PROPERTIES AND DURABILITY OF CEMENT-BASED COMPOSITES WITH CFBCA, GGBFS AND CFA

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ABSTRACT: Reducing the amount of cement production is advantageous on environmental sustainability development because cement production is a highly energy consumption and carbon dioxide emission. Therefore, the utilization of industrial by-products mixed with cement is becoming an important task. This study presents the properties and durability of cement-based composites with circulating fluidized bed combustion ash (CFBCA), ground granulated blast furnace slag (GGBFS), and coal-fired fly ash (CFA). Seven mixtures with varying proportions of ordinary Portland cement (OPC), CFBCA, GGBFS, and CFA were prepared. Flow test, setting times test, water absorption test, compressive strength test, flexural strength test, length change test, and sulfate attack resistance were conducted. Test results show that higher flow ranged from 107 to 134.5% has been obtained for blended cement mixtures than that of plain cement mixture, with approximately 76% of the flow. At the age of 91 days, the compressive and flexural strengths of blended mortars with CFBCA replacement cement of 30% are lower than those of plain cement mortars. In addition, the blended cement mortars have a higher water absorption and sulfate attack resistance and a lower length change, which is comparable to plain cement mortar. It indicated that the amount of cement replacement by CFBCA, GGBFS, and CFA was limited below 20% at the same time, respectively.

Keywords: property, durability, circulating fluidized bed combustion ash, ground granulated blast-furnace slag, coal fly ash

1. INTRODUCTION

The production of cement is a greatly energy-intensive process and the average intensity of carbon dioxide emission is 0.83kg CO₂ per kg of cement[1]. In other words, manufacturing one ton of the ordinary Portland cement (OPC) created about one ton of $CO_2[2]$. Thus, as the attention on environmental sustainability is increasing, reducing CO₂ emission and energy consumption of producing cement without sacrificing the economic capability is much more significant. To reach the goals mentioned above, the use of industrial by-products, such as ground granulated blast furnace slag (GGBFS), coal-fired fly ash (CFA), silica fume (SF), and rice ash (RA), as partial replacement to cement, is becoming an important task. It is not only energy-saving and carbon emissions-reducing but has superior properties compared to OPC[3]. Thus, many researchers have been working on producing concretes with lower OPC or blended cement because of its availability.

Circulating fluidized bed combustion (CFBC) is a comparatively new technology in lowing emission of pollutants and grows intensely in great utility power plant applications. The ash from the CFBC boiler is an industrial by-product[4] that has a large specific surface area and high water requirement. In addition, CFBCA contains relatively high free lime and low SiO₂ and Al₂O₃ compared to CFA. It does not meet the North American standard and not conform to the European standard for components or additives in concretes[5]. CFBCA Therefore, the utility of CFBCA in construction and buildings may result in strength reduction and structural damage [6-11]. However, with the amount of CFBCA increasing and its disposal cost increasing, improving techniques for recycling and reutilizing of CFBCA has become a crucial task even if CFBCA is not as good as other pozzolans.

Ground granulated blast furnace slag (GGBFS) and highcoal-fired fly ash (CFA) are two by-products that have been the most used in concrete. Not only did it be used as the aggregates, but it also is used as binders. Both GGBFS and CFA are good pozzolans that are used in cement to improve the properties of cement-based materials. Chen et al.[12]investigated the properties of hardened paste with GGBFS, Type F fly ash and CFBCA as binders and pointed out that the mixtures with 15-20 wt% CFBCA and 10-30 wt% FA is the optimum mixtures that have the superior properties. Chi [13] found that the mortar with GGBFS and CFBCA has a lower compressive strength than OPC mortar. When CFBCA replacing cement up to 30%, the specimen would result in a much higher length change. Hermawan et al.[14]indicated that the addition of CFBCA by 20% was chosen as the optimum amount to improve the compressive strength for later ages at a higher temperature. Sheng et al. [15] reported that the fineness and the contents of SO₃ and free lime (f-CaO) of pressured fluidized bed combustion ash (PFBCA) have a significant influence on self-cementitious properties. Higher self-cementitious strength has been obtained for PFBCA with higher contents of SO₃ and *f*-CaO. In addition, FA with high contents of SO₃ and *f*-CaO has beneficial self-cementitious properties[16].

In this study, seven mixtures with varying proportions of OPC, CFBCA, GGBFS, and CFA were prepared and relative tests were performed to explore the properties and durability of blended cement-based composites. The test results may provide a better understanding on the utilization of industrial by-products, meanwhile, it can also offer a useful basis for advanced application of the combination of CFBCA, CFA, and GGBFS in construction and building industries.

2. EXPERIMENTAL PROGRAM

2.1 Materials

CFBCA and CFA collected from the ash hoppers of the electrostatic dust collector were supplied by the Mailiao Six Light Naphtha Cracker Plant in Taiwan. GGBFS was from China Steel Corporation (CSC), located at Kaohsiung,

Sci.Int.(Lahore),32(6),693-698,2020

Taiwan. Type I ordinary Portland cement (OPC) conforming with CNS 61 was used. The physical properties and chemical compositions of CFA, CFBCA, GGBFS, and OPC were listed in Table 1. Particle size sieve analysis was conducted and 86% of CFBCA passed the No. 200 (75 μ m) sieve. The Blaine specific surface area and specific gravity are 3680 cm²/g and 3.15 for OPC, 3000 cm²/g and 2.76 for CFBCA, 2370 cm²/g and 2.39 for CFA, 6000 cm²/g and 2.88 for GGBFS, respectively. These raw materials with various mixed ratios were used as binders. Fine aggregate was prepared with river sand and it has 2.33 of fineness modulus, 2580 kg/m³ of bulk density and 2.94% of water absorption, respectively.

Table (1) Physical properties and chemical composition of CFA, CFBCA, GGBFS, and OPC (%wt).

	OPC	CFBCA	GGBFS	CFA
Physical properties				
Specific gravity	3.15	2.76	2.88	2.39
Blaine fineness, cm ² /g	3450	3000	6000	2370
Chemical compositions (%)				
Calcium oxide, CaO	63.8	56.80	40.67	1.94
Sulfur trioxide, SO ₃	2.20	32.40	0.56	0.57
Silicon dioxide, SiO ₂	20.6	5.22	34.58	56.66
Ferric oxide, Fe_2O_3	3.20	0.58	0.44	7.56
Aluminum oxide, Al_2O_3	5.40	2.21	13.69	23.97
Magnesium oxide, MgO	1.98	2.06	7.05	0.93
L.O.I.	1.00	7.83	4.72	2.76

2.2 Mix design and preparation of specimens

The mix design was performed according to ASTM C192 [17]. At first, all of the raw materials (OPC, CFA, CFBCA, GGBFS, and sand) were dry mixed for 1 minute according to the mix proportion. Next, water was poured into the dry mix. Then, the mixes were stirred again till becoming uniform. When the compounds were finished, the uniform mixtures were molded in 50mm \times 50mm \times 50mm to produce mortar specimens. After 24 hours, the specimens were demolded and then placed in the curing room at a relative 80% RH and 25°C. Finally, the mortar specimens were prepared until testing. The mixed proportion of the mortars is given in Table 2. As listed in Table 2, a fixed liquid/binder ratio of 0.5 and seven mixes with various proportions of OPC, CFBCA, GGBFS, and CFA were prepared.

Table (2) Mix proportion of OPM and specimens with CFA, CFBCA, and GGBFS (kg/m³)

Mix no.*	Cement/CFA/ CFBCA/ GGBFS	Water	Fine Agg.	Cement	CFA	CFBCA	GGBFS
OPM	10/0/0/0	268	1474	536	0	0	0
F1C1G1	7/1/1/1	268	1352	375	54	54	54
F2C1G2	5/2/1/2	268	1324	268	107	54	107
F2C2G2	4/2/2/2	268	1318	214	107	107	107
F2C2G4	2/2/2/4	268	1032	107	107	107	214
F1C3G1	5/1/3/1	268	1340	268	54	161	54
F1C3G2	4/1/3/2	268	1332	214	54	161	107

Within mix designation FxCyGz, x, y, and z represent the level of replacement (in wt%) of CFA, CFBCA and GGBFS as cement, respectively.

2.3 Method

The flow test was conducted in light of ASTM C230-14[18]. The mix was put on a flow table and then dropped 25 times within 15 seconds. As the mix was dropped, it spreads out on the flow table. By measuring its spread on a flat surface, the flow was obtained. The initial setting time and final setting time of the mix were measured on the basis of ASTM C191-13[19]. The water absorption rate test was made according to ASTM C642 [20]. Firstly, the specimen was placed into an oven heated at 105±5°C and kept in the oven for 24 hours. After that, the specimen was taken out till it cooled down to room temperature and weighed (W_d) . Then, the specimen was immersed in water and kept in water for 24 hours. After that, the specimen was taken out and the surface water was wiped and then weighed (W_s) again. The water absorption (WA)formula was following [21, 22]: WA(%) = $(W_s-W_d)/W_d \times$ 100%. The compressive strength test was performed conforming with ASTM C109-11[23]. Cubic specimens with $50 \times 50 \times 50$ mm were cast to determine the compressive strength at the ages of 7, 14, 28, and 91 days. Each mix with three specimens was prepared at each testing age. The flexural strength test was done at the ages of 7, 14, 28, and 91 days according to ASTM C348 [24]. The prismatic specimen of 40×40×160 mm for each mix was prepared and three specimens were tested to find the average flexural strength. The length change test at the ages of 3, 7, 14, 28 and 56 days was measured in accordance with ASTM C596[25]. For each mix, prismatic specimens with 250×25×25 mm were prepared and two specimens were measured. After 24 hours, the specimen was demolded and the initial length (L_i) was measured. Then, the specimen was placed in the humidity cabinet and cured. After the specified curing period, the length of the drying shrinkage specimen (L_x) was measured again. Finally, the length change (LC, %) was calculated at x age by the equation: LC (%) = $(L_i - L_x)/G \times 100\%$, where G is 250 mm, the nominal gauge length. The sulfate attack resistance at the age of 28 days was conducted according to the ASTM C88[26]. The specimen at 28 days was immersed exactly in the saturated sodium sulfate solution (Na₂SO₄ solution, pH=8.7) and lasted for 24 hours. After that, it was put into an oven and heated at 105±5 °C for 24 hours. It was called a test cycle. This test cycle was repeated 5 times. Then the compressive strength of specimens with the sulfate attack was tested and the compressive strength reduction rate (SRA) of the specimen was computed by the formula: SRA (%) = $[(S_0-S_1)/S_0] \times 100\%$, where S₀ is the compressive strength cured in water at the age of 28 days and S₁ is the compressive strength after 5 times of test cycle in the sulfate attack.

3. RESULTS AND DISCUSSION

3.1 FLOW

The workability of the mix is the most important and complex property of any fresh mixture. It indicates how easily the mixing, placing, compacting and finishing process can be done with minimum or no loss of relative homogeneity. As given in Table 3, the flow of the mix with CFA, CFBCA, and GGBFS is higher than that of OPM. Commonly, laboratory mixed mortars should have a flow of approximately 100 - 115%. In this study, the flow of OPM is

approximately 76%, which is not good workability. However, when CFA, CFBCA, and GGBFS were used to replace partial cement, the flow of the blended cement mixtures are ranged from 107 to 134.5%. It indicates that the cement replacement by CFA, CFBCA, and

GGBFS increases the flow, thus improves the workability of the mortars.

Table (3) Flow of OPM and specimens with CFA, CFBCA, and GGBFS (%)

GGDI B (70)				
Mix no.	Flow (%)			
OPM	75.88			
F1C1G1	128.00			
F2C1G2	126.75			
F2C2G2	123.50			
F2C2G4	134.5			
F1C3G1	107.0			
F1C3G2	112.5			

3.2 Setting time

The initial setting time and the final setting time depend on the plasticity of paste. The initial setting time is the paste losing its plasticity at the beginning and the final setting time is the paste completely losing its plasticity. It can be seen from Table 4 that initial and final setting times of specimens with CFA, CFBCA, and GGBFS were higher than that of OPM except those of 30% cement replacement by CFBCA. Compared with the setting time of OPM specimen, the initial setting time and final setting time of specimens with CFA, CFBCA, and GGBFS increase 21~97 minutes and 30~124 minutes, respectively. It indicates the cement replacement by CFA, CFBCA (less than 30%), and GGBFS delays the process of hydration or hardening.

Table (4) Initial and final setting time of OPM and specimens with CFA, CFBCA, and GGBFS

Mix no.	Initial setting time	final setting time		
	(hr : min)	(hr : min)		
OPM	3:19	4:45		
F1C1G1	3:40	5:15		
F2C1G2	4:10	5:28		
F2C2G2	4:17	5:53		
F2C2G4	4:56	6:49		
F1C3G1	2:01	4:32		
F1C3G2	1:58	4:28		

3.3 Water absorption test

The water absorption rate of OPM and the specimens with CFA, CFBCA, and GGBFS was given in Table 5. A higher water absorption rate has been obtained for the specimens with CFA, CFBCA, and GGBFS than that of OPM. The OPM specimen has water absorption of 9.03%, whereas the specimens with CFA, CFBCA, and GGBFS have water absorption rates varied from 9.24% to 12.72%. It should be mentioned that specimen containing GGBFS has the relatively lower water absorption rate than the other specimens with CFA, CFBCA, and GGBFS because of the pozzolanic reaction and filling effect by GGBFS.

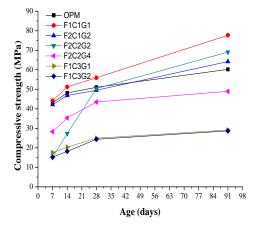
Table (5) Water absorption rate of OPM and specimens with CFA, CFBCA, and GGBFS

Mix no.	Water absorption rate (%)
OPM	9.03
F1C1G1	12.72
F2C1G2	11.49
F2C2G2	10.45
F2C2G4	9.24
F1C3G1	11.26
F1C3G2	10.07

3.4 Compressive strength

Figure 1 shows the compressive strength development of OPM and specimens with CFA, CFBCA, and GGBFS at the ages of 7, 14, 28 and 91 days. At the age of 91 days, the F1C1G1 specimen has the highest compressive strength of 76.6 MPa. It is followed by the specimens F2C1G2 and F2C2G2, with compressive strength of 67.8 MPa and 62.5 MPa, respectively. As the cement replacement by CFBCA is over 30% or by GGBFS is 40%, the compressive strength is lower than that of OPM. It indicates that the amount of cement replacement by CFBCA, GGBFS, and CFA was recommended less than 20% at the same time.

Figure (1) Compressive strength of OPM and specimens



with various CFA, CFBCA and GGBFS replacement rates

3.5 Flexural strength

The flexural strength of OPM and specimens with CFA, CFBCA, and GGBFS at the ages of 7, 14, 28 and 91 days is shown in Figure 2. As shown from Figure 1, except for the F1C3G1 and F1C3G2 specimens with cement replacement by CFBCA over 30%, other specimens with CFA, CFBCA, and GGBFS have higher flexural strength than OPM at the ages of 28 and 91 days. At 91 days, the F2C2G4 specimen has the highest flexural strength, with 8.10 MPa, followed by F2C2G2 and F2C1G2 specimens, with 7.93 MPa and 7.78 MPa of the flexural strengths, and then F1C1G1 and OPM specimens, with 6.47 MPa and 6.19 MPa of the flexural strengths. F1C3G2 specimen is on the other end of the scale, with 4.08 MPa of flexural strength.

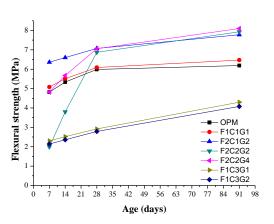


Figure (2) Flexural strength of OPM and specimens with various CFA, CFBCA and GGBFS replacement rates

3.6 Length change

Figure 3 displays the results of the length change of OPM and specimens with CFA, CFBCA, and GGBFS at the ages of 3, 7, 14, 28 and 56 curing days. It can be seen from Figure 3 that all of the specimens have a dramatic increasing length change at the beginning of 14 days. After 14 days, the increase of length change grows slightly till the age of 56 days. The OPM specimen has the highest length change in the seven specimens. Meanwhile, the reduction of the length change increases with an increasing cement replacement by CFA CFBCA and GGBFS. At the age of 56 days, the length change of the OPM specimen was 704×10^{-6} which is 8 -100% higher than those of other specimens with blended cement. The specimen with 20%CFA, 20%CFBCA, and 40% GGBFS (F2C2G4) is on the other end of the length change, with 351×10^{-6} . It indicates that the cement replacement rate by CFA, CFBCA, and GGBFS can reduce the length change of specimens. In the meantime, the more the cement replacement by GGBFS, the lower the length change. It seems that the adding of GGBFS may reduce the length change of blended cement mortars. Except for OPM specimen, F1C1G1 and F1C3G1 specimens with 10% GGBFS are the top two high length change of specimen, respectively.

Previous research pointed out that binders with higher SO₃ content may create excessive ettringite (AFt) and cause the expansion and disintegration of the specimen. As listed in Table 1, the content of SO₃ in CFBCA is 15 times as many as OPC. It means that the specimen with CFBCA replacement may cause an increased length change. However, the content of SO₃ in GGBFS and CFA is 0.56% and 0.57%, which is less than that of OPC. Thus, the length change of specimen with various combinations of CFA, CFBCA and GGBFS is still less than that of OPM.

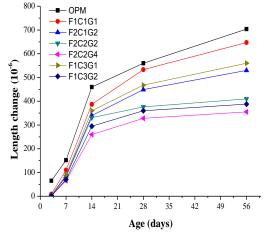


Figure (3) Length change of OPM and specimens with various CFA, CFBCA and GGBFS replacement rates

3.7 Sulfate attack resistance

The compressive strengths of OPM and specimens with various CFA. CFBCA and GGBFS replacement rates before and after sulfate attacks were presented in Table 6. As listed in Table 6, after 5 times of test cycle in the sulfate attack, the compressive strength of the OPM specimen decreases from 51.0 MPa to 43.2 MPa, with a compressive strength loss of 15.4%, but the compressive strength of the specimen with CFA, CFBCA, and GGBFS increase ranged from 4.8% to 66.5% except for the F1C1G1 specimen with 10% CFBCA, 10% CFA and 10% GGBFS. In general, concrete would occur expansion and production of expansive ettringite and gypsum, then cracking, and spalling with sulphate attack and decrease the compressive strength[27]. However, CFBCA has high contents of sulphur oxides (SO_2) , lime (CaO). The compressive strength of the specimen with CFA, CFBCA, and GGBFS increases after sulfate attacks because of the CaSO₄ products stalling the pores, thus condensed the pore structure.

Table (6) Compressive strengths of OPM and specimens with various CFA, CFBCA and GGBFS replacement rates before and after sulfate attacks

	Compressive strength		Strength	
Mix no.	(Mpa)		reduction rate	
	before	after	(%)	
OPM	51.0	43.2	-15.4	
F1C1G1	55.9	55.7	-0.4	
F2C1G2	49.5	55.4	11.8	
F2C2G2	50.4	52.8	4.8	
F2C2G4	43.5	47.2	8.46	
F1C3G1	24.9	30.8	23.4	
F1C3G2	24.4	40.6	66.5	

5. CONCLUSIONS

This study presents the properties and durability of OPM and specimens with CFA, CFBCA and GGBFS. The conclusions are the following:

- (1) By-products, CFBCA, CFA, and GGBFS increase the flow, thus the workability is improved.
- (2) Compared with blended and plain cement mortars, higher water absorption and sulphate attack resistance and a lower length change of blended cement mortars are attained.
- (3) CFBCA would results in a lower strength when it was added up to 30%. Moreover, the amount of CFBCA, GGBFS, and CFA replacement cement is recommended less than 20% at the same time, respectively.

6. ACKNOWLEDGEMENTS

The authors would like to acknowledge the financial support from the Ministry of Science and Technology, ROC. (MOST 103-2221-E-274-004)

7. CONFLICT OF INTEREST

The authors declare no conflict of interest.

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