- Technical Paper -

INFLUENCE OF FLY ASH REPLACEMENT RATIO ON COMPOSITIONS OF C-S-H GEL

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ABSTRACT

This study reports the effect of fly ash replacement ratio on composition of C-S-H gel. The compositions of C-S-H gel were estimated by combination of Rietveld/XRD analysis, selective dissolution and ignition loss. Experiment results confirm the decreasing of CaO/SiO_2 ratio as the increasing replacement ratio of fly ash. Bonding water in hydrated gel decreased as CaO/SiO_2 ratio increased. Such changing of compositions of C-S-H gel affected its density.

Keywords: C-S-H gel, CaO/SiO_2 ratio, Bonding water, fly ash

1. INTRODUCTION

When cementitious materials contact with water, hydrated products such as $Ca(OH)_2$, ettringite, monosulfate and C-S-H gel are formed. Microstructure develops as well. During aging, C-S-H gel becomes main compound in paste matrix.

The C-S-H gel presents many effects on properties of paste and concrete for instance; compressive strength, permeability, chlorine binding capacity, shrinkage, etc. Therefore, properties of C-S-H gel are important topic that must be investigated.

As for fly ash-cement system, it is well known that hydration of fly ash increases the average degree of polymerization of silicate chains and thus decreases CaO/SiO_2 ratio [1, 2]. In practical, replacement ratio of fly ash is varied from 5 to 60% depended on type and requirement of concrete. It is quite likely that changing the replacement ratio of fly ash affects composition of C-S-H gel.

The purpose of this research is to elucidate influence of fly ash replacement ratio on compositions of C-S-H gel. The compositions of C-S-H gel are estimated by combination of quantitative XRD, Rietveld analysis, selective dissolution and loss of ignition. The CaO/SiO_2 ratio and bonding water in C-S-H gel were determined.

2. EXPERIMENT PROGRAMS

2.1 Materials and Mixed Proportions

Ordinary Portland cement was used. Fly ash type II according to JIS A6201 was used. Physical and chemical properties of fly ash and OPC are shown in Table 1. Paste samples were prepared with water-binder ratio of 1.00 by volume. The replacement ratios of fly ash are 0%, 25% and 50%. A polycarboxylate-base type superplasticizer was used to control the fluidity of paste, namely dispersion state of particles.

First, fly ash and cement particles were blended together with 2 liters pan mixer for 60 seconds. Then water was added, paste samples were mixed with low speed for 90 seconds and further mixed with high speed for 90 seconds. Then fly ash-cement paste was poured into 5cm in diameter and 10cm in height cylinder mold.

At one day after mixing, the samples were remolded and cured in water. The temperature was controlled at 20°C. Compositions in hydrated samples were examined at 7, 28, 56, 91 and 182 days.

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Table 1 Physical and chemical properties of fly ash and OPC

| | Ignition loss (%) | Chemical composition (mass) | | | | | | | | | Density (kg/m³) | Blaine surface area (m²/kg) | Mineral composition (mass) | | | |
		SiO_2 (%)	Al_2O_3 (%)	Fe_2O_3 (%)	CaO (%)	MgO (%)	Na_2O (%)	K_2O (%)	TiO_2 (%)	MnO (%)			C_3S (%)	C_2S (%)	C_3A (%)	C_4AF (%)
Fly ash	0.90	59.90	29.10	6.05	1.30	0.00	0.00	0.93	2.32	0.00	2290	376	-	-	-	-
OPC	0.77	20.84	5.95	2.62	63.63	1.79	0.18	0.33	0.34	0.10	3150	347	63.09	12.99	11.78	9.23

2.2 Analyzing Methods

At required age the samples were cracked and soaked in acetone to stop hydration reaction and further dried at 105°C. Then they were ground in a disc mill. Particles smaller than 75μm were used in analysis.

Ignition losses of samples were measured at 950°C. The compositions and hydration degree of hydrated samples were estimated by combination methods between XRD-Rietveld analysis and selective dissolution [3, 4].

As for selective dissolution, 1g of hydrated sample was prepared in 30 cm³ of HCl solution in centrifuge tube. Then the tube was shaken in automatic shaking water bath. Temperature was set at 60°C for 15 minutes. Then the sample was centrifuged at 4000rpm for 1 minutes and liquid phase was separated and decanted. After that, the solid phase in tube was washed with hot water. Next, the centrifuge tube was filled with 30cm³ of Na_2CO_3 solution, and placed in an 80°C hot automatic shaking water bath for 20 minutes. Then the sample was again centrifuged at 4000rpm for 1 minutes and liquid phase was separated and decanted. The solid phase was again washed with hot water. Next, the tube with the residue sample was dried at 110°C and weighed. The residue sample is unhydrated fly ash. According to a references [4, 5], hydration degree of fly ash is the amount of hydrated fly ash divided by unhydrated fly ash at 0 day.

As for XRD-Rietveld analysis, $Cu_{k\alpha}$ X-ray diffraction equipment was used. The experiments were carried out in the range of 5-70°2θ with 0.02 step scan and 1.00 s/step speed. Divergence slit, scattering slit and receiving slit were 1/2°, 1/2° and 0.3 mm respectively. NIST standard corundum , SRM 676, was used as an internal reference. The sample and internal standard were carefully mixed until a homogeneous color and texture was obtained. The Rietveld analysis program used in this study was SIROQUANT version 2.5 software[6]. The program uses a crystal structure databank, which contains information on adsorption coefficients, unit cell data and crystal structures and thus can analyze composition of cement [7-10].

3. RESULTS AND DISCUSSION

3.1 Replacement Ratio of Fly Ash and Amount of C-S-H gel

According to our previous study [3, 4], the amount of C-S-H gel can be estimated as following; First crystal compounds in hydrated cement (C_3S, C_2S, C_3A and C_4AF), crystal compounds in fly ash, crystal compounds in hydrated products ($Ca(OH)_2$, ettringite and monosulfate) were determined by XRD-Rietveld analysis and then total amount of amorphous phase included the fly ash compound was estimated via internal standard; corundum. On the other hand, total amount of unhydrated fly ash (both crystal and amorphous) can be estimated by selective dissolution. By subtracting the unhydrated fly ash with its crystal phases, the amount of unhydrated amorphous phase in fly ash can be calculated. Then amount of amorphous left that we may consider as C-S-H gel can be obtained by subtracting amorphous in fly ash from total amount of amorphous.

Figure 1 shows the amount of C-S-H gel by weight as a function of time and replacement ratio of fly ash [3]. One can see that the amount of
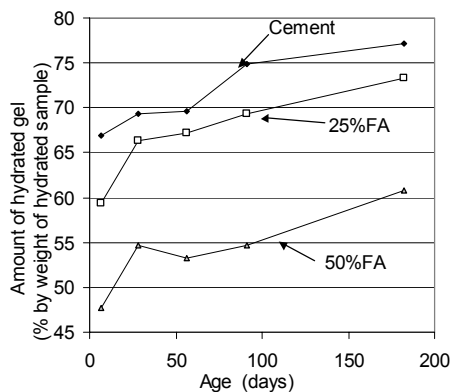

Fig.1 The amount of C-S-H gel by weight as a function of time and replacement ratio of fly ash.

Table 2 Compounds and oxides of fly ash measured by XRD; Rietveld analysis and XRF analysis

Compounds	XRF (% by weight)	XRD (% by weight)	Compound in amorphous (% by weight)	% by weight of total amrophous
	a	b	c=a-b	d= c/Am*100
Al_2O_3	29.11	17.68	11.43	15.42
SiO_2	59.90	7.13	52.77	**71.15**
K_2O	0.93	0.00	0.93	1.26
CaO	1.69	0.07	1.62	2.18
TiO_2	2.32	0.04	2.28	3.08
Fe_2O_3	6.05	0.92	5.13	6.92
Amorphous (Am)		**74.17**		

C-S-H gel increases as age increases and decreases as replacement ratio of fly ash increases. Nevertheless, the unit of amount of C-S-H gel in Figure 1 is percent expressed by ratio to weight of hydrated sample. It is quite likely that the amount of C-S-H gel expressed by volume may differ from that expressed by weight [11] since density of C-S-H gel in 25%FA and 50%FA may differ from those in cement paste.

3.2 CaO/SiO₂ Ratio of C-S-H Gel

CaO/SiO_2 ratio of C-S-H gel can be estimated by following.

In case of cement paste, calcium oxide supplied by C_3S and C_2S was consumed to generate $Ca(OH)_2$ and C-S-H gel. Since amount of $Ca(OH)_2$ was known from XRD-Rietveld analysis, by subtracting calcium oxide in $Ca(OH)_2$ from the calcium oxide provided by dissolution from C_3S and C_2S, the amount of calcium oxide in hydrated gel can be estimated. On the other hand, silica oxide contributed by C_3S and C_2S was supplied to produce hydrated gel only. Since the amount of C_3S and C_2S in hydrated samples are known, CaO/SiO_2 can be estimated.

In the case of fly ash cement paste, the amount of silica oxide contributed from fly ash is necessary to be considered. The compounds and oxides of fly ash measured by XRD-Rietveld analysis and XRF analysis are shown in Table 2. From by XRD-Rietveld analysis and XRF analysis, about 70% of amorphous is SiO_2. In our previous study [4], it was confirmed that the major cementitious material in fly ash is amorphous. In this study, it is assumed that only SiO_2 in amorphous can hydrate. By applied this assumption, the amount of SiO_2 contributed by hydrated fly ash can be calculated via hydration degree of fly ash. Therefore, the total amount of CaO and SiO_2 contributed by C_3S, C_2S and fly ash can be estimated. Accordingly CaO/SiO_2 ratio in fly ash-cement system can be estimated.

It should be noted that in fact, fly ash also contributes Al_2O_3 to hydrated gel. However, the calculation will become much more complicate if Al_2O_3 is considered. Further research is necessary to clarify effect of Al_2O_3 in amorphous phase of fly ash.
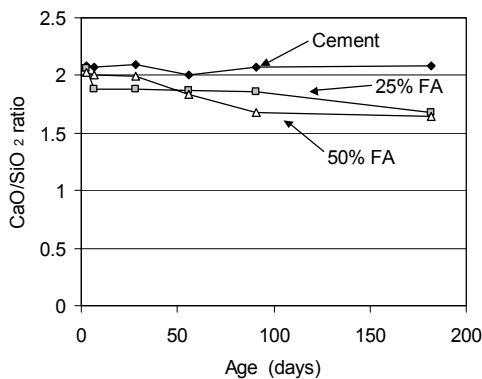

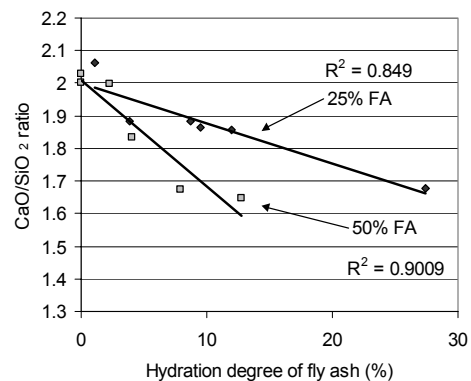Fig. 2 CaO/SiO₂ ratio as a function of time and replacement ratio of fly ash.

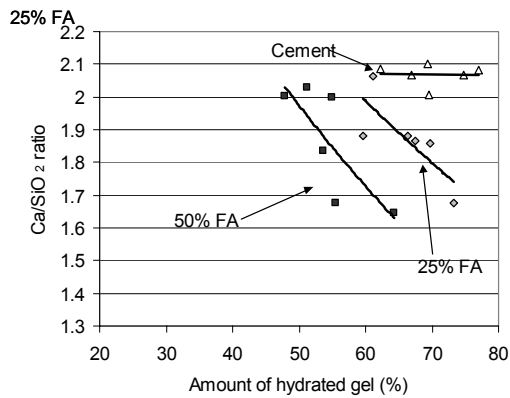Fig. 3 CaO/SiO₂ ratio as a function of hydration degree of fly ash.

Fig. 4 Relation between CaO/SiO$_2$ ratio and amount of C-S-H gel as a function of replacement ratio of fly ash

Fig. 5 Relation between bonding water in C-S-H gel and amount of C-S-H gel as a function of replacement ratio of fly ash.

Figure 2 shows CaO/SiO$_2$ as a function of time. CaO/SiO$_2$ ratio of cement paste is almost constant. As for fly ash cement paste, CaO/SiO$_2$ ratio of sample with 25% and 50% replacement ratio tend to decrease as the age increases. Figure 3 illustrates the CaO/SiO$_2$ ratio as a function of hydration degree of fly ash. CaO/SiO$_2$ ratio decreases as well as increasing of hydration degree of fly ash.

Figure 4 illustrates the relations between CaO/SiO$_2$ ratio and amount of C-S-H gel as a function of replacement ratio of fly ash. The CaO/SiO$_2$ ratio of fly ash-cement system decreases as the amount of hydrated gel increases while that in cement system remains almost constant. At the amount of C-S-H gel, 50%FA shows lower CaO/SiO$_2$ ratio than 25%FA. The results confirm that replacement ratio of fly ash affect CaO/SiO$_2$ ratio of C-S-H gel.

3.3 Bonding Water in C-S-H Gel

The CaO/SiO$_2$ of hydrated gel described in previous section has been discussed by many researchers [1, 2]. However, the bonding water in C-S-H gel has been rarely described. The amount of bonding water in C-S-H gel is not equal to ignition loss of water and thus cannot be measured directly. However, the total amount of bonding water can be estimated via ignition loss of weight of hydrated sample.

Total bonding water is bonding water in Ca(OH)$_2$, ettringite, monosulfate and hydrated gel. Since Ca(OH)$_2$, ettringite and monosulfate are crystal, the amount of bonding water in these compounds can be calculated via it chemical composition. After subtract bonding water in crystal phases from total bonding water, the amount of bonding water in hydrated gel can be estimated.
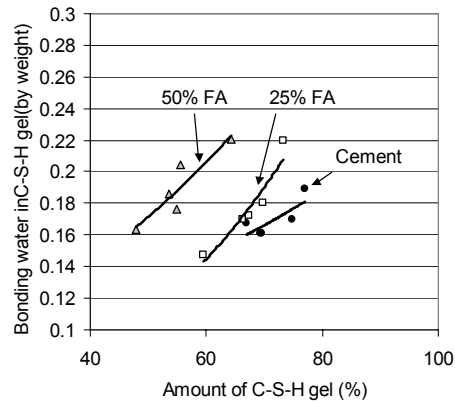
It should be noted that in this research, all samples were dried at 105 °C so that all of free water was eliminated. At this temperature, bonding water from ettringite also evaporated. It was expected that almost ettringite was destroyed so that it was hardly detected. More researches are required in this area.

Figure 5 shows relation between bonding water in C-S-H gel and amount of C-S-H gel as a function of replacement ratio of fly ash. At the same amount of hydrated gel, bonding water in hydrated gel of sample prepared with 50% fly ash is higher than those of samples prepared with of fly ash 25% and 0% respectively. Moreover, it increases when amount of C-S-H gel increases.

It is crucial to find the reason why the composition of hydrated gel is changed. I. G. Richardson [12] reported that the amount of hydroxyl water is flexible within the limits imposed by the need to maintain the layer structure and neutrality; decreased content of Ca^{2+} ions balanced by an increase in Si-OH groups. It seem that there are range of composition of CaO, SiO$_2$ and H$_2$O to make hydrated gel stable.

SiO$_2$ contributed from cement and fly ash has two oxygen atoms. However, SiO$_4$ tetrahedral in hydrated gel has four oxygen atoms. This means SiO$_2$ need two oxygen atoms from other molecule to become tetrahedral.

Figure 6 shows the schematic figure of one kind of C-S-H gel; jennite. There are at least three ways that SiO$_2$ can share other two oxygen atoms; polymerized with another SiO$_2$, sharing oxygen atoms with CaO and sharing oxygen atoms
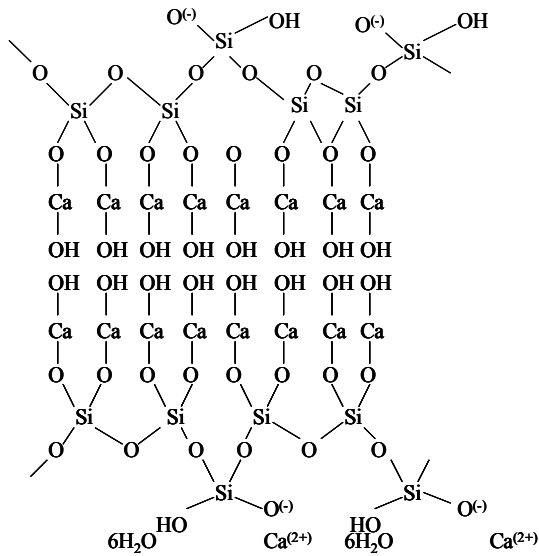
Fig. 6 The schematic figure of C-S-H gel.

Fig. 7 Relation between bonding water in C-S-H gel and CaO/SiO$_2$ ratio.
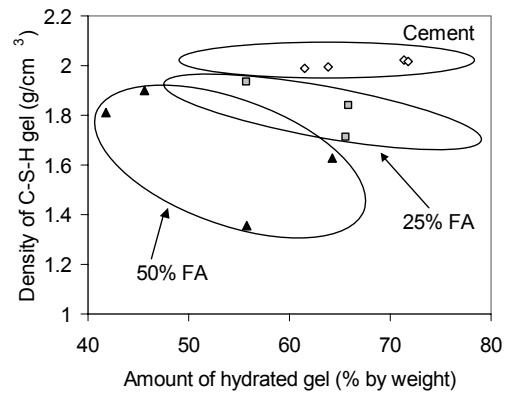
Fig. 8 The density of C-S-H gel.

Fig. 9 The amount of C-S-H gel expressed in % by volume.

with OH$^-$ group. In cement paste, the amount of CaO may be enough so that each Si can share oxygen with two atoms of CaO except bridging tetrahedral. However, in fly ash – cement paste, the amount of CaO may not enough so that Si can share oxygen with only one atom of CaO. Nevertheless, Si atom needs another oxygen to form tetrahedral structure.

It is quite likely that one of CaO next to Si may be replaced with OH$^-$. This may results in the increasing of bonding water when fly ash is used.

The relation between bonding water in C-S-H gel and CaO/SiO$_2$ ratio is shown in Figure 7. Bonding water in C-S-H gel increases when CaO/SiO$_2$ decreased.

The hypothesis described above may be checked by examined density of C-S-H gel. Since molecular weight of OH$^-$ is lower than CaO^{2+}, density of hydrated gel should decrease when bonding water in hydrated gel increases.

The total volume of solid phases can be estimated by mercury intrusion method. On the other hand, from selective dissolution and Rietveld analysis, amount by weight of each compound in fly ash-cement hydrated sample can be estimated. Among these compounds, only density of hydrated gel is unknown. Therefore, the density of C-S-H gel can be estimated.

Figure 8 shows the density of C-S-H gel calculated from combination of Rietveld analysis, selective dissolution and mercury intrution.
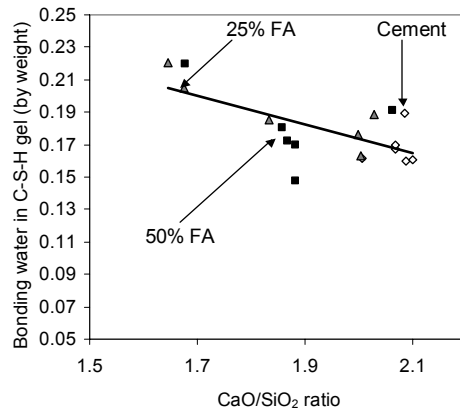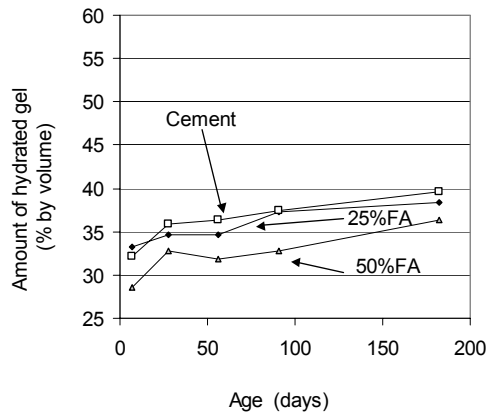
It can be seen that density of C-S-H gel

decreased when fly ash was replaced. The density of C-S-H gel became lower when replacement ratio of fly ash increases. These results express that C-S-H gel is affected by replacement ratio of fly ash.

As mention at the beginning in Figure 1, the amount of C-S-H gel expressed in % by weight of sample decreases as replacement ratio of fly ash increases. However, from result in Figure 8 the tendency of amount of C-S-H gel expressed by volume should be different.

Figure 9 shows the amount of C-S-H gel expressed in % by volume. In calculation, the average density of C-S-H gel in cement paste, 25%FA and 50%FA are 2.00, 1.85, 1.67 g/cm^3, respectively.

4. CONCLUSIONS

(1) Experiment results confirm that CaO/SiO_2 ratio decreases as replacement ratio of fly ash increase.
(2) Bonding water in C-S-H gel is depended on replacement ratio of fly ash; bonding water in hydrated gel of sample prepared with 50% fly ash is higher than those of samples prepared with of fly ash 25% and 0% respectively.
(3) Difference in composition of C-S-H gel cause difference in its density.

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