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Environmentally Friendly Concrete Using Compound Materials

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ABSTRACT

The present study intended to develop clinker-free concrete (hereafter called CFC) that is free of cement as a source matter of CO_2 emissions but uses mainly industrial by-products, such as silica fume, ground granulated blast furnace slag, and fly ash, as chief ingredients and to discuss concrete that helps reduce environment load. The study showed that the use of fly ash Class IV as well as ground granulated blast furnace slag of relatively low fineness is practicable. In the course of capillarization, these are fixed quantity of X-ray determination of the powder and determined using a mercury-sealed porosimeter. Hydration products, such as mullite, gypsum, calcium hydroxide, and ettringite, were found. It was also found that such products filled capillary tubes with the lapse of time, thereby decreasing the pore size.

INTRODUCTION

The problem of a decreasing amount of resources available for construction is becoming evident. Structural construction projects tend to take measures that aim to reduce the life cycle cost (LCC) of the structure.

As far as concrete buildings are concerned, it is believed that a reduction in the LCC may result with the aid of many elements, such as enhanced design freedom that is brought by increased strength and durability of structural members, thus leading to smaller column cross sections and to increased distance between columns. Larger, more comfortable usable space could thus be obtained.

In view of the trend toward increasing the height and durability of concrete structures, it is expected that demand for high-strength concrete will continue to be strong. One of the most recommendable measures for increasing the strength and durability of concrete members is to make the concrete structure more compact. By way of example, high-strength (or super high strength) concrete can be produced by using admixtures, typically silica fumes; increasing the unit amount of cement; reducing the ratio of water-cement (binder); and other means. In certain industrial areas, super high-strength concrete with standard design strength of 150 N/mm^2 or more is already in practical use［H.Jinnai et al, 2007］.

Turning to the industry-wise percentage of CO_2 emissions in Japan, the manufacturing sector accounts for 46% of the total emissions, while the cement sector approximately 4%［Cement Association HP］. Supposedly, CO_2 gas equivalent to about 800 kg in amount is emitted for each tonne of ordinary cement produced［M.Higuchi, 2002］. In particular, production of high-strength (or super high-strength) concrete entails use of large quantities of cement and, therefore, a large volume of CO_2 is emitted, causing grave concerns about air pollution on a global scale. On the other hand, it is not advisable to suppress cement production to any extent since it is called "blood flow through the vein of the whole industry". Such being the case, if the technology to allow the use of less cement and still meet the structural strength requirements demand at the construction site is developed, it will no doubt serve to reduce the emissions of CO_2.

Amid such a situation, this study examines the use of fly ash and ground granulated blast furnace slag in the belief that their effective use will certainly help reduce CO_2 emissions during cement production.

This paper discusses basic characteristics of environmentally friendly concrete (hereinafter referred to as clinker-free concrete (CFC)) consisting mainly of fly ash of different grades as industrial byproducts and ground granulated blast furnace slag with varying specific surface areas. No cement is contained in it. Silica fume, also an industrial byproduct, is used in the study.

EXPERIMENTAL INVESTIGATION

Materials

Materials used in the experiment are listed in Table 1, while grades of fly ash in Table 2 as compared with specified values of JIS A6201 (Fly Ash for Concrete). Specimens of ground granulated blast furnace slag have specific surface areas of 4000 cm^2/g and 8000 cm^2/g, while those of fly ash are FA2 and FA3 coming from different sources. For the comparative study on physical property, pre-mix cement (HSPC) for high-strength concrete containing ordinary portland cement is used as the reference material. Since the specimens are free of cement, calcium hydroxide is not produced, thereby conceivably restraining pozzolanic reaction. As countermeasures in this connection, the authors tried to accelerate that reaction by mixing a multi-porous slaked lime (hereafter called the slaked lime) with a high specific surface area of $45m^2/g$ since the lime is considered highly reactive. In addition, anhydrous gypsum was used to counteract self-shrinkage and other similar problems.

Mixing conditions and powder composition

The mixing conditions applied to the present study are given in Table 3, while the powder composition in Table 4. With 60 N/mm^2 as a target reference design strength in mind, the authors set water-powder ratio to 20%, sand-powder ratio to 32%, and absolute volume percentage of coarse aggregate (Xv) to 37.5% in reference to the findings from the previous study［H. Fujiwara et al, 2006］. Concrete mixing using the reference material was also performed as indicated in Table 3. Varying amounts of a high-range water reducing agent were added and adjusted to have a slump flow rate of 650±50 mm, while an anti-foaming agent was handled likewise until it had an air content of 2.0% or less.

Table 1. Materials

Material	Symbol	Type of material	Density (g/cm^3)
Binder (P)	SF	Silicafume (SiO_2 96.6%, Specific surface 20.0m^2/g)	2.24
	FA2	Fly ash Ⅱ	2.23
	FA4	Fly ashⅣ	2.01
	BS4	Ground granulated blast-furnace slag (Specific surface 4000cm^2/g)	2.90
	BS8	Ground granulated blast-furnace slag (Specific surface 8000cm^2/g)	2.91
	TK	Porous Slaked lime (BET Specific surface 45m^2/g)	2.24
	AG	Anhydrous gypsum	2.90
Water	W	Tap water	1.00
Fine aggregate	S	Crushed sand	2.63
Coarse aggregate	G	Crushed sand	2.63
Admixture	SP	High-range water reducing agent (Polycarboxylic acid ether)	1.08
	DF	Anti-foaming agent (Polyalkylene glycol conductor)	1.00
Comparison	HSPC	High-strength premix cement	2.99

Table 2. Quality of FA

Testing requirement		JIS A6201 Class II	FA2	JIS A6201 Class IV	FA4
SiO_2 (%)		over 45.0	55.3	over 45.0	63.2
Moisture (%)		below 1.0	0.1	below 1.0	0.01
Ignition loss (%)		below 5.0	1.2	below 5.0	0.5
Density (g/cm^3)		over 1.95	2.23	over 1.95	2.01
Fineness	Residue of 45 μ sieve (%)	below 40	4	below 70	-
	Blaine specific surface area (cm^2/g)	over 2500	4410	over 1500	1750
Flow ratio (%)		over 95	110	over 75	92
Activity index	28 days (%)	over 80	90	over 60	74
	91 days (%)	over 90	104	over 70	83

Table 3. Mixing condition

Slump Flow (mm)	Air content (%)	W/P (%)	S/P (%)	Xv (%)
650±50	below 2	20	32	32

Table 4. Powder composition

No.	Percentage by weight (%)						
	SF	FA2	FA4	BS4	BS8	AG	TK
CFC-1	5	35	0	36	0	9	15
CFC-2	5	0	35	36	0	9	15
CFC-3	5	35	0	0	36	9	15
CFC-4	5	0	35	0	36	9	15

Elements of the experiment

Fresh property

Mixing time

A twin-shaft forced mixing unit with a nominal capacity of 2L was used for concrete mixing. The procedure is as follows: mortar having sufficient fluidity was first mixed and then coarse aggregate was added to the mixture. Mixing followed long enough until concrete was produced. Before mortar mixing, powder and fine aggregate were kneaded for 60 seconds and addition of water and high-range water reducing agent followed. After that, water and high-range water reducing agent were added for mixing.

Slump flow test

This test was conducted according to the JIS A1150 “Method of test for slump flow of concrete”.

Air content test

This test was conducted according to the JIS A1128-1999 “Testing Method under Fresh Concrete Pressure (Air Chamber Pressure Method)”.

Characterization

Using a hardened cement paste body based on the powder whose composition is indicated in Table 4, the product was determined by means of an X-ray diffraction, while the body was characterized for pore size distribution with a mercury-sealed porosimeter.

The cement paste was formed using a Forbert mixer; water and added high range water reducing agent were stirred for several seconds at low speed and the paste was visually checked for fluidity. The specimen was thus prepared. The specimen was normally cured in the water.

X-ray determination of the powder

At 1, 3, 7, and 28 days of aging, the hardened body was ground granulated. The specimen was prepared by immersing ground granulated material in the solution of large amounts of acetone and stopping hydration. The specimen was taken out and subjected to X-ray powder diffraction (XRD) to examine the product.

Determination of pore size distribution

At 7 and 28 days of aging, the hardened body was coarsely crushed to particles 2.5 mm or less in size. The specimen was prepared by immersing the particles in the solution of large amounts of acetone and stopping hydration. The specimen was taken out, allowed to dry in air, and determined using a mercury-sealed porosimeter.

Observation of hydration products under the SEM

At 7 and 28 days of aging, the specimen for determination of pore size distribution was subjected to observation under the SEM.

Hardening property

Compressive strength test

This test was conducted according to the JIS A1108 “Testing Method for Compressive Strength of Concrete”. Released from the mold, the specimen was cured in air (for 1 day of aging) and in water (for 3, 7, 28, and 91 days of aging) prior to determination.

Results and Discussion

Fresh property

The test results for fresh property are given in Table 5, while addition rates of the high-range water reducing agent as well as the mixing time in Figure 1. In general, it is believed that workability improves when fly ash and ground granulated blast furnace slag are used as main ingredients and that; moreover, the target slump flow rate is achieved more easily with a less amount of high-range water reducing agent added than the case where cement-only concrete mix is applied. For the CFC, however, a significantly increased amount of high-range water reducing agent seems to be needed as compared with the case of the HSPC. This phenomenon is presumably ascribable to the fact that the slaked lime used as an accelerator of CFC pozzolanic reaction is of such a porous material that it retains much moisture. Since the BET specific surface area of the slaked lime is as fine as 45 m^2/g, the amount of adsorbed high-range water reducing agent concomitantly increases. Consequently, it is highly probable that the addition rate of the water reducing agent which is required to acquire the specified level of fluidity must be increased. When it comes to the difference in specific surface area of the ground granulated blast furnace slag, it is found that the addition rate of the water reducing agent tends to lower for the CFC-1 and the CFC-3 when the BS8 is used. Turning to the subject of a time elapsed until 50-cm distance is reached in the slump flow test, the CFC-3 containing the FA2 fly ash showed the result comparative with the HSPC, while the CFC-2 as well as the CFC-4 containing the FA4 fly ash tends to be about 5 seconds slower than the former. This phenomenon conceivably occurs in the situation where concrete viscosity increases in the presence of the FA4 since a ball bearing effect is almost negligible there. As far as mixing time is concerned, it tends to be lengthened when the BS8 is used.

Table 4. Test results for fresh property

No.	SP (%)	DF (%)	Slump Flow (mm)	50cm time-of arrival (sec.)	Mixing time (min.)	Air content (%)	C.T (℃)
CFC-1	2.65	1.00	700	5.9	7.0	1.0	23.0
CFC-2	2.50	0.80	645	13.1	6.0	1.0	21.5
CFC-3	2.40	1.00	615	8.0	9.0	1.8	24.0
CFC-4	2.50	0.90	640	13.2	8.0	1.3	22.0
HSPC	0.85	0.70	665	8.6	3.0	0.6	16.0

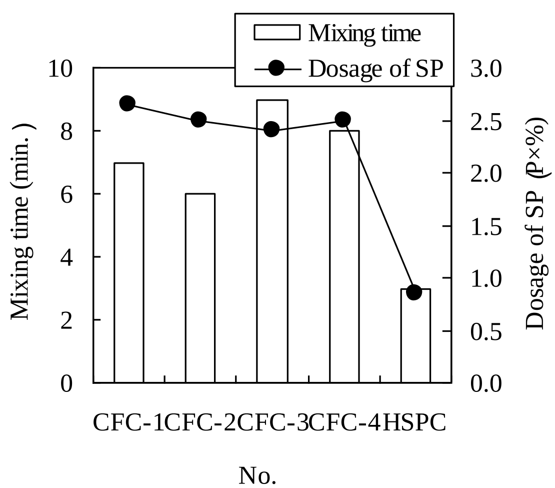


Fig. 1. Dosage of SP and mixing time

Characterization

X-ray determination of the powder

Figures 2 through 5 show the patterns of X-ray diffraction from the CFC-1 to CFC-4 specimens that were cured for 1, 3, 7, and 28 days. Without regard to aging days, products that were found are quartz (SiO_2), anhydrous gypsum ($CaSO_4$), calcium hydroxide

($Ca(OH)_2$), mullite ($3Al_2O_3 \cdot 2SiO_2$), and ettringite ($Ca_3Al2O6 \cdot 3CaAl_2O_6 \cdot 32H_2O$). At 28 days of aging, quartz, mullite, anhydrous gypsum, and calcium hydroxide were found, indicating that difference is not very significant between the 7-day and 28-day aging tests. Presence of quartz and mullite contained in fly ash is constantly observed without regard to the aging period. On the other hand, the amount of calcium hydroxide produced tends to lower from that of the diffraction peak. This tendency is considered to result from the absence of calcium hydroxide, leading to suppression of pozzolanic reaction because the CFC is cement-free. As a means for counteracting such a problem, mixing of the slaked lime is a common practice. The slaked lime so mixed, however, is assumedly consumed during pozzolanic reaction to fly ash.

Ettringite is produced when there is a reaction between SO_4^{2-} that is dissolved in water from gypsum contained in cement and $Ca_3[Al(OH)_6]_2$ ［Y.Arai,1989］ In the tests discussed in the present study, anhydrous gypsum used for self-shrinkage protection probably induced production of ettringite.

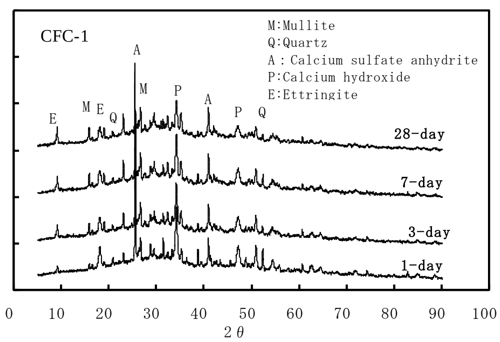


Fig. 2. Patterns of X-ray diffraction (CFC-1)

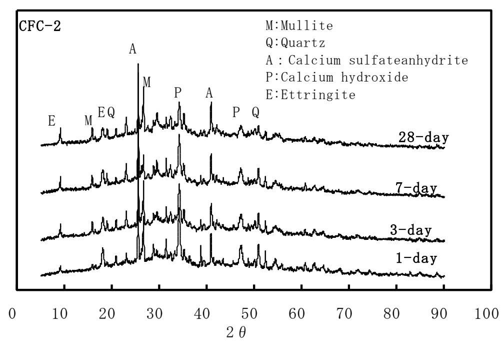


Fig. 2. Patterns of X-ray diffraction (CFC-2)

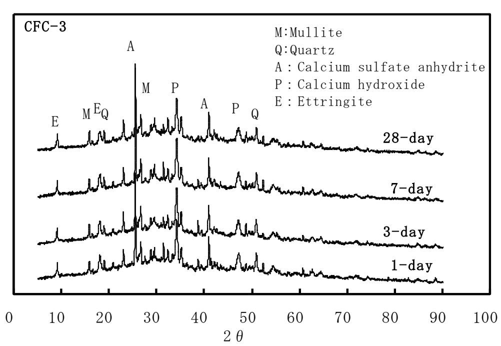


Fig. 3. Patterns of X-ray diffraction (CFC-3)

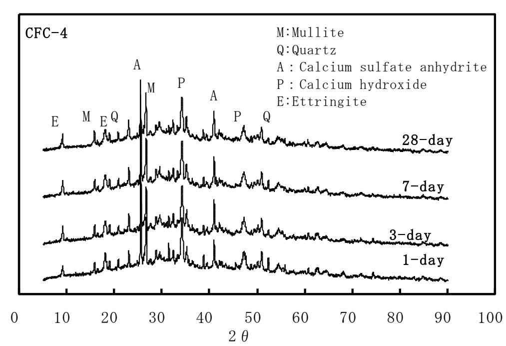


Fig. 4. Patterns of X-ray diffraction (CFC-4)

Determination of pore size distribution

Figures 6 and 7 compare pore size and quantity at each aging day concerned with the CFC-3 and the CFC-4.

As can be seen from these, the amount of coarse capillary pores deceases as the aging days increase. Approximately 0.01-µm sized pores are predominant in number. It seems that, at 28 days of age, the number of pores 0.01 µm in size decreases, thus making the structure more compact with a smaller of number of pores inside. It is most likely that the X-ray diffraction peak of calcium hydroxide tends to go down with increasing age. Progress of pozzolanic reaction is considered to be responsible for increased compactness of the structure of the hardened body, which is attendant on a reduced distribution of pores inside.

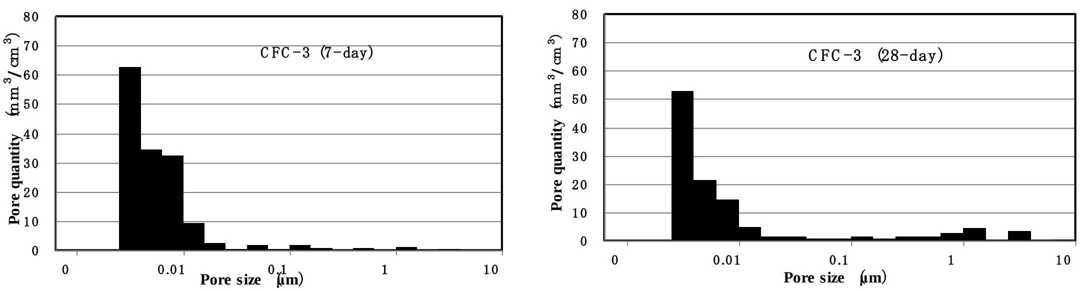


Fig. 6. Pore size and pore quantity (CFC-3)

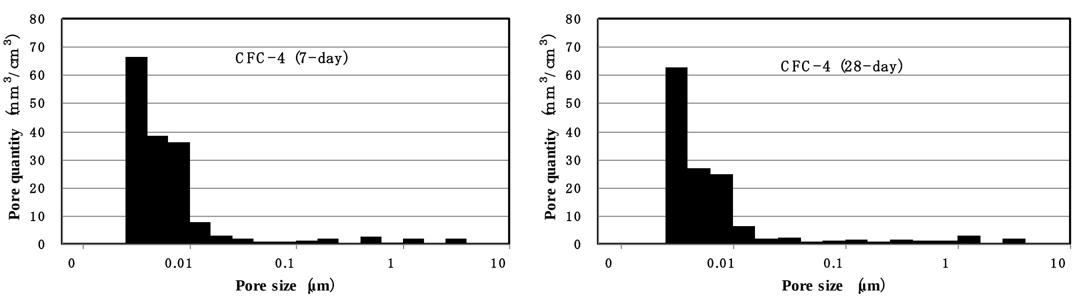
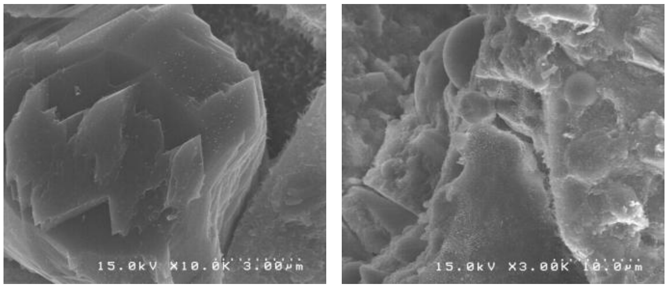


Fig. 7. Pore size and pore quantity (CFC-4)

Observation of hydration products under the SEM

Figure 8 shows the SEM photo of the cross section of the paste at 28 days of aging. As is seen in the CFC-1's SEM photo, there are flat crystals of calcium hydroxide. The CFC-3's photo evidently shows that fly ash is intertwined in the hydration products. On the other hand, ettringite is observed in the form of crystals of a trigonal system.

Hydration products emerging from the X-ray diffraction of the CFC-1 to the CFC-4 include mullite, anhydrous gypsum, calcium hydroxide, and ettringite. Those products are seen under the SEM at all days of aging concerned.



(CFC-1: 28-day) (CFC-3 :28-day)

Fig. 8. SEM Photo

Compressive strength test results

As is clear from Figure 8, the CFC is found inferior to the HSPC as the promoter of development of compressive strength. At 1 day of age, however, the CFC developed its compressive strength at a relatively slow pace presumably because of larger amounts of the high-performance water reducing agent contained than used for the HSPC. At 91 days of age, however, its compressive strength exceeded 80 N/mm^2. The CFC-3 and the CFC-4 were found to have their compressive strength amounting to 80 N/mm^2 or more at 28 days of age when the BS8 was used together. Achievement of that high level of strength conceivably resulted from mixing of the BS8 that has a comparatively large specific surface area. In other words, mixing of the BS8 most likely promoted compactness of the hardened body, while reducing the number of pores inside. Thus, the compressive strength increased.

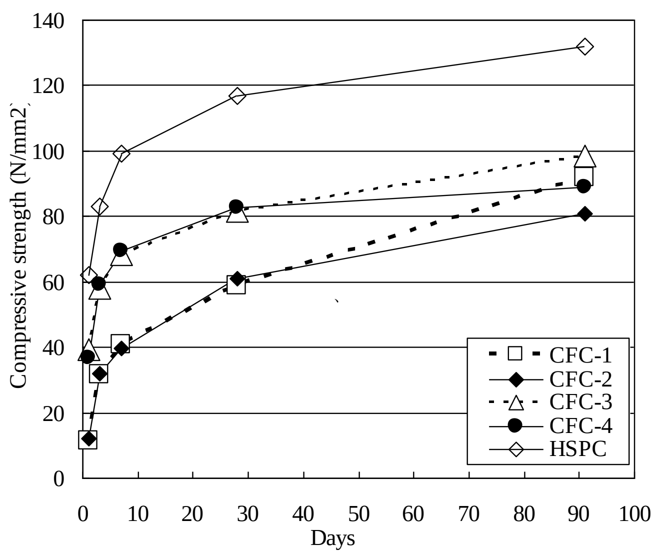


Fig.9. Compressive strength results

On the other hand, the effect expected from each grade of fly ash is compared between the CFC-1 and -2 and also between the CFC-3 and -4 at later than 28 days of age when the effect of the pozollanic reaction presumably begins to become appreciable. The finding is such that the compressive strength of the CFC-1 and the CFC-3 that use the FA2 is greater than that of the rest of specimens. The difference in that strength exceeded 10 N/mm^2 at 91 days of age. As indicated in Table 2, the FA2 exhibits greater activity index than the FA4 at 91 days of age, thereby inducing an increase in the compressive strength. Even in the case where the FA4 was used, an increase in the compressive strength of the CFC-2 that contain the BS4 with lower fineness than that of the BS8 showed greater compressive strength at 28 to 91 days of aging than that indicated by the CFC-3 that used the FA2 and the BS8 together. The finding leads us to believe that full development of compressive strength may be expected even when the FA4 fly ash is used.

Conclusion

One can say with reasonable confidence that the immersion-cured CFC comes to have a compressive strength of 80 N/mm^2 or 60 N/mm^2 or more at 28 days of age.

Use of the FA2 rather than the FA4 is greatly helpful in increasing compressive strength at 28 to 91 days of age.

Products that are found regardless of aging days include quartz, anhydrous gypsum, calcium hydroxide, mullite, and ettringite.

At 28 days of age, a compact structure with relatively small pores develops as the pozollanic reaction progresses, leading to an increase in compressive strength. Even in the case of cement-free application, it is possible to argue that concrete with a compressive strength of more than 60 N/mm^2 can be obtained.

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