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Development of Production Method for Carbon-free Fly Ash (CfFA) and Properties of Concrete Containing CfFA

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ABSTRACT

To enhance the effective use of fly ash in Japan, the method for removing unburned carbon is proposed. The forced air pulverization system with a burning process was developed to produce carbon-free fly ash (here in after referred to as CfFA) with loss on ignition (LOI) as low as 1.0% or less. The characteristics of CfFA were investigated and several tests were performed to examine the applicability of CfFA as a concrete admixture by measuring properties of CfFA concretes. Consequently, it was confirmed that this system is capable of producing three kinds of CfFA with LOI of 1.0% or less which perfectly correspond to Type IV, Type II and Type I in Japan Industrial Standards, *JIS A 6201*. In addition, CfFA was ensured to have no unfavourable effects on concrete but promotes the qualities of concrete regardless of the characteristics of its raw fly ash.

INTRODUCTION

Fly ash is known as a fine concrete admixture because the long-term strength development is promoted by its pozzolanic reaction activity. It is also very effective in chemical resistance and durability, and reduction of alkali silica reaction, water content and drying shrinkage strain. For above respects, fly ash has been standardized by Japan Industrial Standards, *JIS R* 5213(Portland fly-ash cement) and JIS A 6201(Fly ash for use in concrete). Besides, fly ash is one of the sustainable procurement products (also called as green procurement products) designated by Ministry of Land, Infrastructure, Transport and Tourism in Japan. Nevertheless, the effective use of fly ash in concrete has not been widely spread in Japan.

The annual amounts of fly ash produced from coal-fired power stations in Japan are shown in **Fig.1**. According to Japan Coal Energy Centre, approximately 7 million tonnes were produced annually until 1998. In 2007, it had eventually increased to 12 million tonnes, which is about 1.7 times the quantity in 1998. Simultaneously, the beneficial use of fly ash, both in ratio and amount, increased in contrast to landfill use and finally reached 96% of the total production in 2007. However, as shown in **Fig.2**, 66% of the beneficial use was just for the replacement of clay, a cement raw material. Furthermore, even though 18% was used for



the construction-related applications, the use as a mineral admixture or blended cement accounted for only a small portion of it.

What is disturbing the spread of effective use of fly ash in concrete is "carbon content". The presence of carbon in fly ash adversely affects workability of concrete and the variation in carbon content leads to an erratic behavior with respect to air entrainment since the porous carbon particles adsorb a part of air-entraining agents. Carbon content is usually indicated by the value of loss on ignition (LOI). As illustrated in **Fig.3**, the linear relationship between LOI and the unburned carbon content in fly ash proves the identicalness of the two, although LOI is slightly greater than carbon content since it also includes some combined water and carbon dioxide (CO_2) losses. The presence and variation of carbon content even in JIS fly ash is a matter of course, considering the facts that the type and source of coal burned in a power station are not consistently uniform even in a short term; power stations vary their operations in response to power demand (day-to-day variations); the design of coal-fired boiler and the type of dust collection equipment are different in each power station; and moreover, fly ash is only a by-product to which not much attention is paid.

Fig.4 shows how carbon content (LOI) and diversity in characteristics of fly ash affect air content of concrete, where the same amount of air entraining agent were applied to three concretes containing different kinds of fly ash. As can be seen from this figure, the higher the LOI was, the lower air entrainment obtained. When LOI was over 1.0%, the air contents reacted differently, none of them reaching the target air content. When LOI was less than

1.0%, however, all the concretes achieved the target air content easily, implying that the carbon content less than 1.0% has no unfavorable influence on air entrainments regardless of the characteristics of fly ash. In *JIS A 6201*, the various requirements are specified for fly ash to be a fine admixture. However, the upper limits of LOI specified are "5.0% or less" for JIS II and IV, and "3.0% or less" for JIS I fly ash; relatively high numbers which possibly affect the air-entrainment.

Fly ash is very attractive admixture for concrete for its high pozzolanic reaction activity. The variations in the carbon content and characteristics of fly ash, however, make the quality control of concrete very difficult, resulting in the unwillingness for concrete producers to use. Therefore, to extend the effective use of fly ash in concrete in Japan, the unburned carbon should be removed to provide fly ash with a uniform quality

In this research project, first, the forced air pulverization system with a burning process was developed to produce carbon-free fly ash with LOI as low as 1.0% or less. Then, the characteristics of CfFA were investigated. Finally, several experiments on the properties of fresh and hardened concretes with CfFA were conducted to determine the applicability of CfFA as a concrete admixture.

DEVELOPMENT OF CfFA PRODUCTION SYSTEM

Outline of Production System

The CfFA production system, as illustrated in **Fig.5**, consists of 2 processes; a burning process and a pulverization and separation process. The mechanisms of the system are as follows.

Burning Process -Rotary Kiln. The burning process is operated by a rotary kiln which is composed of three parts; heating, stabilizing, and cooling. Fly ash starts self-combustion after reaching 600 degrees Celsius and loses its pozzolanic reactivity when reaching over 950C. In the heating part, the burner is carefully adjusted to maintain the heating temperature between 800 and 900C so that fly ash starts self-combustion. Then, fly ash proceeds to the stabilizing part where its unburned carbons are burned out. The temperature in this part is maintained over 600C by the heat generated from fly ash self-combustion, thus additional combustion supply is unnecessary. Finally, fly ash reaches the cooling part and cools down the temperature so that it dose not go over the critical temperature of 950C by self-combustion. At this point, CfFA with LOI of 1.0 % or less is created.

Pulverization and Separation Process. As illustrated in **Fig. 5**, this process is composed of three equipments; a hyper cyclone, a cyclone separator and a bug filter.

Hyper Cyclone (H/C): The particles of CfFA start to be pulverized by the action of collision and friction caused by the swirl of strong forced wind and also by the rotary wing installed inside the cyclone. The swirl function creates globularity of particles, and the rotary wing makes them much finer. Here coarse and heavy particles of CfFA are collected.



Fig.5 Outline of production system of CfFA

Cyclone separator (B/C): To meet various manufacturing conditions and CfFA qualities, this separator was equipped with a guide vane to control the swirl wind inside the cyclone and became capable of separating CfFA relatively easily. From this equipment, smaller particles of CfFA are collected.

Bug Filter (BG): The finest ashes finally left from the above equipments are collected in this filter.

Through this process, CfFA produced from the rotary kiln are pulverized and separated into three kinds of CfFA, which are much higher value-added CfFA.

Characteristics of CfFA

To testify the quality of CfFAs, two kinds of raw fly ash were experimentally inserted into this system. **Table 1** shows *JIS A 6201* quality requirements on moisture content, ignition loss, density, fineness degree, value of flow, and pozzolanic reaction activity for the four classes of JIS fly ash. **Table 2** reveals the characteristics of the two raw fly ashes ((1) and (2)) and each followed by three CfFAs produced from this experiment. H/C, B/C, and BG refer to the CfFA collected in each equipment.

According to **Table 2**, the ignition loss of raw fly ash (1) and (2) are 7.61% and 5.95%, respectively, and all of the CfFAs are made less than 1.0% of ignition loss. The value of LOI becomes slightly larger in the following order: H/C < B/C < BG. This is because unburned carbon (still remained after the burning process) with low density are blown by the strong forced air into the bug filter.

Fig. 6 shows the particle size distribution of each CfFA. As for a specific surface area of CfFA, H/C shows $2500 \text{ cm}^2/\text{g}$, BC $3800 \sim 4200 \text{ cm}^2/\text{g}$, and BG $9500 \sim 57000 \text{ cm}^2/\text{g}$. The mean particle size is in the order of H/C > B/C > BG. In particular, fly ash collected in BG contains fine particles less than 1µm. SEM (Scanning Electron Microscope) pictures of fly ash are shown in **Fig.7**. It is observed that raw fly ash includes plenty of porous unburned carbons, coarse and irregular particles are included in H/C, and plenty of spherical (globular) particles are included in B/C and BG. For the value of flow, H/C shows the smallest one, and it becomes larger as the mean particle size becomes smaller in B/C and BG.

		J								
	Туре	Ι	II	III	IV					
Moisture c	ontent (%)	≦1.0								
Loss or	n Ignition (%)	≦3.0	≦5.0	≦8.0	≦5.0					
Dens	sity (g/cm³)		≧1.95							
Finanacc	Retained on 45µm sieve (%)	≦10	≦40	≦40	≦70					
Filleness	Specific surface blaine (cm ² /g)	≧5000	≧2500	≧2500	≧1500					
Value	of flow (%)	≧105	≧95	≧85	≧75					
Activity	28-day	≧90	≧80	≧80	≧60					
Index (%)	91-day	≧100	≧90	≧90	≧70					

Table 1 Physical Properties of Fly Ash (JIS A 6201)

Table 2 Physical Properties of CfFA

Type of Fly Ash		Density	Loss on	Mean particle	Retained	Specific	Specific surface	Ratio of	Activity index		
		(g/cm ³)	ignition (%)	size*1 (µm)	45µm*1 (%)	surface*1 (cm ² /cm ³)	Blaine*2 (cm²/g)	flow value (%)	Age of 28days	Age of 91days	
	Raw	2.23	7.61	16.76	17.6	5010	3218	94.6	-	-	
(1)	H/C	2.37	0.35	38.31	42.9	2280	1532	88.3	83.2	80.9	
(1)	B/C	2.26	0.64	13.98	7.54	5270	3540	102.6	98.7	90.2	
	BG	2.41	0.67	5.98	5.53	21330	14329	107.5	102.3	104.7	
	Raw	2.25	5.95	22.29	31.0	5380	3614	-	-	-	
(2)	H/C	2.65	0.13	32.06	34.3	3840	2573	96.1	87.9	79.5	
(2)	B/C	2.74	0.45	11.05	10.2	7960	5333	105.4	88.8	93.6	
	BG	2.79	0.76	2.09	0.00	54390	36441	106.5	95.4	102.8	
JI	S II	2.33	1.69	15.2	9.0	5230	3670	111.2	81.4	101.3	

*1 : measured by laser diffraction particle size distribution analyzer

*2 : apprpximated value based on measured value by laser diffraction particle size distribution analyzer

H/C : CfFA obtained by hyper cyclone

B/C : CfFA obtained by cyclone sepatator

BG : CfFA collected by bug filter



Fig.6 Particle size distribution of various CfFA

Table 3 shows the chemical components and their percentages in the raw fly ash (1), (2) and CfFAs. Among the several components in fly ash, silicon dioxide (SiO_2) , aluminium oxide (Al_2O_3) , iron oxide (Fe_2O_3) and carbon (C) are the major chemical components. After going through the production system (burned under 850 C), no significant changes occurred to the structure of the components and the percentages, except for the considerable reduction in carbon content and the increase in iron content.



Fig. 7 SEM pictures of fly ash (Fly Ash (1))

	Table	3 Chemi	cal compo	onent of C	CfFA			
Comple			Che	emical Cor	nponent ((%)		
Sample		SiO ₂ Al ₂ O ₃ Fe ₂ O ₃ CaO Mg						

Comple										
Sample	SiO ₂	AI_2O_3	Fe ₂ O ₃	CaO	MgO	С				
Raw(1)	67.05	15.1	2.90	0.48	1.09	7.36				
Raw(2)	52.63	25.61	5.52	2.16	1.59	4.69				
CfFA(1)	-	-	3.48	-	-	0.53				
CfFA(2)	-	-	6.48	-	-	0.19				

CfFA: After Burning under 850 deg C

Fly Ash (1)(LOI:7.61%)										
Raw	1000 °C	950 ℃	900 °C	850 °C	800 °C	750 ℃	700 ℃			
		A Castin	Calification		A. Maria	6 Marine	Ster Com			
	1995-1997		the seal	10. TO 45	1000					
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	and the first of		S. Same							
		、								
Fly Ash (2)	(LOI:5.95%))								
Raw	1000° C	950 ℃	900 °C	850 °C	800 °C	750 ℃	700 ℃			
				N.S. CON	Part of the second	A State of the second				
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Fig. 8 Burning temperature and colour of CfFA

It is well known that the colour of raw fly ash varies from light gray to dark black, depending on the amount of unburned carbon content; the lighter the colour the lower the carbon content which can be proved from the pictures of two raw fly ashes in Fig. 8. The Fig.8 also shows the differences in colour of fly ash under various burning temperatures.

CfFAs produced from fly ash (2) are more reddish than those from (1) due to the larger iron content. It is considered that the larger the iron oxide content, the more reddish the colour. It is also observed that the high burning temperatures make the colour of CfFA more reddish. The colour of fly ash can influence the colour of concretes. To be mentioned here, colour is one of the important concerns for the sales value of concrete products, for that reason, the amount of iron oxide should be monitored and the burning temperature should be properly controlled.

By comparing all the findings from the investigation with *JIS A 6201*, it is assured that CfFAs from H/C, B/C and BG satisfy the specifications of Type IV, Type II, and Type I fly ash, respectively. More importantly, however, the ignition loss of all CfFAs is kept 1.0% or less with which stable air entrainment is expected regardless of the characteristics of raw fly ash. In addition, this production system is capable of utilizing approximately 100% of raw fly ash and produce CfFAs without discharging any residues.

EXPERIMENTAL PROGRAM

The objective of this experiment is to examine applicability of CfFA as a concrete admixture by measuring fresh properties, compression strength, and drying shrinkage strain of CfFA concretes in comparison with conventional JIS II fly ash concretes.

Treatment of CfFA in Concrete Mix Proportioning. Fig. 9 shows how CfFA can be treated as a component material in concrete mixture. In this paper, CfFA is treated as a mineral admixture. However, it can be regarded as a substitute of cement or a substitute of fine aggregate; therefore, both cases are examined in the following tests. In addition, since CfFA is powder with pozzolanic reaction, water-to-powder ratio (W/P), in which the powder is the sum of cement and CfFA(C+CfFA), is used in the mix proportions.

Concrete Mix Proportions. The proportioning of the concrete mixtures is summarized in **Table 4**. Mainly two series of concretes were designed; Series I (24-18-20N) as architecture construction concretes and Series II (21-8-20N) as civil engineering concretes.

For each series of concrete, 9 mix proportions are designed; one non-fly ash concrete as a reference (base) concrete, four concretes with fly ash applied as a cement substitute (A); and another four with fly ash used as an aggregate substitute (B). As for the kinds of fly ashes used in this experiment are the CfFA (2) and JIS II fly ash with LOI of 1.69% in Table 2. In detail, CfFA II applied for mix proportion A (as a cement substitute) is a mixture of CfFA from B/C and BG with a ratio of 3:1 by weight, whereas, CfFA IV used for mix proportion B (as a fine aggregate substitute) is large-size particles from H/C. Other physical properties of cement and aggregate used are also written at the bottom of Table 4. Unit water content is set as 182kg/m^3 for Series I and as 171kg/m^3 for Series II concretes. The water-reducing agent is kept constant at 1.5% of P (C+CfFA) in Series I and 1.0% in Series II, and the dosage of air-entraining agent is adjusted in order to meet the target slump of 18 ± 1 cm for Series I and 8 ±1 cm for Series II, and an air content of 4.5 ± 0.5 % for both.

Casting and Curing of Test Specimens. Plastic cylinder moulds with a size of $\varphi 100x200$ mm were used to produce the specimens of concretes for compressive strength test, and the steel prism moulds with a size of 100x100x400mm were used for the measurement of drying shrinkage strain. After casting, all specimens were removed from the moulds at the age of 1 day, and cured in water (temperature of 20 ± 1 C) until the age of testing.

Ref.	W	C		5	5	G	Air	
Part of Cement	W	C CfFA		S		G	Air	
Part of Aggregate	W	С		CfFA	S	G	Air	
Mineral Admixture	W	C Cf		FA	S	G	Air	
	⊢ ⊢ P							

W:Water, C:Cement, S:Sand, G:Gravel, CfFA:Carbon-free Fly Ash, P:Powder(=C+CfFA)
Fig. 9 Treatment of CfFA in mix proportion of concrete

									_				
Type of		Content of	W/C	W/P	s/a	CfFA(FA)		Un	it we	ight (k	(g/m ²)	
Ready-Mixed		Fly Ash	(%)	(%)	(%)	/P	w	С	FA	CfFA	S	G1	G2
Concrete		,	()	(,	(,	(%)				0			
		-	54.3	54.3	47.9	0		336	0	0	839	644	285
		JIS II 10%	60.2	54.3	47.9	10.0		302	34	0	834	639	282
	А	CfFA II 5%	57.0	54.3	47.9	5.0		319	0	17	836	642	282
Corios I		CfFA II 10%	60.2	54.3	47.9	10.0		302	0	34	834	639	282
(24-19-20NI)		CfFA II 20%	67.7	54.3	47.9	20.0	182	268	0	68	826	636	280
(24-10-2011)		JIS II 75kg/m ³	54.3	41.6	43.9	18.0		336	75	0	729	660	290
	В	CfFA IV 50kg/m ³	54.3	44.3	45.9	13.0		336	0	50	776	647	285
		CfFA IV 75kg/m ³	54.3	41.6	43.9	18.0		336	0	75	729	660	290
		CfFA IV 100kg/m ³	54.3	39.2	40.9	23.0		336	0	100	635	705	309
		-	59.2	59.2	48.1	0		289	0	0	876	666	293
		JIS II 10%	65.7	59.2	48.1	10.0		260	29	0	870	663	290
	А	CfFA II 5%	62.3	59.2	48.1	5.0		274	0	15	873	666	293
Corios II		CfFA II 10%	65.7	59.2	48.1	10.0		260	0	29	870	663	290
(21_8_20NI)		CfFA II 20%	74.0	59.2	48.1	20.0	171	231	0	58	865	660	290
(21-0-2014)		JIS II 75kg/m ³	59.2	47.0	42.1	20.60		289	75	0	729	708	312
	В	CfFA IV 50kg/m ³	59.2	50.4	46.1	14.75		289	0	50	810	671	296
		CfFA IV 75kg/m ³	59.2	47.0	42.1	20.60		289	0	75	729	708	312
		CfFA IV 100kg/m ³	59.2	44.0	41.1	25.71		289	0	100	697	708	312

Table / Mix properties of concrete

C: ordinary Portland cement (gravity:3.16g/cm³)

FA: JIS II in Table 2 CfFA: CfFA (2) in Table 2

CrFA (2) in Table 2 S: sand (gravity:2.62 g/cm³, absorption: 2.84%, maximum size:2.5mm) G1: gravel (gravity:2.65 g/cm³, absorption: 1.20%, maximum size: 20mm) G2: gravel (gravity:2.71 g/cm³, absorption:0.31 %, maximum size: 20mm) Chemical Admixture: water-reducing agent & air-entraining agent

Testing of Specimens. For all mixtures of concrete, compressive strength test was performed in accordance with JIS A 1108(Method of test for compressive strength of concrete). Compressive strengths at the age of 7, 28 and 91 days were measured, and at the same time, for the selected five mix proportions (Reference, 10%, JIS10%, 75kg/m³ and JIS75kg/m³), the longitudinal strain was measured by using the compressometer. The secant modulus of elasticity at the stress point of 1/3 compressive strength was obtained.

Drying shrinkage test was carried out in the room where the temperature and relative humidity were maintained at 20±1 C and 60±5% R.H., respectively. They started drying at a age of 7 days, and drying shrinkage strains of five mix proportions (Reference, 10%, JIS10%, 75kg/m³ and JIS75kg/m³) selected from each series were measured by using Contact Micron Strain Gauge with an accuracy of 1/1000mm.

EXPERIMENTAL RESULTS AND DISCUSSIONS

Fresh Properties

The properties of freshly mixed concrete, such as slump, air content, unit weight, and temperature, are investigated and described in Table 5, Fig. 10, and Fig. 11.

Mix. No.	Type of Fly Ash	Notation		Water-re Notation Age (P× ^o		Water-reducing Agent (P×%)	Air-entraining Agent (P×%)	Slump (cm)	Air (%)	Unit volume (t/m ³)	Temp. (deg C)
1	Reference		Ref.		1.00A	18.5	4.9	2.31	12		
2	JIS II		A-JIS10		1.50A	18.0	4.3	2.32	12		
3		^	A-5		1.00A	18.0	4.8	2.31	12		
4	(B/C+BG)	А	A-10] [1.00A	18.5	4.5	2.31	12		
5	(0/0+00)		A-20	1.5	1.00A	19.0	4.1	2.32	12		
6	JIS II		B-JIS75		2.00A	20.0	4.5	2.32	12		
7		Б	B-50		1.00A	18.0	4.9	2.30	12		
8		D	B-75		0.75A	17.5	4.6	2.30	12		
9	(1,0)		B-100		0.75A	17.0	4.4	2.31	12		
10	Reference		Ref.		2.50A	8.5	5.0	2.33	12		
11	JIS II		A-JIS10		3.00A	8.0	4.0	2.32	12		
12		^	A-5		2.25A	8.5	4.8	2.34	12		
13	(B/C+BG)	А	A-10		2.50A	8.0	4.7	2.32	12		
14	(0/0100)		A-20	1.0	2.50A	8.5	4.4	2.33	13		
15	JIS II		B-JIS75		4.00A	16.0	4.2	2.31	12		
16		R	B-50		2.50A	8.5	4.9	2.34	12		
17			B-75		2.25A	9.0	4.1	2.34	13		
18	(1,/C)		B-100		2.25A	8.5	4.0	2.32	12		

Table 5 Properties of fresh concrete

Air-entraining Agent: 1A is 0.02% of (C+CfFA) by weight A : replacement of cement B : replacement of sand



Fig.10 Dosage of water-reducing agent in each mix proportion





Fig. 10 shows the dosage of water-reducing agent for each mix proportion. As can be seen from the graph, the dosage of water-reducing agent is the same for the reference and mix proportion A in Series I and II (No.1 to 5 and 10 to 14). For mix proportion B in Type I

and II(No.6 to 9 and 15 to 18), however, the larger the powder contents the higher the dosage of water-reducing agent since the percentages of the agent are fixed to the amount of powder.

Regarding the air content, **Fig. 11** indicates that, to satisfy the target air content, JIS II fly ash concretes requires a larger dosage of air-entraining agent than CfFA concretes. This is considered that the large amount of unburned carbon (LOI of 1.69%) in JIS II fly ash adsorbed the air-entraining agent.

As can be seen from **Table 5**, the mix proportions of No.6 and No.15 with JIS II fly ash as an aggregate substitute showed higher slump values than the target values, on the other hand, all other mix proportions were able to obtain the target slump. This implies that a target slump of JIS II fly ash concretes cannot be achieved by the use of chemical admixtures since the influence of large amount of unburned carbon is rather significant.

For unit weight and temperature, no major differences were observed among all the mix proportions.

Compressive Strength and Modulus of Elasticity. The test results of compressive strength for all mixtures and modulus of elasticity for five concrete mixtures at the age of 7, 28, and 91 days are described in **Table 6**.

Strength ratio is defined as a ratio of compressive strength of fly ash concrete to that of reference concrete. The strength ratios of CfFA were plotted in **Fig. 12.** In case of mix proportion A (a cement substitute) in both series, CfFA concretes initially showed the smaller strength gain compared to the reference concretes, and the ratios are lower for the concretes with larger CfFA content. However, the small strength gain became larger as the age of concrete increased because of the pozollanic reactivity of CfFA, and finally approached to almost 1.0, meaning that the same strength gain as the reference concretes were achieved at the age of 91 days.

Mix	Type of		Compressive Strength (N/mm ²)			Young's Modulus (10 ⁴ N/mm ²)			
No	Ready-Mixed	Notation	Age of	Age of	Age of	Age of	Age of	Age of	
NO.	Concrete		7days	28days	91days	7days	28days	91days	
1		Ref.	27.9	40.1	45.5	2.73	3.10	3.47	
2		A-JIS10	27.5	34.6	44.5	2.37	3.01	3.32	
3		A-5	27.2	37.1	49.7	-	-	-	
4	Corioc I	A-10	26.1	35.4	43.6	2.68	3.19	3.45	
5	$(24_{-}18_{-}20N)$	A-20	24.1	31.3	42.0	-	-	-	
6	(27-10-2011)	B-JIS75	31.9	42.4	52.6	2.25	3.04	3.28	
7		B-50	29.3	38.4	46.3	-	-	-	
8		B-75	30.4	40.0	49.0	2.53	2.82	3.16	
9		B-100	30.7	38.9	50.1	-	-	-	
10		Ref.	24.2	32.9	40.1	2.63	3.59	3.79	
11		A-JIS10	21.7	30.5	39.9	2.47	3.22	3.46	
12		A-5	22.5	31.7	39.4	-	-	-	
13	Corioc II	A-10	21.4	29.6	38.5	3.01	3.16	3.32	
14	(21_8_20NI)	A-20	18.8	25.8	35.9	-	-	-	
15	(21-0-2014)	B-JIS75	24.9	36.0	44.7	2.73	3.07	3.36	
16		B-50	26.0	33.1	41.5	-	-	-	
17		B-75	27.3	36.0	47.4	2.04	2.78	3.05	
18		B-100	28.6	37.1	46.3	-	-	-	

Table 6 Compressive strength of CfFA concrete



In the case of mix proportion B (aggregate substitute) in both series, the strengths of CfFA concretes were almost equal to or slightly larger than those of reference concretes because the water-to-cement ratio of both reference and CfFA concretes are equivalent. Moreover, the larger strength gain was observed with the concretes with higher CfFA content even in 7-day curing, which can be considered that the addition of CfFA led to the condensing or compacting the structure of hydration products due to its fine particles, and that it eventually helped to increase a long-term strength by the pozzolanic reactivity.

Fig. 13 shows the relationships between cement-to-water ratio (C/W) and compressive strength, and powder-to-water ratio (P/W) and the one. It is found that both relationships can be expressed by a linear equation which means that the compressive strength of CfFA concrete can be controlled by both C/W and P/W.

Fig.14 shows the relationship between compressive strength and modulus of elasticity. It is found that although the test data are slightly scattered, the higher the compressive strength the higher the modulus of elasticity, regardless of concretes with and without CfFA. The calculated values by using the prediction formula for this relationship, which is proposed by JASS 5 (Japanese Architectural Standard Specification, JASS 5 Reinforced Concrete Work) published by AIJ (Architectural Institute of Japan), are also plotted in this figure. It is found that the calculated values underestimate the test data.

Drying Shrinkage Strain. Fig. 15 shows relationships between the drying shrinkage strain and time. As seen in this figure, CfFA concretes show the less drying shrinkage than reference concretes, and the replacement of fine aggregate led to a smaller drying shrinkage than the replacement of cement. According to JASS 5, the drying shrinkage strain of ordinary concrete is limited to less than 8×10^{-4} at the drying time of 180 days. It is found that



Fig.16 Relationship between water loss and drying shrinkage strain

only the reference concrete in Series I showed a higher drying shrinkage strain than this maximum value; the drying shrinkage strain of other concretes was less than 8×10^{-4} . The predicted values of drying shrinkage strain by using the prediction formula proposed by JASS 5 are also plotted in Fig.15, and it is found that they agree with test data.

Fig. 16 shows the relationship between water loss and drying shrinkage strain. As illustrated in this figure, the drying shrinkage strain of reference concretes is larger than that of other concretes although they show the smallest amount of water loss. It is also found that concrete mixtures with a cement replacement show a greater ratio of drying shrinkage strain to water loss than that with a fine aggregate replacement; concrete mixtures with greater unit water content show greater drying shrinkage strain.

CONCLUSIONS

In this research project, to enhance the effective use of fly ash in concrete in Japan, the authors proposed the method for removing unburned carbon in raw fly ash to produce CfFA (carbon-free fly ash), and investigated on the characteristics of CfFAs and the fresh and hardened properties of concrete containing CfFA. The following conclusions can be drawn from the present study:

- (1) The CfFA production system consisted of the burning process (rotary kiln) and the pulverization and separation process (a hyper cyclone, a cyclone separator, and a bug filter) is capable of producing the three kinds of CfFAs which perfectly accord with the specifications of Type I, II, and IV in *JIS A 6201*. Furthermore, all the CfFAs keep the ignition loss 1.0% or less, which is considerably lower than the maximum limits in *JIS A 6201*. In addition, this production system can utilize approximately 100% of raw fly ash without discharging any residues.
- (2) CfFA content up to 20% as a cement substitute and up to 100 kg/m³ as a fine aggregate substitute can achieve the target fresh properties under the same mixture condition as the reference concrete.
- (3) Compressive strength showed the tendency to increase with the increase in CfFA content and less drying shrinkage strain is observed in CfFA concretes than in non-fly ash concretes. CfFA concretes also show the less drying shrinkage than non-fly ash concretes, and the replacement of fine aggregate led to a smaller drying shrinkage than the replacement of cement.
- (4) It is found that when a carbon content of 1.0 % or less, fly ash has virtually no unfavourable effects on the properties of fresh and hardened concrete regardless of the kinds and characteristics of fly ash.

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