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### VALUE-ADDITION OF RESIDUAL ASHES FROM DIFFERENT BIOMASS ORIGINS IN CEMENT BASED MATERIALS: A COMPARATIVE STUDY

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**ABSTRACT** The rising fuel prices and growing concern about global warming associated with greenhouse gases emissions have increased the interest for clean bioenergy production. Conventionally, the use of biomass as an energy source is considered as carbon neutral or low carbon, which has potential of sustainable energy supply in future. However, production of ash from different bioenergy transformation processes can become an important source of pollution if appropriate disposal schemes are not implemented. The utilization of ashes from biomass origins in cement based materials could be an environmentally friendly and valuable approach. Currently, fly ash from coal is used in cement production. However, utilisation of biomass ashes as cement constituents is limited due to ASTM norm C618. In this research, ashes from different biomasses produced by different transformation processes have been compared and discussed. For example, ash obtained from biochar by pyrolysis of swine manure has high percentages of elements such as K, P, Ca, and Mg which are suitable for soil fertility but not useful in cement manufacture. However, application of this ash on agricultural soil is restricted by norms to avoid overloading of nutrients in soil as well as leaching of heavy metals in natural water sources. Similarly, ashes from commercial wood pellets and switchgrass could be suitable for agricultural as well as for construction materials. Properties such as particle-size and bulk density of these ashes can be favourable for using them as substitute for sand and filler materials in construction materials.

**Keywords:** Ash, biomass, cement, combustion, bioenergy, swine, willow, switchgrass, wood pellet

**INTRODUCTION** The rising fossil fuel prices and growing concern about global warming associated with greenhouse gas emissions has increased the interest for energy production from renewable sources (e.g. biomass, solar, wind, etc.). Conventionally, the use of biomass as an energy source is considered as carbon neutral or low carbon because the CO<sub>2</sub> emitted during the transformation of material to recover the energy, is absorbed again by the biomass through the photosynthesis process. Though, such consideration is true only if the production of biomass is carried out in a sustainable way.

Ash-forming elements are present in biomass as salts, bound in the carbon structure (inherent ash) as mineral particles from dirt and clay introduced into the biomass fuel during harvesting or transportation (entrained ash) (Van Loo and Koppejan, 2008). During combustion, a fraction of such elements is volatilized and released to the gas phase. Later they form the fine mode of the fly ash characterized by a particle size of < 1 µm. On the other hand, the non-volatile ash compounds remain in the char and results in residual ash particles with a wide range of compositions, shapes and sizes, related to the characteristic of the parent mineral particles. A fraction of the residual ash will be entrained with the flue gas and form the coarse part of fly ash (> 5 µm), while the other fraction will stay on the grate and form bottom ash (Van Loo and Koppejan, 2008).

The increased utilisation of biomass materials for the production of heat and power, especially in large power plants, increase the amount of ashes derived from such production. The review carried out by Reijnders (2005) listed the pollutants and hazardous elements that ash may contain. These include significant quantities of relatively mobile inorganic compounds (e.g. As, Cu, Cd), elements that give rise to significant aqueous leaching (Ba, Br, Ca, Cl, F, Fe, K, Mg, Na, Mn, P and S) and persistent hazardous organic pollutants (POP) such as polycyclic aromatic compounds (PAH), polychlorinated biphenyls (PCB) and chlorinated dioxins and benzofurans. Thus it is necessary to implement appropriate schemes for utilisation of ash disposal.

Nowadays, uses of ashes from different origins include soil stabilisation, mine backfill and agriculture. Benefits and barriers in each case are presented by Smith (2005). Ashes have also emerged as construction or geotechnical materials or have been proposed for such applications. Ashes, principally from the combustion of coal, had been used to replace a portion of cement in the concrete. The ASTM norm C618 covers fly ash for use in concrete where cementitious or pozzolanic action is desired. Using ash in concrete shows distinct quality advantages: improves workability, reduces segregation, bleeding, heat evolution and permeability, inhibits alkali-aggregate reaction, and enhances sulphate resistance (FHWA, 2011). There are additionally economic and ecological benefits.

Currently, most of fly ash used in cement production comes from coal. The quality of these ashes is controlled by standard specifications or classification systems. Usually, the ASTM norm C618 is applied. Additional standards include the AASHTO M 295 and the EN 450. However standard specifications were not specifically prepared for biomass or biomass co-firing ash (Van Loo and Koppejan, 2008). Even the use of biomass ash in concrete is prohibited by the ASTM norm C618 (Wang and Baxter, 2007). According to Rajamma *et al.*(2009), chemistry and mineralogy of biomass ashes differ from those of coal ashes. Although in some researches where results from the characterisation and analysis of biomass ash or co-firing biomass ash showed a similarity compared to the coal fly ash and to the specifications given by norms (Wang and Baxter, 2007; Wang *et*

*al.*, 2008; Rajamma, *et al.*, 2009 and Esteves, *et al.*, 2011). Thus the exclusion of biomass fly ash in concrete by norms seems inappropriate. Standards in a number of European countries have been drafted to permit the ashes from the co-combustion of coal with biomass to be used in concrete production (Van Loo and Koppejan, 2008).

ASTM norm C618 defines fly ash as the finely divided residue that results from the combustion of ground or powdered coal and that is transported by flue gasses. Two major classes of fly ash are specified in ASTM C618 on the basis of their chemical composition resulting from the type of coal burned: Class F (normally produced from burning anthracite or bituminous coal) and Class C (normally produced from the burning of subbituminous coal and lignite). Class C fly ash usually has cementitious properties in addition to pozzolanic properties due to free lime, whereas Class F is pozzolanic fly ash and shows rarely cementitious properties when mixed with water alone. Table 1 shows the chemical and physical requirements listed in the ASTM C618 specification.

Table 1. ASTM Specification C618-08a. Chemical requirements

| Chemical properties   | Class |      |
|---|-------|------|
|   | F     | C    |
| SiO <sub>2</sub> + Al <sub>2</sub> O <sub>3</sub> + Fe <sub>2</sub> O <sub>3</sub> , (Σ), min., % | 70.0  | 50.0 |
| SO <sub>3</sub> , max, %  | 5.0   | 5.0  |
| Moisture content, max, %  | 3.0   | 3.0  |
| Loss on ignition, max, %  | 6*    | 6.0  |

\* The use of Class F pozzolan containing up to 12.0 % loss on ignition may be approved.

This research focuses on the use of ashes from biomass origins in cement based materials as an environmentally friendly and valuable approach. A comparative analysis of ashes from different biomass origins via different thermal transformation processes is discussed.

## MATERIAL AND METHOD

**Biomasses** The ashes used come from four different biomasses: (i) commercial wood (a mix of black spruce and grey pine pellets), (ii) dried solid fraction of pig manure (SFPM), (iii) switchgrass, and (iv) willow. All biomasses, which were previously pelleted, were submitted under direct combustion via a pellet heater.

One additional biomass was evaluated. There is the biochar from the SFPM, when it was submitted into a pyrolysis process. The swine manure, procured from the collection pit of a local swine farm (St-Lambert, Quebec) in the form of 35% dry solids of swine manure, was pre-treated prior to the thermochemical conversion via pyrolysis. For this, the samples were put in an oven maintained at 105°C for a maximum of 72 hours on aluminium trays or until a constant weight. The dried samples were ground in a custom rotary cutter using 2 mm mesh size screen. The particles thus obtained were then transferred to a closed plastic container until used in the pyrolysis process. The physical and chemical properties of the biomasses are listed in table 2. The SFPM has the most important ash content of all biomasses tested under direct combustion (8.8 and 9.57 % d.b. at 750°C and 1100°C respectively), and the wood has the less important (0.5 and 0.38 % d.b. at 750°C and 1100°C respectively).

Table 2. Physical and chemical properties of the biomasses

|                                |                      | Wood  | SFPM  | Switchgrass | Willow | Biochar                 |
|--------------------------------|----------------------|-------|-------|-------------|--------|-------------------------|
| <b>Physical properties</b>     |                      |       |       |             |        |                         |
| Diameter                       | (mm)                 | 6.5   | 8.4   | 5.5         | 6.8    |                         |
| Humidity                       | (% w.b.)             | 6.6   | 10.5  | 14.1        | 12.7   | 1.97 <sup>a</sup>       |
| Density                        | (g/cm <sup>3</sup> ) | 1.1   | 1.26  | 0.94        | 1.03   |                         |
| Bulk density                   | (kg/m <sup>3</sup> ) | 686   | 769   | 509         | 590    |                         |
| Ash content (750°C)            | (% d.b.)             | 0.5   | 8.8   | 3.7         | 2.8    | 15.3 <sup>a</sup>       |
| Ash content (1100°C)           | (% d.b.)             | 0.38  | 9.57  | 4.3         | 4.0    |                         |
| High heating value             | (MJ/kg w.b.)         | 17.9  | 15.6  | 18.7        | 18     |                         |
| <b>Chemical properties</b>     |                      |       |       |             |        |                         |
| SiO <sub>2</sub>               | (% w.b.)             | 0.041 | 0.986 | 2.405       | 0.716  | 6.13                    |
| Al <sub>2</sub> O <sub>3</sub> | (% w.b.)             | 0.014 | 0.180 | 0.168       | 0.153  | 0.95                    |
| Fe <sub>2</sub> O <sub>3</sub> | (% w.b.)             | 0.005 | 0.521 | 0.062       | 0.053  | 2.16                    |
| CaO                            | (% w.b.)             | 0.153 | 1.945 | 0.624       | 1.367  | 16.2                    |
| Na <sub>2</sub> O              | (% w.b.)             | 0.010 | 0.343 | 0.033       | 0.034  | 5.62                    |
| MgO                            | (% w.b.)             | 0.028 | 0.698 | 0.153       | 0.159  | 10.0                    |
| P <sub>2</sub> O <sub>5</sub>  | (% w.b.)             | 0.006 | 1.464 | 0.157       | 0.215  | 20.9                    |
| SO <sub>3</sub> <sup>b</sup>   | (% w.b.)             | 0.008 | 0.834 | 0.089       | 0.145  |                         |
| K <sub>2</sub> O               | (% w.b.)             | 0.047 | 1.321 | 0.229       | 0.588  | 20.9                    |
| Cl                             | (mg/kg)              | 13.8  | 3053  | 129         | 34.4   |                         |
| C                              | (% w.b.)             | 47.1  | 40.5  | 43.5        | 45.1   | 36.9 (d.b) <sup>a</sup> |
| N                              | (% w.b.)             | 0.108 | 2.26  | 0.624       | 0.584  | 3.24 (d.b) <sup>a</sup> |
| TiO <sub>2</sub>               | (% w.b.)             | 0.000 | 0.009 | 0.009       | 0.005  | 0.05                    |
| V <sub>2</sub> O <sub>5</sub>  | (% w.b.)             | 0.000 | 0.001 | 0.000       | 0.000  |                         |
| CrO <sub>3</sub>               | (% w.b.)             | 0.000 | 0.003 | 0.001       | 0.001  | 0.03                    |
| MnO                            | (% w.b.)             | 0.015 | 0.025 | 0.010       | 0.013  | 0.31                    |
| CoO                            | (% w.b.)             | 0.000 | 0.000 | 0.000       | 0.000  |                         |
| NiO                            | (% w.b.)             | 0.000 | 0.001 | 0.000       | 0.000  |                         |
| CuO                            | (% w.b.)             | 0.000 | 0.022 | 0.001       | 0.001  |                         |
| ZnO                            | (% w.b.)             | 0.001 | 0.039 | 0.004       | 0.027  |                         |
| SrO                            | (% w.b.)             | 0.000 | 0.004 | 0.002       | 0.004  |                         |
| ZrO <sub>2</sub>               | (% w.b.)             | 0.000 | 0.001 | 0.000       | 0.001  |                         |
| Nb <sub>2</sub> O <sub>5</sub> | (% w.b.)             | 0.000 | 0.000 | 0.000       | 0.000  |                         |
| BaO                            | (% w.b.)             | 0.001 | 0.001 | 0.002       | 0.004  |                         |

<sup>a</sup> Values corresponding to swine raw manure

### Thermal processes

Direct combustion of the pellet biomass The direct combustion experiments were carried out in a 60,000 BTU/h (17.58 kW) output biomass pellet heater (Enviro; model: Omega). The method used is part of a study aiming to evaluate the emissions and the energy produced when such biomasses are employed for heat production by direct combustion (Godbout *et al.* 2011a; 2011b). In order to test the biomasses under their own optimal combustion conditions, a preliminary experiment were carried out to determinate the ideal input air flow for each biomass (Godbout *et al.*, 2011a). The stove control board allowed five different burning rates (amount of pellets per unit of time), from which, three rates were used in the present experiments: (i) maximal, (ii) intermediate and (iii) minimal burning rate. Each test included the biomass burning at the three rates continuously. The experiments were carried out burning each biomass during 50 min at

each burning rate (in steady state) with their own ideal input air flow. Three repetitions were carried out for each. Before each test and at each burning rate change, the biomass burned during 60 and 50 min respectively in order to get stable burning conditions. Moreover, the pellet heater was installed on a scale ( $\pm 0.05$  kg) which collected the weight at regular intervals during the combustion process. After each test, the ash in the stove (bottom ash) and the ash in the chimney (fly ash) were collected and weighed.

Heating by oven after the biomass pyrolysis The Auger pyrolysis reactor used in this study is an interesting biomass pyrolysis technique which is a continuous type, equipped with computer control to maintain temperature of the pyrolysis zone at required level. The automated reactor control system also provided collection of data for temperature of different zones, pressure and rotational velocity of the Auger reactor. The heating block consisted of a solid copper block with lengthwise rod-type heating elements of about 300 W/inch capacity with 10 inches in length. The biochar collection system used gravity settling of heavier char particles from the pyrolysis vapor, alternatively, for a higher scale process this can be suitably replaced with a cyclone separator. Finally, the pyrolysis vapor was condensed using a cylindrical type condenser of about 12 L volume with a spiral cooling element (-10 to -15°C recirculating fluid) and a 2 L round bottom flask heat quenching system with 250 ml initial liquid volume. A vapor trap was installed before condenser to collect heavier bio-oil fraction and another vapor trap was installed after the condenser to trap the remainder lighter bio-oil fraction, if any. The pyrolysis vapor was extracted from the pyrolysis zone using a vacuum pump at the end of the vapor exit. The inside pressure of around 500 mm Hg during the pyrolysis operation was observed to be effective in evacuating the pyrolysis vapor. The biomass feeding control was calibrated with respect to particle size of the dried swine manure and it was verified at the end of each pyrolysis batch by measuring the remaining biomass. The whole Auger pyrolysis reactor system was cleaned at the end of each batch to minimize cross contamination of samples. The ash obtained from swine manure biomass was resulted from the combustion of the pyrolysis product, biochar. For this, the biochar was put in a crucible and heated in an oven at 550°C for 30 min followed by 950°C for another 30 min.

**Characterization of ashes.** Elemental composition of ashes were studied by X-ray fluorescence spectrometry (XRF). Chlorine content was measured by titration with silver nitrate ( $\text{AgNO}_3$ ). C and N content was determined using a TruSpec analyser (LECO). The norm ASTM C311-11 was followed in order to determine the loss on ignition (LOI). In order to determine moisture content (MC), the collected ashes samples were dried in a laboratory oven at 105°C. The ashes were not sieved before the analysis. On the other hand, the mineral analysis of the biochar ash samples was performed at a local mineralogy laboratory (COREM, Quebec City) as per standard procedures.

## RESULTS AND DISCUSSION

**Characterisation of fly ash from the direct combustion of the raw biomass.** The total recovered ashes (fly and bottom ash) were 0.9 %, 10.2 %, 4.1 % and 4.1 % of the burned biomass, for wood, SFPM, switchgrass and willow respectively. Fly ash recovered represented a very small portion of total recovered ashes. In average, fly ashes recovered included 1.0 % and 2.8 % of total recovered ashes. Total biomass fly ash presented visually different colors. In the case of ashes recovered from wood, switchgrass and willow, they are predominantly grey but their tone is markedly different. The wood ashes are darker than those of the willow, and the switchgrass ashes are darker than the other two. The ashes from SFPM had a particularly different color. They presented a light brown color with some white fine particles produced by the metal oxides. Additionally, some particles completely unburned were noticed into the switchgrass ash samples. That could be caused by the fact that the pellets of such biomass were very fragile. Thus, high quantities of dust and fractured material were produced that they were easily and quickly transported by the airflow once arrived into the combustion chamber.

The chemical properties of the sampled biomass fly ashes are listed in Table 3. Results showed that all samples were predominantly made of  $\text{SiO}_2$  (11.4–41.9%),  $\text{CaO}$  (16.5–29.3%) and  $\text{C}$  (9.6–14%). Generally, the ashes' chemical properties were proportional to those of the initial biomass. For instance, switchgrass showed a significantly high  $\text{SiO}_2$  content before and after the combustion. Furthermore, the trace elements with the most important contents ( $\text{ZnO}$ ,  $\text{MnO}$  and  $\text{TiO}_2$ ) were the same in the biomasses and in the ashes. On the other hand, high  $\text{Cl}$  content were found in fly ashes (13,806–35,223 mg/kg).

When compared with ASTM chemical requirements, the fly ashes of the evaluated biomasses did not meet all ASTM parameters in order to be classified by such norms. In fact, none of the fly ashes meet the minimal sum of  $\text{SiO}_2 + \text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3$  content and the LOI parameter. The switchgrass fly ashes showed a sum value close to ASTM class C designation, i.e. 47.7 %. In fact, the switchgrass fly ash presented a high and predominantly  $\text{SiO}_2$  content (41.9 %). With respect to LOI results, no biomass respected the maximal allowed value to ASTM requirements (6.0 % max.). The switchgrass ashes had the closest value (14.8 %). In the other hand, the  $\text{SO}_3$  and the moisture contents of fly ashes of all tested biomasses were into the ASTM limit values. However, because fly ash from our biomasses did not meet all chemical ASTM requirements, they should not be used in concrete materials as replacement of a part of the cement. In fact, such ashes would not have an enough pozzolanic propriety because of the important deficit in  $\text{Al}$  and  $\text{Fe}$  content.

Table 3. Chemical requirements of ASTM specification (C618-08a) for fly-ash and properties of the biomass fly ash samples.

|   | ASTM requirements |      | Biomass fly ash properties |        |             |        |
|---|-------------------|------|----------------------------|--------|-------------|--------|
|   | F                 | C    | Wood                       | SFPM   | Switchgrass | Willow |
| SiO <sub>2</sub> (% w.b.)               |                   |      | 11.4                       | 13.0   | 41.9        | 16.4   |
| Al <sub>2</sub> O <sub>3</sub> (% w.b.) |                   |      | 2.3                        | 2.0    | 3.8         | 2.6    |
| Fe <sub>2</sub> O <sub>3</sub> (% w.b.) |                   |      | 3.7                        | 4.3    | 2.0         | 2.4    |
| Σ <sup>a</sup> (% w.b.)                 | 70.0              | 50.0 | 17.3                       | 19.3   | 47.7        | 21.4   |
| CaO (% w.b.)                            |                   |      | 24.8                       | 20.4   | 16.5        | 29.3   |
| Na <sub>2</sub> O (% w.b.)              |                   |      | 1.9                        | 2.9    | 1.4         | 1.5    |
| MgO (% w.b.)                            |                   |      | 5.8                        | 6.9    | 3.8         | 5.1    |
| P <sub>2</sub> O <sub>5</sub> (% w.b.)  |                   |      | 9.5                        | 12.8   | 4.6         | 7.7    |
| SO <sub>3</sub> <sup>b</sup> (% w.b.)   | 5.0               | 5.0  | 4.4                        | 3.9    | 1.5         | 3.2    |
| K <sub>2</sub> O (% w.b.)               |                   |      | 2.6                        | 5.1    | 4.1         | 4.1    |
| Cl (mg/kg)                              |                   |      | 34,314                     | 35,223 | 13,436      | 13,806 |
| C (% w.b.)                              |                   |      | 14                         | 11.5   | 9.6         | 10.7   |
| N (% w.b.)                              |                   |      | 0.646                      | 0.883  | 0.366       | 0.494  |
| TiO <sub>2</sub> (% w.b.)               |                   |      | 0.13                       | 0.12   | 0.23        | 0.14   |
| V <sub>2</sub> O <sub>5</sub> (% w.b.)  |                   |      | 0.01                       | 0.01   | 0.00        | 0.01   |
| CrO <sub>3</sub> (% w.b.)               |                   |      | 0.09                       | 0.06   | 0.05        | 0.06   |
| MnO (% w.b.)                            |                   |      | 0.65                       | 0.46   | 0.40        | 0.46   |
| CoO (% w.b.)                            |                   |      | 0.00                       | 0.00   | 0.00        | 0.00   |
| NiO (% w.b.)                            |                   |      | 0.03                       | 0.02   | 0.01        | 0.02   |
| CuO (% w.b.)                            |                   |      | 0.06                       | 0.08   | 0.03        | 0.06   |
| ZnO (% w.b.)                            |                   |      | 1.25                       | 0.97   | 0.45        | 0.78   |
| SrO (% w.b.)                            |                   |      | 0.07                       | 0.06   | 0.05        | 0.09   |
| ZrO <sub>2</sub> (% w.b.)               |                   |      | 0.01                       | 0.01   | 0.01        | 0.01   |
| Nb <sub>2</sub> O <sub>5</sub> (% w.b.) |                   |      | 0.00                       | 0.00   | 0.00        | 0.00   |
| BaO (% w.b.)                            |                   |      | 0.10                       | 0.06   | 0.07        | 0.10   |
| PbO (% w.b.)                            |                   |      | 0.00                       | 0.00   | 0.00        | 0.00   |
| MC <sup>c</sup> (% w.b.)                | 3.0               | 3.0  | 1.6                        | 1.3    | 0.8         | 0.8    |
| LOI <sup>d</sup> (%)                    | 6.0 <sup>e</sup>  | 6.0  | 22.6                       | 22.2   | 14.8        | 20.3   |

<sup>a</sup> Sum of SiO<sub>2</sub> + Al<sub>2</sub>O<sub>3</sub> + Fe<sub>2</sub>O<sub>3</sub>, (min, %); <sup>b</sup> SO<sub>3</sub> (max, %); <sup>c</sup> Moisture Content (max, %); <sup>d</sup> Loss on Ignition (max, %); <sup>e</sup> The use of Class F pozzolan containing up to 12.0 % loss on ignition may be approved.

### Characterisation of bottom ash from the direct combustion of the raw biomass.

Higher quantity of ash was recovered from the bottom of the heater, between 97.2 % and 99% of total ashes recovered. As expected, the wood produced the less (0.9 % w.b. of which 97.2 % were bottom ash) and the SFPM produced the most (10.2% w.b. of which 99 % were bottom ash). The switchgrass and willow produced both 4.1 % w.b. of which 98 % were in bottom ash.

Visually, bottom ashes showed the same color difference as corresponding fly ashes. Equally, CaO, SiO<sub>2</sub> and C were the principal chemical elements constituting bottom ashes for each biomass as fly ashes (table 4). However, the P<sub>2</sub>O<sub>5</sub> and K<sub>2</sub>O content in SFPM ash were more important than C. In fact, important quantities of such elements were present in the initial biomass. Thus, these elements are hardly decomposed and volatilized during combustion; they remain attached to the solid waste fraction. Additionally, wood ash presented a significant high carbon content (41.7 %). Based on the organic matter and

carbon content ratio (1.2), it can be deduced that C in wood ash is present in a graphitic form.

Table 4. Chemical requirements of ASTM specification (C618-08a) for fly-ash and properties of the biomass bottom ash samples.

|   | ASTM requirements  |                   | Biomass bottom ash properties |        |             |        |
|---|--------------------|-------------------|-------------------------------|--------|-------------|--------|
|   | F                  | C                 | Wood                          | SFPM   | Switchgrass | Willow |
| SiO <sub>2</sub> (% w.b.)               |                    |                   | 6.7                           | 10.8   | 55.2        | 17.2   |
| Al <sub>2</sub> O <sub>3</sub> (% w.b.) |                    |                   | 1.5                           | 2.0    | 4.5         | 3.1    |
| Fe <sub>2</sub> O <sub>3</sub> (% w.b.) |                    |                   | 4.2                           | 5.7    | 4.2         | 1.7    |
| Σ <sup>a</sup> (% w.b.)                 | 70.0 <sup>a</sup>  | 50.0 <sup>a</sup> | 12.5                          | 18.5   | 63.9        | 22.0   |
| CaO (% w.b.)                            |                    |                   | 19.7                          | 22.0   | 16.2        | 30.2   |
| Na <sub>2</sub> O (% w.b.)              |                    |                   | 1.1                           | 3.8    | 1.0         | 1.0    |
| MgO (% w.b.)                            |                    |                   | 3.7                           | 8.0    | 3.7         | 3.6    |
| P <sub>2</sub> O <sub>5</sub> (% w.b.)  |                    |                   | 1.8                           | 16.4   | 3.8         | 5.1    |
| SO <sub>3</sub> (% w.b.)                | 5.0 <sup>b</sup>   | 5.0 <sup>b</sup>  | 1.4                           | 6.1    | 0.3         | 1.7    |
| K <sub>2</sub> O (% w.b.)               |                    |                   | 5.0                           | 11.0   | 5.2         | 11.0   |
| Cl (mg/kg)                              |                    |                   | 1,238                         | 11,829 | 543         | 594    |
| C (% w.b.)                              |                    |                   | 41.7                          | 8.2    | 2.6         | 13.1   |
| N (% w.b.)                              |                    |                   | 0.3                           | 0.3    | 0.1         | 0.3    |
| TiO <sub>2</sub> (% w.b.)               |                    |                   | 0.07                          | 0.11   | 0.26        | 0.13   |
| V <sub>2</sub> O <sub>5</sub> (% w.b.)  |                    |                   | 0.00                          | 0.01   | 0.01        | 0.00   |
| CrO <sub>3</sub> (% w.b.)               |                    |                   | 0.33                          | 0.06   | 0.30        | 0.07   |
| MnO (% w.b.)                            |                    |                   | 1.79                          | 0.29   | 0.25        | 0.30   |
| CoO (% w.b.)                            |                    |                   | 0.00                          | 0.00   | 0.00        | 0.00   |
| NiO (% w.b.)                            |                    |                   | 0.10                          | 0.03   | 0.49        | 0.02   |
| CuO (% w.b.)                            |                    |                   | 0.04                          | 0.21   | 0.02        | 0.02   |
| ZnO (% w.b.)                            |                    |                   | 0.17                          | 0.27   | 0.07        | 0.24   |
| SrO (% w.b.)                            |                    |                   | 0.06                          | 0.05   | 0.04        | 0.09   |
| ZrO <sub>2</sub> (% w.b.)               |                    |                   | 0.01                          | 0.01   | 0.01        | 0.02   |
| Nb <sub>2</sub> O <sub>5</sub> (% w.b.) |                    |                   | 0.00                          | 0.00   | 0.00        | 0.00   |
| BaO (% w.b.)                            |                    |                   | 0.15                          | 0.02   | 0.05        | 0.10   |
| PbO (% w.b.)                            |                    |                   | 0.00                          | 0.00   | 0.00        | 0.00   |
| MC <sup>c</sup> (% w.b.)                | 3.0 <sup>c</sup>   | 3.0 <sup>c</sup>  | 1.6                           | 0.3    | 0.3         | 0.4    |
| LOI <sup>d</sup> (%)                    | 6.0 <sup>d,c</sup> | 6.0 <sup>d</sup>  | 50.1                          | 10.8   | 3.9         | 21.6   |

<sup>a</sup> Sum of SiO<sub>2</sub> + Al<sub>2</sub>O<sub>3</sub> + Fe<sub>2</sub>O<sub>3</sub>, (min, %); <sup>b</sup> SO<sub>3</sub> (max, %); <sup>c</sup> Moisture Content (max, %); <sup>d</sup> Loss on Ignition (max, %); <sup>e</sup> The use of Class F pozzolan containing up to 12.0 % loss on ignition may be approved.

With regard to Cl content, SFPM showed a value significantly higher than other biomasses (Pr<0.0001). The wood, willow and switchgrass ashes did not present significant differences among themselves (Pr>0.1) due to the large variability in the data. The cause of such variability was not identified. On the other hand, relative high values were found for MnO (0.3–1.79 %), ZnO (0.07–0.27 %) and TiO<sub>2</sub> (0.07–0.26 %). The same trace elements were reported in fly ash.

Excluding switchgrass, the biomasses bottom ash could not be classified into the ASTM norm because of the high values of LOI (10.8–50.1 %) and also, in the case of the SFPM ash, with the higher SO<sub>3</sub> content (6.1 %). The switchgrass bottom ash met the requirements for class C designation. Critical properties found in fly ash were different than in bottom ash for switchgrass. In fact, ash had a significantly higher SiO<sub>2</sub> content

(55.2%) and a low LOI result (3.9%) that allowed being classified as class C ash. Thus it should be showing pozzolanic behavior in a concrete material. Further studies should be focused in the study of the physical properties of concrete materials when using switchgrass bottom ash.

**Characterisation of ash from biomass submitted to a pyrolysis process.** The ash composition of minerals in biochar ash is showed in table 5. Results evidently suggest that it might not be a suitable option for integration with concrete constituents as major constituents such as  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{Fe}_2\text{O}_3$  had substantially lower concentrations than required as per ASTM norms for concrete. In principle, the ash obtained from biochar from pyrolysis of animal manure is very different from those of wood and other biomasses. On the other hand, it might be interesting to investigate the maximum concentration of ash from biochar by pyrolysis of animal manure, which can be mixed with concrete without compromising structural properties and environmental safety. As a matter of fact, ash obtained from biochar by pyrolysis of animal manure is recommended for agricultural land and regarded as safe; therefore, it might also be safe for mixing with concrete.

Table 5. Chemical properties of the biochar samples from swine manure pyrolysis (%).

| <b>Constituent</b>      |              |
|-------------------------|--------------|
| $\text{SiO}_2$          | 6.13         |
| $\text{Al}_2\text{O}_3$ | 0.95         |
| $\text{Fe}_2\text{O}_3$ | 2.16         |
| CaO                     | 16.2         |
| MgO                     | 10.0         |
| $\text{Na}_2\text{O}$   | 5.62         |
| $\text{K}_2\text{O}$    | 20.9         |
| $\text{TiO}_2$          | 0.05         |
| MnO                     | 0.31         |
| $\text{P}_2\text{O}_5$  | 20.9         |
| $\text{Cr}_2\text{O}_3$ | 0.03         |
| LOI                     | 11.3         |
| <b>Total</b>            | <b>83.25</b> |

**CONCLUSION** The chemical proprieties of biomass ash were analyzed to determine their potential use as a replacement of a part of the cement in the concrete. The biomasses tested included wood, solid fraction of pig manure, switchgrass and willow. Results led to the following conclusions: 1. There is a close relation between the chemical properties of the initial biomass and both fly and bottom ashes. 2. Biomass fly ash present high Cl content (13,806–35,223 mg/kg). 3. Biomass fly ash has not enough  $\text{SiO}_2 + \text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3$  content and LOI value to meet ASTM specifications. Thus they are not suitable as cement replacement. 4. Cl content in biomass ash was high and very variable. 5. Switchgrass bottom ash show a potential use in concrete materials. In fact it met ASTM chemical specifications for the class C designation. However, further studies should be focused in the study of the physical properties of concrete materials when using such ash. 6. Ash from biochar produced from swine manure pyrolysis is not suitable for integration with concrete constituents. Further studies could consider studying the chemical proprieties of a biomass ash with coal fly ash mix.

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