

The Fluidity of Cement Pastes with Fly Ashes Containing a Lot of Unburned Carbon

Seung-Heun Lee,[†] Akira Kawakami,* Etsuo Sakai,* and Masaki Daimon*

Faculty of Materials & Chemical Engineering, Kunsan National University, Kunsan 573-701, Korea

*Department of Metallurgy and Ceramic Science, Graduate School,

Tokyo Institute of Technology, 2-12-1 Ookayama, Meguro-ku, Tokyo 152-8552, Japan

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ABSTRACT

Fly ashes containing 6.1-16.5 wt% of unburned carbon were treated thermally at 500°C for 3 h and thus, the content of unburned carbon was decreased below 2.1 wt%, the range of particle size distribution became narrower and the mean particle size became smaller. Besides, the properties of particles in fly ashes were improved, particularly the particle shape became close to a spherical type. The fluidity of cement pastes containing fly ashes treated previously at 500°C for 3 h was increased much than that of cement pastes containing original fly ashes. When the added amount of superplasticizer was over the saturation amount, there was no correlation between the amount of unburned carbon in fly ashes and the apparent viscosity of cement pastes actually. On the contrary, when the added amount of superplasticizer was below the saturation amount, there was a correlation.

Key words : Fly ash, Carbon, Superplasticizer, Cement paste, Fluidity

1. Introduction

Coal-fired power plants have been tried to decrease the combustion temperature on account of environmental problems.¹⁾ Therefore, the quality of fly ashes varies severely and fly ashes including a great deal of unburned carbon tend to increase in its generated amount. Hence, in view of an efficient use for resources, new techniques should be developed acutely in order to improve the quality of fly ashes.²⁻⁵⁾ Presently, the amount of unburned carbon is the most important factor for the quality of fly ashes discharged from coal-fired power plants. The unburned carbon in fly ashes causes some effects, particularly when fly ashes are used as a mineral admixture for concrete.⁶⁻⁸⁾ It reduces entrained air and can also decrease water reducing effect and retarding effect due to the organic admixture.^{1,6,9)}

In order to reduce the amount of unburned carbon in fly ashes, several methods have been tried but can be classified broadly as follows. Concretely, one method is that the power plant operational process is improved, in which the enhancement of boiler heat efficiency, the improvement of collection method for fly ashes are included.⁶⁾ Another method is that once discharged as a by-product, unburned carbon can be separated or removed. The techniques for

removing unburned carbon from fly ashes comprise various kinds of air classification, electrostatic separation, column flotation and the like.^{7,8,10)} Two types of unburned carbons existing in fly ashes have been reported.^{1,11)} One is of relatively large size particles since carbon particles are generated from incomplete combustion. The other which is made of volatile matter from coal and usually called as lace carbon, is of very small size particles below 5 μm . The air classification and the electrostatic separation are suitable for separating unburned carbon having large size particles. The column flotation can separate unburned carbon having very small sizes.⁷⁾ However, there are some disadvantages in the column flotation. The effects of flotation agent upon properties of concrete and economical efficiency in accordance with wet process should be solved. The removal of unburned carbon by heat treatment is economical, since this procedure can save fuel from carbon portion mainly by re-combustion. Unfortunately, it costs more additionally and the pozzolan property of fly ashes tends to become worse, after the re-combustion, which is caused by being crystallized in a part of glassy phase and by being agglomerate due to the high temperature for heat treatment.

In this experiment, fly ashes containing 6.1-16.5 wt% of unburned carbon were used and the removal of unburned carbon have been tried by lowering heat treatment temperature in which the glassy phase was not crystallized and the agglomeration phenomenon did not occur. Then, the change of properties of fly ashes and the variation of fluidity of cement pastes were investigated.

[†]Corresponding author : Seung-Heun Lee

E-mail : shlee@kunsan.ac.kr

Tel : +82-63-469-4733 Fax : +82-63-466-2086

Table 1. Chemical Compositions of Original Fly Ashes

Fly ash	SiO ₂	Fe ₂ O ₃	Al ₂ O ₃	CaO	MgO	SO ₃	TiO ₂	Na ₂ O	K ₂ O	C	Ig. loss
A	56.76	2.56	19.13	1.52	0.47	0.42	0.65	0.22	0.77	16.47	17.46
B	55.21	7.52	19.01	3.90	0.93	0.29	0.62	0.57	1.02	10.50	10.98
C	60.95	2.96	20.91	2.35	0.31	0.41	0.75	0.51	1.14	9.54	10.30
D	47.94	5.18	34.42	0.87	0.16	0.34	1.16	0.57	0.52	8.63	9.08
E	50.43	6.29	23.63	6.49	0.93	1.09	1.22	1.99	0.78	6.09	6.57

2. Experimental

2.1. Materials

Five kinds of fly ashes containing 6.09~16.47 wt% of unburned carbon were selected and experimented. These fly ashes were labeled as A, B, C, D and E, in accordance with the higher content of unburned carbons. In order to remove unburned carbon in fly ashes, fly ashes were heat-treated in an electric furnace at 500°C for 3 h in air and the heat treated fly ashes were labeled as A', B', C', D', E' respectively.

Ordinary Portland cement (Blaine 3560 cm²/g, specific gravity 3.15) was used.

2.2. Measurement of physical and chemical properties of fly ashes

The fly ashes were examined by using chemical analysis with an atomic absorption spectrophotometer (SHIMADZU Co., AA-680, Japan) and the amount of unburned carbon was measured by using Carbon Analyzer (HORIBA Co., Chromatic-C, Japan) and the loss on ignition was analyzed on the basis of KS L 5401. Blaine (KS L 5106), BET (Micromeritics, ASAP 2010C, USA), specific gravity (KS L 5110) and particle size distribution (Microtrack-9320 HRA, USA) was measured to characterize physical properties of the fly ashes. The crystalline phases of fly ashes were examined by X-ray diffraction analysis (MAC SCIENCE Co., Japan) and the morphologies of fly ash particles were observed by SEM (AKASHI Co. SR-50, Japan).

2.3. Measurement of apparent viscosity of cement pastes

In order to prepare pastes for samples, the parts of cements were replaced with fly ashes and then mixed with water/(cement + fly ash) 0.40 for 3 min. At this moment, the replacement ratio of fly ashes was adjusted from 20 wt% to 50 wt%. Polycarboxylic acid superplasticizer was added over saturation amount. Viscosities were measured by using cone and plate type rotary viscometer (Hakke Co., RT 20, German) in the shear rate range of 0.3/s – 1000/s – 0.3/s (1 cycle : 6 min.) at 20°C. At the 1000/s of shear rate, the apparent viscosities were estimated.

3. Results and Discussion

3.1. Physical and chemical properties of fly ashes

The chemical compositions of the fly ashes are repre-

Table 2. Physical Properties of Original Fly Ashes

Fly ash	Specific gravity	Blain value (cm ² /g)	BET value (m ² /g)	Mean particle size (μm)
A	2.15	4350	17.42	22.27
B	2.13	3048	7.86	49.49
C	2.16	3953	5.88	13.91
D	2.06	3312	4.09	26.82
E	2.09	3697	4.04	27.62

sented in Table 1. The total amount of SiO₂ and Al₂O₃ were over 74.0 wt%. The loss on ignition was in the range of 6.57~17.46 wt% and contents of unburned carbon were relatively high in the range of 6.09~16.47 wt%. Table 2 shows the physical properties of fly ashes. The specific gravity was in the range of 2.06~2.15 and Blaine value in the range of 3048~4350 cm²/g. The correlation between the amount of unburned carbon and Blaine value did not seem clear, but BET value tend to increase in the range of 4.04~17.42 m²/g, which showed that the more unburned carbon was included in its content, the bigger BET value was.

For the removal of unburned carbon, the optimal temperature and the time period were decided as 500°C and 3 h, respectively. In order to elucidate the change of crystalline phases and the morphologies of particles according to heating temperatures of fly ashes, Lee *et al.*¹²⁾ have examined and reported as below. Fly ashes were heated at the temperature range of 400~1200°C for 3 h and as a result, fly ashes heated at 500°C rarely had the variation of particles. But from at 600°C, fly ashes went through sintering phenomena between particles and at 1000°C, anorthite caused by crystallization was also produced. In this experiment, 500°C was adopted as a temperature for the heat treatment that the crystallization could not happen and the agglomeration of particles might not occur. In order to decide the time period for the heat treatment, the loss of ignition according to time was investigated at 500°C (Fig. 1). Up to 3 h, the loss on ignition increased drastically and it became slower afterward. Therefore, the time period for the heat treatment was determined as 3 h.

Table 3 shows the physical properties of fly ashes after the heat treatment. The unburned carbons were reduced below 2.1 wt% by heat treatment at 500°C for 3 h in air. Before and after the heat treatment, the changes of crystalline phases were observed by X-ray diffraction analysis. The results are shown in Fig. 2. The major crystalline phases of fly ashes were identified as α-quartz and mullite

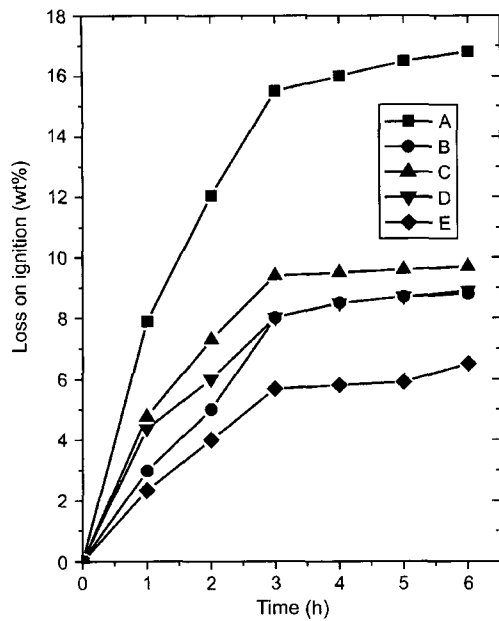


Fig. 1. Loss on ignition of fly ashes according to time.

Table 3. Physical Properties of Fly Ashes after Heat Treatment at 500°C for 3 h in Air

Fly ash	Specific gravity	BET value (m ² /g)	Mean particle size (μm)	Carbon (wt%)
A'	2.39	2.5	12.47	1.5
B'	2.35	0.8	22.08	2.1
C'	2.24	1.1	12.23	0.5
D'	2.20	1.0	17.63	0.7
E'	2.16	0.8	22.50	0.7

and in fly ash B, the minor crystalline phase was detected as magnetite since the content of Fe₂O₃ was higher than any other fly ashes. Fly ash B and E containing a lot of CaO were depicted as peaks of weak lime. As shown in Fig. 2(b), fly ashes obtained after heat treatment did not happen the crystallization according to the heat treatment.

As shown in Table 3, BET values of fly ashes as they can be after the heat treatment reduced radically, compared with the value before the heat treatment in Table 2. Fig. 3 shows the relationship between unburned carbon content and BET value. The correlation with unburned carbon content was confirmed to be linear. And thus, when the specific surface area of fly ash containing high content of unburned carbon is analyzed, BET value measured by N₂ adsorption is elucidated to be more effective than Blaine value measured by the air permeability method.

Fig. 4 shows the changes of particle size distribution before and after the heat treatment. Since unburned carbon having a large particle size induced by the heat treatment, the particle size was decreased and so the mean particle size was also reduced. When the fly ashes were heat-treated at 500°C for 3 h, the particle agglomeration did not happen and the range of particle size became narrower. As shown in

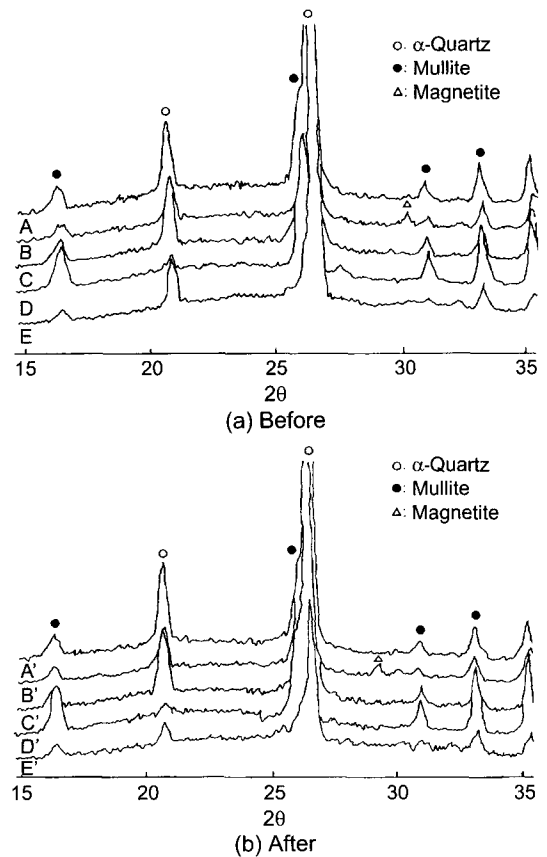


Fig. 2. XRD patterns of fly ashes before and after heat treatment at 500°C for 3 h in air.

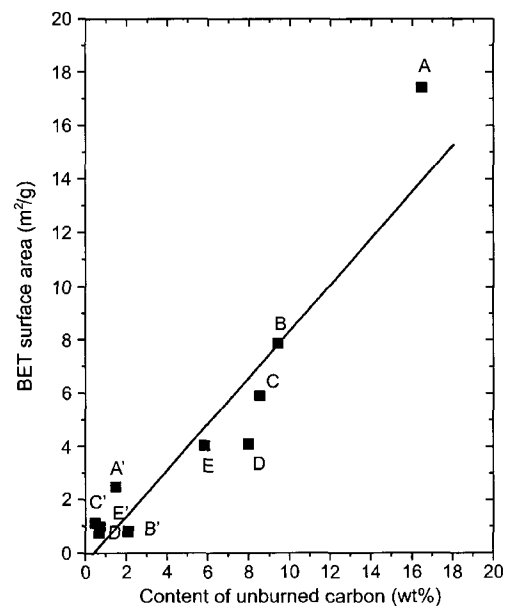


Fig. 3. The relationship between BET surface area and content of unburned carbon in fly ashes.

Fig. 5, porous and irregular shape particles were reduced due to the heat treatment and their morphologies became close to a spherical type.

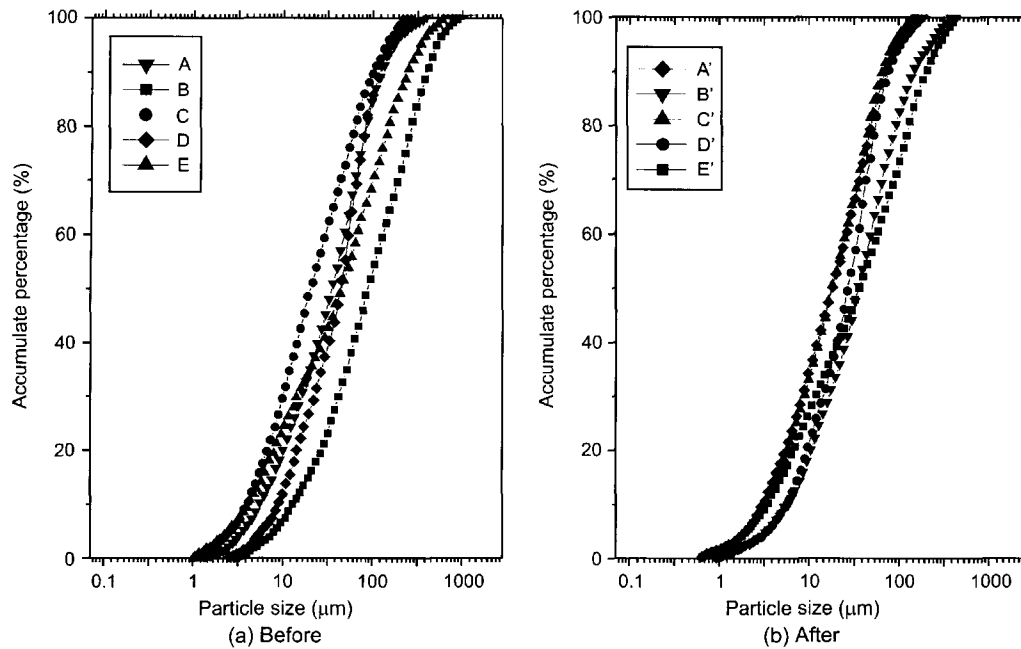


Fig. 4. Particle size distribution curves for fly ash (a) before and (b) after heat treatment at 500°C for 3 h in air.

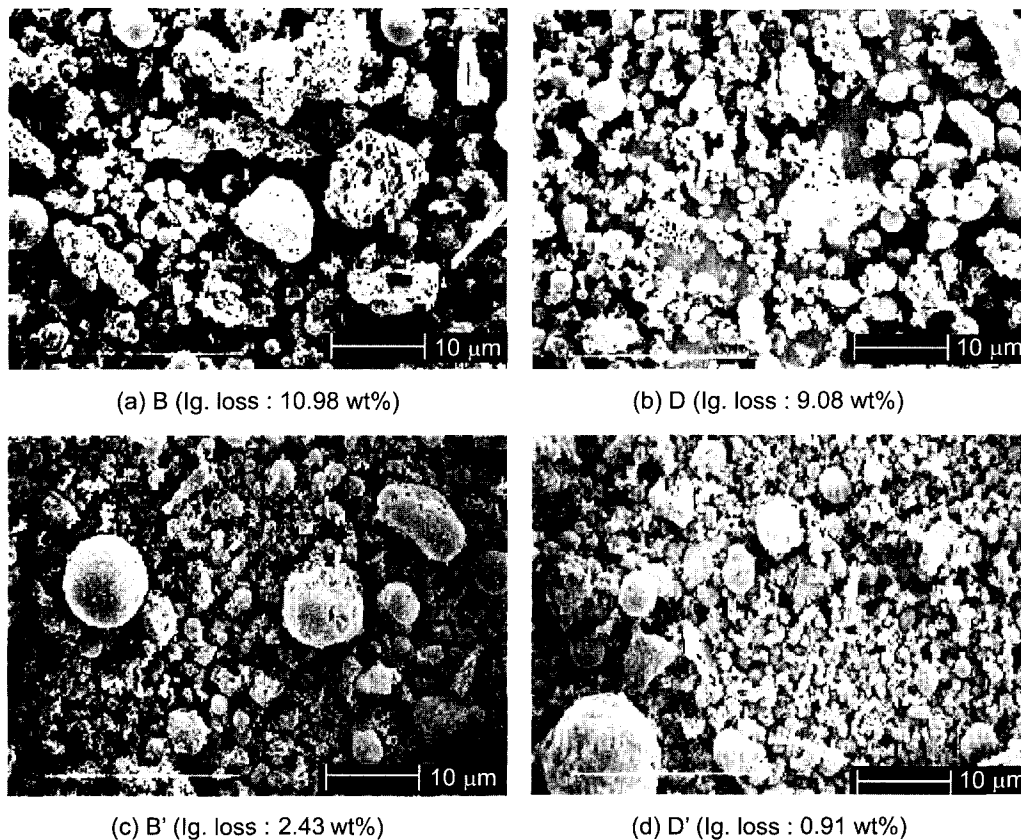


Fig. 5. SEM images of fly ashes (a), (b) before and (c), (d) after heat treatment at 500°C for 3 h in air.

The specific gravity was increased by the heat treatment (Table 3). The reason was that by heat treatment, unburned carbons having smaller specific gravities in the range of 1.2~2.0 were decreased.¹¹⁾

3.2. Fluidity of cement pastes

In the cement paste which was mixed with fly ash A having the highest content of unburned carbon, the relationship between the apparent viscosity and the added amount of

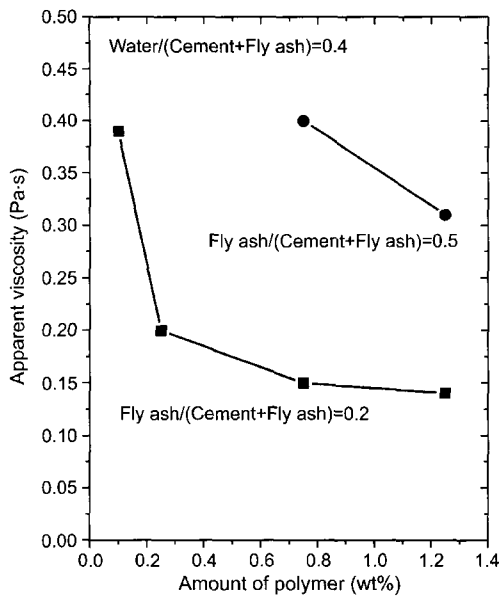


Fig. 6. The relationship between apparent viscosity of cement paste and added amount of superplasticizer.

superplasticizer was investigated. The result is shown in Fig. 6. In the paste containing 20 wt% of fly ash A, the apparent viscosity tended to reduce in addition to the superplasticizer until reaching 0.7 wt% and then, over this content, the apparent viscosity had a constant value. When the content was near 0.7 wt%, the adsorption amount of superplasticizer was considered to reach the saturation point. However, in case of the paste with 50 wt% of fly ash, when the content of superplasticizer reached even over 0.7 wt%, the apparent viscosity seemed to be reduced. As a result, it is verified that the saturation point was over 0.7 wt%.

The unburned carbon among fly ashes adsorbs a great deal of superplasticizer, compare with other particle and thus into the cement paste mixed with fly ashes containing a lot of unburned carbon, a great deal of superplasticizer are added to reach the saturation amount. Therefore, in the paste mixed fly ashes with a more amount of unburned carbon, the amount of superplasticizer is increased to maintain the viscosity constantly.

Fig. 7 shows the relationship of the apparent viscosity of cement pastes and the content of unburned carbon in fly ashes when 0.7 wt% of superplasticizer and 20 wt% of fly ashes were mixed. In any case, the fluidity was improved by heat treatment. This result seems to be a phenomenon that the adsorbed amount of superplasticizer is reduced by the removal of carbon and the superplasticizer is adsorbed onto cement and fly ashes effectively. In addition, because the unburned carbon is porous and irregular shape, it diminishes ball bearing effect and worsens packing density.¹³⁾ And the cement paste with fly ashes is decreased fluidity. But these effects are thought to be reduced by the removal of carbon. As shown in Fig. 7, there might be little correlation between the amount of unburned carbon among fly ashes and the fluidity of cement pastes. Since the added amount of

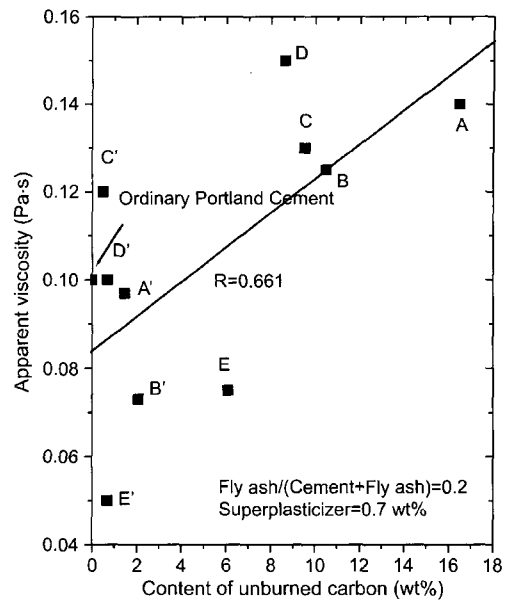


Fig. 7. The relationship between apparent viscosity of cement pastes and content of unburned carbon.

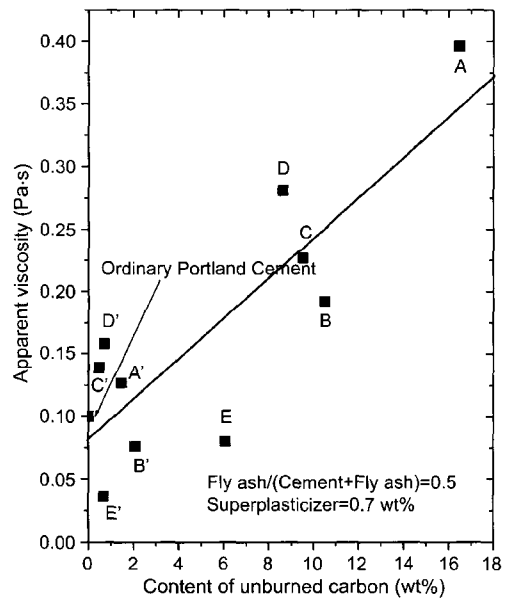


Fig. 8. The relationship between apparent viscosity of cement pastes and content of unburned carbon in fly ashes.

superplasticizer was more than the saturation amount, the fluidity of cement pastes was affected by particle size distribution, particle shape and surface state rather than the effect of superplasticizer.

Fig. 8 shows the relationship of the apparent viscosity of cement pastes and the content of unburned carbon in fly ashes when 0.7 wt% of superplasticizer and 50 wt% of fly ashes were mixed. In adding fly ash, if the added amount of fly ash was varied from 20 wt% to 50 wt%, the viscosity was increased rapidly. This result means that when the substitution ratio of fly ash was 50 wt%, the adsorption amount of plasticizer on the unburned carbon in fly ashes did not

become saturated. In case that the fly ash including unburned carbon massively is utilized, the balance between the adding ratio of superplasticizer and the adding ratio of fly ash is an important factor.

On the other hand, when fly ashes obtained after heat treatment are substituted, the fluidity of cement paste was not changed much, even though substitution ratio increases. Besides, when even fly ash E' was mixed, the viscosity was decreased according to the substitution ratio. The reason is that since the particle size distribution of fly ash E' is wider, the packing density becomes higher. That is to say, it is considered that if the packing density of powder is increased, the retention water remained on the inside of particle cluster should be reduced and the amount of the water participating in the fluidity becomes larger.^{14,15)}

4. Conclusions

The following conclusions can be drawn from this study.

1. Fly ashes including 6.09~16.47 wt% of unburned carbon were treated at 500°C for 3 h and were lowered in unburned carbon content below 2.09 wt%. And thus, there was a correlation between the content of unburned carbon and BET value.

2. Since fly ashes containing a great deal of unburned carbon was treated at 500°C for 3 h, the particle size distribution became narrower and the mean particle size was decreased and then the morphology of particles became close to a spherical shape.

3. The fluidity of cement pastes with fly ashes treated at 500°C for 3 h was improved. When the added amount of superplasticizer was over the saturation amount, the correlation between unburned carbon in fly ashes and the apparent viscosity of cement pastes did not appear. But, when the added amount of superplasticizer was less than the saturation amount, the correlation between unburned carbon in fly ashes and the apparent viscosity of cement paste seemed to be clear.

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