

# The binding properties of cementitious materials using circulating fluidized bed co-fired fly ash and pulverised coal fly ash

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**Abstract.** This study aims to investigate the binding properties of co-fired fly ash (CFFA) in paste and mortar specimens. Paste specimens containing various CFFA proportions (25%, 50%, 75%, 100% by weight of cement) were conducted and evaluated using setting time tests, water demand tests and compressive strength tests. Mortar specimens containing various CFFA and Pulverised coal fly ash (PCFA) proportions (10%, 20%, 30% by weight of cement) were also conducted and compared with regard to flowability and compressive strength. The test results indicated that the water demand increased as the amount of CFFA replacement increased on the flow level at  $110\pm 3\%$ ; this is due to the higher ignition loss (L.O.I.). Higher L.O.I. values mean that there are more unburned carbon particles in the CFFA and that most of these carbon particles are porous. The compressive strength of mortar specimens decreased as the amount of CFFA replacement increased. Compared to the chemical compositions of cement ( $C_3S$ ,  $C_2S$ ), the main components of CFFA ( $Ca(OH)_2$ ,  $CaCO_3$ ,  $CaO$ ) have lower crystalline strength and compactness. Therefore, the higher amount of CFFA replacement would inevitably cause a reduction of the cement contents of specimens, thereby reducing the compressive strength of the mortar specimens. Thus, an appropriate amount of superplasticiser and CFFA replacement in the mixture is useful with regard to the binding properties of cementitious materials.

## 1 Introduction

Green energy and environmental protection are two major issues of the global energy industry which are important concerns in the world. In recent years, energy demand has increased day by day due to increases in living standards and demand, and energy production is one of the main sources of environmental pollution [1, 2]. According to previous literature, around 80% of global energy is provided through the burning of fossil fuels, which emits a large amount of carbon dioxide ( $CO_2$ ) as greenhouse gases. This is one of the main causes of global warming. In addition, fossil-fuel power stations and thermal power plants also produce

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pollutants such as sulphur oxides (SO<sub>x</sub>) and nitrogen oxides (NO<sub>x</sub>), which are harmful to the environment [3, 4]. At present, the main reserves of fossil fuels in the world are primarily coal. How to improve the efficiency of coal combustion and reduce pollution is a matter of great significance to the energy industry [5].

In recent years, circulating fluidized bed (CFB) boilers have been widely used; however, the co-fired fly ash (CFFA) produced by CFB has not been properly treated using a sustainable recycled method [6]. Pulverised coal fly ash (PCFA) produced from thermal power plants is now widely used as an ingredient in construction materials. Although CFB technology has been widely used in various countries, CFFA has not been routinely and properly processed and there is a lack of appropriate applications for it. The method of disposal of CFFA in Taiwan is mostly landfill or in-plant stacking. However, this causes heavy metals to infiltrate the ground and pollute the groundwater. New and proper disposal methods must be sought and created [7, 8, 9].

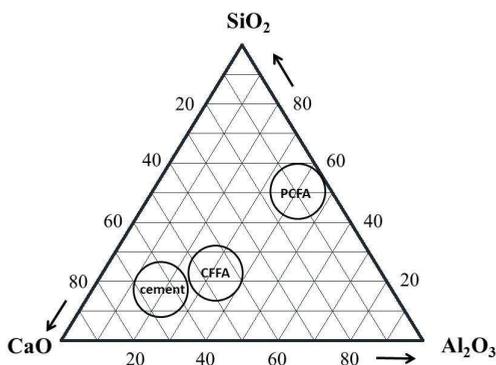
The CFFA produced by CFB boilers has a low combustion temperature (850 to 900 degrees Celsius) and limestone is added as a desulphurising agent during the combustion process. Its physical and chemical properties are different from PCFA [10, 11, 12]. Thus, CFFA cannot be directly used in construction materials in the using the same current technology as PCFA. This study intends to use CFFA to replace the substitutes of cement-based materials, and discuss the mechanism and hydrated characteristics of CFFA applied to cement-based materials. It is expected that it can be applied in construction materials and achieve the purpose of the sustainable utilisation of resources in civil engineering.

## 2 Materials and test procedures

The specific gravity and chemical compositions of Portland type I cement, CFFA and PCFA are summarised in Table 1. The chemical compositions of PFFA are different to those of cement and CFFA. The ternary phase diagram for the CaO-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> is shown in Fig. 1. The comparison of results show that CFFA has higher Al<sub>2</sub>O<sub>3</sub> and SO<sub>3</sub> content than cement and PCFA; lower SiO<sub>2</sub> than PCFA; lower CaO than cement. The specific gravity, water absorption rate, and fineness modulus of the fine aggregates are 2.52, 1.20%, and 2.89, respectively. The mix design of mortar specimens is summarised in Table 2. The cement replacement of CFFA or PCFA was used at the levels of 0%, 10%, 20% and 30%. The water/binder ratios (W/B) used were 0.45 and 0.55.

**Table 1.** Specific gravity and chemical compositions of cement, CFFA and PCFA.

Chemical compositions	cement	CFFA	PCFA
Fe <sub>2</sub> O <sub>3</sub>	2.98 %	2.25 %	23.97 %
Al <sub>2</sub> O <sub>3</sub>	5.46 %	13.80 %	7.56 %
SiO <sub>2</sub>	21.04 %	21.10 %	56.66 %
MgO	2.52 %	2.29 %	0.57 %
SO <sub>3</sub>	-	10.06 %	1.34 %
CaO	63.56 %	48.50 %	1.94 %
Specific gravity	3.15	2.57	2.32



**Fig. 1.** Ternary phase diagram for CaO-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>.

The mix design of the mortar specimens is shown in Table 2. The specimens are numbered as follows: M4 and M5 (for which W/B was 0.45 and 0.55, respectively); F10, F20 and F30 (for which the replacement of cement was 10%, 20% and 30% of PCFA, respectively); C10, C20 and C30 (for which the replacement of cement was 10%, 20% and 30% of CFFA, respectively). Table 3 presents the test methods, the dimensions of the test specimens and testing standard. In addition, the use of superplasticiser (SP) was set at 2 wt.% of binder in this study.

**Table 2.** Mix design of mortar specimens (kg/m<sup>3</sup>).

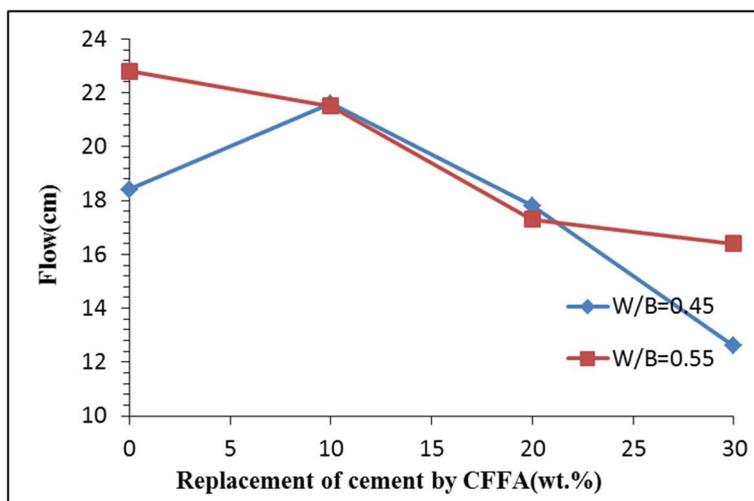
Mix no.	W/B	water	cement	CFFA	PCFA	fine aggregates	SP
M4	0.45	242.1	538	0	0	1479.5	0
M4F10		242.1	484.2	0	53.8	1479.5	0
M4F20		242.1	430.4	0	107.6	1479.5	0
M4F30		242.1	376.6	0	161.4	1479.5	0
M4C10		231.4	484.2	53.8	0	1479.5	10.7
M4C20		231.4	430.4	107.6	0	1479.5	10.7
M4C30		231.4	376.6	161.4	0	1479.5	10.7
M5	0.55	280.5	510	0	0	1402.5	0
M5F10		280.5	459	0	51	1402.5	0
M5F20		280.5	408	0	102	1402.5	0
M5F30		280.5	357	0	153	1402.5	0
M5C10		280.5	459	51	0	1402.5	0
M5C20		280.5	408	102	0	1402.5	0
M5C30		280.5	357	153	0	1402.5	0

**Table 3.** Test methods.

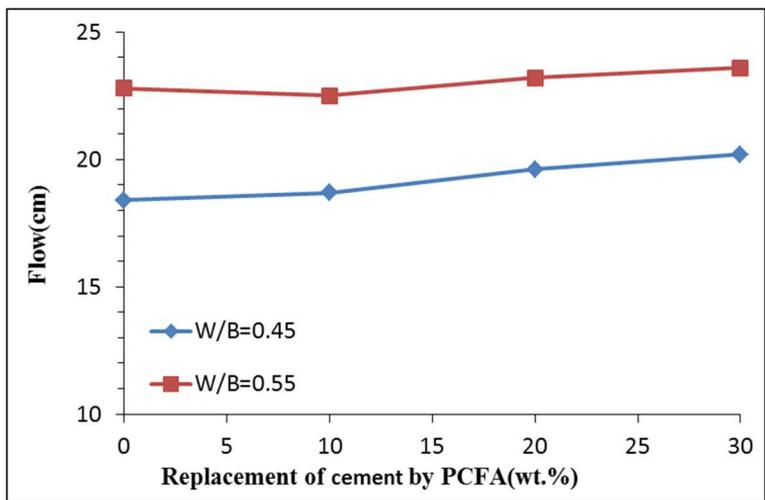
Test methods	Specimen dimensions (mm)	Testing standard	Testing age (days)
Flow test	-	ASTM C1437	-
Compressive strength test	50x50x50	ASTM C109	7, 28, 56, 91
Shrinkage test	285x25x25	ASTM C596	7, 28, 56
Water absorption	50x50x50	ASTM C642	7, 91

### 3 Results and discussion

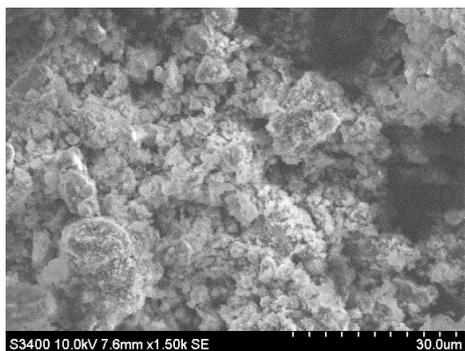
The results of flowability for all mixes are shown in Figs. 2 and 3. The fluidity of mortar increased with increases of W/B. The main reason is that the increase of W/B would increase the amount of lubricating water used per unit of cement. The fluidity of the CFFA specimens decreased with increases in the proportion of CFFA replacement. The particles of CFFA had larger water absorption, and these particles were polygonal with a rough surface and irregular shape (as shown in Fig. 4) resulting in an increase of the friction between the fine aggregates and the cement pastes. CFFA reacted with water to produce irregularly shaped small particles, it was also affected the fluidity. However, the fluidity of the PCFA specimens increased with increases in the proportion of CFFA replacement due to its smooth and spherical particles.



**Fig. 2.** Flow tests of the mortar specimens containing CFFA.

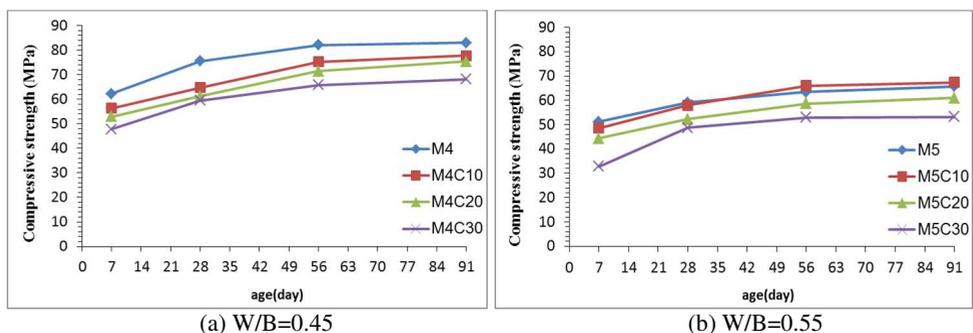


**Fig. 3.** Flow tests of the mortar specimens containing PCFA.

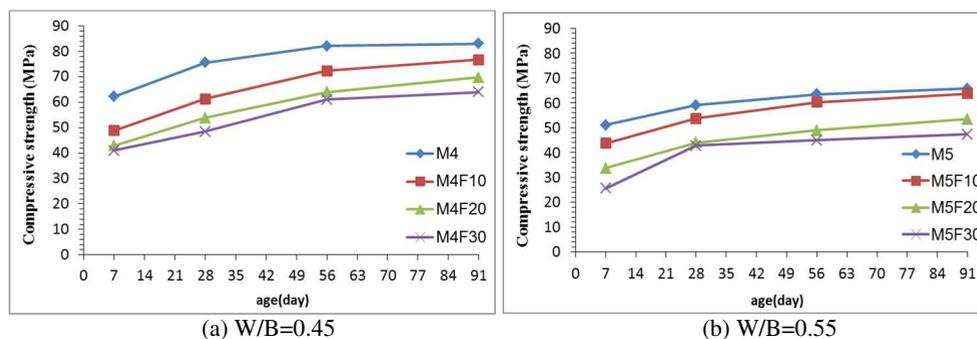


**Fig. 4.** Scanning electron microscope image of CFFA.

The results of compressive strength for all mixes are shown in Figs. 5 and 6. The compressive strength of the CFFA specimens decreased with increases in the proportion of CFFA replacement. Compared with the main components of cement (including  $C_3S$ ,  $C_2S$ ,  $C_3A$ , and  $C_4AF$ ), CFFA (including  $Ca(OH)_2$ ,  $CaCO_3$ ,  $CaO$ ) had poorer crystalline strength and compactness of micro-structures. The inclusion of CFFA in mortar specimens inevitably caused the reduction of the original cement paste, and then reduced the compressive strength of the pastes.



**Fig. 5.** Compressive strength development curves of the specimens containing CFFA.



**Fig. 6.** Compressive strength development curves of the specimens containing PCFA.

However, the compressive strength of the PCFA specimens also decreased with increases in the proportion of PCFA replacement. The pozzolanic reaction of PCFA was relatively slow compared to that of cement. The compressive strength of the mortar was mainly contributed by the hydrated cement, and the compressive strength decreased with increases of PCFA replacement. The PCFA specimens continued to exhibit the pozzolanic reaction after the age of 91 days, it is inferred that the compressive strength was eventually increased when the curing age was exceeded 91 days than M4 and M5 specimens.

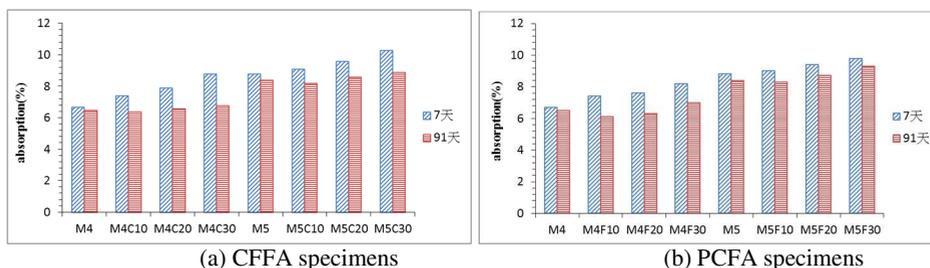
The results of compressive strength for all mixes are shown in Table 4. These indicate that the shrinkage of CFFA specimens decreased with increases in the proportion of CFFA replacement. CFFA contained 10.06%  $SO_3$  and a small amount of gypsum. These two components reacted with calcium aluminate salts ( $C_3A$ ,  $C_4AF$ ) in cement to form calcium vanadate and monosulphate calcium aluminate [12]. These hydrated products produced exothermic expansion at an early age and this phenomenon also helped to inhibit the shrinkage. However, the shrinkage of PCFA specimens had the same effect as the proportion of CFFA replacement. PCFA itself had no obvious hydrated reaction at an early age. Most of the shrinkage was affected by the amount of cement. Therefore, the shrinkage decreased with increases in the amount of PCFA instead of cement. This indicated that the amount of cement would be reduced, resulting in a decrease in shrinkage. The shrinkage of CFFA or PCFA specimens at all ages was almost as low as that of the control specimens, which proves that the inclusion of CFFA and PCFA helps reduce the shrinkage of mortar.

**Table 4.** Results of shrinkage.

Mix no.	Shrinkage ( $\times 10^{-6}$ mm/mm)			Mix no.	Shrinkage ( $\times 10^{-6}$ mm/mm)		
	7 days	28 days	56 days		7 days	28 days	56 days
M4	-69.0	-191.8	-202.8	M4	-69.0	-191.8	-202.8
M4C10	-77.3	-187.8	-194.4	M4F10	-81.2	-198.5	-207.7
M4C20	-74.3	-174.7	-181.3	M4F20	-77.4	-179.0	-185.3
M4C30	-67.2	-155.0	-167.5	M4F30	-58.7	-174.2	-181.2
M5	-126.5	-230.5	-250.0	M5	-126.5	-230.5	-250.0
M5C10	-82.0	-192.5	-198.3	M5F10	-92.3	-209.5	-211.2
M5C20	-78.8	-186.8	-197.5	M5F20	-82.0	-196.4	-205.1

M5C30	-66.3	-181.0	-193.6	M5F30	-72.0	-187.2	-194.8
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The results of water absorption for all mixes are shown in Fig. 7. They indicated that the absorption of CFFA specimens increased with increases in the proportion of CFFA replacement. As the amount of cement replacement of CFFA increased, it inevitably caused the original cement pastes to shrink, which affect the compactness and lead to increased pores in the microstructures. However, the absorption of PCFA specimens had the same effect as the proportion of CFFA replacement. Cement in the specimens has significantly reacted with water as a hydrated reaction and there is no significant hydrated reaction between PCFA particles. Therefore, the pores between the PCFA and cement particles also increased as the amount of PCFA replacement increased. Compared with the control specimens at the W/B of 0.45, CFFA specimens had lower water absorption when the replacement was 10% and the PCFA specimens had lower water absorption in the M4F10 and M4F20 specimens.



**Fig. 7.** Water absorption histograms of the mortar specimens.

## 4 Conclusions

Based on the concept of sustainable development of resources and the sustainable utilisation of materials, it is feasible to apply CFFA and PCCF to cement-based materials. The comprehensive conclusion is as follows:

1. Flow test results show that the inclusion of PCFA in mortar specimens would help improve workability; CFFA in specimens would reduce the workability significantly.
2. The compressive strength shows that the compressive strength of CFFA mortar was higher than that of PCFA specimens; therefore, the inclusion of CFFA to replace the cement had the most substantial benefit for the improvement of compressive strength.
3. The results show that the CFFA specimens had lower shrinkage than that of PCFA specimens, and the shrinkage tended to decrease as the amount of CFFA or PCFA replacement increased.
4. The results show that the M4F10, M4F20, M5F10 and M5F20 specimens had lower absorption than that of the CFFA specimens. However, M4F30 and M5F30 had higher absorption than that of the CFFA specimens. Overall, M4F10, M4F20, M5F10, M5F20, M4C10 and M5C10 had lower absorption than that of the control specimens.

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