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# Influence of sulfur trioxide on volume change and compressive strength of eco-mortar

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## HIGHLIGHTS

- When fly ash from a CFB co-fired boiler is mixed with water, it has a highly exothermic reaction, expansion of the particulate matter and a high pH value.
- Some producers of concrete use co-fired fly ash as a controlled low strength material (CLSM).
- The $SO_3$ content might have been a factor that induced the volumetric expansion of the composite cement mortar.
- The volumetric expansion of the composite cement mortar might have been primarily induced by $C\text{-}A\text{-}\bar{S}\text{-}H$ and $CaSO_4{\cdot}(H_2O)_8$.

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## ABSTRACT

GGBS was mixed with circulating fluidized bed boiler (CFBB) co-firing fly ash (CFFA) to produce mortar, which was then subjected to compressive strength and volume stability testing. The test results revealed that the mortar composed of CFBB CFFA, and GGBS demonstrated improved strength; specifically, mixture ratio of 30%:70% by weight yielded the most optimal compressive strength (65%). When the CFBB CFFA exceeded 40%, apparent volume expansion and unstable compressive strength performance were observed. The SEM and XRD analysis revealed that $C\text{-}A\text{-}\bar{S}\text{-}H$ and $CaSO_4{\cdot}(H_2O)_8$ were generated; this result was attributed to the presence of excessive sulfur trioxide, causing volume expansion.



## 1. Introduction

The industrial revolution at the end of the eighteenth century steered technological development toward a new direction, gradually replacing manual labor with mechanical equipment. Thus, humans are bestowed with a more convenient and comfortable lifestyle. However, while relishing themselves in a better quality of life, humans are also faced with the potential threats caused by such technological developments. According to past studies, the global environment began to deteriorate since the beginning of the industrial revolution; such adverse effect intensified beginning in 2006, when global warming, ozone depletion, resource exploitation, and excess generation of industrial wastes started to endanger humans' living environments. As humans grow accustomed to the benefits brought by technologies, returning to a primitive lifestyle is no longer possible. Therefore, satisfying human needs while conserving the environment and ensuring sustainable development have become a crucial global concern. Concrete is one of the materials most widely used in construction engineering. However, concrete is primarily mixture using Portland cement as its binder. Portland cement emits a large amount of carbon dioxide during its manufacture. Carbon emission is the primary factor aggravating the unproven greenhouse effect, and according to referenced papers [1–3], carbon emission from Portland cement has amounted to 5% of the total global carbon emissions. Therefore, if the production process for Portland cement can be improved or an alternative raw material can be found, the chance to mitigate the global carbon emission increases slightly.

Previous studies have [4,5] indicated that ground granulated blast-furnace slag (GGBS) is currently one of the most applicable materials for partial replacement of Portland cement. GGBS originates primarily from the byproducts of the steel industry and comprises large amount of $SiO_2$, CaO, and $Al_2O_3$. GGBS undergoes a second-order hydration reaction when mixed with Portland cement to form $Ca(OH)_2$. This second-order reaction is known as

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the Pozzolanic reaction. Therefore, GGBS has been extensively applied as a partial substitute to Portland cement. A research report published in 2014 [4] also indicated that GGBS can undergo similar reactions with other industrial byproducts (e.g., basic oxygen furnace [BOF] slag) when Portland cement is not used. Because of its pH value, BOF slag can activate GGBS. In addition, BOF slag contains large amounts of CaO, which in the presence of water can undergo Pozzolanic reaction or alkali-activated reaction [4] with the compositions of GGBS (i.e., $SiO_2$, CaO, and $Al_2O_3$).

Bio-mass, an otherwise wasted material, is one of several clean fuels, which can be burned in a boiler system to produce energy. Its use has had a most rapid increase recently. Combustion of coal and bio-mass can be mostly used in pulverized coal (PC) boiler, stoker boiler or fluidized bed (FB) boiler in the typical cogeneration plant. The circulating fluidized bed boiler (CFBB) is a proven cost-effective and environmental friendly combustion system [5,6] and is a very effective for burning multiple fuels. A CFBB can easily burn fuels such as bituminous, sub-bituminous, lignite, anthracite, petro-coke and bio-mass, which covers wood, sludge, tire derived fuel(TDF), refused derived fuel (RDF), industry wastes etc. [7]. CFBB also has low operating temperature in combustor which is around 800–900 °C. The low combustion temperature does not melt the ashes, and the ashes are standing as crystalline. The residues, including fly ash and bottom ash of CFBB are strongly alkaline and contain trace metals, which may impact the environment if disposed by landfill. Fly ash of CFB coal fired boiler contains a calcium content of around 20–30% of CaO due to the limestone ($CaCO_3$) being injected into the combustor to capture $SO_2$ by forming $CaSO_4$ and thus reducing SOx emission into atmosphere [5]. CFBB co-firing multiple fuels will produce co-firing fly ash (CFBB CFFA), which used in this study. It contains CaO (37.8%), $SiO_2$ (26.4%), $Al_2O_3$ (13.9%), and $SO_3$ (12.9%). It is speculated that CFBB CFFA is also likely to undergo Pozzolanic or alkali-activated reaction with GGBS [8]. Fly ash of coal fired CFB boilers contain around 20–40% by weight of CaO because excess limestone ($CaCO_3$) is injected into CFBB to capture the maximum amount of $SO_2$ [9]. When fly ash from a CFB co-fired boiler is mixed with water, it has a highly exothermic reaction, expansion of the particulate matter and a high pH value. CFBB CFFA has a large specific surface area, which can result more water requirement for the blended cement mortar. The additional water may cause the harmful pores when the mortar has hardened [10]. This is main reason why mixing CFBB CFFA with Portland cement is not popular. This paper presents co-firing fly ash produced in CFBB, which co-fires bituminous coal, sludge and shredded tires. Fly ash of co-firing boilers for use in concrete are not addressed in Taiwan. Fly ash is not allowed to be directly blended with Portland cement in concrete. Recently, fly ash is being disposed by landfill or special permission to be as raw materials of a cement kiln. Some producers of concrete use it as a controlled low strength material (CLSM) for road paving.

This study adopted GGBS as the primary binder material and selected ratios of CFBB CFFA to GGBS as the primary variable for producing blended cement mortar. The GGBS in the wet mortar generates free CaO and MgO. Then, those two elements continuously combine with water forming $Ca(OH)_2$ and $Mg(OH)_2$ causing volume expansion. This reaction creates the alkaline environment, which is similar to using only Portland cement [11]. Subsequently, compressive strength tests were conducted to verify the feasibility of mixing GGBS with CFBB CFFA to form blended cement mortar. However, because the blended cement mortar contains a large amount of $SO_3$, which causes volume expansion in solidified cement mortar, volume stability testing was also conducted. The test results obtained were used as the basis for deducing the optimal mixture ratio for CFBB CFFA. Furthermore, scanning electron microscopy (SEM) and X-ray diffraction (XRD) analysis were performed to identify potential problems.

## 2. Experimental

The chemical composition of CFBB CFFA, GGBS, Portland cement and the mixture are described below.

### 2.1. Materials

Test materials include cement, water, aggregates, CFBB CFFA and GGBS powder. The cement used ordinary Portland cement and fine aggregate with gravity of 2.65 g/cm$^3$ are selected. The chemical composition and physical analysis of test materials are shown in Table 1 [4,5]. The description of OPM, CFBB CFFA and GGBS powder are specified below sub-sections.

#### 2.1.1. Ordinary Portland cement

Ordinary Portland cement I is used as a bench mark material (OPM) for comparing all blended material's characteristics and properties. Its main ingredients are 63.5% CaO and 21.04% $SiO_2$ with specific gravity 3.15 and 3713 cm$^2$/g specific surface.

#### 2.1.2. CFBB CFFA

CFBB CFFA is the residues derived from the CFBB co-combustion using a fuel mix of bituminous coal (65%, wt.), waste paper sludge (30%, wt.) and shredded tires (5%, wt.). The co-firing fly ash is deemed as non-reusable waste material in Taiwan and to be landfilled or other disposal process. The total content of major ingredients $Fe_2O_3$, $SiO_2$, and $Al_2O_3$ is approximately 42.55%, which is less than 70% total required ASTM-593 [12] for fly ash cement. CFFA has a higher content of CaO (37.8%, wt.). A serious concern is the 12.9% $SO_3$ content, which is over than normal limit of less than 4% requirement of blended cement.

#### 2.1.3. GGBS powder

GGBS powder was supplied by local commercial market and is readily available. It is a byproduct of iron manufacturing process. Refer to the referenced papers [4,5], major chemical compositions consist of 41.16% CaO (wt.), 33.42% $SiO_2$ (wt.), 13.35% $Al_2O_3$ (wt.) and 7.76% MgO (wt.) respectively. The specific gravity is 2.89 with 5892 cm$^2$/g as the specific surface.

### 2.2. Mixture proportion for mortar

The variable factor was to change the mixing proportioning ratio of CFFA to GGBS powder in 9:1, 8:2, 7:3, 6:4, 5:5, 4:6 and 3:7 by weight (CFFA weight ratio to GGBS powder) as shown in Table 2 of proportion of CFBB CFFA and GGBS. The ratio of binder and aggregates was 1:2.75. The water-cement ratio was 0.5 for all test specimens.

## 3. Experimental procedures

### 3.1. Compressive strength test

For each mixture, 50 mm × 50 mm × 50 mm cubes were used and three specimens of each mixture were tested at the age of 7, 14, 28, 56 and 91 days curing to investigate the average compressive strength. Each mixture has three test specimens.

**Table 1**
Chemical composition and physical analysis of test specimens (%).

| Chemical composition (wt%) | CFBB CFFA(F) | GGBS(G) | Cement(C) |
|---|---|---|---|
| Cl | 0.13 | NA | NA |
| Zn | 0.86 | NA | NA |
| Mn | NA | 0 | NA |
| MgO | 2.36 | 7.76 | 2.52 |
| $Al_2O_3$ | 13.9 | 13.35 | 5.46 |
| $SiO_2$ | 26.4 | 33.42 | 21.04 |
| $SO_3$ | 12.9 | NA | NA |
| $K_2O$ | 0.54 | NA | NA |
| CaO | 37.8 | 41.16 | 63.56 |
| $Fe_2O_3$ | 3.73 | 0.21 | 2.98 |
| $P_2O_5$ | 0.43 | NA | NA |
| $TiO_2$ | 0.69 | NA | NA |
| Others | 0.26 | 4.1 | 4.44 |
| *Physical properties* | | | |
| Specific gravity | 2.75 | 2.89 | 3.15 |
| Specific surface (cm$^2$/g) | 3886 | 5892 | 3713 |

Notes: Data showing above refer to the referenced paper [4,5].