Recycling of switchgrass combustion ash in cement: Characteristics and pozzolanic activity with chemical accelerators

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HIGHLIGHTS

- Hazardous ash from switchgrass combustion could be recycled in cement.
- Tested the physiochemical, thermal and microstructural properties of ash.
- Switchgrass ash was an effective pozzolan in the late stage of cement curing.
- Pozzolanic activity of ash was enhanced with chemical accelerators.
- Cement with 10% ash and chemical accelerator was as strong as conventional cement.

ARTICLE INFO

ABSTRACT

Biomass combustion produces renewable energy, but generates hazardous ash that must be disposed. High-volume of fine ash from the biomass combustion could be a harmful pollutant which causes lung cancer. Recycling the ash in cement is an environmentally-friendly solution especially for the cement industry. The objectives of this paper were to (1) characterize the ash from switchgrass combustion in a lab-designed furnace and (2) evaluate the material properties of cement containing switchgrass combustion ash. Cement-ash blends tested in this study contained 10% and 20% of ground ash (by weight) and chemical accelerators (5% Na_2SO_4 or 5% $CaCl_2·2H_2O$). Switchgrass combusted at 411 °C generated 5% ash by weight. After grinding for 30 s, ground ash had a porous structure with 65.0 μm of mean particle size and 41.2 m^2/g of BET surface area. Ground ash consisted of 67.2% of SiO_2 and its structure contained 72.2% of amorphous crystal. This ash was a good pozzolan in blended cement, and its pozzolanic activity was improved by adding chemical accelerators (5% Na_2SO_4 and 5% $CaCl_2·2H_2O$ were equally effective). Blended cement with 10% ash and either 5% Na_2SO_4 or 5% $CaCl_2·2H_2O$ had similar material properties (strength and expansion resistance) as conventional Portland cement. Hence, recycling the switchgrass ash in the cement proved to be technically applicable.

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1. Introduction

Biomass combustion generates renewable energy, which is appealing to energy-intensive industries such as cement producers. Since cement is produced at ≈1450 °C, an average-size cement plant uses 3–6 GJ of fossil fuel per tonne of cement fabricated [1]. Cement industry can use biomass fuel to supplement fossil fuel and partially reduce its carbon footprint. For instance, Lafarge Canada accom-plished full-scale cement production trials with biomass fuel in 2010, but noted several obstacles for the biomass fuel. Burning 1 kg of the biomass fuel would generate 0.05–0.2 kg of fine ash, and the fine ash was a hazardous contaminant that could potentially cause lung cancer [2]. Owing to large volume of the fine ash when it was present on-site, it was not appropriate to adopt conventional industrial waste treatments, such as land fill. Consequently, one challenge was how to dispose of the ash generated from the biomass fuel in an efficient, sustainable and economical way.

It is technically possible to recycle the ash produced during bio-mass combustion in cement. The most important constituent of ash that can enhance the strength and durability of concrete is SiO_2, owing to the supplementary formation of calcium silicate hydrate

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((CaO)$_x$·(SiO$_2$)$_y$·(H$_2$O)$_z$, C–S–H) from calcium hydroxide (Ca(OH)$_2$, CH) by the pozzolanic reaction [3]. Pozzolans are siliceous or siliceous and aluminous materials with virtually no cementing value; however, in the presence of water, they react with CH to form C–S–H, which is the main contributor to concrete strength [4]. A satisfactory pozzolan should have small particle size and contain more than 70% of SiO$_2$ + Al$_2$O$_3$ + Fe$_2$O$_3$ [5]. Yet, compared to the conventional pozzolans like silica fume (containing ≈99% SiO$_2$), the pozzolanic activity of biomass ash is still inferior due to its lower SiO$_2$ content (≈50–80%). Hence, it is critical to consider how to enhance the pozzolanic reaction when biomass ash is used in cement.

To stimulate the pozzolanic activity of ash, chemical acceleration is achieved by adding 3–5% Na$_2$SO$_4$ or CaCl$_2$·2H$_2$O in cement–ash mixtures. By adding Na$_2$SO$_4$, the reaction between Na$_2$SO$_4$ and Ca(OH)$_2$ produces NaOH, which accelerates the dissolution of SiO$_2$ in the cement–pozzolan–water system, thus enhancing the pozzolanic reaction rate. Blended cement pastes (with 10% or 30% of oil shale ash) possessed stronger mechanical properties after being accelerated by 2.25%, 4.5% or 6.25% Na$_2$SO$_4$ [6]. Adding 4% Na$_2$SO$_4$ efficiently accelerated the pozzolanic activity of low grade ash (reject fly ash) when cement was replaced by 10%, 25% and 40% ash [7]. Moreover, when cement pastes contained a high volume of fly ash (≈80%), Na$_2$SO$_4$ effectively reduced the setting time and increased the compressive strength [8], and improved both of the early and later strengths at 23–65 °C [9]. In contrast, mixing CaCl$_2$·2H$_2$O with cement generates a new crystal C$_3$A·CaCl$_2$·10H$_2$O–C$_3$A·Ca(OH)$_2$·12H$_2$O, which provides a more robust microstructure than C–S–H but also improves cementing characteristics [10]. In cement pastes containing 80% of volcanic ash, mixing 4% CaCl$_2$·2H$_2$O decreased the early strength but increased the later strength at 23 °C, and advanced both of the early and later strengths at 35–65 °C [9]. Meanwhile, CaCl$_2$·2H$_2$O was also effective in the cement mortar with 20% bagasse ash [11] and 20% pozzolanic clay [12]. Therefore, the chemical acceleration by Na$_2$SO$_4$ or CaCl$_2$·2H$_2$O has the potential to improve the pozzolanic activity of biomass ash.

Switchgrass (*Panicum vigratum L.*) is an emerging biomass fuel in North America and Europe [13]. Compared to other biomass sources, it has an excellent calorific value (17–20 MJ/kg) and is rich in silicon (4.0–6.3%) [14], which implies that its ash might have a positive pozzolanic activity. However, there is no research heretofore to evaluate the recycling of switchgrass ash in the cement, or to explore the solution to make this concept technically applicable.

This paper aimed to characterize the ash from switchgrass combustion in a lab-designed furnace, and evaluate the material properties of cement containing switchgrass combustion ash. The cement–ash blends tested in this study contained 10% and 20% of ground ash (by weight) and chemical accelerators (5% Na$_2$SO$_4$ or 5% CaCl$_2$·2H$_2$O). To compare the results to other studies, the pozzolanic activities and cement properties were evaluated by standard methods, including Frattini test, lime–ash test, concrete compressive strength test, and expansion test.

2. Material and methods

2.1. Switchgrass preparation and characterization

Switchgrass was gathered from a farm in Williamsburg, Ontario, Canada, and characterized in lab with two replications. Before combustion, switchgrass was manually sheared to 2 cm long roughly. About 10 mg of ground switchgrass (≈500 μm) was used for the proximate analysis by the sequential thermogravimetric method [15]. Ultimate analysis was performed by micro-combustion method, with ≈25 mg of dried ground switchgrass, using an elemental analyzer equipped with thermal conductivity detectors. As defined in ASTM D4239-13e1 [16], the sulfur content was measured by combustion method on a sulfur analyzer at 1350 °C. The calorific value (higher heating value) of the dried switchgrass was tested in an oxygen bomb calorific meter following the ASTM D5865-13 method [17].

2.2. Switchgrass combustion

2.2.1. Design of combustion furnace

A multiple-purpose stove was connected into a combustion furnace in the lab (Fig. 1). Dimension of combustion chamber was 84 × 38 × 51 cm. An exhaust expelling system was set up to provide sufficient air (≈2500 cm^3/s) for complete combustion. During combustion, temperature of the sample surface was monitored by an infra-red thermometer outside the furnace. One thermocouple was installed on the exhaust gas outlet and a second thermocouple was placed in the chamber interior. Both thermocouples were linked to a data acquisition card (DAQ) for data recording every 5 s. In addition, an aluminum wire mesh (2 mm) was placed at the exhaust exit port to block the exit of fine burnout residue carried by exhaust gas.

2.2.2. Combustion test

Combustion temperatures and yields of burnout residue were measured by the combustion tests with various initial switchgrass load (492, 590, 639, 648, 924, 960 and 1323 g). During each test, the switchgrass sample was placed evenly on the bottom of chamber without packing or compressing it to minimize delay in heat and mass transfer, which could make the ash free of char maximally. Then, the ventilation system was switched on and switchgrass was ignited by a propane torch. Combustion was maintained for 5 min, and throughout this period, temperatures of switchgrass surface, exhaust gas, and chamber interior were measured by thermocouples and recorded by the DAQ. After combustion, burnout residue was collected and weighted. Any unburned char was separated by removing the residue that did not pass through a 2 mm mesh sieve, and the ash was assumed to be all material that were less than 2 mm in size.

2.3. Characterization of switchgrass ash

As-received ash was then characterized for its physiochemical, thermal and microstructural properties. Before characterization, it was ground in a vibratory pulverizing mill for 30 s. Particle size distribution of ash, as well as the Portland cement (used in the following pozzolanic evaluation section) was visualized by a laser scattering particle size analyzer. Range of distribution was set from 0.020 to 2000 μm. Brunauer Emmett Teller (BET) surface area of ash was determined with a BET analyzer. X-ray fluorescence (XRF) quantified the major mineral oxides in ash, silica fume and Portland cement by a XRF spectrometer. A powder X-ray Diffractometer helped distinguish the crystal structure of ground ash. Based on the X-ray diffraction (XRD) observation, amorphous content was estimated by Rietveld refinement [18]. Generator power of X-ray was 40 kV/20 mA with Cu anode material, and scanning angle ranged from 5 to 100 °2θ. Scanning step size was set at 0.04 °2θ/s. Thermal properties of ash were evaluated by a Thermogravimetric-Differential Scanning Calorimetry (TG-DSC) analyzer. Specifically, ≈10.6 mg of ground ash was placed in an Al$_2$O$_3$ crucible, and heated up to 900 °C, in an atmosphere of 20% O$_2$ + 80% N$_2$ (by volume). Volume rate of gas was 20 mL/min, and heating rate was 10 °C/min. Consequently, mass loss and enthalpy change were recorded. Lastly, microstructure of ground ash (coated in carbon) was observed by a Scanning Electron Microscope (SEM).

2.4. Evaluation of pozzolanic activity

Experimental designs of the following four tests (including sample designation and mixture proportion) were provided in Tables 1 and 2. All of the tests were replicated three times to assure the repeatability of results.

2.4.1. Frattini test

Pozzolanic activity of ash was chemically determined by the Frattini test [19], which quantified the reduction of Ca^{2+} in the pozzolanic reaction. Specifically, 20 g of sample consisting of 80% Portland cement and 20% ash were mixed in 100 mL distilled water. To investigate chemical acceleration, 1 g of Na$_2$SO$_4$ was added into a mixture (S-AN). Because adding CaCl$_2$·2H$_2$O disturbed the measurement of Ca^{2+} reduction, we neglected CaCl$_2$·2H$_2$O in this test. Samples with 20% silica fume or without any pozzolan were also included as positive and negative controls. Samples were preserved for 8 d in sealed plastic bottles at 40 °C. Afterwards, samples were vacuum-filtered and cooled to ambient temperature in sealed Buchner funnels. The filtrate was tested for OH$^-$ and Ca^{2+} by titration. To compare the pozzolanic activity of each sample, maximal Ca^{2+} concentration (M[CaO]) at a certain [OH$^-$] was calculated by Eq. (1),

$$M \, [\text{CaO}], \text{ mmol/L} = \frac{K_{sp} \times 10^9}{[\text{OH}^-, \text{ mmol/L}]^2} \qquad (1)$$

where [OH$^-$] was the actual OH$^-$ concentration. K_{sp} was the solubility product constant, and equaled to 4.405 × 10^{-6} mol^3/L^3, determined by [Ca^{2+}] and [OH$^-$] in saturated Ca(OH)$_2$ solution at 25 °C. Hence, the ratio of Ca^{2+} reduction, as the index of pozzolanic activity was determined by Eq. (2),

$$\text{Pozzolanic activity index, } \% = \frac{M \, [\text{CaO}], \text{ mmol/L} - [\text{CaO}], \text{ mmol/L}}{M \, [\text{CaO}], \text{ mmol/L}} \qquad (2)$$

where [CaO] was the actual Ca^{2+} concentration in solution.