Fresh properties and Compressive strength of Ultra high strength mortar using fly ash finely powdered from single micron to submicron region

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Abstract: This research examined the application possibility of fly ash discharged from coal-fired power plant as an admixture for Ultra High Strength Fiber Reinforced Concrete (designated below as UFC). Silica fume is generally used as an admixture in order to enable mixing at very low water to binder ratio in Japan. However, the quality fluctuation of silica fume is large. Therefore, there are problems with the quality variations of fresh properties and strength characteristics of the UFC. In this study, fly ash finely powdered with particle diameter of 0.4 to 2μm in 50% cumulative volume passing diameter was prototyped. This is aimed at expanding the applications of fly ash generated in large quantities in Japan and to increase its added value. Utilizing this prototype fly ash as the admixture, fresh properties and compressive strengths of the mortars were tested. As a result, mortar with fly ash ultrafine powder displayed better fresh and strength performance than when silica fume is used. Based on the above, the possibility of applying fly ash ultrafine powder as an admixture for UFC was discovered.

Keywords: Fly ash ultrafine powder, Silica fume, Compressive strength, Admixture, mortar

1. Introduction

Fly ash has pozzolanic reaction like silica fume. There are several studies on application of ultrafine fly ash powder as high strength mortar and concrete admixture. There have been multiple studies[1)] in the past which focuses on the strength characteristics using fly ash ultrafine powder with particle diameter of around 5 μm in 50% cumulative volume passing diameter (below D_{50}). However, there are only few studies focusing on the workability and mixing properties with diameter region of 5 μm or less (D_{50} = about 0.8 to 2 μm). Also, wet grinding is mostly used for the production of fly ash ultrafine powder with particle size in the submicron range, which the manufacturing cost is higher than dry grinding.
In this study, fly ash was finely powdered to single micron to submicron region with D_{50} = 0.4 ~ 2 μm by dry grinding. Using the produced fly ash ultrafine powder, the fresh properties and compressive strengths of the mortars were checked, followed by examination of the optimum

particle diameter of the fly ash ultrafine powder and its mixing ratio. As an application comparison, we also examined the fresh properties and strength characteristics of mortars with silica fume.

2. Characteristics of fly ash ultrafine powder

2.1. Fly ash ultrafine powder used

In this study, the fly ash ultrafine powder was made from fly ash type II, a fly ash type that is standardized within Japanese Industrial Standards - JIS A 6201. The fly ash ultrafine powder was classified into two types, cyclone powder collected by a classifier after dry grinding (designated below as Cy powder), and back filter powder collected by a dust collector after classification (designated below as BF powder). The particle size of Cy powder was D_{50} = 1.8 ± 0.2 μm and BF powder was D_{50} = 0.7 ± 0.2 μm. By combining these two types of fly ash ultrafine powders, prototypes of different particle sizes were manufactured and the optimum particle size and replacement rate were examined.

2.2. Particle size distribution of fly ash ultrafine powder

Table 1 shows the particle sizes and specific surface areas of the fly ash ultrafine powders produced. Here, the Blaine specific surface area was measured by a method which do include porosity into consideration[2)]. The BET specific surface area was calculated from the adsorption amount of nitrogen gas after preliminary vacuum suction at 105 °C for 5 hours. The particle size distribution was measured by a laser diffraction based particle size distribution measuring instrument (Microtrac MT 3300 EX II).

Table 1. The particle size and specific surface area of the fly ash ultrafine powder

Name	Particle size (μm)				Blaine specific surface area (cm^2/g)	BET specific surface area (m^2/g)
	D_{25}	D_{50}	D_{90}	D_{99}		
Fly ash type II	3.82	9.96	32.4	83.3	3,960	1.76
Cy powder	1.13	1.87	3.49	5.88	14,240	4.69
BF powder	0.49	0.67	2.54	12.1	36,920	12.0

2.3. Chemical composition and mineral composition of fly ash ultrafine powder

Table 2 shows the methylene blue adsorption quantity, density, and the chemical composition of Cy powder and BF powder. The methylene blue adsorption quantity was measured for the purpose of evaluating the unburned carbon amount and was measured according to JCAS I-61, standard test method of cement association. Chemical components were measured according to JIS R 5202 "Methods for chemical analysis of cement". Density was measured according to JIS R 5201 "Physical testing methods for Cement".

Smaller the particle size of Cy powder and BF powder, greater the ignition loss and the methylene blue adsorption quantity. Particularly as for the BF powder, it is considered that the value of unburnt carbon increased due to classification. Also, it is found that smaller the particle size, higher the density when compared with fly ash type II. It seems that the increase in density was caused by the decreased voids in the particles due to grinding of the hollow particles of the fly ash. Figure 1 shows the SEM images of before and after grinding. As the particle diameter of Cy powder and BF powder became smaller, the shape changed from spherical particles to irregular shape. From this SEM image, it is thought that the particles are well dispersed.

Figure 2 shows patterns obtained from X-ray diffraction. Mullite and quartz have been identified. Both fly ash type II, Cy powder and BF powder had similar peaks. Therefore, no major change has occurred in the crystal structure.

Table 2. Adsorption amount of methylene blue, density, and chemical composition

Name	MB adsorption amount (mg/g)	Chemical composition(%)													Density (g/cm^3)
		ig-loss	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	Na_2O	K_2O	TiO_2	P_2O5	MnO	total	
Fly ash type II	0.46	1.72	56.58	30.90	3.84	2.07	0.59	0.10	0.50	0.78	1.67	0.54	0.04	99.33	2.29
Cy powder	0.61	2.20	56.00	30.79	4.31	1.86	0.49	0.20	0.50	0.79	1.47	0.60	0.04	99.25	2.61
BF powder	2.72	4.45	55.10	28.85	5.19	1.83	0.48	0.29	0.48	0.68	1.31	0.61	0.04	99.31	2.63

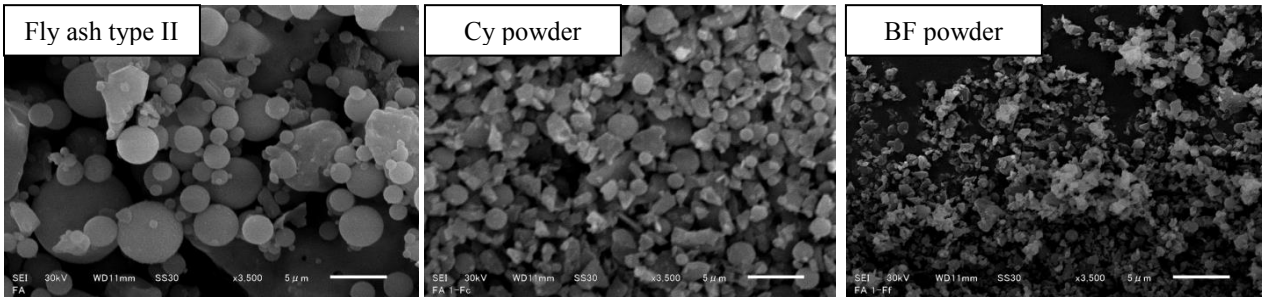

Figure 1. SEM images of before and after grinding

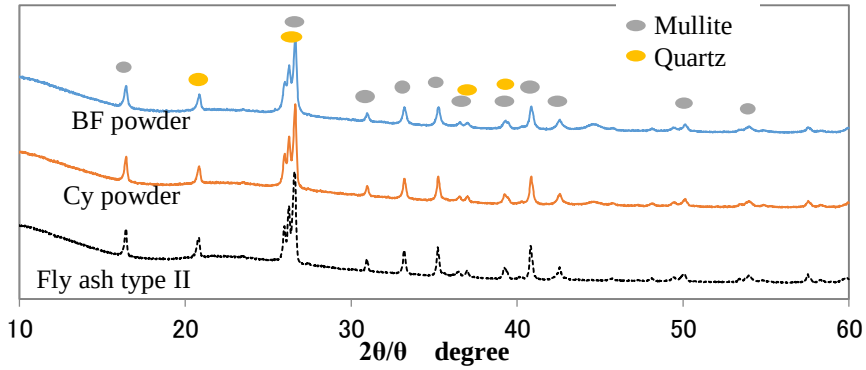

Figure 2. X-ray diffraction patterns

2.4. Comparison of Activity Index of Mortar

Table 3 shows the test results of activity index by mortar, which was tested with reference to JIS A 6207 Annex C "Test method of activity index by mortar of silica fume". For comparison and for reference, standard mortar with silica fume was also tested. Mortar with 100% ordinary portland cement (OPC) and no admixture was used as the base standard. With water to binder ratio set to 30%, experiments were conducted on five levels where various admixtures (Fly ash type II, Cy powder, BF powder and Silica fume) were replaced with 10 weight% relative to OPC. The mortar flow value was adjusted with the superplasticizer to be 260 ± 10mm and the targeted air content was less than 2.0%. The specimens for the compressive strength tests were molded to φ50 × 100mm cylindrical shape. 1 day strength refers to the strength at 24 hours after the addition of water. Specimens for 3, 7, 28 and 91 days strengths were stored and cured in water at 20 °C.

The superplasticizer dosage required for adjusting the flow value was about half with the mortar using Cy powder and BF powder compared to mortar using silica fume. This is because the BET

specific surface area of the silica fume is about 20 m^2 / g, which is very large compared with 4.7 m^2 / g of Cy powder and 12 m^2 / g of BF powder. Therefore, the adsorption amount of the superplasticizer to the silica fume itself increased to obtain the same flow value. Also, BF powder has higher dosage of superplasticizer compared to Cy powder. This can also be due to the BF powder having larger BET specific surface area and ignition loss than Cy powder, resulting in the increased adsorption amount of the superplasticizer to the unburned carbons.

The level of activity index using Cy powder and BF powder was equivalent or higher than the level using silica fume at all ages except for 28 days. Compressive strength was higher with the level using BF powder than with the case using Cy powder. This is considered to be due to the improved reaction rate of the fly ash, caused by smaller particles sizes of BF powder compared to Cy powder. Alternatively, it may be due to fine powder effect. Meaning that the mortar becomes denser by the formation of a large amount of calcium silicate around the fine powder by hydration. The reason activity index at 28 days is smaller than that of silica fume is likely due to lower pozzolanic reaction of fly ash compared to silica fume. A fine powder effect can also be considered as one of the reasons why the activity index of the mortar using Cy powder and BF powder is larger than that of silica fume at 3 and 7days. Therefore, it is necessary to quantitatively evaluate the pozzolanic reactions and clarify which of the potential causes is the true reasoning behind higher compressive strength. As for the compressive strength at 1 day, since it shows a tendency slightly different to results from 3 days, the influence of the superplasticizer dosage is also considered.

From the above it was found that strength characteristics was near same as silica fume when fly ash is grinded to D_{50} = 1.0 μm. This case however, was an experiment with a water to binder ratio of 30%, which as a high strength mortar can be considered to be relatively large. Therefore, to confirm crucial properties of high-strength mortars such as workability and mixing performance, experiment with lower water to binder ratio is necessary. In the next section, optimum substitution rate and particle size of fly ash ultrafine powder at lower water to binder ratio is investigated.

Table 3. Mortar test result (JIS R 6207)

Name	SP/B (%)	DF/B (%)	Flow Value (mm)	Air(%)	Compressive strength (N/mm^2)					Activity Index (%)				
					1 day	3 days	7 days	28 days	91 days	1 day	3 days	7 days	28 days	91 days
Fly ash type II	0.89	0.020	261	0.5	28.7	72.2	86.8	109	125	86	90	92	96	103
Cy powder	0.85	0.010	262	0.5	28.7	76.2	95.0	122	143	86	95	101	108	118
BF powder	1.15	0.001	266	0.1	27.4	81.0	105	129	148	82	101	111	114	122
Silica fume	1.80	0.020	255	1.5	26.4	74.3	97.0	131	143	79	93	103	116	118
OPC	1.05	0.020	259	0.4	33.4	79.9	94.2	113	121	100	100	100	100	100

3. Optimum replacement rate and particle size of fly ash ultrafine powder at low water binder ratio

3.1. Materials used

Table 4 shows the materials used. The fly ash ultrafine powders 2 to 4 were prototyped by adjusting the mixing ratio of Cy powder (D_{50} = 1.8 ± 0.2 μm) and BF powder (D_{50} = 0.7 ± 0.2 μm). For comparison, fly ash ultrafine powder 1 (FA 2.4) was separately prepared by dry grinding. In addition, fly ash ultrafine powder 5 (FA 0.4) having the same particle size as silica fume was prototyped by wet grinding. The numerical values of the symbols in Table 4 displays the D_{50} of fly ash ultrafine powder and silica fume.

Table 4. Materials used

Name	Material	Symbol	D_{50}(μm)
Water	Water	W	-
Cement	Ordinary portland cement	OPC	-
Admixture	Fly ash ultrafine powder 1	FA2.4	2.37
	Fly ash ultrafine powder 2	FA1.5	1.52
	Fly ash ultrafine powder 3	FA1.0	1.08
	Fly ash ultrafine powder 4	FA0.6	0.61
	Fly ash ultrafine powder 5	FA0.4	0.38
	Silica fume	SF0.4	0.39
Fine aggregate	Standard silica sand	S	2.64
Super plasticizer	Polycarboxylic acid-based polymer	SP	-

3.2. Mix proportions of mortars and methods

Table 5 shows the levels compared in this study. The contents of the mortar and the mixing method were referred to JASS 5M - 701: 2015. Here, JASS5 is the Japanese Architectural Standard Specification for Reinforced Concrete Work. The ratio of the binder and the fine aggregate (dry quartz sand) was B:S = 1:1.4 by weight, and the water to binder ratio was 17%. The water to binder ratio was set to 17% as this value was the minimum ratio which SF 0.4-15 could be mixed with the upper limit of recommended superplasticizer dosage. For mixing of mortar, an ASTM mixer was used. The rotation speed of the mixer was set to 139 rpm and the method was as follows;

Dry mixed for 30 seconds → Add water and superplasticizer → Mortarization time + 2 minutes mixing → 5 minutes stopping mixing → 30 seconds mixing.

OPC, fly ash ultrafine powder and silica fume were weighed separately. The mortar flow value was adjusted with the superplasticizer to be 260 ± 10mm.

Table 5. The levels compared in this study and results of this experiment

Symbol	W/B (%)	Admixture type	Ratio of admixture (%)	SP/B (%)	Flow Value (mm)	mortarization time (s)	Compressive Strength (N/mm^2)	
							7 days	28 days
FA2.4-30	17	FA2.4	30	It is not mortarized and can not be mixed.				
FA1.5-30		FA1.5	30	1.1	270	40	110	135
FA1.0-30		FA1.0	30	1.1	254	20	108	136
FA0.6-30		FA0.6	30	1.8	270	90	105	129
FA0.6-15		FA0.6	15	1.6	252	240	109	132
FA0.4-15		FA0.4	15	2.5	262	180	112	139
SF0.4-15		SF0.4	15	4.0	254	120	106	138

In this experiment, mortarization time, flow value and compressive strength were measured. As shown in Figure 3, the mortarization time was measured from the start of mixing until the mortar was homogenized by visual observation. The motarization time was set as the time taken for the water, binder and the sand to completely homogenize and judged that the state would not change, shown in the right photograph in figure 3. The evaluation method for mortarization time was uniquely determined for this experiment. The specimens for the compressive strength tests were molded into φ50 × 100mm cylindrical shape. Specimens for compressive strengths at 7 and 28 days were stored and cured in water at 20 ° C.

Figure 3. Judgment as mortarization time

3.3. Experimental Results

The results of this experiment are shown in Table 5. The superplasticizer dosage required to maintain same flow value was significantly lower with the level using the fly ash ultrafine powder compared to that of silica fume. This was the same result as the previous section.

Mortarization time was faster in order of FA 1.0 - 30, FA 1.5 - 30, FA 0.6 - 30, SF 0.4. 15, FA 0.4 - 15, FA 0.6 - 15. At the level of mixing ratio of 30%, FA 2.4-30 was mixed for more than 10 minutes with the maximum limit of recommended superplasticizer dosage and still could not be mortarized. Also, as the FA 1.5 - 30, FA 1.0 - 30 and the fly ash became finer, the mortarization time became shorter. However, when it became finer to the level of FA 0.6 - 30, the mortarization time became longer.

The Fuller-Thompson curve is an ideal particle size distribution curve in which powder particles are closest packed. Closer to the curve, the particles of the binder are in the closest packed state, and good fluidity can be obtained with a smaller amount of water. Figure 4 shows the particle size distribution of the binder used in this experiment and also the ideal particle size curve of Fuller-Thompson. With FA 2.4-30, the proportion of powder of 1 μm or less was small, and optimal packing properties could not be obtained. Therefore, it is presumed that this is the reason why mortarization was not successful. On the other hand, it is speculated that FA 0.6-30 have lengthened the mortarization time as the particle size of about 0.6 to 3 μm is too large.

From Figure 4, while SF 0.4 - 15 and FA 0.4 – 15 displays almost the same particle size distribution, mortarization time was longer for FA 0.4 - 15 by approximately 60 seconds. This is presumed that the mortarization time became longer since the fly ash ultrafine powder is more angular than the silica fume. There were also differences in superplasticizer dosage between SF 0.4 - 15 and FA 0.4 - 15.

The mortarization time of FA 1.0 - 30 was 20 seconds whilst the mortarization time of SF 0.4 - 15 was 120 seconds. FA 1.0 - 30 was able to significantly shorten mortarization time compared to SF 0.4 - 15. Compared with Fuller-Thompson's ideal particle size curve, FA 1.0 - 30 lacks particle sizes of 0.6 μm or less and also, compared to FA 1.0 - 30, SF 4 - 15 and FA 0.6 - 15 contains particles with larger diameter of about 0.4 μm and only few with particle sizes of around 2 μm. On the other hand, when replacing cement with silica fume, it is reported that closest packing tends to occur by setting the substitution rate to 10 to 20%[3)]. From Figure 4, SF 0.4 - 15 shows the particle size distribution closest to the ideal particle size curve of Fuller - Thompson. However, the mortarization time was significantly longer than FA 1.0 - 30. For fly ash ultrafine powder with different in particle shape and silica fume, it is considered that the particle size of

about 0.6 to 2 μm is most effective for improving the mortarization time. Consequently, the influence of the filling state of particles containing fine particles on the fluidity of mortar is a future subject.

7 and 28 days compressive strength was equal to the mortar with silica fume.

From the above, it shows that it is possible to shorten the mixing time by using fly ash ultrafine powder having D_{50} = 0.6 to 1.5 μm as the binder, to an amount twice lower as that of the UFC with silica fume.

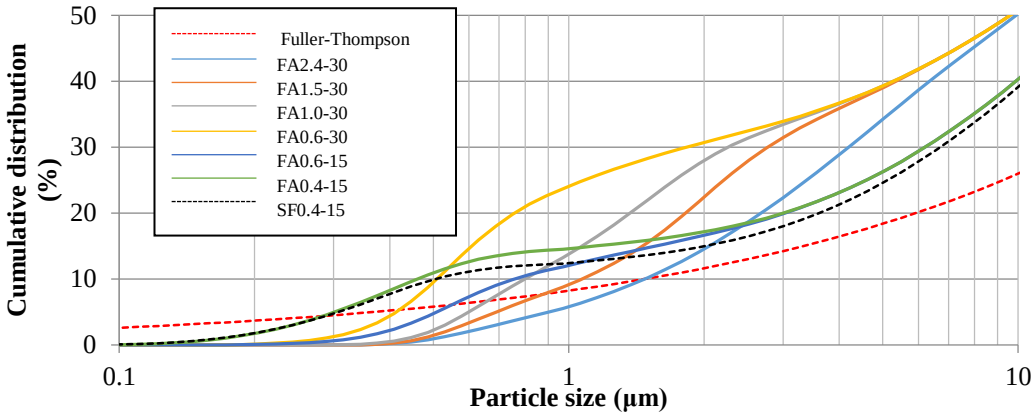

Figure 4. Particle size distribution of the binder used in this experimental level

4. Comparison with high strength fiber reinforced mortar

4.1. Used materials and experimental level and method

The materials used except for fly ash ultrafine powder are the same as in Table 4. The fly ash ultrafine powder was adjusted to D_{50} = 0.93 μm. The water to binder ratio was set to 15.7%. Experiments were conducted on two levels where fly ash ultrafine powder and silica fume were replaced with 15 weight% relative to OPC. The superplasticizer dosage was fixed at 2.5 weight%. The fiber was steel fiber (diameter: 0.2 mm, length: 15 mm, density: 7.85 g / cm^3) and the added ratio was 2.0 vol%. For mixing of mortar, an ASTM mixer was used. The rotation speed of the mixer was set to 216 rpm and mixing method was as follows;

Dry mixed for 30 seconds → Add water and superplasticizer → 10 minutes mixing → 3 minutes stopping mixing → 2 minutes mixing after addition of fiber. In the previous section, flow test, compressive strength and flexural strength test were conducted. The specimen size for flexural strength determination was 40 × 40 × 160 mm. Flexural strength was measured in accordance with JIS A 1106 "Method of test for flexural strength of concrete". 1 day compressive strength refers to the strength at 24 hours after addition of water. Compressive strength and flexural strength after steam curing was also tested. Specimens for flexural strengths at 7 days were stored and cured in water at 20 °C. Here, the steam curing was pre-aged in an environment of 20 °C before removing the mortar from the mold next morning, and cured for 24 hours at a temperature of 90 °C.

4.2. Experimental Results

The results of this experiment are shown in Table 6. Even with the same dosage of superplasticizer, the flow value of the mortar became larger with fly ash ultrafine powder than

the mortar with silica fume. Even after mixing the fibers, same tendency was observed. Compressive strength of mortar with fly ash ultrafine powder was 10 N / mm^2 higher than the mortar with silica fume at 1 day. The reason for this seems to be that the activity of the pozzolanic reaction of fly ash ultrafine powder has improved by steam curing. Or it is thought that it is because the porosity of mortar with fly ash ultrafine powder became small. Therefore, it is possible to add prestress at a stage earlier than silica fume, which may lead to improvement in productivity. Compression and flexural strength after steam curing of specimen with fly ash ultrafine powder was equal to or higher than that of silica fume.

From the above it was found that high strength fiber reinforced mortar with ultrafine powder as the admixture displays equal or greater fresh and strength characteristics compared to the mortar with silica fume as the admixture. In future work, it is also necessary to grasp shrinkage characteristics.

Table 6. The results of this experiment

Symbol	W/B (%)	Admixture type	Ration of admixture (%)	SP/B (%)	Flow Value (mm)		Compressive Strength (N/mm^2)		Flexural Strength (N/mm^2)	
					Before fiber mixing	After fiber mixing	1 day	After steam curing	After steam curing	7 days
FA0.8-16	15.7	FA0.8	15.0	2.5	309	279	52.7	201	32.7	30.6
SF0.4-16		SF0.4			295	262	39.5	205	32.3	30.1

5. Conclusions

In this study, the fresh properties and compressive strength characteristics of mortar mixed with the prototype fly ash ultrafine powder as an admixture for high strength mortar were tested. As a result, the following knowledge was obtained.

- In regards to mortar with the water binder ratio of 30%, it was found that by grinding the fly ash to D_{50} = 1.0 μm, the compressive strength performance is the same as the mortar with silica fume.
- In regards to mortar with water to binder ratio of 17%, it is possible to shorten the mixing time by using the fly ash ultrafine powder having D_{50} = 0.6 to 1.5 μm as the binder, to an amount twice lower than that of the UFC with silica fume.
- It was found that when fly ash ultrafine powder is used as admixture for high strength fiber reinforced mortar, it shows fresh properties and strength characteristics equal to or higher than that of silica fume.

6. References

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