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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.

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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% $CaCl_2{\cdot}2H_2O$). 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% $CaCl_2{\cdot}2H_2O$ were equally effective). Blended cement with 10% ash and either 5% Na_2SO_4 or 5% $CaCl_2{\cdot}2H_2O$ 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 accomplished 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 biomass 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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($(CaO)_x·(SiO_2)_y·(H_2O)_z$, 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 $SiO_2 + Al_2O_3 + Fe_2O_3$ [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_2SO_4 or $CaCl_2·2H_2O$ in cement–ash mixtures. By adding Na_2SO_4, the reaction between Na_2SO_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_2SO_4 [6]. Adding 4% Na_2SO_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_2SO_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 $CaCl_2·2H_2O$ with cement generates a new crystal $C_3A·CaCl_2·10H_2O$–$C_3A·Ca(OH)_2·12H_2O$, 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% $CaCl_2·2H_2O$ 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, $CaCl_2·2H_2O$ was also effective in the cement mortar with 20% bagasse ash [11] and 20% pozzolanic clay [12]. Therefore, the chemical acceleration by Na_2SO_4 or $CaCl_2·2H_2O$ 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_2SO_4 or 5% $CaCl_2·2H_2O$). 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_2O_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_2SO_4 was added into a mixture (S-AN). Because adding $CaCl_2·2H_2O$ disturbed the measurement of Ca^{2+} reduction, we neglected $CaCl_2·2H_2O$ 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),

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

where $[OH^-]$ was the actual OH^- concentration. K_{sp} was the solubility product constant, and equaled to $4.405 \times 10^{-6}\ mol^3/L^3$, 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),

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

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

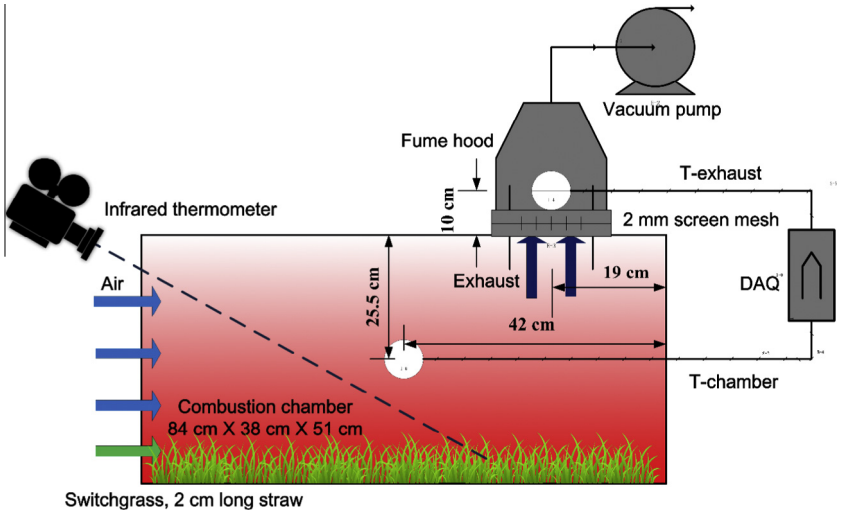

Fig. 1. Schematic diagram of the lab-designed furnace for switchgrass combustion. DAQ was the data acquisition system. T-exhaust and T-chamber were the thermocouples linked to DAQ for measuring the temperatures of exhaust gas and chamber interior. An infrared thermometer was set up to monitor the temperature of fuel surface.

Table 1
Designations and mixture proportions (g) of Frattini test and lime–ash test.

Mixture (g)	Frattini test				Lime–ash test			
	S-C	S-S	S-A	S-AN	S-S	S-A	S-AN	S-AC
Portland cement	20	16	16	16	–	–	–	–
Hydrated lime	–	–	–	–	180	180	180	180
Sand	–	–	–	–	1480	1480	1480	1480
Silica fume	0	4	0	0	360	0	0	0
Ash	0	0	4	4	0	360	360	360
5% Na_2SO_4	0	0	0	1	0	0	27	0
5% $CaCl_2{\cdot}2H_2O$	–	–	–	–	0	0	0	27
Water	100	100	100	100	297	297	312	312

2.4.2. Lime–ash test

When mixed with lime and sand, the pozzolanic mix should gain a strength of 4.1 MPa or higher after cured at 54 °C for 7 d, and another 21 d at 23 °C in water [20]. Lime:pozzolan:standard sand ratio was 180 g:360 g:1480 g by weight. The 5% chemical accelerators (Na_2SO_4 or $CaCl_2{\cdot}2H_2O$ powder) were added in some batches of mixtures, and water/(lime + pozzolan) ratio was 0.55. Lime-silica fume sample was also tested as reference to. Samples were cast into 50 mm cube molds, and were cured at 54 °C. Strength was checked for each sample after 7 d curing at 54 °C, and then after another 21 d curing at 23 °C in water.

2.4.3. Compressive strength of concrete cylinder

Compressive strength of concrete cylinders (50 mm diameter, 100 mm height) was tested to assess the influence of ash and chemical accelerators on concrete. Replacement ratio of ash to cement was 0% (as control), 10%, and 20% by weight, respectively. Sample with 10% silica fume was also included as a positive control. Water/(cement + ash) ratio was 0.55 for the satisfactory workability, and coarse/fine aggregate was 65/35. Chemical accelerators (5% Na_2SO_4 or 5% $CaCl_2{\cdot}2H_2O$ powder) were blended in the batches containing 10% ash to appraise the chemical acceleration. After casting, samples were cured in water at 23 °C for 3, 7 and 28 d. As per ASTM C618 [5], pozzolanic activity index was defined as the percentage of the compressive strength compared to the control.

2.4.4. Expansion of mortar bar due to alkali–silica-reaction (ASR)

A qualified pozzolan could reduce the expansion due to alkali–silica-reaction (ASR), thus enhancing the durability of concrete [21]. Expansion test was carried out in accordance with ASTM C1260 [22]. Specifically, 25 × 25 × 100 mm mortar bars were made from reactive sand, cement, and ash (substituting 0%, 10%, and 20% of cement by weight). Chemical acceleration by 5% Na_2SO_4 or 5% $CaCl_2{\cdot}2H_2O$ powders was investigated on mortar bars with 10% ash. Water/(cement + pozzolan) ratio was 0.47, and cement/fine aggregate ratio was 1/2.25. Mortar bars with 10% of silica fume were also prepared as a positive control, and samples without any additive were the negative control. Reference length was obtained by curing mortar bars in water at 80 °C for 24 h. Afterwards, samples were transferred in 1 mol/L NaOH solution at 80 °C for 14 d. During this period, the length of samples was measured at 12 h intervals with a length comparator.

Table 2
Designations and mixture proportions (kg/m^3) of concrete compressive strength test and expansion test.

Mixture (kg/m^3)	Relative density	S-C	S-S10	S-A10	S-A20	S-AN10	S-AC10
Concrete compressive strength test							
Portland cement	2.87	330	297	297	264	297	297
Fine aggregate	2.81	660	594	594	528	594	594
Course aggregate	2.61	1226	1103	1103	980	1103	1103
Silica fume	2.70	0	33	0	0	0	0
Ash	1.79	0	0	33	66	33	33
5% Na_2SO_4	–	0	0	0	0	9	0
5% $CaCl_2{\cdot}2H_2O$	–	0	0	0	0	0	9
Water	–	182	182	182	182	182	182
Mortar bar expansion test							
Portland cement	2.87	440	396	396	352	396	396
Fine aggregate	2.81	990	891	891	792	891	891
Course aggregate	2.61	–	–	–	–	–	–
Silica fume	2.70	0	44	0	0	0	0
Ash	1.79	0	0	44	88	44	44
5% Na_2SO_4	–	0	0	0	0	10	0
5% $CaCl_2{\cdot}2H_2O$	–	0	0	0	0	0	10
Water	–	207	207	207	207	207	207

2.5. Statistical interpretation

The effect of ground ash from switchgrass combustion on pozzolanic activity in cement and materials properties of concrete, with or without chemical accelerators, was statistically compared using a Fisher's Least Significant Difference (LSD) test at the 95% confidence level.

3. Results and discussions

3.1. Switchgrass combustion in lab-designed furnace

Table 3 showed the proximate and ultimate analysis, and the calorific value (higher heating value) of switchgrass. On a dry basis, switchgrass had 5% ash and 17.5 MJ/kg of higher heating value (HHV). Switchgrass has higher energy content than other biomass fuels, which are normally around 15 MJ/kg, but the high ash content of switchgrass means that that ash remaining after combustion must be disposed or they could be recycled by blending with cement materials [23].

Combustion in the lab-designed furnace occurred at average temperatures of 411 °C on switchgrass surface, 275 °C in chamber interior and 89 °C in exhaust gas. In previous research, maximal decomposition rate during switchgrass combustion occurred at 300–350 °C [24]. Temperature of the switchgrass surface (411 °C) demonstrated adequately high temperature for combustion within this lab-designed furnace.

Before removing the large unburned char, mean yield of burnout residue was 14% by weight when initial switchgrass load was from 492 g to 1323 g. This value was more than double the switchgrass ash content (5%), which was attributed to different testing apparatus and conditions. Combustion test was repeated seven times and standard deviation of the mean yield was ±0.72%. There was a linear correlation (Adj. $R^2 = 0.9835$) between initial switchgrass load and burnout residue yield (Fig. S1), indicating that the initial fuel load did not alter the burnout residue yield in the lab-designed furnace and that 2500 cm^3/s of air supply assured complete combustion after 5 min. Thereafter, we combined all ash samples and considered them to be homogeneous, physically, chemically and microstructurally, for the following experiments.

3.2. Characterization of switchgrass ash

Ground ash was gray in color (Fig. S3). Mean particle size of cement was 21.95 μm, with 12,820 m^2/m^3 of specific surface area (Table 4). According to ASTM C618 [5], a physically satisfactory pozzolan should pass a 45 μm sieve, but the ground ash in this study was slightly coarser (65.00 μm) (Fig. S2). This suggests that grinding more finely could improve the pozzolanic activity of ash. BET surface area of ground ash was 41.25 m^2/g (Table 4), thus ground ash had ample porosity, confirmed by microscopic examination at 10,000 times magnification by SEM (Fig. 2(b)), which is important for the microstructure of cementing materials and the resulting concrete.

Chemically, ash contained less $SiO_2 + Al_2O_3 + Fe_2O_3$ (68.17%) than silica fume (95.14%), and also substantially less SiO_2

Table 3
Proximate and ultimate analysis, and calorific value of the switchgrass.

Proximate analysis, wt.%					
Basis		Moisture	Volatile matter	Ash	Fixed carbon
Air		6.55	80.55	4.69	8.21
Dry		–	86.20	5.02	8.78
Ultimate analysis, dry basis, wt.%					Calorific value, MJ/kg
C	H	N	S	O	HHV
41.30	5.86	0.60	0.06	52.18	17.46

Table 4
Major mineral oxides, specific surface area, mean particle size, BET surface area, thermal property and color of ground ash from switchgrass combustion, silica fume, and Portland cement.

Mineral elements (wt.%)	Switchgrass ash	Silica fume	Ordinary Portland cement
SiO_2	67.18	95.01	19.67
Al_2O_3	0.68	0.02	4.82
Fe_2O_3(T)	0.31	0.11	2.79
MnO	0.07	0.02	0.07
MgO	2.05	0.76	2.53
CaO	12.28	0.82	61.77
Na_2O	0.11	<0.01	0.20
K_2O	1.24	0.55	0.73
TiO_2	0.06	<0.01	0.22
P_2O_5	1.15	0.08	0.22
Cr_2O_3	0.01	<0.01	0.01
V_2O_5	<0.003	<0.003	0.02
Loss on ignition (LOI)	14.77	3.20	2.21
Total	99.91	100.60	95.27
$SiO_2 + Al_2O_3 + Fe_2O_3$	68.17	95.14	27.28
Specific surface area (m^2/m^3)	6251.4	–	12820
Mean particle size (μm)	65.00	–	21.95
BET surface area (m^2/g)	41.25	–	–
Color	Gray	Dark	Gray

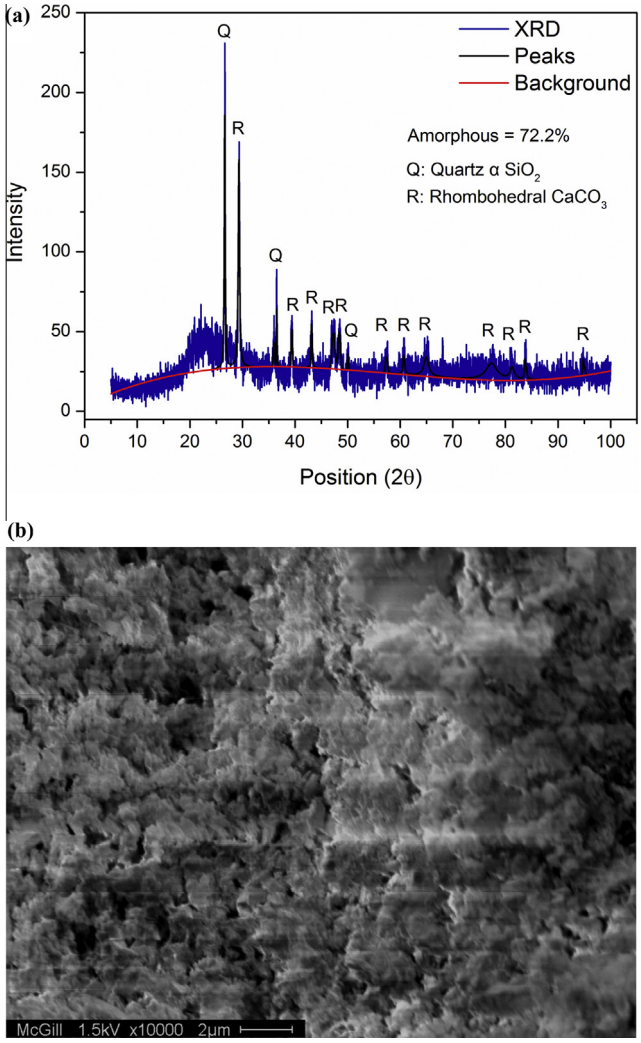

Fig. 2. (a) Crystal structure of the ground ash from switchgrass combustion, investigated by XRD. Peaks, background curve and amorphous content were determined by the Rietveld refinement and (b) microstructural observation of the ground ash.

(67.18%) than silica fume (95.01%) (Table 4). The XRD profile above the background line revealed that SiO_2 in ground ash was predominately amorphous (72.2%), especially in the zone of 20–40 °2θ (Fig. 2(a)). Crystalline phase mostly consisted of Quartz-α SiO_2 (52%) and rhombohedral $CaCO_3$ (48%). Therefore, ground ash in this study featured a sufficient proportion of amorphous SiO_2 in the crystal structure, which could be pozzolanic-active.

The ground ash was thermally stable from 25 °C to 900 °C (Fig. S4), losing 14.10% mass and releasing 0.7588 J/g of heat when subjected to these conditions (Table 4). This implies that most of the switchgrass carbon was lost during combustion in the lab-designed furnace and the additional mass lost during this test was a combination of carbon decomposition and metal element evaporation.

3.3. Evaluation of pozzolanic activity

3.3.1. Frattini test

In the Frattini test, diminution of Ca^{2+} and OH^- chemically reflects the activity of pozzolans. Points of Portland cement were close to the solubility curve of $[Ca^{2+}]$–$[OH^-]$ ($K_{sp} = 4.405 \times 10^{-6}$ mol^3/L^3, 25 °C), affirming that 8 d curing at 40 °C was sufficient for cement hydration to create a saturated $Ca(OH)_2$ solution (Fig. 3(a)). However, cement with silica fume and cement–ash blends tested in this study were all located below the curve, which indicated that they were all pozzolanic-active. Furthermore, silica fume had stronger ability to decrease OH^- (to 28.67 mmol/L) than ash (to 42.33 mmol/L) and the ash with Na_2SO_4 (to 46.50 mmol/L). Decrease of alkali concentration was attributed to the pozzolanic reaction, which is an acid-base neutralization between $Ca(OH)_2$ and silicic acid, and is proportional to the quantity of reactive SiO_2 in the pozzolan. Greater alkali consumption by silica fume was expected, due to fact it contains more reactive SiO_2 than switchgrass ash.

The pozzolanic activity of the test materials (Fig. 3(b)) revealed that cement was slightly pozzolanic-active due to small amounts of SiO_2 (19.67%) and Al_2O_3 (4.82%). Silica fume had the highest SiO_2 content and greatest pozzolanic activity (75.15%). Still, ash and the ash with Na_2SO_4 possessed pozzolanic activities of 30.89% and 33.89%, respectively (Fig. 3(b)) and these were similar statistically ($P = 0.0729$, Fisher's LSD test).

Although the SiO_2 content of pozzolan was correlated to its pozzolanic activity chemically, the crystal structure of pozzolan could also be important in microstructure development and mechanical properties of the cementing materials containing ash.

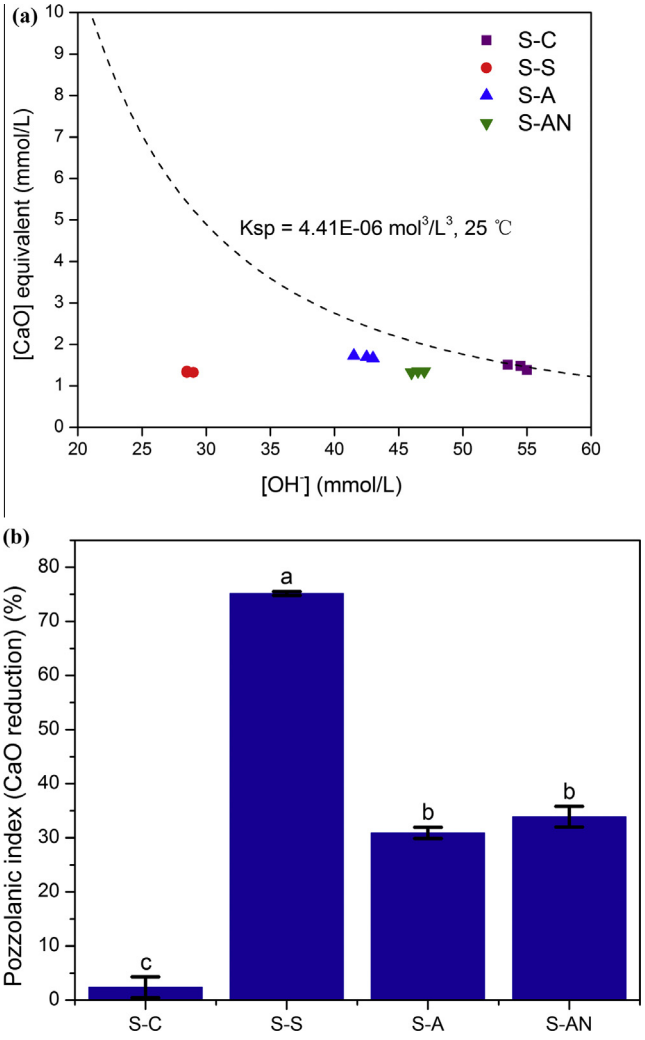

Fig. 3. (a) Results of Frattini test, showing the solubility profile (dotted line) of the saturated $Ca(OH)_2$ solution at 25 °C. Points below the solubility profile indicated positive pozzolanic activity and (b) pozzolanic activity index derived from Frattini test. Values above 0% suggested a positive pozzolanic activity. Columns with different letters were significantly different at $P < 0.05$, Fisher's LSD test.

3.3.2. Lime–ash test

In lime–ash tests, the positive control was cement with silica fume (S-S), which exhibited the greatest pozzolanic activities at both 7 and 28 d curing ages (6.3 and 6.9 MPa) (Fig. 4). Ash sample after 7 d curing had a 3.9 MPa of compressive strength, which was marginally below the strength criteria of 4.1 MPa [20]. This lack of strength was ascribed to the lower content of SiO_2 in ash than silica fume. Yet, because the progress of cement hydration and pozzolanic reaction benefited from the prolonged curing duration, the compressive strength of ash cube increased to 4.2 MPa after 28 d (Fig. 4). This demonstrates that switchgrass ash was an effective pozzolan in the late stage. Mixing 5% Na_2SO_4 or 5% $CaCl_2{\cdot}2H_2O$ in lime–ash mixtures showed that both chemical accelerators manifestly fortified the strength to 4.8 and 4.4 MPa after 7 d, and to 5.1 and 4.9 MPa after 28 d, respectively. There was a consistent, significant ($P < 0.05$, Fisher's LSD test) improvement in compressive strength with Na_2SO_4 than with $CaCl_2{\cdot}2H_2O$. We attribute this finding to changes in the alkali concentration with Na_2SO_4, which could hasten the dissolution of SiO_2 in ash and transform it to

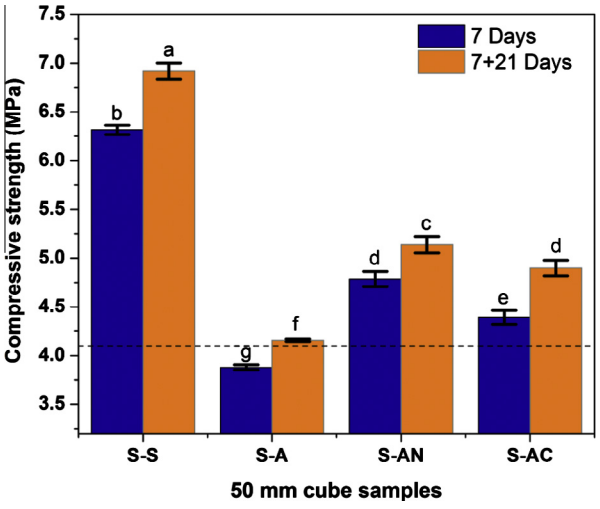

Fig. 4. Strength of 50 mm lime–ash cubes. Horizontal dash in graph was at 4.1 MPa, which was the strength criteria required by ASTM C593-06. Columns with different letters were significantly different at $P < 0.05$, Fisher's LSD test.

$Si(OH)_4$ or H_4SiO_4 [25]. Generating more alkalinity of the cement–water–ash system or stimulating the dissolution of SiO_2 in the pozzolan might effectively enhance the strength of the cement–ash mixture during the curing stage.

3.3.3. Compressive strength of concrete cylinder

As shown in Fig. 5(a), concrete with 10% silica fume possessed the strongest compressive strength after 3, 7 and 28 d curing (23.4, 27.5, and 39.1 MPa, respectively). Cement with 20% of ash had the lowest compressive strength of 5.6, 14.8 and 28.4 MPa after 3, 7 and 28 d curing. While 10% ash in the cement–ash blend improved the strength to 28.6 MPa after 28 d curing, this was significantly less ($P = 0.0495$, Fisher's LSD test) than the Portland cement control with 32.5 MPa of compressive strength after 28 d (Fig. 5(a)). These results are interpreted as follows: partial replacement of cement by ash reduced the proportion of primary hydration reactants tricalcium silicate ($(CaO)_3{\cdot}SiO_2$, C_3S) and dicalcium silicate ($(CaO)_2{\cdot}SiO_2$, C_2S) in the mixture. Less C_3S and C_2S consequently led to insufficient formation of C–S–H (main strength contributor) and CH (chief reactant in pozzolanic reaction) [26,27]. Since the pozzolanic reaction is controlled by CH formation and diffusion of hydrated products [28], it was retarded when less CH formation occurred in the early stage (3 and 7 d) and to a greater extent in the cement-ash blend with 20% ash than 10% ash (Fig. 5(a)). More importantly, the low SiO_2 content in ash reduced the production of C–S–H from the pozzolanic reaction and shortage of C–S–H compounds weakened the strength of concrete. Therefore, we assert that compressive strength of concrete was greatly influenced by the initial quantity of C_3S and C_2S. This is further supported by the fact that the compressive strength of cement–ash blends with 10% and 20% switchgrass ash converged after 28 d (Fig. 5(a)). Replacement ratio of ash did not affect the strength of concrete considerably in the late stage, whereas the lack of initial C_3S and C_2S always had a negative impact.

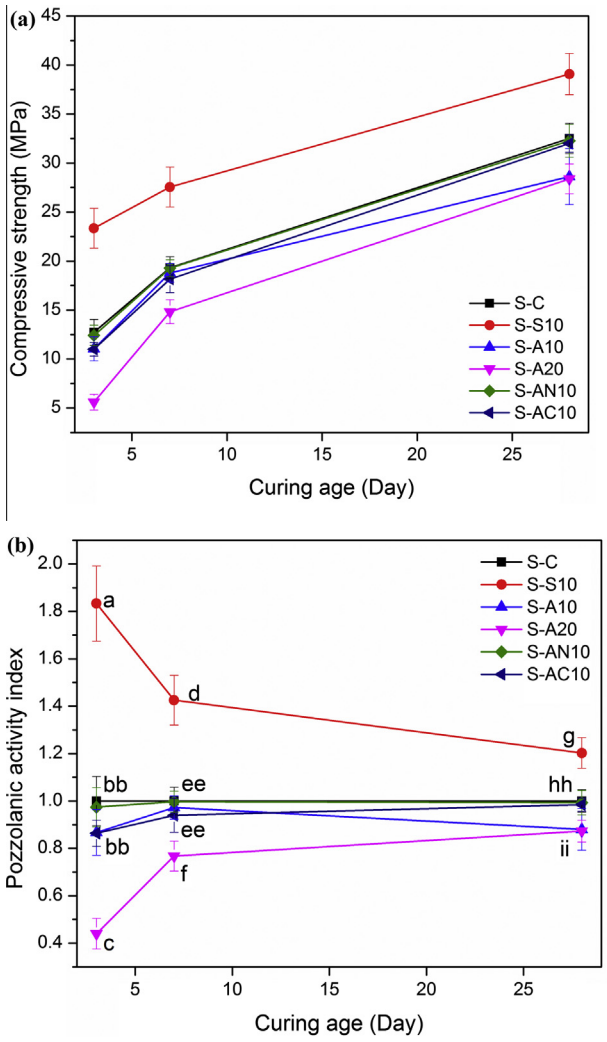

Fig. 5. (a) Compressive strength of 50 mm × 100 mm concrete cylinders and (b) pozzolanic activity index based on the compressive strength of concrete cylinders. Value above 1.0 indicated a positive pozzolanic activity. Results with different letters were significantly different at $P < 0.05$, Fisher's LSD test.

Adding 5% Na_2SO_4 or 5% $CaCl_2{\cdot}2H_2O$ to a cement–ash blend with 10% ash was an effective way to overcome the shortcomings of ash alone, giving strength comparable to the Portland cement control throughout the curing period (Fig. 5(a)). This improvement was attributed to chemical acceleration, namely (1) more alkali generated by Na_2SO_4 and (2) stronger crystals of $C_3A{\cdot}CaCl_2{\cdot}10H_2O$–$C_3A{\cdot}Ca(OH)_2{\cdot}12H_2O$ induced by $CaCl_2{\cdot}2H_2O$. Compared to the S-A10 treatment (cement with 10% ash, without chemical accelerators), both chemicals produced similar compressive strength in the short term (3 and 7 d curing) and improved the compressive strength in the long term (28 d curing, Fig. 5(a)). It appears that chemical acceleration can offset lower C–S–H formation in cement-ash blends, which occurs due to the lower proportion of cement, by enhancing the pozzolanic reaction and thereby producing more C–S–H for strength.

As the pozzolanic activity index was defined as the percentage of the compressive strength compared to the control, an index that is greater than 1.0 suggested a positive pozzolanic activity (Fig. 5(b)). Silica fume possessed the greatest pozzolanic activity, which diminished with increasing curing time (1.8 after 3 d, 1.4 after 7 d, and 1.2 after 28 d). This trend was attributed to the following: high amorphous SiO_2 content in silica fume promoted the development of pozzolanic reaction, thus using up the crystallized CH. More expenditure of crystallized CH provoked the additional formation of C–S–H in the early stage. Depletion of free crystallized CH and free SiO_2 reserves in the cement-silica fume blend progressively reduced the pozzolanic activity.

Compared to Portland cement, the cement–ash blend with 10% ash and 5% Na_2SO_4 gave the consistent pozzolanic activity, close to 1.0, during the 28 d period (Fig. 5(b)). There was a lag in the pozzolanic activity of the cement-ash blend with 10% ash and $CaCl_2{\cdot}2H_2O$, but by 7 d and 28 d of curing, it was statistically similar ($P < 0.05$, Fisher's LSD test) to Portland cement and had a pozzolanic activity of nearly 1.0 after 28 d (Fig. 5(b)). Cement–ash blends with 10% ash and 20% ash had the lowest pozzolanic activity at most measurement times (0.88 and 0.44 at 3 d, 0.97 and 0.77 at 7 d, and 0.88 and 0.87 at 28 d). Lower SiO_2 content, as well as smaller proportions of cementitious compounds in these blends, inhibited both pozzolanic and hydration processes in the cement–ash mixtures. Prolonged curing probably stimulated formation of crystalline CH and boosted the pozzolanic activity, particularly in the cement–ash mixture containing 20% ash which increased from 0.45 to 0.88 between 3 d and 28 d of curing (Fig. 5(b)). Our findings support the use of chemical accelerators, particularly 5% Na_2SO_4, in cement–ash blends to sustain the pozzolanic activity more efficiently.

3.3.4. Expansion test

Expansion of mortar bars due to ASR provides insight into pozzolanic activity whereby $\leqslant$0.1% of expansion at 16 d after casting is considered an innocuous behavior [22]. The Portland cement control (mortar bar without any additives) expanded by 0.0886% after 16 d (Fig. 6), which met the ASTM standard and indicated the sand used in this study was reactive enough to cause ASR [29].

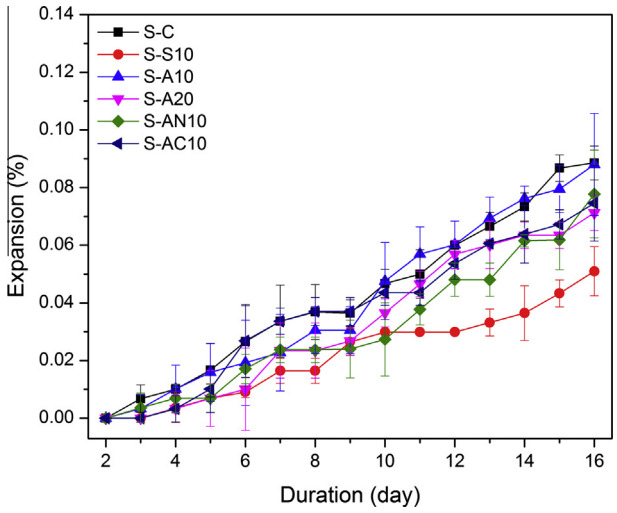

Fig. 6. Expansion results of 25 mm × 25 mm × 100 mm mortar bars. Points were the mean ± standard error of $n = 3$ replicates, except $n = 2$ for S-A10 at the 16th d because one outlier was omitted from the analysis.

Compared to other samples in Fig. 6, mortar bar with 10% silica fume had the least expansion (0.0510%), which was interpreted to mean that silica fume satisfactorily inhibited ASR because it had the strongest pozzolanic activity. Expansion was similar and non-significant ($P = 0.8690$) in mortar bars with 20% ash (0.0713%), 10% ash + 5% Na_2SO_4 (0.0778%) and 10% ash + 5% $CaCl_2{\cdot}2H_2O$ (0.0756%) (Fig. 6). Less expansion in cement-ash blends suggested an advantageous contribution from ash, due to either the pozzolanic reaction, or the reduction of hydration heat, or both simultaneously. The mortar bar with 10% ash had the similar expansion (0.0883%) with the control after 16 d ($P = 0.9714$). Possibly the ash contained appreciable quantities of Na_2O and K_2O (1.35% in total, Table 4) compared to Portland cement (0.93% in total, Table 4), which may have increased the alkalinity and the ASR phenomena, but why this was the case with 10% ash and not 20% ash is unknown and warrants further study.

4. Conclusions

Switchgrass combusted for bioenergy generates a large amount of hazardous ash (5% by weight) for disposal. 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% $CaCl_2{\cdot}2H_2O$ were equally effective). Chemical acceleration was continuously effective, but it was more efficient in the early stage than late stage. The compressive strength and the resistance to ASR expansion of blended cement containing 10% switchgrass ash (with a chemical accelerator) was comparable to conventional Portland cement. The further studies might enhance the pozzolanic activity of switchgrass ash by controlling the combustion temperature and retention time, thus removing the carbon and increasing the amorphous crystal content in ash.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.conbuildmat.2014.09.114.

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