C for 91 days. Likewise, the reaction ratio of the sample cured at 40°C for 28 days is almost the same as that of the sample cured at 20°C for 1 year. These reaction ratios determined from the insoluble residue and the amount of Al_2O_3 dissolved up until the age of 91 days are almost equal each other. Various factors affect the rate of the pozzolanic reaction until the age of 182 days. The higher the curing temperature and the water/powder ratio, the higher the reaction ratio.

The reaction ratios of fly ash determined from the insoluble residue using the samples prepared at the curing temperature of 40°C and at the water/powder ratio of 50% and at different substitution rates of fly ash are illustrated in Fig. 5. The reaction ratio of fly ash decreases with increases in the substitution rate. Its reaction ratio at the age of 7 days is almost the same as in any substitution rate, continuously enlarging the difference between reaction ratios at each substitution rate up until the age of 182 days. The reaction ratios of fly ash corresponding to the substitution rates at the ages of 91 and 365 days using the samples prepared at the curing temperatures of 20°C and 40°C and at the water/powder ratios of 30% and 50% are illustrated in Fig. 6.

The reaction ratio of the sample cured at 40°C constantly increases independently of the curing temperature, the water/powder ratio, and the substitution rate of fly ash during the period of time from 91 days to 365 days. Meanwhile, the smaller the substitution rate of fly ash and the higher the water/powder ratio in the sample cured at 20°C, the larger the increase of the reaction ratio of fly ash during the same period of age.

The consumptions of calcium hydroxide are the downward estrangements from the linear line, which is the assumed amount of calcium hydroxide produced due to the hydration of cement, to the measured values in Fig. 2. The relationship between the consumptions of calcium hydroxide per 1 g of fly ash converted from the measurements in Fig. 2 and the reaction ratio of fly ash determined from the insoluble residue are illustrated in Fig. 7. Both items are so strongly correlated with each other that the consumptions of calcium hydroxide and the decrease of the insoluble residue are jointly related to the reaction ratio of fly ash.

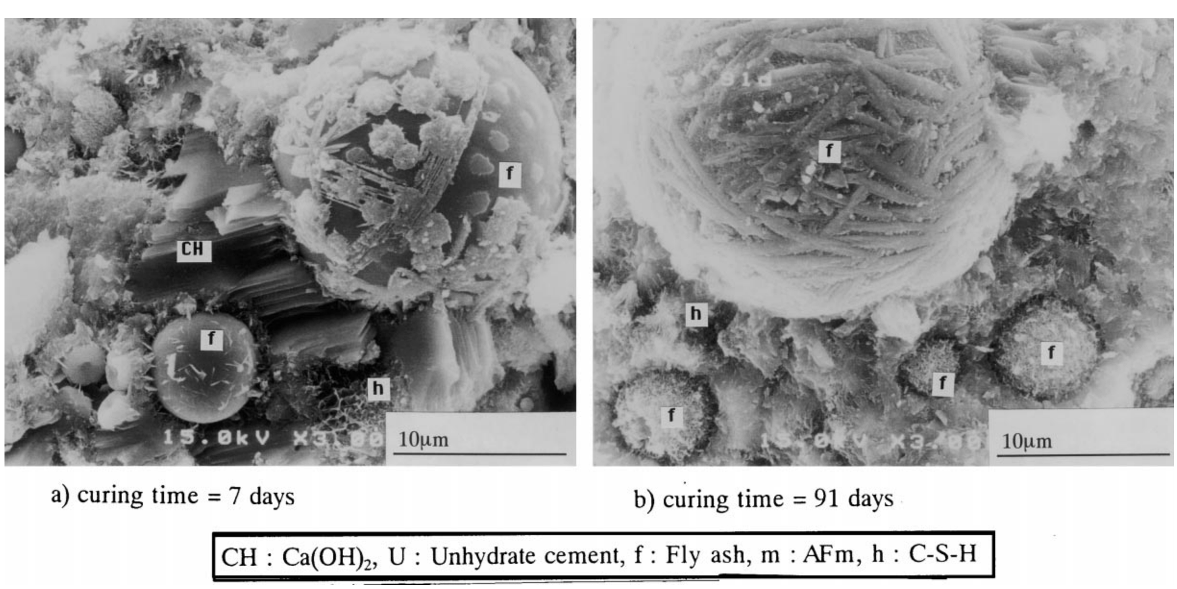

Fig. 8. SEI of reacted fly ash cement paste made with 30% and 50% water/powder, and 40% fly ash.

3.4. Hardened structure of cement paste

The SEIs of hardened paste which were prepared by curing at 40°C with a fly ash substitution rate of 40% and a water/powder ratio of 50% at the ages of 7 and 91 days are shown in Fig. 8.

The reaction on the surface of fly ash at the age of 7 days hardly proceeds. Small amounts of hydrate are radially produced around the fly ash. At the age of 91 days as illustrated in the picture, some fly ash particles approximately 5 μm in diameter have completely reacted and have been substituted by hydrates as shown in the picture. The fly ash particles with large diameter hardly react in most cases.

The SEIs of hardened pastes prepared with a fly ash substitution rate of 40% and different water/powder ratios and curing temperatures at the age of 1 year are shown in Fig. 9. A lot of fly ash particles substituted by hydrates are observed in the hardened cement paste cured at 40°C. The pozzolanic reaction proceeds more slowly in the hardened cement paste cured at 20°C than in the hardened cement paste cured at 40°C. Each fly ash particle has its own conditions for the pozzolanic reaction. The difference in the SEIs caused by the water/powder ratio was not clearly observed.

The BEIs of hardened pastes prepared by the curing temperature of 40°C, the water/powder ratio of 50%, and the fly ash substitution rates of 0% and 40% at the ages of 7 days and 1 year are shown in Fig. 10.

A lot of unhydrated cement and the reacting layer approximately 3 μm thick around cement particles are observed in hardened paste prepared at the fly ash substitution rate of 0% at the age of 7 days. At the age of 1 year, however, the unhydrated cement particle is reduced

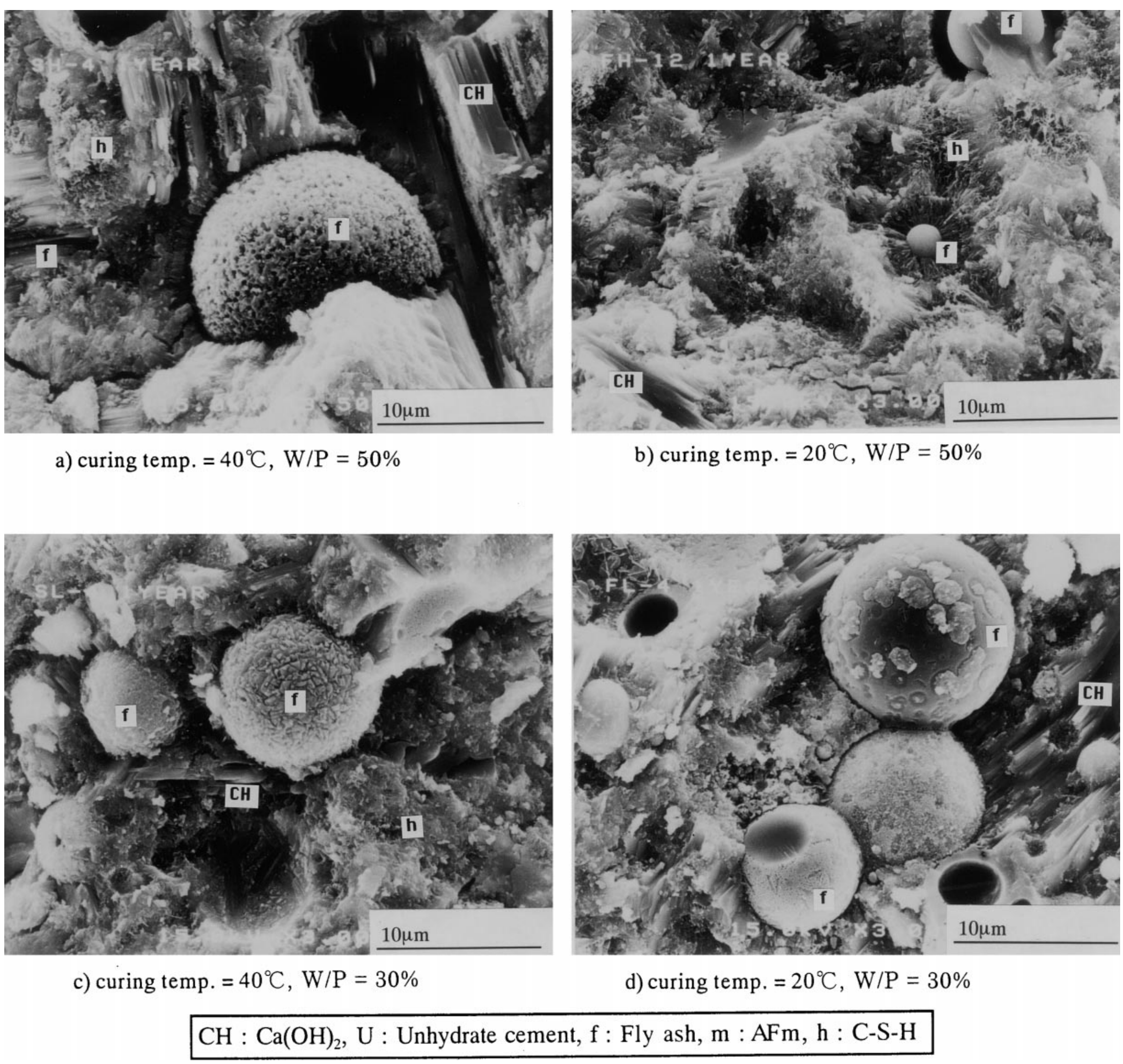

Fig. 9. SEI of hardened fly ash cement paste made with 30% and 50% water/powder, and 40% fly ash.

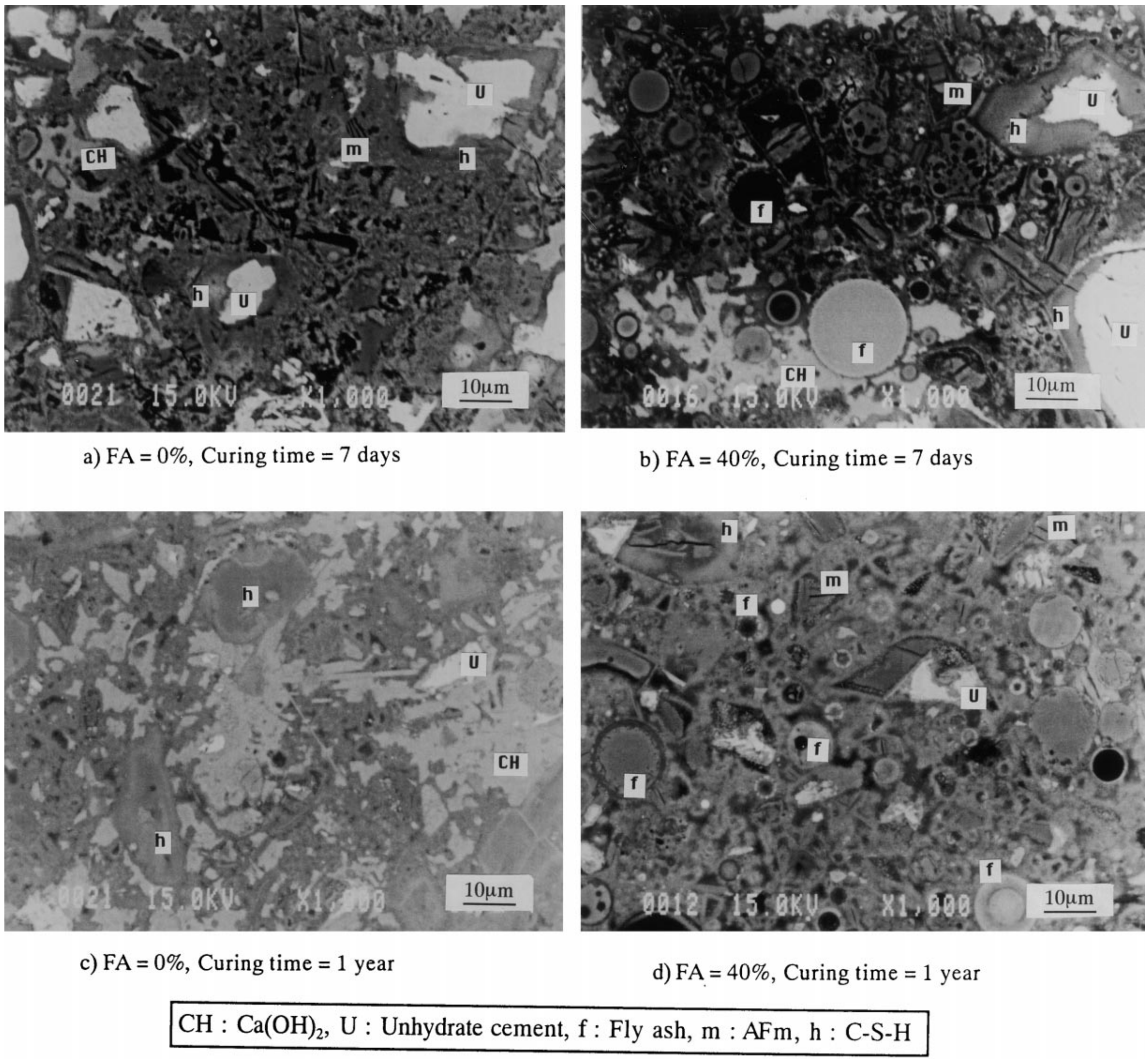

Fig. 10. BEI of polished surface of hardened cement paste made with 50% water/powder, and 0% and 40% fly ash.

and the pore space becomes smaller, hence, the hardened paste is densified.

The unhydrated cement particle is little because the hydration reaction is accelerated in hardened paste, which is prepared with a fly ash substitution rate of 40% at the age of 7 days. Also, calcium hydroxide deposited between the cement particles is observed. There are many fly ash particles with clear borders between the particles. More monosulfate hydrate (AFm) is observed in this than in hardened paste prepared by the fly ash substitution rate of 0%. Maybe this is because the Al ion is supplied by the reaction of fly ash. This agrees with the change of Al_2O_3 in the filtrate in the insoluble residue test. Unhydrated cement hardly remains at the age of 1 year and the borders between the fly ash particles become unclear. The reaction is promoted inside some fly ash particles, and every fly ash particle has its own conditions for the reaction.

4. Conclusions

The hydration reaction of cement and the pozzolanic reaction of fly ash were investigated using hardened fly ash cement. The following conclusions were obtained.

(1) It is possible to quantitatively analyze the reaction ratio of fly ash using the insoluble residue in and the amount of Al_2O_3 dissolved from hardened paste according to proposed methods. The reaction ratio determined from the insoluble residue per unit weight of fly ash and the consumptions of calcium hydroxide agree with the calculated values.

(2) The pozzolanic reaction of fly ash in the hardened paste cured at 20°C begins at the age of 28 days. The pozzolanic reaction of fly ash in the hardened paste cured at 40°C has already started at the age of 7 days and shows a reaction ratio of 12%. The pozzolanic reaction largely depends upon the temperature.

(3) The reaction ratio of fly ash at the age of 1 year in the hardened paste prepared by employing the curing temperature of 40°C and the water/powder ratio of 50% was approximately 30%. The reaction ratio in the hardened paste prepared by employing the water/powder ratio of 30% was approximately 20%, which was the same as that obtained in the hardened paste prepared by employing the curing temperature of 20°C and the water/powder ratio of 50%.

(4) The effects of various factors on the rate of the pozzolanic reaction of fly ash are large until the age of 182 days. The higher the curing temperature and/or the higher the water/powder ratio, the higher the reaction ratio. It is feared that self-neutralization may occur in the hardened paste with the substitution rate of fly ash of 60%. From the results of the pozzolanic reaction, the maximum substitution of fly ash is approximately 40%.

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