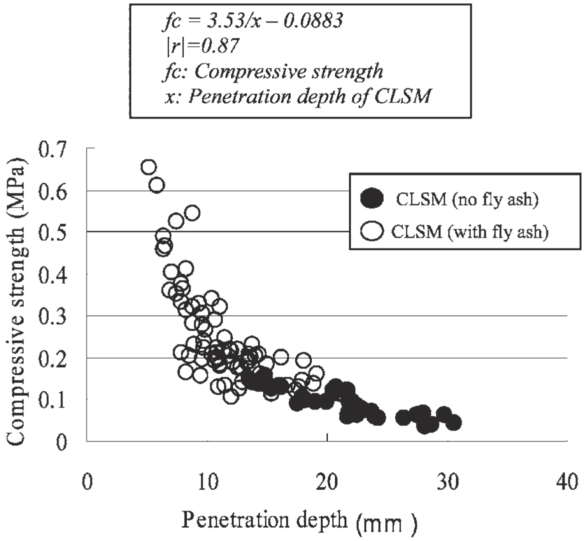

Figure 3 — Relationship between compressive strength and penetration depth.

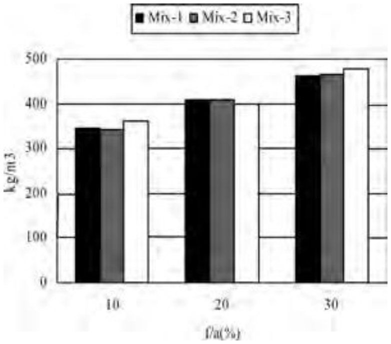

Figure 4 — Unit water content versus filler-aggregate ratio, f/a.

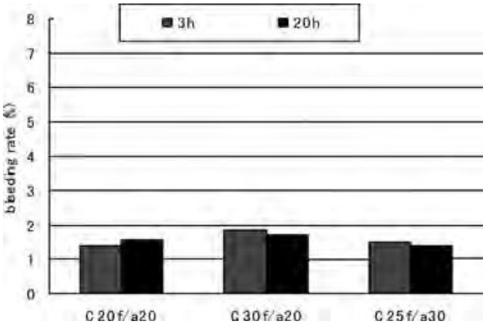

Figure 5 — Bleeding rate (mix-o series).

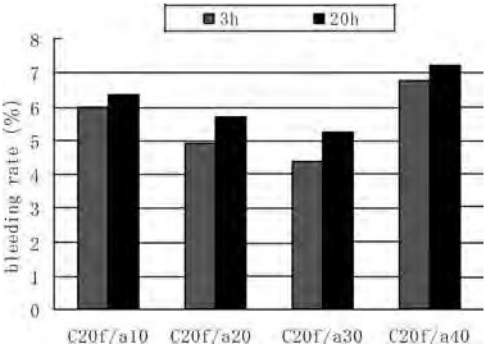

Figure 6 — Bleeding rate (mix-1 series).

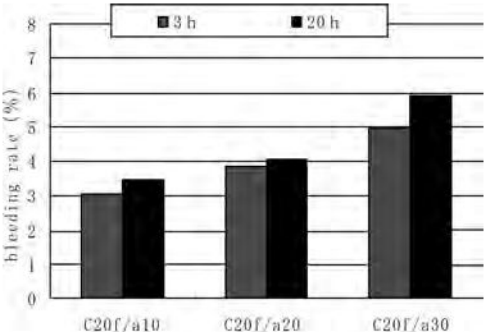

Figure 7 — Bleeding rate (mix-2 series).

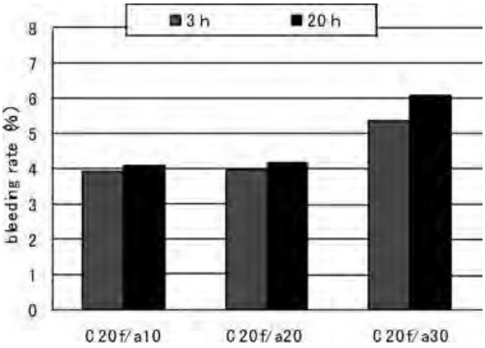

Figure 8 — Bleeding rate (mix-3 series).

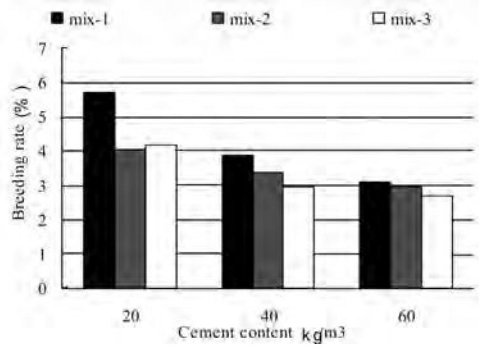

Figure 9 — Bleeding rate versus cement content.

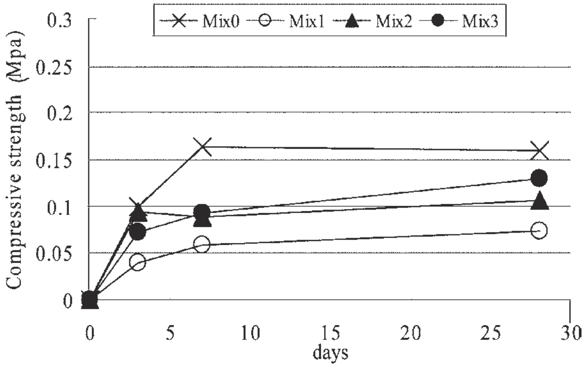

Figure 10 — Compressive strength development C20f/a20.

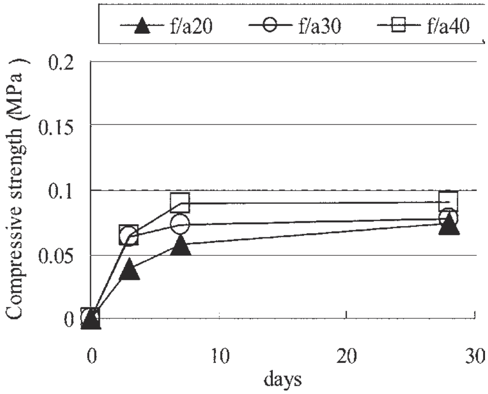

Figure 11 — Compressive strength development (Mix-1 series) C20.

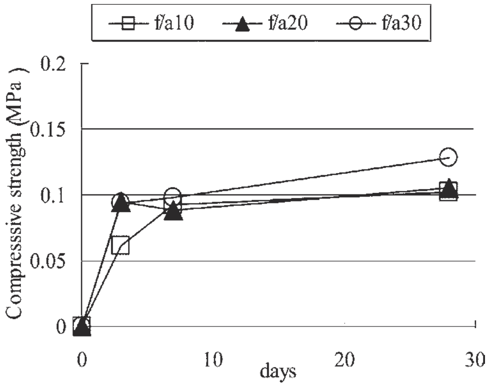

Figure 12 — Compressive strength development (Mix-2 series) C20.

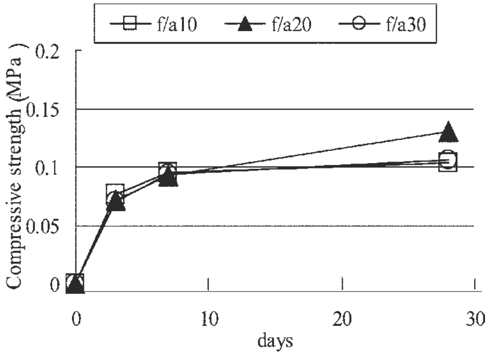

Figure 13 — Compressive strength development (Mix-3 series) C20.

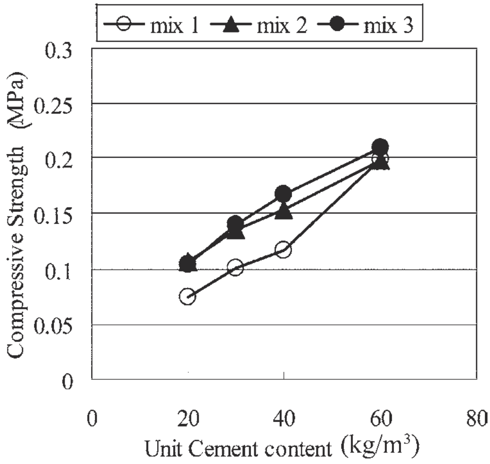

Figure 14 — Compressive strength versus unit cement content.

SP-242—28

Composition of C-S-H in the Hydration Products of Fly Ash-Cement System

by P. Termkhajornkit and T. Nawa

Synopsis: This paper describes the effect of fly ash on composition of C-S-H gel. The CaO/SiO_2 ratio and chemical bonding water of C-S-H gel were estimated by the combination of the Rietveld analysis by XRD, the selective dissolution analysis and loss of ignition measurement. The results indicated that the CaO/SiO_2 ratio of hydrate gel in fly ash-portland cement paste decreased as the hydration of fly ash proceeds, while the CaO/SiO_2 ratio of C-S-H gel in portland cement paste did not vary with the progress of hydration. At the same amount of produced C-S-H gel, bonding water in C-S-H gel of paste prepared with 50% fly ash was higher than those of pastes prepared with of fly ash 25% and 0%. The corresponded results can be seen from decreasing of density of C-S-H gel when replacement ratio of fly ash increases. The bonding water in C-S-H gel decreases as its CaO/SiO_2 ratio increases. The effect of chemical bonding water in C-S-H gel can be applied to modify the gel/space-strength model.

Keywords: bonding water; C-S-H gel; fly ash; rietveld analysis; selective dissolution

Pipat Termkhajornkit, Doctor in Socio-Environmental Engineering has been working at Hokkaido University, Japan since 2005 in the field of recycling of waste products, repairing agents, and pozzolanic materials.

Toyoharu Nawa is a Professor of Socio-Environmental Engineering at Hokkaido University, Japan. His research interests are recycling of aggregate, repairing agents, and recycling of waste products and pozzolanic materials. He is the chairman of Civil Engineering Committee JSCE333 on Properties and performance evaluation of concrete with several admixtures. He is also the chairman of Architectural Institute of Japan JASS5 Committee on cement and admixture.

INTRODUCTION

It is well known that the microstructure in hardening cement paste develops as a result of progress in hydration reaction of cementitious materials. When cementitious materials are dispersed in water, the liquid phase gets rapidly saturated with various ionic species. After that hydration products such as $Ca(OH)_2$, ettringite, monosulfate and calcium silicate hydrate(C-S-H) gel are formed. Among the hydration products, the major one is C-S-H gel.

There are numerous reports on utilization of fly ash in concrete. This is because fly ash has been found to modify many properties of concrete such as workability, strength, shrinkage and heat evolution (1-6). Fly ash performs at least two important functions to improve the properties of concrete; a micro filler and pozzolanic reaction. As a pozzolan, fly ash reacts with calcium hydroxide and produces very small fibers of C-S-H gel. There are many reports about the effect of fly ash on calcium silicate ratio of C-S-H gel (7, 8). Hydration of fly ash increases the average degree of polymerization of the silicate chains, accordingly decreasing the CaO/SiO_2 ratio of C-S-H gel. However, C-S-H gel is not composed of only calcium and silicate. Chemical bonding water is also an important component of the C-S-H gel composition.

The purpose of this study was to investigate the effect of fly ash on the composition of C-S-H gel, especially the chemical bonding water. The CaO/SiO_2 ratio of C-S-H gel was determined by the a quantitative analysis for hydration degree of Portland cement and fly ash, which is determined by a combination of a Rietveld analysis by XRD data and a selective dissolution analysis using HCl and Na_2CO_3 solutions, respectively. The chemical bonding water in C-S-H gel was also determined by loss of ignition test. Further, it is shown that the effect of the chemical bonding water on the density of C-S-H gel in fly ash-portland cement paste can be used to modify the gel/space ratio-strength model for pastes containing fly ash.

EXPERIMENTAL

Cement and fly ash used in this study were ordinary Portland cement and fly ash meeting JIS R5210 and JIS A6201 specification, respectively. The replacement ratios of fly ash were 0%, 25% and 50% by volume of the blended cement. Cement pastes were made with water-cementitious ratio of 1.00 by volume. In order to adjust the fluidity of paste, a polycarboxylate-based type (PC) superplasticizer was used. The chemical and physical properties of the cementitious materials are shown in Table 1.

The flow value of paste was measured by a flow test according to JASS15 M-103. After mixing, the paste was poured into the cylindrical cone, 50 mm in diameter and 51 mm in height. Then, the cone was slowly pulled up vertically. The flow value was the averaging value of two crossing diameters of the spreading paste. The amount of superplasticizer was adjusted until the flow value was between 200 and 250 mm. The paste was placed in cylindrical molds, 5mm in diameter and 10mm in height. At one day after mixing, the paste specimens were demolded. The specimens were cured in water at 20°C until the required age. Measurements of the compressive strength and the degree of hydration were made at 7, 28, 56, 91 and 182 days.

After the compressive strength test the fractured pieces of the specimen were further crushed with a hammer into 2.5 to 5.0 mm fragments. To stop the hydration, the paste samples were soaked in acetone for 24 hours. The samples were allowed to dry at room temperature (20°C) for six hours and oven-dried 105°C for three hours. A part of the samples was used for measuring porosity by the mercury intrusion method and the rest was ground in a disk mill. The amount of unhydrated fly ash was directly estimated by a selective dissolution method using HCl and Na_2CO_3 solutions (5). The amounts of crystal compound and total amorphous material were measured and analyzed by XRD-Rietveld analysis (9). SIROQUANT version 2.5 was used as the software for the Rietveld analysis. The loss on ignition (LOI) of was measured by ignited the sample at 950 °C.

RESULTS

Calcium/silicate ratio

Calcium/silicate molar ratio can be estimated by a combination of the selective dissolution and the XRD-Rietveld analysis. The amount of each crystalline phase of OPC such as C_3S, C_2S, C_3A and C_4AF, fly ash and hydrated products such as $Ca(OH)_2$, ettringite and monosulfate were estimated by the XRD-Rietveld analysis. Furthermore, by using the reference known the amount of crystalline compounds, the total amount of amorphous phase in paste can also be determined. On the other hand, the selective dissolution analysis can give us the total amount of unhydrated fly ash that includes both crystalline and amorphous compounds. Further measuring the crystalline phases in unhydrated fly ash by the XRD-Rietveld analysis, and subtracting the crystalline phases from the unhydrated fly ash, one can estimate the amount of unhydrated amorphous phase in fly ash. Then amount of remaining amorphous phase was considered as C-S-H gel (9).

Figure 1 shows the amount of C-S-H gel by weight as a function of time and the replacement ratio of fly ash (10). It is evident that the amount of C-S-H gel increases as age increases but decreases as replacement ratio of fly ash increases. It should be noted that the unit of amount of C-S-H gel in Fig. 1 is in weight percent. When the amount of C-S-H gel is expressed by volume, the effect of replacement ratio of fly ash on the amount of C-S-H gel produced may differ from that expressed by weight (11).

In the case of cement paste, the ratio of calcium oxide and silicon dioxide of C-S-H gel can be estimated by using mass balance since the C-S-H gel is produced by the hydration of C_3S and C_2S only. Lime contributed by C_3S and C_2S was used to produce $Ca(OH)_2$ and C-S-H gel. Since the amount of $Ca(OH)_2$ was known, by subtracting the calcium oxide present in $Ca(OH)_2$ from the calcium oxide provided by C_3S and C_2S, the amount of calcium oxide present in C-S-H gel can be estimated. On the other hand, silicon dioxide contributed by C_3S and C_2S was supplied to produce C-S-H gel only. Therefore, CaO/SiO_2 can be estimated. In the case of fly ash-cement paste, it is necessary to consider the amount of silicon dioxide contributed by fly ash.

Table 2 shows the compound composition and oxide analysis of fly ash by XRD- Rietveld and XRF analysis, respectively. About 70% of amorphous phase consists of SiO_2. From a previous study (9), the authors had confirmed that the amorphous phase was the major component in fly ash that hydrated. In this study, it is assumed that fly ash contributes to supply only SiO_2 to the formation of C-S-H gel. Based on this assumption, the amount of SiO_2 contributed by hydrated fly ash can be calculated by the hydration degree of fly ash. In this way, the total amount of CaO and SiO_2 dissolved from C_3S, C_2S and fly ash can be estimated, and accordingly the CaO/SiO_2 molar ratio in fly ash-cement system can be evaluated.

It should be noted that, in fact, fly ash also provides Al_2O_3, and C-S-H gel contains Al_2O_3. However, the model will become much more complicate if the effect of Al_2O_3 is considered. Thus, in this study, the effect of Al_2O_3 component was not taken into account. However, further study will be necessary to clarify the effect of Al_2O_3 in amorphous phase of fly ash on the formation of C-S-H gel.

Figure 2 shows the CaO/SiO_2 ratio of C-S-H gel as a function of time. The CaO/SiO_2 ratio of cement paste is almost constant regardless of the age. In contrast, for fly ash cement paste, the CaO/SiO_2 ratios of C-S-H gel for pastes with fly ash of 25% and 50% replacement tend to decrease as the age increases. Figure 3 expresses the relation between the CaO/SiO_2 ratio and the amount of C-S-H gel as a function of replacement ratio. The CaO/SiO_2 ratio of C-S-H gel for fly ash-portland cement paste decreases as the amount of produced C-S-H gel increases, while that in portland cement paste remains almost constant. Figure 4 illustrates the CaO/SiO_2 ratio as a function of hydration degree of fly ash. This figure confirms that the CaO/SiO_2 ratio decreases as the hydration degree of fly ash increases, and their correlation vary depending on replacement ratio of fly ash.

Chemically bonded water in C-S-H gel

The change in CaO/SiO_2 ratio of C-S-H gel has been reported by many researchers (7, 8). However, the little information on chemically bonded water has been reported. The bonding water in C-S-H does not correspond to LOI of the paste because this includes the chemically bonded water from other cement hydration products. Thus the amount of chemically bonded water in C-S-H cannot be measured directly. Total LOI of the paste is equal to the sum of chemically bonded water in $Ca(OH)_2$, ettringite, monosulfate hydrate and C-S-H gel. Since $Ca(OH)_2$, ettringite and monosulfate hydrate are crystalline, the amount of chemically bonded water in these crystalline compounds can be stoichiometrically calculated. After subtracting the chemically bonded water in crystalline phases from the total bonding water, the amount of chemically bonded water in C-S-H gel can be estimated.

It should be noted that in this research, all samples were dried at 105 °C so that all of evaporable water was eliminated. At this temperature, however, the chemically bonded water from ettringite also evaporated. It was expected that almost all of the ettringite was destroyed so that it was not detected. Indeed, in this study, after heating the amount of ettringite detected by XRD-Rietveld analysis was negligible.

Figure 5 illustrates the relation between the chemically bonded water in C-S-H gel and the amount of C-S-H gel. With the same amount of C-S-H produced, the bonded water in C-S-H for the sample prepared with 50% fly ash was higher than the samples prepared with of 25% fly ash or no fly ash.

DISCUSSION OF RESULTS

Why the chemically bonded water in C-S-H gel increases

It is crucial to find the reason why the composition of C-S-H gel is changed. Richardson (12) reported that since the amount of hydroxyl group in C-S-H gel is rather flexible within the limits imposed by the need to maintain the layer structure and electric neutrality: a decrease in Ca^{2+} ions in C-S-H gel is balanced with an increase in Si-OH groups. As a result, a range of compositions of CaO, SiO_2 and H_2O is possible in C-S-H. Figure 6 shows the schematic diagram of chemical structure of Jennite which is one kind of C-S-H. As shown in this figure, the morphology of silicate existed in C-S-H is not SiO_2 that has two oxygen atoms, but tetrahedral SiO_4 that has four oxygen atoms. This means that SiO_2 component dissolved from cement and fly ash need two oxygen atoms from other molecule to from C-S-H. According to Fig. 6, there are 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 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 the fly ash – cement pastes, the amount of CaO may not be enough so that Si can share oxygen with only one molecule of CaO. Nevertheless, Si atom needs oxygen to form tetrahedral structure. Accordingly, one of CaO next to Si may be replaced with OH^-. Therefore, chemically bonded water in C-S-H should decrease as CaO/SiO_2 increases. The relation between bonded water in C-S-H and CaO/SiO_2 is shown in Figure 7. It should be noted that the schematic diagram of C-S-H in Fig. 6 is simplified in order to consider the mechanism of change in C-S-H structure. It may show the features of the C-S-H structure, but does not show precisely the actual structure of C-S-H.

The result in Fig. 5 might be confirmed indirectly from the experimental results for the density of C-S-H. Since molecular weight of OH^- is lower than that of CaO^{2+}, it can be expected that the density of C-S-H may decrease when the bonding water in C-S-H increases. From selective dissolution and XRD-Rietveld analyses, the weight fraction of each compound in hydrated fly ash-cement paste can be estimated. Among these compounds, only density of C-S-H is unknown. On the other hand, the total volume of solid phases in paste can be estimated by mercury intrusion method. From these results, density of C-S-H gel can be estimated. Figure 8 shows the estimated density of C-S-H gel. It can be seen that the density of C-S-H for paste with fly ash of 25% replacement is little lower than those from portland cement paste, while that for paste with fly ash of 50% replacement is significantly lower. This results correspond to our expectation.

Application of effect of bonding water in C-S-H gel/space model

The gel/space model is the classic strength prediction model, which has been proposed by Powers (13). The gel/space ratio is defined as the ratio of the volume of the solid hydration products such as C-S-H to the volume of the total space. For Portland cement, it is assumed that 1.0 ml of cement on full hydration occupies 2.06 ml space; not all the hydrated material is gel, but as an approximation we can call it a gel (14). In the case of fly ash-cement paste, Lam et. al. (11) proposed that 1 ml of reacted fly ash occupies 2.52 ml of space. Thus the gel/space ratio of fly ash cement paste can be calculated as following (11);

x = gel/(space which is originally occupied by water + space due to inner product)

$$= \frac{2.06V_c\alpha_c + 2.52V_f\alpha_f}{w_o + V_c\alpha_c + V_f\alpha_f} \qquad (1)$$

where x is gel/space ratio, V_c and V_f are volume fraction of cement and fly ash, respectively; α_c and α_f are the hydration degree of cement and fly ash respectively; w_o is the volume of space, which is originally occupied by water; $V_c\alpha_c + V_f\alpha_f$ represents the volume of the inner product.

Figure 9 shows the relation between compressive strength and gel/space ratio. The compressive strength increases as gel/space ratio increases. At the same time, it is also evident that the relationship of paste with fly ash of 50% replacement is different from the others. In equation (1), the difference between 2.06 and 2.52 is due to significant deference in the apparent density of C-S-H gel of cement and fly ash, respectively. As previously described, the density of C-S-H for the paste with 25% fly ash is a little lower than that from the neat portland cement paste, where as that for the paste with 50% fly ash is significantly lower. Therefore, in Fig. 9, the data for paste with fly ash of 25% replacement can be plotted on the same line as portland cement paste. On the other hand, the data for paste with fly ash of 50% replacement is not consistent with the relationships for paste with fly ash of 25% replacement and the paste without any fly ash.