- Technical Paper -

A STUDY OF FLY ASH-CEMENT HYDRATION BY RIETVELD ANALYSIS AND SELECTIVE DISSOLUTION

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ABSTRACT

Recent improvements in concrete research have shown the importance of durable concrete with environmental materials such as fly ash. Mechanical properties and durability of cementitious material are related to its microstructure. In order to understand the microstructure of concrete, it is necessary to quantitatively determine its cementitious hydration. However, until now there is no proper method to measure hydration degree of fly ash-cement system. In this paper, we purpose the new method; superposition between quantitative XRD analysis/ Rietveld analysis and selective dissolution. By using this method the amount of unhydrated cement, unhydrated fly ash, $Ca(OH)_2$ and hydrated gel can be estimated.

Keywords: hydration, fly ash, selective dissolution, Rietveld analysis, $Ca(OH)_2$

1. INTRODUCTION

Recently, the issue of microstructure of concrete draws attention of many researchers. Understanding in microstructure will lead to understanding in mechanical properties of concrete such as strength and its durability. In order to understand the microstructure of concrete, it is necessary to understand its cementitious hydration. In conventional cement system, hydration degree of cement can be estimated by many method such as heat of hydration, thermal analysis (DTA), thermo gravimetric (TG) analysis, non-evaporate water content or ignition loss of samples, XRD peak or peak area and backscattered electron image analysis (BSE). However, until now it there is no proper method to measure hydration degree of binary system such as fly ash-cement system.

It was reported that the amount of $Ca(OH)_2$ can be quantitatively measured by thermal analysis (DTA) and thermo gravimetric (TG) analysis. However, in fly ash-cement system, in its reaction process, cement produces $Ca(OH)_2$ while fly ash consumes $Ca(OH)_2$. Thus, the amount of $Ca(OH)_2$ can no longer represent the hydration degree in binary cementitious system.

As for backscattered electron image analysis (BSE), it was reported that this method could quantitatively measure amount of unhydrated Portland cement. In fly ash-cement system, Igarashi et al. [1] reported that brightness of fly ash particles were sufficiently different from that of unhydrated cement particles. However in hydrated sample, it is quite difficult to measure the area of

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fly ash distinguished through its brightness by computer since calcium silicate hydrate gel (C-S-H gel) also has similar brightness.

As for non-evaporate water or bonding water content, the amount of non-evaporate water is interpreted from its ignition loss. The hydration degree of cement is calculated based on assumption that 1g of anhydrous cement produce 0.23 g of non-evaporate water when it hydrates completely [2]. In the case of fly ash-cement system, hydration degree cannot be calculated directly from non-evaporate water because it is not constant since major component in fly ash is amorphous.

As for the hydration degree of fly ash, selective dissolution method is often used to measure amount of unhydrated fly ash [3, 4]. The procedure of this method is that firstly the acid solution is used to dissolve all Ca components in the sample. After that the base solution is used to dissolve gel components (Al, Si, Fe gel). In the final stage, only unhydrated fly ash is left. By applying this method, the hydration degree of fly ash can be estimated. However, amount of unhydrated cement or its hydration is still unknown.

For XRD analysis, in conventional XRD analysis, it can detect when crystal hydrate products appear. However, it cannot determine the amount of compound quantitatively.

From the above reasons, there is no method to measure hydration degree in fly ash-cement system yet. The purpose of this study is to find the quantitative method to measure hydration degree in fly ash-cement system.

In 1969, Rietveld successfully found the method that can interpret all information from the XRD technique [5]. He stated that XRD patterns should be analyzed using each point on the profile step-scan as a data rather than the integrated intensities of the individual lines. At first, Rietveld analysis was used to refine structure of crystal phase from powder neutron diffraction data. In 1987, this method was extended to multiphase XRD patterns and phase abundance analysis by Hill and Howard [6].

In the case that amorphous is coexisted, the amount of crystal phases calculated from Rietveld analysis seem to be higher than the true value. This problem can be solved by putting standard reference. The analysis can be corrected by dividing the values by the ratio of the measured value to the true amount of standard value. The difference between the total of the phase quantities after corrected and 100% provides the amount of amorphous content.

Many researchers mentioned that Rietveld analysis can be applied to complex system, however, there are at least 2 problems. First problem is that in Rietveld analysis, large numbers of parameters are applied. This means that good fitting may be obtained from unrealistic values of parameters resulting in wrong values of the amount of phases. Therefore, we need to compare the result of Rietveld to other quantitative methods. In this study BSE image analysis was used to compare amount of unhydrated cement. The amount of $Ca(OH)_2$ was compared to result from thermal analysis. Second problem is that Rietveld analysis cannot distinguish kinds of amorphous. In fly ash-cement system we need to know amount of two kinds of amorphous; amorphous in unhydrated fly ash and those in hydrated product. Therefore, using only Rietveld analysis seems not to be enough to analyze hydration in fly ash-cement system.

To solve these problems, we would like to purpose new concept; superposition of Rietveld analysis and selective dissolution.

The amount of each crystal phase component (crystal phases of OPC, fly ash and hydrated product) and total amount of amorphous can be extracted by Rietveld analysis. On the other hand, selective dissolution can give us the total of unhydrated fly ash.

By subtracting the unhydrated fly ash with its crystal phases, the amount of unhydrated amorphous phase in fly ash can be calculated. Finally the amount of C-S-H gel can be obtained. By using this concept, at least two useful data can be extracted; the amount of C-S-H gel and total unhydrated particles. The explanation can be seen in the following equation.

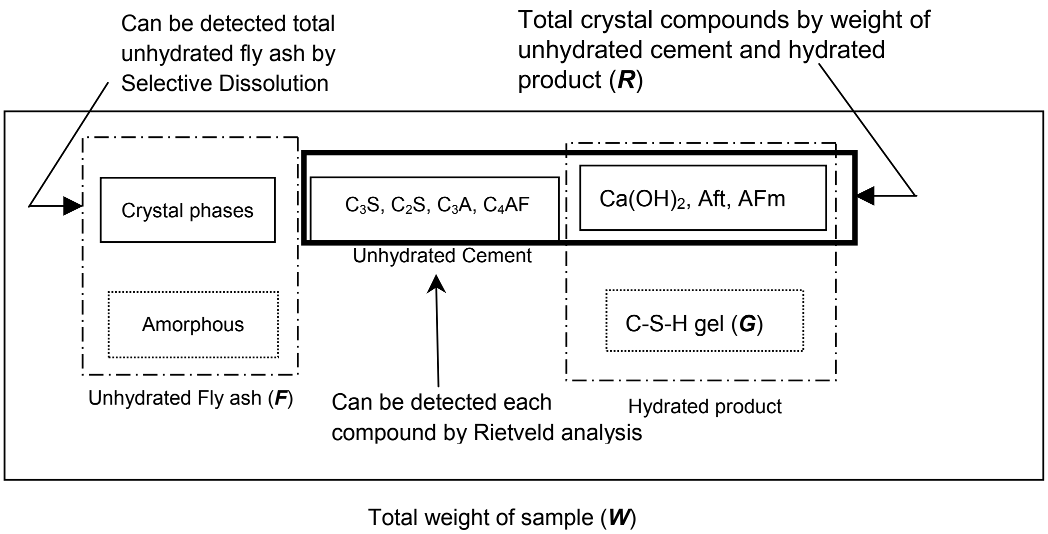

Fig 1. Superposition of Rietveld analysis and selective dissolution

Table 1 The physical and chemical properties of fly ash and OPC

	Ignition loss	Chemical composition (mass)									Density	Blaine surface area	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
	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(kg/m^3)	(m^2/kg)	(%)	(%)	(%)	(%)
Fly ash	0.90	59.90	29.60	4.80	1.30	0.60	0.00	0.70	0.00	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

$$G = W - R - F \quad (1)$$

Where, G is C-S-H gel, W is the total weight of sample, R is total crystal compounds by weight of unhydrated cement and hydrated product which can be found by Rietveld analysis, F is total unhydrated fly ash from selective dissolution. The schematic figure is illustrated in Figure 1.

2. EXPERIMENTS

Ordinary Portland cement (OPC) was used. Fly ash type II classified by JIS A6201 was used. A Polycarboxylate - based superplasticizer was used. Physical and chemical properties of fly ash and OPC are shown in Table 1.

Replacement ratio of fly ash is 25 and 50% by volume. Water binder ration is 1.00 by volume. First, fly ash and cement particle were mixed together with 2 liters pan mixer for 60 seconds. After water was added, paste samples were mixed low speed for 90 seconds and further mixed with high speed for 90 seconds. Then fly ash-cement paste was poured into cylinder mold. Height and diameter of cylinder mold is 100 and 50 mm, respectively. At 24 hours after mixing, samples were demolded. Samples were cured in water at 20 °C. The compressive strength of cylinder samples; 100mm height and 50 mm diameter were measured at7, 28, 56, 91 and182 days.

At required age, the samples were cracked and soaked in acetone to stop hydration reaction. The amount of unhydrated fly ash was measured by selective dissolution method using HCl and Na_2CO_3 solution [4].

1g of hydrated sample was dissolved in 30 cm^3 of HCl solution in centrifuge tube. Then the tube was further stirred in 60°C hot water for 15 minutes. Next the liquid phase was separated and decanted. After that, the solid phase in tube was washed with hot water for 3 times. Following this, the centrifuge tube was filled with 30cm^3 of Na_2CO_3 solution, and placed in an 80°C hot water bath for 20 minutes and stirred occasionally. Then the liquid phase was decanted. The solid phase was again washed with hot water for 3 times. Next, the tube with the residue sample was dried at 110°C and weighed.

The amount of crystal compound and

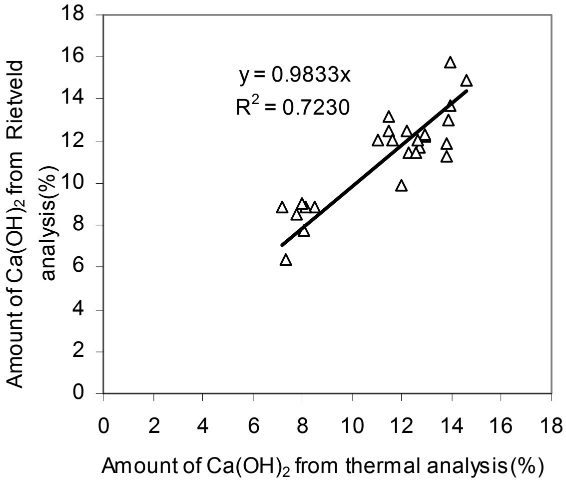

Fig. 2 The comparison between $Ca(OH)_2$ from Rietveld analysis and those from thermal analysis

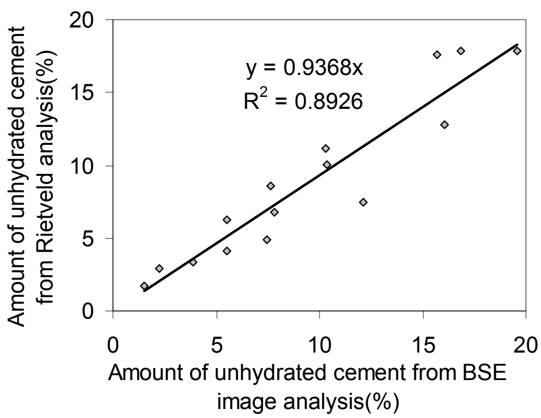

Fig. 3 The comparison between unhydrated cement from Rietveld analysis and those from BSE image analysis

total amorphous compound was measured and quantified by XRD and Rietveld analysis respectively. Rikaku, $Cu_{k\alpha}$ 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.10 % of X-ray standard corundum known as SRM 676 was used as NIST standard. The sample and internal standard were carefully mixed until a homogeneous color and texture was obtained.

As for analysis, SIROQUANT version 2.5 software was used. The unhydrated cement, crystal compound in unhydrated fly

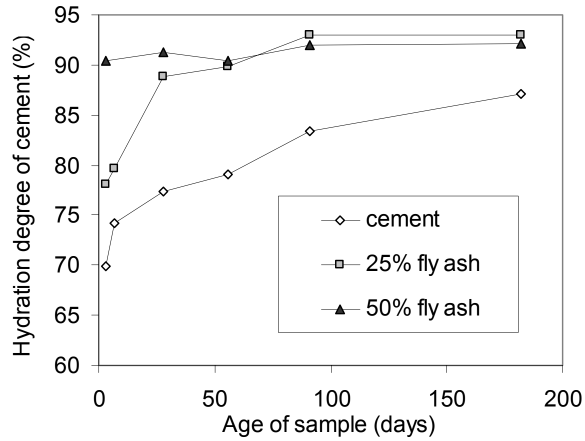

Fig. 4 Hydration degree of cement

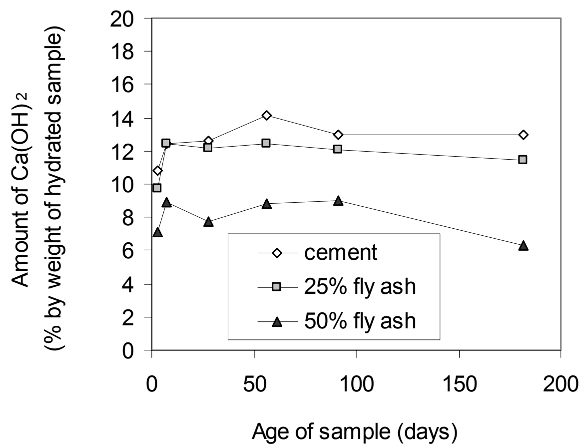

Fig. 5 The amount of $Ca(OH)_2$ at different age

ash and crystal compound in hydrated product and total amount of amorphous compound were quantified.

3. RESULTS AND DISCUSSION

3.1 Verification of Rietveld Analysis

It was reported that the amount of $Ca(OH)_2$ from thermal analysis (DTA) and thermo gravimetric (TG) is the most accurate. On the other hand, it is well known that the amount of unhydrated cement from Backscattered electron image analysis (BSE) is realistic. In this paper, these two methods were used to verify the results of Rietveld

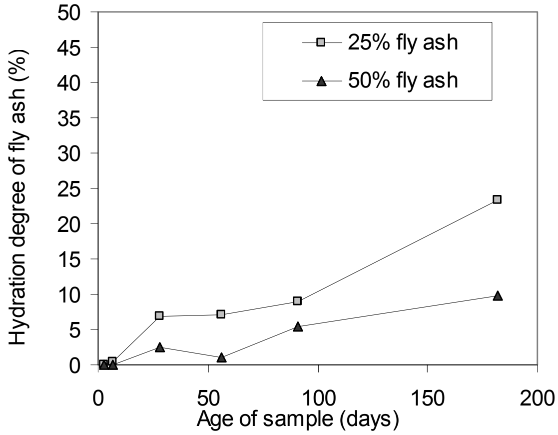

Fig. 6 The degree of hydration of fly ash

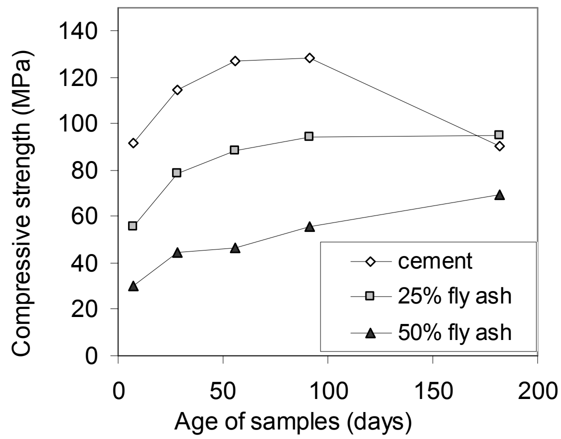

Fig. 8 Compressive strength as a function of time

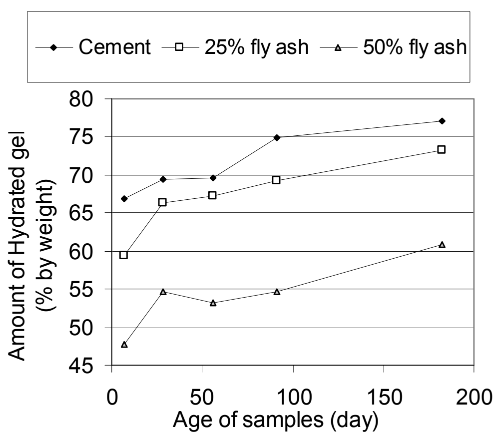

Fig. 7 The amount of hydrated gel at different age

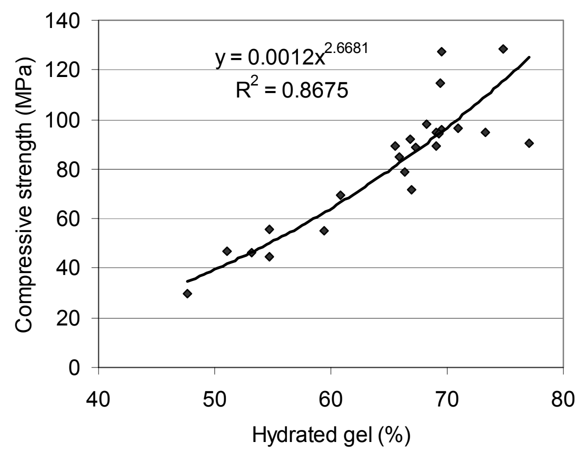

Fig. 9 The relation between compressive strength and hydrated gel

analysis. Figures 2 and 3 show the comparison between $Ca(OH)_2$ from Rietveld analysis and those from thermal analysis, the comparison between unhydrated cement from Rietveld analysis and those from BSE image analysis, respectively. In figure 2, there is good general agreement between two techniques. In figure 3, close agreement between two different measurement techniques is also obtained.

From these results, we can conclude that the quantitative analysis of unhydrated cement and $Ca(OH)_2$ using XRD-Rietveld method are very accurate.

3.2 Data From Rietveld Analysis

At least two data can be extracted from Rietveld analysis: the amount of unhydrated cement and $Ca(OH)_2$. From the amount of unhydrated cement, we can estimate hydration degree of cement. Figures 4 and 5 show hydration degree of cement and the amount of $Ca(OH)_2$ as a function of time, respectively. By using Rietveld analysis, we can know how fly ash effect the hydration of cement. From figure 4, the hydration degree of cement increased when fly ash was replaced. Figure 5 shows that, the amount of $Ca(OH)_2$ reduced as the replacement ratio of fly ash increased.

3.3 Data from Selective Dissolution

Rietveld analysis cannot directly estimate hydration degree of fly ash because anhydrous fly ash originally includes a large amount of amorphous component. However, the amount of unhydrous fly ash in cement-fly ash mixes can be measured by selective dissolution. The validity of this method was described in our previous paper [4]. The hydration degree of fly ash is shown in figure 6. The hydration degree decreased as the replacement ratio of fly ash increased.

3.4 Combining Rietveld Analysis and Selective Dissolution

In unitary system such as Portland cement paste, the amount of hydrated gel can be calculated from data extracted from Rietveld analysis. However, in the case of fly ash-cement system, we need to combine the Rietveld analysis and the selective dissolution to calculate the amount of hydration gel. The amount of hydrated gel is shown in figure 7. By using this method, we can find amount of hydrated gel, which affects the strength and durability of concrete.

3.5 Strength

Compressive strength is shown in figure 8. The compressive strength of cement paste increases until 91 days but suddenly drops at 182 days. As for samples including fly ash, of which replacements ratio is 25% and 50%,the compressive strength continually increases until 182 days. At 182 days, the compressive strength of sample with 25% of fly ash replacement ratio is higher than that of cement paste.

The relation between compressive strength and hydrated gel is shown in figure 9. The relationship between them can represent by a single curve, regardless of replacement ratio of fly ash. The compressive strength increases as the amount of hydrated gel increases.

4. CONCLUSIONS

This study is the first attempt to understand quantification of hydration of binary cementitious system. The amount of $Ca(OH)_2$ and unhydrated cement were verified by thermal analysis and backscattered electron image analysis, respectively. From the above result, we can conclude that by using our purposed method, the amount of unhydrated cement, unhydrated fly ash, hydration degree of cement, hydration degree of fly ash, $Ca(OH)_2$ and hydrated gel can be found.

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