Characterization of optimum fluidized bed combustion ash-based geopolymer concrete

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Abstract: The fluidized bed combustion (FBC) ash was evaluated for value-added use in the production of geopolymer concrete where alkali aluminosilicate hydrates are the primary binder constituents. The FBC was supplemented with other raw materials in order to achieve chemical balance, and they were milled with CO₂ and air to evaluate the benefit from CO₂ uptake. An experimental study on the properties of the optimum FBC ash-based hydraulic cement and the concrete fabricated from it was conducted. Also, the corresponding properties of Portland cement concrete were also investigated as the reference group. For the FBC ash-based cement, tests were performed to measure the CO₂ uptake and heat of hydration; for FBC ash-based hydraulic cement concrete, measurements were made on the compressive strength of hardened material, residual compressive strength after immersion in boiling water and sulfates resistance. The results of this study suggest that, the FBC ash-based geopolymer with the mechanochemical activation can provide desired mechanical attributes, sulfates resistance when compared with normal Portland cement concrete.

1. Introduction

FBC is a very effective technology for power generation, which has met the environmental requirement for large reductions in SO₂ and NOₓ emissions [1]. The relatively high silica and alkali contents of FBC ash makes it suitable for production of alkali aluminosilicate hydrate binders in high-performance and sustainable geopolymer concrete materials [2]. However, low combustion temperature leads to a low glassy phase in FBC ash which hinders it does not favor its use as a cement replacement in conventional portland cement concrete.

A lot of aluminosilicate source materials, like metakaolin [3, 4], blast-furnace slag [5], rice husk ash [6] and red mud [7] have been used as source materials for the synthesis of geopolymer. FBC ash [8-10] is another alternative source material as it contains silica and the conventional two-part geopolymers are produced by mixing the aluminosilicate precursor with an alkaline solution. However, the FBC fly ash-based geopolymer has a low strength. Proper grinding of FBC fly ash removed pores and cavities and increased the surface area [9].

The utilization of FBC ash is limited for making the geopolymer, non-cement binding, as it is a material with low reactivity. This research attempted to improve FBC ash for geopolymer preparation through mechanochemical activation.

Concrete specimens made with the optimum FBC ash-based hydraulic cement developed in this research was prepared and subjected to a comprehensive experimental program for characterization of some key aspects of their performance. For the FBC ash-based cement, tests
were performed to measure the CO$_2$ uptake, blaine fineness and heat of hydration. For FBC ash-based hydraulic cement concrete, measurements were made on compressive strength of hardened material, residual compressive strength after immersion in boiling water and sulfates resistance. A conventional Portland cement concrete was also investigated together with the new FBC ash-based hydraulic cement concrete in order to assess the competitive position of the new hydraulic cement in terms of key engineering properties.

2. Experiment
Carbonization of recycled coarse aggregate and its performance analysis
2.1 Materials
The optimum FBC ash-based hydraulic cement incorporating CO$_2$ was prepared through mechanochemical activation. A blend of FBC ash: conventional coal ash at 70:30 weight ratio was milled in CO$_2$ in the presence of 23.2% Na$_2$SiO$_3$, 7.5% NaOH and 3.9% MgO by mass of the blended ash. This was the optimized FBC ash-based hydraulic cement formulation developed in the research. The chemical composition and blaine fineness of the binders are given in Table 1. The concrete mix design incorporating this hydraulic cement is shown in Table 2. The Portland cement concrete mix design used as reference group is presented in Table 3.

| Material          | SiO$_2$ | Al$_2$O$_3$ | Fe$_2$O$_3$ | CaO | MgO | Na$_2$O | K$_2$O | Blaine fineness(cm$^2$/g) |
|-------------------|---------|-------------|-------------|-----|-----|---------|-------|--------------------------|
| FBC ash           | 21.73   | 9.26        | 14.15       | 26.52| 5.2 | 3.0     | 2.62  | 4610                     |
| Coal fly ash      | 43.10   | 23.30       | -           | 14.30| -   | 0.90    | 1.70  | 4702                     |
| Portland Cement   | 20.10   | 7.10        | 4.40        | 64.70| -   | 1.10    | 1.00  | 11.640                   |

Table 2. Mix proportions of the FBC ash-based hydraulic cement concrete

| Material                  | Quantity, kg/m$^3$ |
|---------------------------|--------------------|
| Optimum geopolymer cement | 324                |
| Coarse aggregate          | 797                |
| Fine aggregate            | 530                |
| Water-to-cement ratio     | 0.46               |

Table 3. Mix proportions Portland cement concrete

| Material                  | Quantity, Kg/m$^3$ |
|---------------------------|--------------------|
| Portland cement type I    | 320                |
| Coarse aggregate          | 728                |
| Fine aggregate            | 1092               |
| Water-to-cement ratio     | 0.55               |

2.2 Preparation of Test Specimens
The FBC ash-based hydraulic cement concrete and the Portland cement concrete were mixed in a laboratory mixer, molded, consolidated by external vibration, sealed, and retained at room temperature for 24 hours. They were then demolded and sealed at 95% relative humidity and room temperature until a test age of 7 days.

2.3 Test Methods
The FBC ash-based hydraulic cement was tested for assessment of its CO$_2$ uptake, morphology
(via scanning electron microscopy), blaine fineness, and heat of hydration. The FBC ash-based hydraulic cement and the control Portland cement concrete were subjected to an experimented program for assessment of their fresh mix workability and set time, compressive and flexural strength, density, void content, water absorption capacity, sorptivity, and acid, sulfate and fire resistance. The test methods employed in this research are reviewed in the following.

2.3.1 CO$_2$ Uptake
FTIR spectroscopy and mass loss with temperature rise (LOI) were used to assess the CO$_2$ uptake of FBC ash-based hydraulic cements processed mechanochemically in a CO$_2$ medium. FTIR spectra of hydraulic cements were used to identify bonds associated with carbonate anions or physically adsorbed carbon dioxide. A JASCO FTIR-4100 system was used for FTIR spectroscopy. LOI was used as an approximate measure of CO$_2$ uptake. Approximately 5g of hydraulic cement powder was heated up to 950°C at a temperature rise rate of 10°C/min. The %CO$_2$ uptake was calculated using the following equations:

$$\text{LOI} = \frac{\text{wt. of powder at } 25^\circ\text{C}}{\text{wt. of powder at } 950^\circ\text{C}} \times 100\%$$

% CO$_2$ uptake = LOI for CO$_2$ milled – LOI for blend of as-received powders

2.3.2 Heat of Hydration
The heats of hydration of FBC ash-based hydraulic cement and the control Portland cement were measured via calorimetry (I-cal 2000 HPC). Immediately before the test, 20 g of cementitious material was mixed with sufficient amount of water (depends on the w/c ratio of concrete) by hand for a fixed length of time. The paste was then placed inside the calorimeter, and the heat release was monitored for up to 4 days.

![Figure 1. The calorimetry test setup.](image)

2.3.3 Compression Tests
Compression tests were performed at the age of 7 days on room-temperature-cured 50 mm concrete cube specimens. Compression loads were applied quasi-statically at a stress rate of 20 MPa/min.

2.3.4 Sulfate Resistance
Sulfate resistance of concrete specimens was evaluated by visual inspection and measuring the residual compressive strength after their exposure to a sulfate solution. Test specimens were immersed in a sulfate solution (5% Na$_2$SO$_4$ in water) at 7 days of age [11]. Average of two compression tests were taken as the compressive strength prior to and after exposure to sulfate solution. FBC ash-based hydraulic cement concrete and Portland cement concrete specimens were immersed in the sulfate solution in separate containers (Figure 2); the volume proportion of sulfate solution to specimens was 4 to 1. The change in compressive strength after sulfate exposure was determined by testing the compressive strength of specimens after selected periods of exposure. The specimens were tested in saturated surface dry condition.
3. Test Results and Discussion

3.1 CO₂ Uptake

Figure 3 shows the FTIR spectra of the FBC ash-based hydraulic cement milled in air and in CO₂. The 1440 cm⁻¹ peak corresponds to the carbonate anions incorporated into the hydraulic cement. Milling in CO₂ produces a sharper peak at this wave number, which is indicative of uptake of CO₂ when milling is performed in a carbon dioxide gas medium. Based on the thermogravimetry (LOI) measurements, the CO₂ uptake of the FBC ash-based hydraulic cement processed mechnochemically in carbon dioxide gas environment was 15.01% by mass of the hydraulic cement.

3.2 Heat of Hydration

The rate of heat evolution and the total heat of hydration, respectively, of Portland and FBC ash-based hydraulic cement are presented in Figures 4 and 5. The FBC ash-based hydraulic cement, when compared with Portland cement, exhibits a higher rate of heat release during the first ten hours, but a smaller total heat of hydration. This observation indicates that the hydration reactions and thus the strength gain for FBC ash-based hydraulic cement occurs more rapidly at early stages of hydration when compared with Portland cement for which hydration reactions are extended over time.
Figure 4. Rate of heat release versus time associated with hydration of Portland cement and FBC ash-based hydraulic cement.

Figure 5. Total heat release versus time associated with hydration of Portland cement and FBC ash-based hydraulic cement.

3.3 Compressive Strength and Residual Compressive Strength

Figure 6 presents the visual appearances of FBC ash-based hydraulic cement concrete and Portland cement concrete compression test specimens. Figure 14 presents the compressive (and residual compressive) strength test results for FBC ash-based hydraulic cement concrete and Portland cement concrete (both at 7 days of age). The residual compressive strength of concrete was measured after immersion in boiling water and subsequent drying (steps involved in measurement of density). The mean 7-day compressive strengths obtained with the FBC ash-based hydraulic cement and Portland cement are 18 and 24 MPa, respectively. While the 7-day compressive strength obtained with the first-generation FBC ash-based hydraulic cement is 25% less than that obtained with Portland cement, the 18 MPa compressive strength of FBC ash-based hydraulic cement concrete is within the viable range for concrete construction applications. The particular Portland cement concrete considered here provides a relatively high 7-day compressive strength of 24 MPa (when compared with the typical 28 MPa compressive strength of normal-strength concrete at 28 days of age). The residual compressive strengths of both concrete materials were statistically comparable (at 5% level of significance) to those obtained prior to immersion in boiling water. There is a minor and statistically insignificant drop in the compressive strength of the FBC ash-based hydraulic
cement concrete after immersion in boiling water.

Figure 6. Compression test specimens of Portland cement concrete (left) and FBC ash-based hydraulic cement concrete (right).

Figure 7. Seven-day compressive strength and residual compressive strength test results for FBC ash-based hydraulic cement concrete and Portland cement concrete (means & 95% confidence intervals).

3.4 Sulfate Resistance

The sulfate resistance of the FBC ash-based hydraulic cement concrete and normal Portland cement concrete were assessed based on visual inspection and measurement of compressive strength after different durations of exposure to sulfate solution. Figure 8 shows visual appearances of the FBC ash-based hydraulic cement concrete and Portland cement concrete specimens after different periods of exposure to sodium sulfate solution. The trends in surface deterioration were similar for the two types of concrete. This also applied to the trends in compressive strength loss under sulfate attack (Figure 9). The high sulfate content of FBC ash raises the internal surface content of concrete. The FBC ash-based hydraulic cement concrete is thus exposed to a higher internal sulfate concentration than Portland cement concrete. In spite of that, the trends in sulfate attack are comparable for the two types of concrete, which reflects upon the better barrier qualities and chemical stability of FBC ash-based concrete when compared with Portland cement concrete. The predominantly aluminosilicate- and carbonate-based chemistry of the new hydraulic cement limits its susceptibility to sulfate attack. This is why the presence of sulfates in FBC ash does not rule out its use in the new type of cement, which is not the case in use of FBC ash as a partial replacement for Portland cement.
Figure 8. Visual appearances of the FBC ash-based hydraulic cement concrete and Portland cement concrete after different periods of sulfate attack.

Figure 9. The trends in compressive strength loss with time of exposure to sulfate attack for the FBC ash-based hydraulic cement concrete and Portland cement concrete.

4. Conclusions:
Concrete materials were prepared with FBC ash-based hydraulic cement concrete (incorporating carbonate complexes) and control Portland cement Concrete. A comparative investigation was conducted on the two cements and the resulting concrete materials. Tests performed on cement concerned their CO$_2$ uptake, specific surface area, and heat of hydration. Concrete materials were tested for compressive and resistance to sulfate.

1. The experimental results indicated that the FBC ash-based hydraulic cement developed in the research had a CO$_2$ uptake of 15% in the course of mechanochemical processing. Its specific surface area (fineness) was somewhat greater than that of Type I Portland cement. Total heat of hydration of the FBC ash-based hydraulic cement, however, was smaller than that of Portland cement because hydration of Portland cement was extended over time. The compressive strengths of the FBC ash-based hydraulic cement concrete approached those provided by Portland cement concrete.

2. The trends in surface deterioration and strength loss under sulfate attack were similar for FBC ash-based hydraulic cement concrete and Portland cement concrete. The high sulfate content of FBC ash raises the internal surface content of concrete. The FBC ash-based hydraulic cement concrete is thus exposed to a higher internal sulfate concentration than Portland cement concrete. In spite of this, the trends in sulfate attack are comparable for the two types of concrete, which reflects upon the better barrier qualities and chemical stability of FBC ash-based concrete when compared with Portland cement concrete.

3. The predominantly aluminosilicate- and carbonate-based chemistry of the new
hydraulic cement limits its susceptibility to sulfate attack. This is why the presence of sulfates in FBC ash does not rule out its use in the new type of cement, which is not the case in use of FBC ash as a partial replacement for Portland cement.

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Reference:
[1] E.J. Anthony, E.E. Berry, J. Blondin, E.M. Bulewicz, S. Burwell. Advanced ash management technologies for CFBC ash. Waste Manage, 23 (2003), p. 503-516.
[2] Matalkah, F., Sorouhian, P., and Peyvandi, A. Use of non-wood biomass combustion ash in development of alkali-activated concrete. Constr. Build. Mater., 121, 491-500.
[3] Palomo A, Glasser FP. Chemically-bonded cementitious materials based on metakaolin. Br Ceram Trans 1992;91:107.
[4] Gao K, Lin KL, Wang DY, Hwang CL, Shiu HS, Chang YM, et al. Effects SiO2/Na2O molar ratio on mechanical properties and the microstructure of nano-SiO2 metakaolin-based geopolymers. Constr Build Mater 2014;53:503.
[5] Cheng TW, Chiu JP. Fire-resistant geopolymer produced by granulated blast furnace slag. Miner Eng 2003;16:205.
[6] Rattanasak U, Chindaprasirt P, Suwanvitaya P. Development of high volume rice husk ash alumino-silicate composite. Int J Miner Metall Mater 2010;17:654.
[7] He J, Jie Y, Zhang J, Yu Y, Zhang G. Synthesis and characterization of red mud and rice husk ash-based geopolymer composites. Cem Concr Compos 2013;37:108.
[8] Xu H, Li H, Shen L, Zhang M, Zhai J. Low-reactive circulating fluidized bed combustion (CFBC) fly ashes as source material for geopolymer synthesis. Waste Manage (Oxford) 2010;30:667.
[9] Chindaprasirt P, Rattanasak U. Utilization of blended fluidized bed combustion (FBC) ash and pulverized coal combustion (PCC) fly ash in geopolymer. Waste Manage (Oxford) 2010;30:667.
[10] Chindaprasirt P, Rattanasak U, Jaturapitakkul C. Utilization of fly ash blends from pulverized coal and fluidized bed combustions in geopolymeric materials. Cem Concr Compos 2011;33:55.
[11] Nasser, A. and U. Mingelgrin, Mechanochemistry: A review of surface reactions and environmental applications. Applied Clay Science, 2012. 67: p. 141-150.