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# Hydration of fly ash cement

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## Abstract

It is necessary to establish the material design system for the utilization of large amounts of fly ash as blended cement instead of disposing of it as a waste. Cement blended with fly ash is also required as a countermeasure to reduce the amount of $CO_2$ generation. In this study, the influences of the glass content and the basicity of glass phase on the hydration of fly ash cement were clarified and hydration over a long curing time was characterized. Two kinds of fly ash with different glass content, one with 38.2% and another with 76.6%, were used. The hydration ratio of fly ash was increased by increasing the glass content in fly ash in the specimens cured for 270 days. When the glass content of fly ash is low, the basicity of glass phase tends to decrease. Reactivity of fly ash is controlled by the basicity of the glass phase in fly ash during a period from 28 to 270 days. However, at an age of 360 days, the reaction ratios of fly ash show almost identical values with different glass contents. Fly ash also affected the hydration of cement clinker minerals in fly ash cement. While the hydration of alite was accelerated, that of belite was retarded at a late stage.

*Keywords:* Fly ash; Hydration; Glass content; Basicity; Reactivity

## 1. Introduction

Blended cement has been noted for its property of reducing $CO_2$ generation. In Japan, the amount of fly ash produced in coal fired power plants total nearly 7 million tons per year [1]. For this reason, its use as a raw material for blended cement is anticipated. Fly ash has been used mainly for mass concrete, utilizing its property of low heat for hydration, development of fluidity and suppression of alkali-aggregate reaction. However, fly ash-blended cement tends to be vulnerable to carbonation. In addition, the quality of fly ash varies widely. Accordingly, the characterization of fly ash cement should be clarified, and a material design technique for the effective utilization of characterized fly ash should be established. Furthermore, a shifting in the specification standards for concrete structures with respect to performance verification type is underway in Japan. Under the new specification, various materials can be used freely, but the material design methods of various cementitious materials must be established in order to satisfy the performance requirements of concrete. As variation in the quality of fly ash are significant compared with slag, its utilization in blended cement and additives is limited to dam concrete. The reactivity of fly ash is supposed to be particularly influenced by the glass content and its composition, but few studies with quantitative data for the hydration of fly ash cement and the reaction ratio of fly ash exist. Organization of quantitative reaction data, including those already clarified, is necessary for the material design.

In this study, basic research was carried out to establish a material design method for using fly ash in fly ash cement or as an additive. Further, the glass

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Table 1
Chemical composition of portland cement and fly ash (%)

| Samples | Ignition loss | $SiO_2$ | $Al_2O_3$ | $Fe_2O_3$ | CaO | MgO | $TiO_2$ | $SO_3$ | $Na_2O$ | $K_2O$ | Relative density |
|---|---|---|---|---|---|---|---|---|---|---|---|
| OPC | 1.6 | 21.2 | 4.9 | 2.8 | 65.0 | 1.5 | 0.25 | 2.05 | 0.29 | 0.41 | 3.16 |
| Fly ash F | 1.1 | 56.3 | 34.2 | 3.2 | 1.2 | 1.3 | 1.87 | 0.26 | 0.27 | 0.50 | 2.24 |
| Fly ash F′ | 1.2 | 62.0 | 25.5 | 4.3 | 2.2 | 1.2 | 1.10 | 0.40 | 1.30 | 0.80 | 2.22 |

content, its chemical composition and the hydration ratio of fly ash and cement clinker minerals were determined, using two types of fly ash with different compositions. The hydration of fly ash cement is discussed, and the influence of glass content and the basicity of the glass phase of fly ash on the hydration of fly ash cement was investigated.

## 2. Materials and methods

### 2.1. Materials

The chemical composition and density of ordinary portland cement (OPC) and fly ashes (FA) are shown in Table 1. The mineral compositions of OPC as calculated by conventional Bougue's equation are $C_3S$ 55.8%, $C_2S$ 20.9%, $C_3A$ 8.3%, $C_4AF$ 8.9% and $CaSO_4$ 3.49%. The Blaine specific surface area of OPC is 344 $m^2/kg$. The mineral composition and the Blaine surface area of fly ash are shown in Table 2. The amounts of mullite, $\alpha$-$SiO_2$, hematite and magnetite were analyzed by XRD (internal material: $CaF_2$)[2]. $SO_3$ was assumed to exist as $CaSO_4$. The glass content of fly ash was calculated from the determined crystal amounts, which consists of mullite, $\alpha$-$SiO_2$, hematite, magnetite and $CaSO_4$, and loss on ignition. In this study, two kinds of fly ash with glass contents of 38.2% (F) and 76.6% (F′) were used. The basicity of the glass phase in fly ash was estimated by the calculation procedure stipulated in JIS (Japan Industrial Standard) of blast furnace slag additives for concrete, i.e., basicity=$(CaO+MgO+Al_2O_3)/SiO_2$. The basicities of glass phase for F and F′ were 0.24 and 0.40, respectively, as shown in Table 3. Fig. 1 shows the relationship between the amount of mullite and the glass content of fly ash produced in Japan. The low and high glass content values of 38.2% and 76.6% are typical of fly ash produced in Japan [3]. When the mullite content is reduced, the glass content and the basicity of the glass phase of fly ash become high. The basicities of fly ash are low when compared with that of granulated blast furnace slag, which is about 1.8.

### 2.2. Preparation of specimens

The replacement ratios of two kinds of fly ash OPC were 0(OPC), 20 (F20, F′20), 40 (F40, F′40) and 60 (F60, F′60)% by mass. These were mixed with water to a water/powder ratio of 0.4 and kept for 7, 28, 56, 91, 180, 270 and 360 days at 20 °C in sealed bottles. After the prescribed time, these specimens were ground, immersed in acetone, and D-dried for 24 h.

### 2.3. Measurement of unreacted fly ash and formed $Ca(OH)_2$

The reaction ratio of fly ash was determined by measuring unreacted fly ash using 2 M HCl and 5% $Na_2CO_3$ aqueous solution [4]. The amounts of $Ca(OH)_2$ were determined by measuring the mass loss between 405 and 515 °C in TG–DTA.

### 2.4. Hydration of cement clinker minerals in fly ash cement

The reaction ratios of cement minerals (alite, belite, $C_3A$ and $C_4AF$) in OPC and in fly ash cement (F20 and F′20) were measured by the XRD internal standard method. The diffraction peaks which were used in the XRD quantitative analysis were as follows: alite: 51.7° ($2\theta$) [040](hkl), 51.9° [620]; belite: 31.0° [121]; $C_3A$: 33.15° [440]; $C_4AF$: 12.2° [020]; $\alpha$-$Al_2O_3$: 52.5° [024]. The diffraction peak of belite at 31.0° is overlapped with that of the hydration product, monosulphate, so that the influence was removed by heating the specimens at 200 °C for 6 h [5]. By this treatment, the peak halo at around 12° from aluminate hydrate can be removed. After the heating treatment, 10% $\alpha$-$Al_2O_3$ was mixed as internal standard, and XRD measurement was carried out. The area of diffraction peaks was estimated by the figure integral of the function after curve fitting of the peak profile by means of the minimum square root method. In

Table 2
Mineral composition of fly ash (%)

| FA | Glass content | Mullite | $\alpha$-$SiO_2$ | Hematite | Magnetite | $CaSO_4$ | Ignition loss | Blaine ($m^2/kg$) |
|---|---|---|---|---|---|---|---|---|
| F | 38.2 | 41.9 | 17.1 | 0 | 0 | 1.7 | 1.1 | 406 |
| F′ | 76.6 | 12.4 | 8.7 | 0 | 0.4 | 0.7 | 1.2 | 418 |

Table 3
Basicity of glass phase in fly ashes

| FA | Basicity of glass phase $(CaO+MgO+Al_2O_3)/SiO_2$ |
|---|---|
| F | 0.24 |
| F′ | 0.40 |

calculating the reaction ratio, a correction for the ignition loss was added. This was estimated using the ignited base.

### 2.5. Measurement of pore size distribution

The pore volume and pore size distribution of hardened specimens D-dried for 24 h were measured by mercury penetrating porosimeter.

## 3. Results and discussion

### 3.1. Reaction ratio of fly ash in fly ash cement

The amounts of formed $Ca(OH)_2$ are shown in Fig. 2. The straight line shows the amount of $Ca(OH)_2$ formed in OPC and multiplied by cement content ratio. The difference between the straight line and the experimentally measured data gives the amount of $Ca(OH)_2$ consumed by pozzolanic reaction. This figure indicates that the pozzolanic reaction proceeds between 91 and 360 days, while consuming $Ca(OH)_2$. At the end of this period, the amount of $Ca(OH)_2$ present in the samples is almost identical, regardless of the glass content.

The reaction ratios of fly ash in fly ash cement are shown in Fig. 3. Fly ash did not react for the first 7 days, independent of the glass content and replacement ratio. Therefore, it can be assumed that the mineral and chemical compositions or glass content of fly ash do not influence the effect by which the heat of hydration is reduced in massive concrete with fly ash cement.

The reaction ratio of fly ash F′ with a high glass content is large in comparison with fly ash F with a low glass content during a period from 28 to 270 days. This tendency is evident when the replacement ratio of fly ash is low. The reaction ratio of fly ash at 360 days was almost the same for each fly ash replacement ratio. A spherical particle covered with a glass layer was considered as a model of fly ash. The difference in the glass content was assumed to be the difference in the thickness of the covering glass layer. Taking into consideration the particle size distribution, it was estimated that the thickness of the glass phase in fly ash with a low glass content is 0.54 μm, and that of fly ash with a high glass content is 2.09 μm. Reaction of F′ was particularly stopped even though a large amount of the glass phase remained. The mean particle radius for both kinds of fly ash is about 4 μm. At 360 days, the reaction layers of fly ash F and F′ were 0.32 and 0.39 μm thick, respectively. The pozzolanic reaction proceeds gradually from the surface of fly ash, and a thin film of hydrates is formed. The reaction is almost complete when a certain film thickness is obtained (about 0.3–0.4 μm), restraining the material transfer. When the glass content of fly ash is low, almost all of $Al_2O_3$ has already been crystallized as mullite crystals, and the basicity of glass phase then tends to decrease. The reactivity of fly ash is controlled by the basicity of the glass phase in fly ash during the period from 28 to 180 days.

The results mentioned above clarified that differing glass content and glass phase compositions only have a small influence on the reaction over the long curing periods such as 1 year, but the differences in the reaction before that time pose a great problem. Consequently, the glass content of fly ash should be taken into consideration during the materials design process.

### 3.2. Reaction ratio of cement clinker minerals in fly ash cement

The reaction ratio of alite in portland cement is shown in Fig. 4. Early hydration of alite is accelerated more by cement with fly ash than that with OPC. This is based on the fine powder effect in which hydration products are also formed on the surface of fly ash and the layer of the hydrates formed on the alite surface thins. From Fig. 2, it can be seen that the amount of $Ca(OH)_2$ at 28 days increases with the replacement of cement by fly ash. This should be ascribed to the acceleration of the reaction of cement itself. This results in a decrease in the thickness of the film of hydration product covering the surface of alite on the addition of fly ash. No marked difference between the kinds of fly ash can be seen. Hydration of alite is inhibited after 91 days.

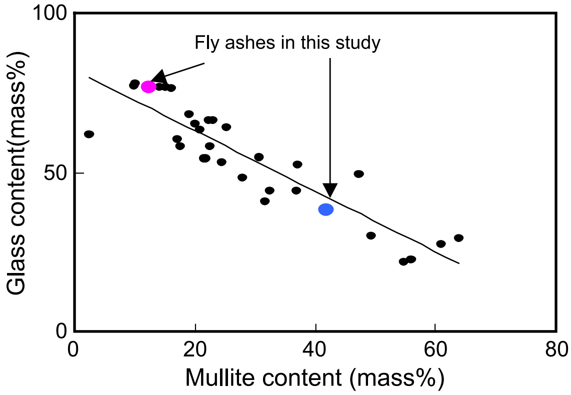

Fig. 1. Glass contents of fly ash in Japan. (This figure was drown by using of the data of Ref. [3].)

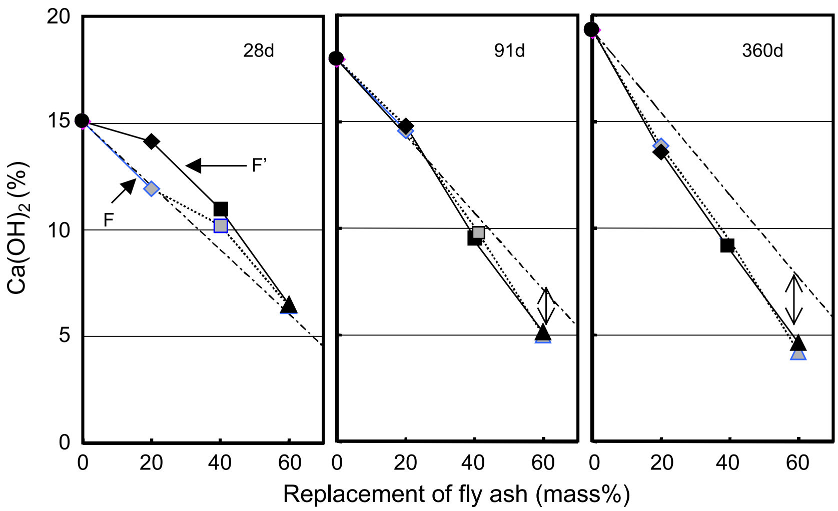

Fig. 2. Relation between the amounts of $Ca(OH)_2$ and the replacement ratios of fly ash in hardened fly ash cements.

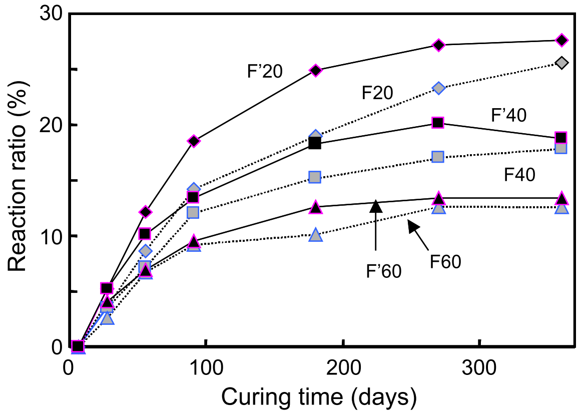

Fig. 3. Reaction ratio of fly ash.

Fig. 5 shows the hydration ratio of belite in fly ash cement or OPC. Initially, the hydration reaction of belite is accelerated together with alite. However, after 91 days, hydration of the belite is retarded in samples with added fly ash. The hydration mechanism of belite is the same as that of alite, but there are two accelerated period for belite: around 4.4 and 30 days [6]. In the blast furnace slag cement with high belite contents, hydration of belite is delayed, because at 30 days the saturation ratios of calcium hydroxide are not increased in the samples with blast furnace slag [7]. This is the acceleration stage of belite. However, abundant calcium hydroxide is still present after 28 days in the fly ash cement. Therefore, it is possible to conclude that hydration of the belite is delayed, since densely hydrated products were formed on the surface of belite or hydrated belite in fly ash cement.

In the case of $C_3A$, the presence or kind of fly ash appears does not appear to have any appreciable influence. Many other XRD peaks appeared around 33° ($2\theta$), which was where the $C_3A$ peak also appeared, so further improvement is required for this XRD quantitative analysis technique. If the X-ray diffraction peak of $C_4AF$ appeared at a lower angle and was not overlapped by other peaks, the quantitative analysis could be carried out with comparatively high accuracy. Addition of fly ash increases the reaction ratios of F20 and F'20 so they are slightly larger than that of OPC, up to 56 days. After that, hydration of

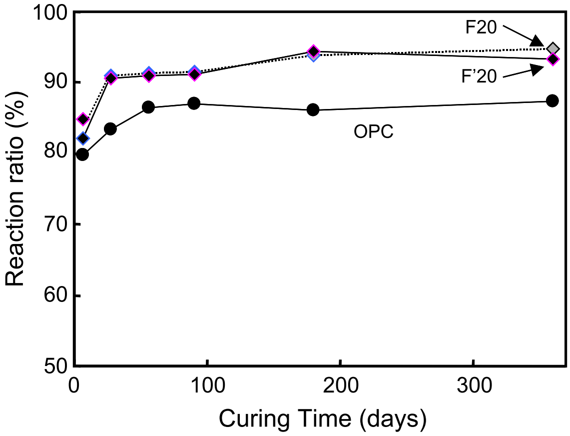

Fig. 4. Reaction ratio of alite in OPC or fly ash cement.

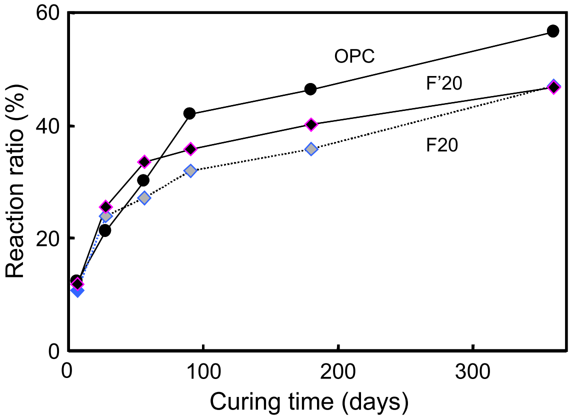

Fig. 5. Reaction ratio of belite in OPC or fly ash cement.

Table 4
$CaO/SiO_2$ ratio of C–S–H in hardened samples

| Samples | 28 days | 360 days |
|---|---|---|
| OPC | 1.72 | 1.54 |
| F20 | 1.76 | 1.39 |
| F′20 | 1.54 | 1.39 |

$C_4AF$ in OPC proceeds gradually, whereas it levels off in the presence of fly ash.

Table 4 shows the $CaO/SiO_2$ ratio of C–S–H in hydrated OPC and fly ash cement (F20, F′20: replacement ratio of fly ash is 20 mass% by mass). These values are calculated from the amount of produced $Ca(OH)_2$, and the reaction ratio of fly ash, alite and belite. At 28 days, the $CaO/SiO_2$ ratios of OPC and fly ash cement with a low glass content fly ash (F20) are higher than that of fly ash cement with a high glass content fly ash (F′20), because the reaction ratio of fly ash F′ is larger than that of fly ash F at 28 days. However, when fly ash is present, the $CaO/SiO_2$ ratio in C–S–H is significantly lower after 28 days than in OPC. The $CaO/SiO_2$ ratios at 360 days were 1.54 for OPC and 1.39 for F20 and F′20, suggesting that the low $CaO/SiO_2$ ratio of C–S–H was produced by pozzolanic reaction. However, the $CaO/SiO_2$ ratio of C–S–H is changed by the mineral composition of OPC. Therefore, more detailed investigation into methods for determining the mineral content of portland cement is necessary.

### *3.3. Pore size distribution of hardened fly ash cement*

The accumulated pore volume (%) in the specimens of hardened OPC paste and fly ash cement (F20 and F′20: replacement ratio of fly ash is 20%) at 91 and 360 days, are shown in Fig. 6. At 91 days, the pore volume of the specimen replaced with F′fly ash having a high glass content showed a smaller value than that of OPC. However, despite the low pozzolanic reactivity due to the low glass content, fly ash F led to high porosity of the hardened sample at 91 days. At 360 days, the reaction of fly ash with low glass content had proceeded, and the pore volumes in the specimens with two different glass contents were almost the same. These results agree well with the results for the reaction ratios of fly ash.

## 4. Conclusion

Using two types of fly ash with different composition, hydration of fly ash cement was examined. In addition to the results achieved in the present work, results from previous report and textbooks are given. This was done so that the properties of fly ash cement, based on quantitative data for the reaction ratio of each mineral and fly ash, could be collected and organized.

(1) Regardless of glass content and composition, fly ash in fly ash cement paste cured at 20 °C did not react in any specimens until 7 days, so the glass content and the composition of fly ash do not need to be taken into consideration for the heat liberation of initial hydration, which is important for mass concrete.
(2) The glass content, namely the basicity of the glass phase, affects the reaction of the fly ash during a period from 28 to 270 days, and the pore structure of hardened body varies, depending on the type of fly ash.
(3) The hydration ratios of fly ash and the porosity of hardened samples with fly ash at 360 days were similar with each other and were not affected by glass content.
(4) Fly ash affected the hydration of cement clinker minerals in the fly ash cement. The long-term hydration of alite was accelerated, while on the other hand, that of belite and $C_4AF$ was retarded.
(5) Addition of fly ash resulted in a low $CaO/SiO_2$ ratio of C–S–H in hardened samples. The $CaO/SiO_2$ ratios at 360 days were 1.54 for ordinary portland cement and 1.39 for fly ash cement.

These quantitative data for the hydration of fly ash cement are also useful for confirming simulated concrete properties based on the hydration model.

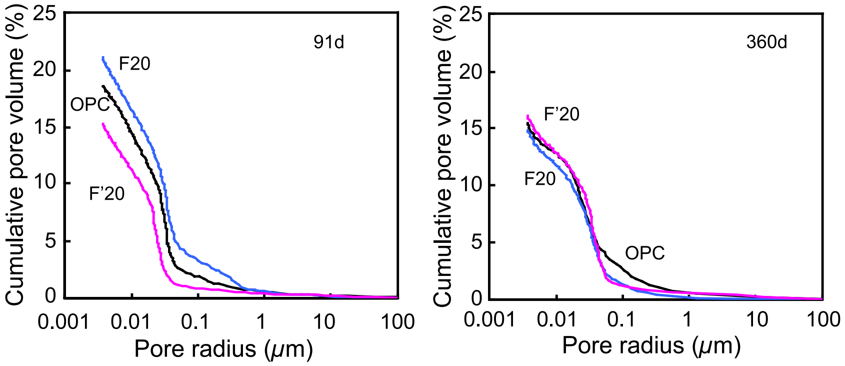

Fig. 6. Pore size distribution of hardened samples at 91 or 360 days.

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