MECHANICAL STRENGTH AND MICROSTRUCTURAL INVESTIGATIONS OF CIRCULATING FLUIDIZED BED COMBUSTION ASHES - GROUND VITRIFIED BLAST FURNACE SLAG BLENDS

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Abstract:

Paste of Circulating Fluidized Bed Combustion (CFBC) ashes - Ground Vitrified Blast Furnace (GVBF) slag blends has been investigated at different ages concerning their mechanical strength and microstructure. Each blend was made from a mixture of 15% CFBC ash and 85% GVBF slag by weight. The result of this investigation notes that all hardened pastes show good strength developing tendency. According to the type of CFBC ash, the flexural and compressive strength at 28 days can reach about 2.6-5.4 MPa and 30.7-54.0 MPa respectively. After 360 days, these values are about 5.6-7.0 MPa and 45.5-75.0 MPa respectively. This interesting development can be essentially attributed to the massive formation of C-S-H gel combined with certain quantity of ettringite, which produces a small amount of expansion. These products of hydration have been identified by X-ray diffraction and differential thermal analysis.

Keyword: CFBC ashes, GVBF slag, Strength, Thermal analysis, X-ray Diffraction

Pasta dari *Fluidized Bed Combustion* (CFBC) debu - *Ground Vitrified Blast Furnace* (GVBF) *slag* diinvestigasi pada waktu yang berbeda untuk menyelidiki kekuatan mekanikalnya dan mikrostruktur. Setiap campuran dibuat dengan pencampuran 15% CFBC dan 85% GVBF berdasarakan berat. Hasil investigasi menunjukkan bahwa semua perkerasan pasta menunjukkan kecenderungan kekuatan yang baik. Berdasarkan tipe CFBC, kekuatan lentur dan tekan pada usia 28 hari mencapai kurang lebih 2.6 – 5.4 MPa dan 30.7 – 54.0 MPa. Setelah 360 hari, nilai ini mencapai kurang lebih 5.6 – 7.0 MPa dan 45.5 – 75.0 MPa. Peningkatan yang menarik ini dapat memberikan pengaruh kepada formasi masif dari C-S-H gel yang dikombinasikan dengan *ettringite* dengan takaran tertentu, dimana dapat yang memproduksi ekspansi dalam jumlah kecil. Hasil dari panas hidrasi ini dapat diidentifikasi dengan difraksi *X-ray* dan *differensial thermal analysis*.

Kata kunci : CFBC, GVBF, kekuatan, *thermal analysis*, difraksi *X-ray*

1. INTRODUCTION

Circulating Fluidized Bed Combustion (CFBC) represents one of the clean technologies for burning high sulfur combustibles in order to reduce the atmospheric pollution. This technology is particularly interesting because of its capacity to burn low quality combustibles and to reduce SO_2 and NO_x production. However, the addition of SO_2 removing sorbents and the use of a lower combustion temperature (850-900°C) produce different kinds of ash compared to conventional coal combustion systems and create a future management problem.

The properties of CFBC ashes vary according to the nature and the quality of the coal burnt in the power plant. Generally, their specific gravity and specific surface are higher than for ashes produced from pulverized coal power plants that are usually used in the field of civil engineering. Due to desulphurising process in the power plant boiler, CFBC ashes contain freer CaO and SO_3.

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Furthermore, there is fewer glass particles in this type of ash, which can be attributed to the lower combustion temperature used in this technology. Theses conditions render their characteristics quite different from those of ashes obtained from coal pulverized power plants.

The hydraulic/pozzolanic property of CFBC ashes is possibly the most useful for civil engineers (Bland, 1991; Charles-Gibergues et al., 1994; Tassart et al., 1997; Salain et al., 2000). However, their use is still very limited because of the exothermic and expansive characteristics of certain CFBC ashes usually related to the presence of free lime (CaO) and anhydrite ($CaSO_4$). Moreover, large variations in their physical, chemical and mineralogical properties increase the risk of using this ash. One author has proposed a process that allows for the selective hydration of quick lime content in fly ashes before use (Blondin et al., 1995). Another recommends the use of these ashes as raw materials for the synthesis of calcium sulphoaluminate cements (Bernardo et al., 2000).

In the present study, the blend of 3 types of CFBC ashes and GVBF slag has been studied from the point of view of strength and mineralogy. It is well known that both lime and anhydrite can be used respectively as the alkaline and sulfate activators of slag. This combined activator essentially stimulates the formation of C-S-H and ettringite, which will develop slag strength (Voinovitch et al., 1976; Dron, 1984; Alexandre, 1988). In the same way, the free lime and anhydrite present in these ashes will be used for activating slag hydration.

The characteristics of the materials studied are first described. Then the results drawn of the experimental study, carried out by hydrating blends of CFBC ash and GVBF slag, are presented and discussed.

2. MATERIALS AND EXPERIMENTAL METHOD

Some physical and chemical properties of two CFBC fly ashes (A1 and A2), a mix of 50% CFBC fly ash and 50% of CFBC bottom ash (A3) and GVBF slag used in this study are given in table 1 and 2 separately.

Table 1
Chemical Analysis of CFBC ashes and GVBF slag (% by Weight)

Materials	Al_2O_3	CaO	SiO_2	Fe_2O_3	SO_3	Free CaO	LOI
A1	16.28	15.34	39.36	6.67	7.40	4.98	10.30
A2	6.92	41.65	21.27	4.45	18.30	14.41	4.55
A3	4.56	50.85	10.45	3.57	25.49	20.49	2.40
GVBF slag	9.80	41.10	36.70	1.35	0.30	-	0.80

Each ash sample was used to prepare three blends, B1, B2 and B3 which respectively contain 15% A1, A2 and A3 and 85% GVBF slag by weight. Plain paste of each blend was used to cast 40x40x160 mm prisms. The water-cementitious materials ratio (w/cm) of each blend, given in table 3 was adjusted in order to produce a paste with a standard consistency according to European standard EN 196-3 (EN 196-3, 1994). These prisms were kept in molds at 20°C and 100% RH for 2 days, then cured in water at 20°C until used for the strength test. At 28, 90, 180 and 360 days of hydration, three prisms were used to measure flexural and compressive strength in accordance with European standard EN 196-1 (EN 196-1, 1994).

Table 2
Physical properties of CFBC ashes and GVBF slag

Materials	Fineness Blaine (cm^2/g)	Specific gravity (g/cm^3)	d_{50} (μm)
A1	6450	2.56	22.9
A2	6875	2.62	37.8
A3	-	2.78	50.0
GVBF slag	5650	2.93	6.9

The hydration products and the relative comparison of their progress over time were identified by X-ray diffraction (XRD) and Differential Thermal Analysis (DTA) after 1 day of hydration as well as after hydration and cured in water for 7, 28, 90, 180 and 360 days. The samples used for these analyses were taken from the central zone of the specimens, dried at 25°C and then crushed less than 100μm.

3. RESULTS AND DISCUSSION

3.1 Mechanical Strength

Figure 1 illustrates the development of flexural and compressive strength of blends as a function of curing time. The development of both flexural and compressive strength is greatly influenced by the type of ash used. In general, the strength increases during the first 180 days and then it tends to stabilize or increases slowly. At 28 days, the flexural strength in the blends containing A1, A2 and A3 was 2.6, 3.5 and 5.4 MPa respectively and after 360 days it reached 5.8, 5.6 and 7.0 MPa. A strong increase was also observed in the development of the compressive strength. At the same period of hydration, the compressive strength in the blends using A1, A2 and A3 increased from 30.7, 47.0 and 54.0 MPa to 45.5, 68.5 and 75.0 MPa respectively.

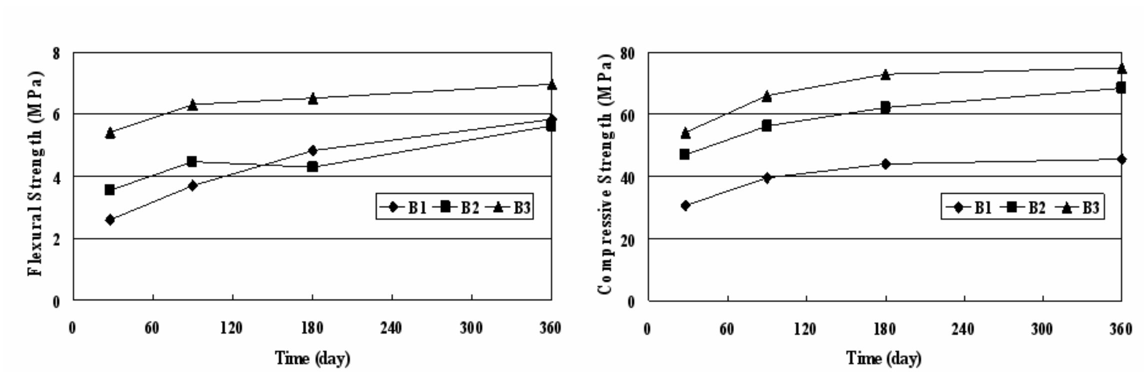

Figure 1
Evolution of Flexural and Compressive Strength of Blends

3.2 Mineralogy

3.2.1 X-Ray Diffraction

The results of XRD analysis indicate a quite similar phenomenon for all the samples. In general, while the anhydrite and the lime content in the blends disappears quickly, the formation of ettringite (3CaO Al_2O_3 3$CaSO_4$ 32H_2O) was clearly identified. The formation of calcite ($CaCO_3$) due to carbonation of the remaining lime can also be noted in each blend. On the other hand, quartz and merwinite are almost constant before and after hydration. Figure 2 shows an evolution of the X-ray diffractograms of the blend containing 15% A3 and 85% GVBF slag.

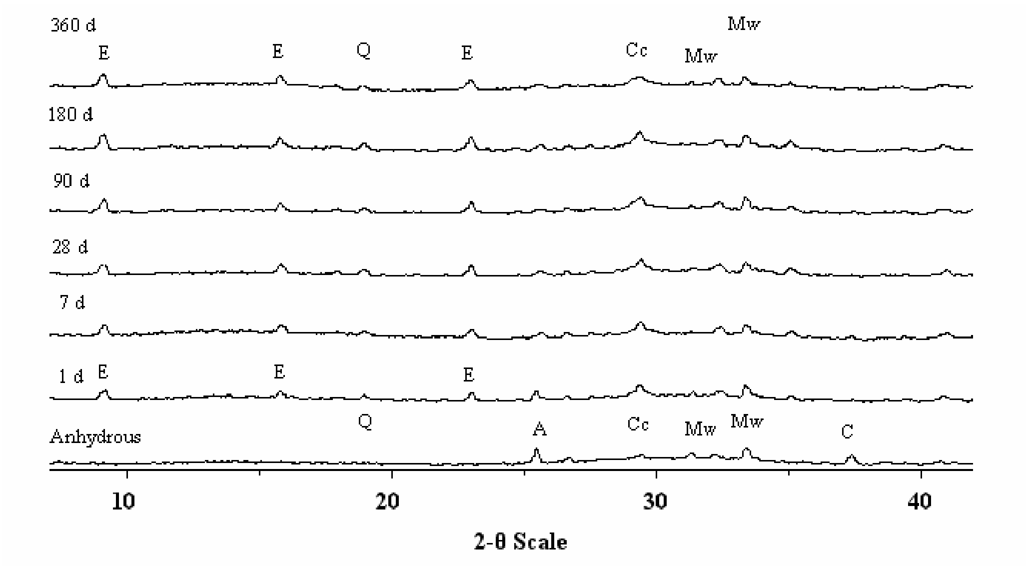

Figure 2
X-ray diffractograms of blend of 15% A3 and 85% GVBF slag
A : Anhydrite, C : Free lime, Cc : Calcite, E : Ettringite, Mw : Merwinite, Q :Quartz

These diagrams show that the formation of ettringite in the blends increases essentially from the beginning until 7 days of hydration and tends to stabilize or slightly decrease in certain blends after this period. These diagrams also show that ettringite persists until 360 days of hydration. The intensity of ettringite increases according to the type and quantity of the CFBC ashes used in the blends. The blends containing more free lime and sulfate produced more ettringite than the others.

3.2.2 Differential Thermal Analysis

Figure 3 shows DTA diagrams of the blend containing 15% A3 and 85% GVBF slag, obtained from 20°C up to 600°C, after 1, 7, 28, 90 and 180 days of hydration. Three principal endothermic peaks have been generally identified in these diagrams at the temperature ranges: 105-115°C, 120-130°C and 135-150°C.

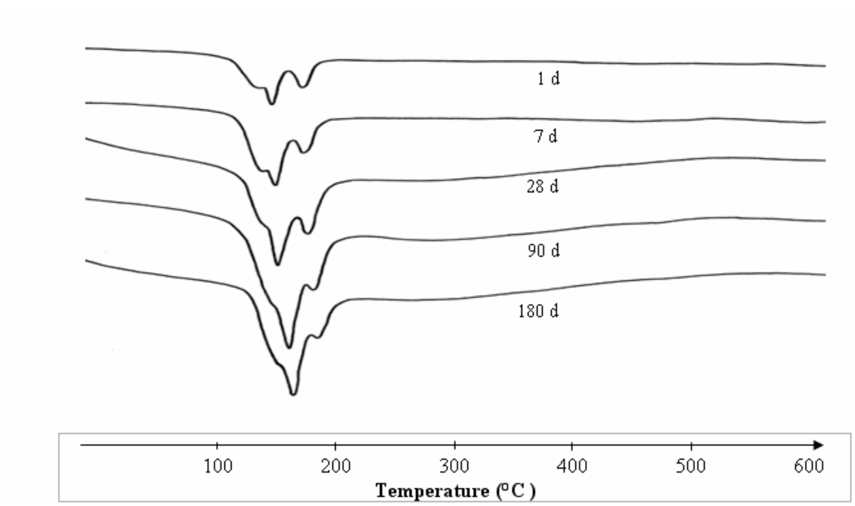

Figure 3
DTA diagrams of blend of 15% A3 and 85% GVBF slag

The first peak indicates the dehydration of free water. During the long hydration process, it tends however to superimpose on the left side of the second peak, which is attributed to the water loss of, hydrated calcium silicate (C-S-H). The presence of this compound could not be observed by XRD analysis probably due to its amorphous structure. The C-S-H peak grows significantly during the curing time for all blends and tends to stabilize after 180 days. The third peak corresponds to the dehydration of ettringite. The presence of this compound observed by DTA confirms the previous result of XRD. The ettringite peak increases noticeably during the first seven days of hydration and tends to stabilize after that.

3.2 Discussion

The mechanical performances presented by the blends are strongly influenced by the type of the CFBC ashes used. This can essentially be related to their different chemical compositions, especially their free CaO and $CaSO_4$ content. The presence of these elements in the blend stimulates the slag hydration and the strength development of the blends. This is clearly indicated by the formation of ettringite and C-S-H in the blends as suggested by the XRD and DTA.

The formation of ettringite combined with the massive formation of C-S-H develops the blend strengths. In fact, the presence of a certain quantity of ettringite reinforces paste solidification which produces a small amount of expansion (Salain, 2001). This is also confirmed by other studies of slag cement hydration (Moranville, 1980; Li et al., 2000). However, it is also probable that the reactive silica and alumina existing in the CFBC ash play an important role in strength development on account of certain hydraulic property (Salain et al., 2000).

Thus, the presence of CFBC ash in the blends activates slag hydration attributed to the free CaO and $CaSO_4$, which act as the alkaline and sulfate activators respectively. Moreover, it simultaneously reinforces the hardening process of the blend supplied by those activators and also the reactive silica and alumina existing in the CFBC ash.

4. CONCLUSION

- The mechanical performances presented by the blends are strongly influenced by the chemical composition of the CFBC ashes used, especially on their free lime and sulfate contents.

- By using 15% of CFBC ash, the flexural and compressive strength of the blends, at 28 days, can reach about 2.6-5.4 MPa and 30.7-54.0 MPa respectively, according to the type of CFBC ash used. These strengths reach about 5.6-7.0 MPa and 45.5-75.0 MPa respectively after 360 days.

- This increased performance can be related to the combination of the massive formation of C-S-H gel and a certain quantity of ettringite that does not produce any significant expansion in the blends.

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