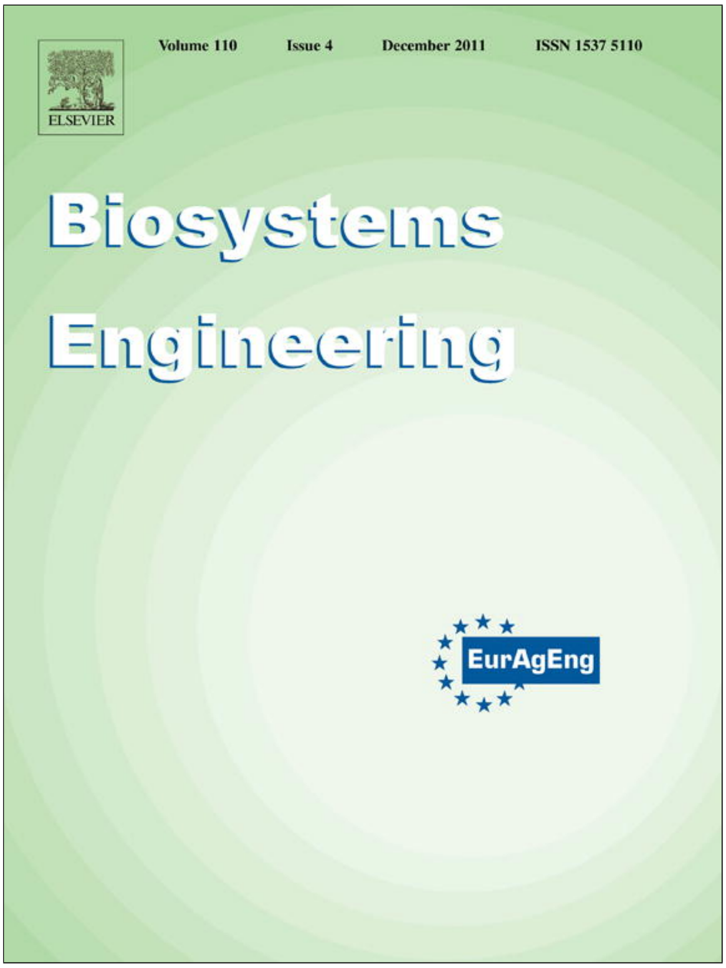
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Review

Biocement production from silicon-rich plant residues: Perspectives and future potential in Canada

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The cement industry produces about 5% of the global anthropogenic carbon dioxide (CO_2) emissions. Global demand for cement is forecast to grow by 4.7% annually, which will increase CO_2 emissions. One way to mitigate the CO_2 generated during cement manufacturing is to use biocement. Biocement is a blend of bio-silica, produced from combustion of organic residues, with Portland cement. Biocement requires less energy intensive clinker, with its related carbon emission, to produce a good cementing agent. Small scale biocement production in tropical areas has shown that blending cement with bio-silica can have environmental, economic and technical benefits. It is also found that a number of crops grown in temperate regions of Canada with high silicon concentration and calorific content have the potential to make biocement. In addition, the combustion process can be integrated into energy production to simultaneously gain the energy and the bio-silica ash. The results indicated that switchgrass, barley, oat and sunflower produce silicon-rich residues and could be good candidates to consider for both energy and biocement production in Canada.

1. Introduction

The cement industry emits about 814–935 kg of CO_2 for every 1000 kg of cement produced (Metz, Davidson, Bosch, Dave, & Meyer, 2007). The chemical decomposition of limestone accounts for 40–50% of CO_2 emissions, and fossil fuel combustion is responsible for the remaining CO_2 emissions (Initiative, 2002; van Oss & Padovani, 2003; Worrell, Price, Martin, Hendriks, & Meida, 2001). In 2000, global cement production was about 1536.6 million tonnes and the associated CO_2 emissions were estimated to be 1578.8 Mt (van Oss & Padovani, 2003). Cement plants account for 5% of global emissions of carbon dioxide, the main cause of global warming (Worrell et al., 2001).

There are three strategies to reduce CO_2 emissions from the cement industry: (1) improve energy efficiency, thus use less fossil fuel, (2) replace fossil fuel with renewable energy sources such as biofuel and other biomass feedstocks, and (3) substitute part of Portland cement with other cementitious materials such as bio-silica (Initiative, 2005). The third option is the main focus of this paper.

Typical raw materials in cement production are limestone or chalk ($CaCO_3$), sand (SiO_2), clay (SiO_2, Al_2O_3, and Fe_2O_3), iron ore (Fe_2O_3), and gypsum ($CaSO_4$). Limestone and clay are

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Nomenclature

CCA	corn cob ash
PMSA	paper mill sludge ash
RHA	rice husk ash
RSA	rice straw ash
SCBA	sugar cane bagasse ash
SCSA	sugarcane straw ash
OPA	oil palm ash
SDA	saw dust ash
BLA	bamboo leaf ash
SSA	sewage sludge ash
VGA	vetiver grass ash
WSA	wheat straw ash

crushed and blended in a ratio of about 75% limestone to 15% clay, and pre-heated to drive off water and decompose the limestone into lime and CO_2. The material is then transferred to a rotary kiln, which heats up to 1450 °C, fusing the calcium from limestone and silicon from clay into calcium silicates (Ca_3SiO_5 and Ca_2SiO_4). The resulting clinker is then cooled, ground and combined with 5% gypsum to control setting (Bye, 1999; Hewlett, 2004; Worrell et al., 2001). To reduce CO_2 emissions and improve cement quality, reactive silica (amorphous silica with average particle size finer than 45 μm) is often used as additive in modern cement production to reduce clinker consumption (Uchikawa & Okamura, 1993, 83). Successful examples include fly ash collected from coal-fired power plants and silica fume produced from silicone industry.

Reactive silica can also be produced from combustion of organic residues. As long as the ash contains sufficient amorphous silica with particle sizes finer than 45 μm, it can be used as cement additive as well. Because of the organic nature, reactive silica so produced is often called bio-silica. Plant by-products like rice husks, sugar cane, and corn cobs can produce bio-silica. When residues containing bio-silica are burned and then blended with Portland cement, the final product is called biocement. The use of biocement has showed environmental, economic and technical benefits. It reduces clinker consumption and its related energy use and CO_2 emissions. The raw feed for cement production becomes renewable. The final concrete can have better performance due to the pozzolanic reaction with bio-silica ash.

Small scale biocement production is underway in tropical areas, but has received little attention in Canada.

This paper presents a literature review on recent development of biocement research. Examples come mainly from pilot-scale biocement production in tropical regions. The objectives of this review were to (1) examine biocement characteristics, (2) to explore the feasibility of simultaneously producing energy by combustion of organic residues and bio-silica ash that exhibits cementitious behaviour, and (3) to propose plants with high silicon concentration and calorific content that grow well in the cold temperate and temperate regions of Canada and have the potential to make biocement.

2. Biocement: sources and characteristics

Biocement is cement containing amorphous bio-silica (SiO_2) generated from the combustion of organic residues, which serve as pozzolanic materials and partial replacements for Portland cement (the most common type of cement in general use around the world).

The process of producing biocement involves two stages. In the first stage, the organic residues are burned to produce ash having reactive bio-silica. In the second stage, the ash produced is blended with Portland cement to produce biocement. The pozzolanic reaction is a simple acid–base reaction between calcium hydroxide and silicic acid (H_4SiO_4or $Si(OH)_4$) that proceeds as follows:

$$Ca(OH)_2 + H_4SiO_4 \rightarrow Ca^{2+} + H_2SiO_4^{2-} + 2H_2O \rightarrow CaH_2SiO_4 \cdot 2H_2O \quad (1)$$

The pozzolanic reaction between amorphous bio-silica and calcium hydroxide must be optimised to produce biocement with good mechanical and physical properties. It is optimised when an amorphous (non-crystalline) silica form with high surface area (particle size less than 45 μm) is combined in the appropriate proportion with Al_2O_3 and Fe_2O_3 (at least 70% by weight) (ASTM, 2003). For example, Adesanya and Raheem (2009a) showed that corn cob ash improved the properties of cement materials, based on their pozzolanic properties. The corn cob ash contained more than 70% (mass basis) of SiO_2, Al_2O_3, and Fe_2O_3. Chemical composition of plant by-products and sewage sludge, relative to Portland cement, is shown in Table 1. Ash from plant by-products may contain 26–94% SiO_2 content. Good pozzolanic properties are obtained when the combined mass of SiO_2, Al_2O_3, and Fe_2O_3 exceeds 70%. By this standard, plant by-products such as sawdust, rice husk, corn cob and bamboo leaf are excellent candidates for biocement (Table 1).

After oxygen, silicon (Si) is the second most abundant element in the Earth's crust. Under natural growing conditions, plants obtain Si from soil. Silicic acid (H_4SiO_4), a non-charged molecule, is absorbed by plant roots when the soil pH is below 9 (Ma & Takahashi, 2002). As water is lost through transpiration, Si bound in silicic acid is translocated from the roots to the shoots and finally deposited as opal (SiO_2), a type of amorphous silica. The Si concentration in the shoot ranges from 0.1% to 10% Si (dry weight basis), depending on the plant species (Epstein, 1999; Ma & Takahashi, 2002; Richmond & Sussman, 2003). An immobile element, Si accumulates preferentially in older tissues. Its deposition is not uniform among plant tissues. In tomato, radish, green onion, and Chinese cabbage, all of which have a rather low Si content (<1%), the Si content of the roots was equal to or greater than that of the shoots. In plants with high Si content (>1%) like wheat and rice, the Si is generally concentrated in aerial parts such as the leaf blade, leaf sheath and stem nodes.

Table 1 – Chemical composition of ash produced from organic residues following combustion at the specified temperature and duration. Values for Portland cement are included for reference.

Organic residue	SiO_2%	Al_2O_3%	Fe_2O_3%	CaO%	MgO%	Na_2O%	K_2O%	Loss on ignition, %	Combustion temperature, °C	Combustion time, h	Reference
Sawdust	67.20	4.09	2.26	9.98	5.80	0.08	0.11	4.67	ND[a]	ND	Elinwa and Mahmood (2002)
Paper mill sludge	25.70	18.86	0.87	43.51	5.15	1.56	1.31	ND	ND	ND	Mozaffari et al. (2006)
Rice husk	93.2	0.4	0.1	1.1	0.1	0.1	1.3	3.7	650	ND	Chindaprasirt et al. (2008)
Vetiver grass	57.48	3.73	1.71	5.45	1.24	0.12	15.49	11.76	900	9	Nimityongskul et al. (2003)
Corn cob	66.38	7.48	4.44	11.57	2.06	0.41	4.92	1.30–1.47	650	8	Adesanya and Raheem (2009a)
Sugar cane straw	59.06	4.75	3.18	19.59	2.25	0.73	4.75	2.05	800	1	Martirena Hernández et al. (1998)
Oil palm shell	63.6	1.6	1.4	7.6	3.9	0.1	6.9	9.6	ND	ND	Chindaprasirt et al. (2008)
Wheat straw	54.24	4.55	1.05	12.54	2.39	ND	ND	7.22	670	5	Biricik et al. (2000)
Bamboo leaf	75.90	4.13	1.22	7.47	1.85	0.21	5.62	ND	600	2	Dwivedi et al. (2006)
Sewage sludge	50.6	12.8	7.21	1.93	1.48	0.32	1.70	ND	700	3	Pan et al. (2003)
Portland cement	22.0	6.0	3.0	65.0	1.0	0.2	0.8	1.29	1400	–	Nimityongskul et al. (2003)

a ND, no data.

In addition to plant species, other factors that affect the Si content include genotypic variation, environmental conditions, growing season, and Si fertiliser application. Genotypic variation generally affects the Si concentration in the plant shoot and intra-specific variation is usually less than inter-specific variation. A survey of about 400 barley cultivars reported 1.24–3.80 mg Si g^{-1} in the grain of hulled barley cultivars (Ma, Sato, & Takeda, 2003). Environmental conditions related to climate and growing season affect Si accumulation, probably due to their influence on plant water relations (adsorption and transpiration). Motomura, Mita, and Suzuki (2002) showed that Si accumulation in long-lived leaves of Kuma bamboo grass was rapid during summer and spring when water consumption by plants was high, but it slowed during winter months. Overall, the quantity of Si deposited per unit dry matter depended on the quantity of silicic acid per unit water transpired and the quantity of water transpired per unit dry matter. Application of Si fertiliser, which confers plant protection against insects, pathogenic fungi, and water stress, also affects plant Si concentration. Mecfel et al. (2007) showed that in *Triticum aestivum* L., the deposition of Si occurs predominantly in the leaves and can be increased by adding Si fertiliser to the soil.

Silicon is found in the non-food portion of many crop plants and could be readily collected from food processors. The suitability for biocement production of each organic residue depends both on its Si content and the reactivity of bio-silica generated upon combustion. Amorphous silica with fine particle size and large surface area has the highest reactivity, and these characteristics can be optimised by controlling the temperature and incineration time. After a suitable ash is blended with Portland cement, the compressive strength of the resultant biocement should be considered. The compressive strength of mortar containing plant by-products ranges from 18 to 103 MPa when added to replace 6–20% of the Portland cement in a mixture (Table 2).

Biocement is an environmentally friendly product that reduces CO_2 emission by partially replacing Portland cement, thereby reducing the volume of this material produced by cement manufacturers. Additionally, plant by-products and other organic residues could be substituted as biofuel for fossil fuel, further reducing CO_2 emissions. For example, substituting rice husk (biofuel) for fossil fuels in cement manufacturing could reduce CO_2 emissions by 50%. The amount of CO_2 emitted from burning 1 kg rice husk is 1.49 kg (Yamamoto, Kihara, Coimbra, & Montanheiro, 1997) and from burning of 1 kg of lignite (brown coal) is 2.93 kg (Quick, 2010). Environmentally, it is better to emit CO_2 that was recently fixed into photosynthates by biofuel or biomass crops than to use fossil fuels, as the latter contain CO_2 that was fixed thousands of years ago.

Plant by-products and other organic residues that generate energy during the combustion process are desirable for this application. Energy generation is affected by the moisture content and type of combustible matter, but the release of undesirable contaminants and cost must also be considered when choosing a viable biofuel. Moisture content influences the recoverable energy level, since moisture vaporisation requires energy during the combustion process. An organic residue with more combustible matter such as cellulose fibres gives higher energy yield (McKendry, 2002). The calorific value of selected organic residues, an indicator of their potential as biofuel, is provided in Table 3.

3. Bio-silica and energy potential from combustion of plant by-products

3.1. *Sawdust ash as bio-silica*

Sawdust is a plant by-product from the processing of timber and forest products. Sawdust can be used as a mulch to

Table 2 – Compressive strength of mortar containing organic residues. Values for 0% ash were included for reference.

Organic residue	Ash content, %	Age days	Compressive strength, MPa	Compressive strength with 0% ash, MPa	Reference
Sawdust	10	28	18.1	23.1	Elinwa and Mahmood (2002)
Paper mill sludge	10	28	62	58	García et al. (2008)
Rice husk	20	28	58.5–103	57.0–100	Chindaprasirt et al. (2008)
Vetiver grass	20	28	55.1	68	Nimityongskul et al. (2003)
Corn cob	8	28	20–36	21–44	Adesanya and Raheem (2009b)
Sugar cane	10	28	42.1	36.1	Ganesan, Rajagopal, and Thangavel (2007)
Oil palm shell	20	28	57.5–102	57.0–100	Chindaprasirt et al. (2008)
Wheat straw	6	28	29	26	Binici et al. (2008)
Bamboo leaf	20	3	62	70	Dwivedi et al. (2006)
Sewage sludge	15	28	47	41	Monzo, Paya, Borrachero, and Corcoles (1996)

improve soil quality, bedding for livestock, as fuel, and for the manufacture of particleboard. Canada is the second largest producer of sawmill products (boards, dimension lumber, timber, poles, and ties from logs) in the world. In 2009, Canada processed an estimated 32×10^6 m^3 of sawn wood (Food and Agriculture Organization of the United Nations, 2011). Sawdust can be used in biocement manufacturing, both as a fuel and as cement replacement material. Recent studies on the use of sawdust ash (SDA) for biocement production have shown that it is cost effective and offers a large potential market for SDA (Sumaila & Job, 1999; Udoeyo & Dashibil, 2002). Yet most studies have focused on sawdust as a fuel due to its high calorific value and there has been limited investigation of the pozzolanic properties of SDA and its viability as a cement replacement. Elinwa and Mahmood (2002) reported that SDA was a silicon-rich residue (67.2% SiO_2) with appreciable quantities of Al_2O_3 and Fe_2O_3 (Table 1). They obtained SDA by open burning and grinding, then mixed the SDA powder with Portland cement in various ratios (by weight), ranging from 0% SDA:100% Portland cement to 30% SDA: 70% Portland cement. With an increasing ratio of SDA: Portland cement, the average consistency of the paste increased. In another study, a blend of 10% SDA: 90% Portland cement showed good performance, giving mortar with the desired workability and strength. The workability and strength of this biocement declined when a higher SDA content was selected, and both initial and final setting times increased with a higher percentage of SDA. However, The setting times were within the British and American standard requirement (Udoeyo & Dashibil, 2002).

3.2. *Paper mill sludge ash as bio-silica*

Paper mill sludge is the residue left over from the paper recycling process and is of interest for biocement production because it contains vegetable fibres. It is used as a soil conditioning agent, and as a bulking agent in compost and fuel. The pulp and paper industry is one of the most important industries in North America, ranking fifth largest in the U.S. economy (Nemerow & Dasgupta, 1991). Each Canadian pulp mill produces an average 40 t (oven-dry) of sludge per day (Clean Air Clean Water Pulp Info Centre, 2010), which can be used both as fuel and in biocement. Paper mill sludge has a high content of cellulose fibres and a gross calorific value of about 15–18 MJ kg^{-1}, making it a good biofuel (Table 3). It also contains calcium carbonate, china clay, and residue chemicals that could promote the pozzolanic reaction. The

Table 3 – Energy obtained upon combustion of organic residues at the corresponding moisture content.

Organic residue	Calorific value[a] MJ kg^{-1}	Type	Moisture, %	Reference
Sawdust	17–18	ND	ND	Fungtammasan and Jittrepit (1994)
Paper mill sludge	14.7–17.6	Gross	Dry	Gavrilescu (2008)
Rice husk	14.7	ND	Dry	Barkakati et al. (1994)
Vetiver grass	16.3	ND	Dry	Islam, Khairul Hassan Bhuiyan, and Hossain (2009)
Corn cob	17	ND	Dry	Demirbas (1997)
Sugar cane	17.6	Gross	Dry	Kilicaslan et al. (1999)
Oil palm shell	17.5	Gross	10	Mahlia, Abdulmuin, Alamsyah, and Mukhlishien (2001)
Wheat straw	17	ND	Dry	Demirbas (1997)
Sewage sludge	17.5	ND	ND	Werther and Ogada (1999)
Fossil fuel (coal)	15-27		Dry	http://www.engineeringtoolbox.com/fuels-higher-calorific-values-d_169.html, March 2011

a The calorific value is the energy content, or heat value, released when the organic residue is burnt in air.

potential of paper mill sludge ash (PMSA) as 'clinker' in cement manufacture was investigated by García, Vigil de la Villa, Vegas, Frías, and Sánchez de Rojas (2008). When burnt to approximately 700 °C, ground, and sieved to a particle size of less than 45 μm, the ash contained reactive silica and alumina, which suggests that PMSA has potential as a replacement for Portland cement in biocement production. Mozaffari, O'Farrell, Kinuthia, and Wild (2006) showed that the biocement containing PMSA as a binder needs more water to make mortar, as compared to Portland cement. Mixing PMSA with a secondary binder, such as granulated blast furnace slag, can reduce water demand because the binder improves the hydration properties and the strength development of the mortar.

3.3. *Rice husk and rice straw ash as bio-silica*

Rice husk, a plant by-product, comprises about one fifth of the 500 Mt of rice produced annually in the world (Mehta, 1992, pp. 407–430). A few uses of risk husk bio-silica are: filler in polymeric materials, a substitute for condensed silica fume in high strength concrete, and starting material for high performance silicon compounds (Chandrasekhar, Satyanarayana, Pramada, Raghavan, & Gupta, 2003). In certain regions, husks are used as fuel for parboiling paddy in the rice mills.

Rice husk ash (RHA) generated from controlled incineration contains more than 87% SiO_2 (Table 1), favourable for pozzolanic reactions, making RHA a good candidate for biocement production or as an additive for blended cement (Ganesan, Rajagopal, & Thangavel, 2008; Nair, Jagadish, & Fraaij, 2006; Nehdi, Duquette, & El Damatty, 2003). Barkakati, Bordoloi, and Borthakur (1994) showed that the reactive silica and calorific value of rice husk make it a practical organic residue for biocement production. Under controlled incineration, RHA contains amorphous silica; the particle size and specific surface are dependent upon the burning conditions, but an average particle size of 5–10 μm and specific surface area of 20–50 $m^2\ g^{-1}$ are generally achieved (Zhang, Lastra, & Malhotra, 1996). The reactivity of amorphous silica is directly proportional to the specific surface area of ash. Therefore, RHA should be ground finely to improve the mechanical strength of concrete.

The most common use of RHA is in blended cement, such as lime-RHA and Portland-RHA cements. The RHA is pulverised or ground to the required fineness and mixed with Portland cement to produce biocement. Using RHA in biocement is cost effective and yields several beneficial properties such as resistance to chemicals and improved strength. Ganesan et al. (2008) prepared RHA from the boiler-burnt husk residue of a rice mill and evaluated the optimal level of RHA substitution in biocement. Results indicated that up to 30% (by weight) of RHA could be blended with Portland cement without adversely affecting the strength and permeability properties of the concrete. Another study showed that up to 40% replacement of RHA was possible with no significant change in compressive strength, compared with Portland cement alone (Al-Khalaf & Yousif, 1984). Addition of RHA to Portland cement not only improves the early strength of concrete, but also forms a C–S–H (calcium silicate hydrate) gel around the cement particles, increasing the density and reducing the porosity of concrete. This may increase concrete strength and prevent cracking (Saraswathy & Song, 2007). The compressive strength of concrete containing up to 30% RHA was similar to that prepared with Portland cement alone, but declined when a higher proportion of RHA was included in the blend. Adding up to 30% RHA in biocement improved the resistance to water permeability of the resulting concrete. These results indicate that RHA is appropriate pozzolanic material that yields concrete with acceptable strength and permeability resistance (Saraswathy & Song, 2007). Biocement with up to 40% RHA had also good sulphate resistance (Chindaprasirt, Kanchanda, Sathonsaowaphak, & Cao, 2007). Additionally, biocement with RHA had greater resistance to chloride penetration than ordinary Portland cement (Chindaprasirt, Rukzon, & Sirivivatnanon, 2008).

Energy requirements for the production of RHA were lower than for Portland cement and most mineral admixtures (Ramachandran, 1995). This supports the use of RHA as an economical bio-silica source. The cost of cement production is expected to decline when Portland cement is partially replaced by RHA (Ahmadi, Alidoust, Sadrinejad, & Nayeri, 2007). Dried rice husk has a calorific value of around 14.65 MJ kg^{-1} (Table 3). It would be environmentally and economically beneficial to burn rice husk as biofuel and use the residue ash for biocement production.

Rice straw ash (RSA) is another potential replacement material for Portland cement. After burning, rice straw is reduced to about 15% ash containing about 82% silica. El-Sayed and El-Samni (2006) showed that RSA is pozzolanic and satisfies the requirements of ASTM. Both initial and final setting times for concrete were found to increase with increasing the percentage of RSA replacement.

3.4. *Vetiver grass ash as bio-silica*

Vetiver grass is a perennial grass cultivated widely in the tropical regions of the world. It is used for soil and water conservation and medicine production. Nimityongskul, Panichnava, and Hengsadeekul (2003) investigated the potential of using vetiver grass ash (VGA) as an additive in cement. Dried vetiver grass was combusted in a ferrocement incinerator at 900 °C. Vetiver grass is self-burning and it does not need extra fuel after the igniting stage. Because VGA proved to have pozzolanic properties, it was blended with Portland cement in the proportions of 20, 40 and 60%, by mass. Biocement made with VGA considerably improved mortar resistance against acid attack, probably because calcium hydroxide reacts with the silica in VGA to form C–S–H gel. The coefficient of water permeability increased as the amount of VGA in the mixture increased. Moreover, VGA-Portland cement mortar had better resistance to water permeability than cement from Portland cement alone (Nimityongskul et al., 2003).

3.5. *Corn cob ash as bio-silica*

Corn cob is a by-product from maize, which is grown on 20% of agricultural land worldwide (Amos & Walters, 2006). About 817 Mt of maize were produced worldwide in 2009, of which 9.5 Mt were harvested in Canada (Food and Agriculture Organization of the United Nations, 2011). Corn cob is used as livestock feed, in charcoal and furfural production, and is a source of xylan for paper production, textile printing, and in the pharmaceutical industry. Corn cob has appreciable calorific value (Table 3) and could serve as fuel when combusted to produce ash for biocement production.

Adesanya and Raheem (2009a) used corn cob ash (CCA) as a pozzolan and determined the physical and chemical properties of concrete from blended cement. Corn cobs were ground and burnt in a furnace using charcoal as a fuel at 650 °C. The CCA was mixed with Portland cement and the mixture contained 0, 2, 4, 6, 8, 10, 15, 20 and 25% CCA, by weight. All CCA-blended cements had higher setting times than Portland cement (Adesanya & Raheem, 2009a), thus, they are suitable for situations where a low rate of heat development is required, such as in mass concreting. This shows that CCA-blended cement is comparable to low heat cement. The authors concluded that at levels lower than 15% substitution, CCA was a good pozzolan for blended cement.

Adesanya and Raheem (2009b) tested the workability and compressive strength of nine mixtures of CCA-blended cement containing 0–25% CCA in the total mass. Based on structural load criteria, the optimum blend contained 8% CCA. The maximum strength gain was achieved in concrete cured for at least 120 days. The durability of concrete made with CCA-blended cement was investigated with respect to permeability and acid resistance. The CCA-blended cement reduced water absorption in concrete. Resistance to chemical attack (HCl and H_2SO_4) was improved with the addition of up to 15% CCA (Adesanya & Raheem, 2010). Additionally, Binici, Yucegok, Aksogan, and Kaplan (2008) showed that an increase in ash content caused a significant increase in the sodium sulphate resistance of the concretes. Microscopic analysis showed that CCA as an additive had a more condensed physical structure than Portland cement, making it more resistant to sulphate attack (Binici, Zengin, Zengin, Kaplan, & Yucegok, 2009).

3.6. Sugar cane ash as bio-silica

Sugar cane straw and bagasse are the wastes from sugar and alcohol factories and are often recycled as fuel for heat generation and vaporisation in these factories. Sugar cane is used as animal feed, fertiliser, alcohol production and bioplastic. Brazil is the leading producer of sugarcane worldwide (Food and Agriculture Organization of the United Nations, 2011). Sugar cane waste is a potential fuel with a gross calorific value of 17 MJ kg^{-1} when dry (Table 3). Wet waste has a lower calorific content (Kilicaslan, Sarac, Özdemr, & Erm, 1999). To date, no information could be found describing the simultaneous use of sugarcane by-products as biofuel and cement replacement material.

Frias, Villar-Cocina, and Valencia-Morales (2007) calcined sugar cane straw and bagasse residues at 800 and 1000 °C. They designated the resultant sugar cane straw ash (SCSA) and sugar cane bagasse ash (SCBA) as potential cement replacement materials because of their high content of amorphous silica and associated pozzolanic activity. The maximum activation was reached by calcined at 800 °C. The pozzolanic activity of SCBA increased with smaller particle size, improving the performance and compressive strength of cement blends (Cordeiro, Toledo Filho, Tavares, & Fairbairn, 2008). The pore structure of lime-SCSA (30:70% by weight, respectively) pastes was similar to Portland cement pastes (Martirena Hernández, Middendorf, Gehrke, & Budelmann, 1998). In other investigations, cement blends with 20% SCBA had the highest compressive strength, greatest reduction in water permeability and greatest resistance to chloride permeation (Chusilp, Jaturapitakkul, & Kiattikomol, 2009). There was a direct inverse relation between the compressive strength of mortar containing SCBA and the particle size of SCBA. Substitution of 10% SCBA in cement caused the setting time to increase, while the compressive strength increased with hydration time. This biocement was resistant when exposed to sulphuric acid (Singh, Singh, & Rai, 2000).

3.7. Oil-palm ash as bio-silica

Malaysia is the world's largest producer and exporter of palm oil, holding about 47% of the global market share (Food and Agriculture Organization of the United Nations, 2011). The oil palm industry produces a considerable amount of solid waste in the form of fibres, empty fruit bunches, and nut shells. The empty fruit bunches, trunk, and shells are produced by 28 Mt per year in Malaysia (Sumathi, Chai, & Mohamed, 2008). The shell and fibre are used as fuel in oil palm mills and reduce to 5% ash after combustion. Additionally, these wastes are also used as soil amendment to improve soil structure and prevent soil erosion.

Oil palm waste is of interest to researchers because its ash contains 64% SiO_2 (Table 1). Oil palm ash (OPA) showed low pozzolanic activity due to its large particles and porous structure. This could be improved by grinding. Tangchirapat, Saeting, Jaturapitakkul, Kiattikomol, and Siripanichgorn (2007) mixed two different particle sizes of OPA, 15.9 μm and 7.4 μm, at concentrations of 10, 20, 30, and 40% (by weight) with Portland cement. Their results suggested that ground OPA is an excellent pozzolanic material and can be used as a Portland cement replacement. The optimum replacement levels were 20% OPA having 15.9 μm particles or 30% OPA with 7.4 μm particles. Concrete strength was evaluated with blends of 10, 20, 30, 40, and 50% (by weight) of OPA mixed with Portland cement. Tay (1990) showed that strength was optimised in biocement with 10% by weight of OPA and the fresh concrete had good workability. Concrete made from biocement containing more than 20% OPA would be more porous and absorbed more water than concrete made from Portland cement alone (Tay & Show, 1996). Resistance against chloride penetration is positively correlated with OPA content in mortar (Chindaprasirt et al., 2008). Ground OPA could also improve the sulphate resistance of concrete (Jaturapitakkul, Kiattikomol, Tangchirapat, & Saeting, 2007).

3.8. Wheat straw ash as bio-silica

Wheat is one of the main agricultural products grown in North America. Globally in 2009, about 682 Mt were produced, of which 26.5 Mt were produced in Canada (Food and Agriculture Organization of the United Nations, 2011). An estimated 9.5 Mt of wheat residues were produced in Canada in 2008 (Table 5).

Wheat residues are used as fertiliser, bio-plastic, and alcohol production.

There is little information regarding wheat straw ash (WSA) as a cement replacement material. Biricik, Akoz, Berktay, and Tulgar (1999) and Biricik, Akoz, Turker, and Berktay (2000) reported that wheat straw reduced to 8.6% ash and contained 73–74% SiO_2 (Table 1) when burned in controlled electrical furnace at 670 and 570 °C for 5 h. The results showed that the pozzolanic properties obtained at 670 °C are higher than those obtained at 570 °C. Mortar containing WSA (burned at 670 °C for 5 h) was resistant against sodium sulphate and optimal resistance against magnesium sulphate (10,000 and 40,000 mg l^{-1} during the 180 days of immersion) was achieved with up to 24% WSA in biocement (Biricik et al., 2000). Binici et al. (2008) mixed WSA with Portland cement to create biocements of 2, 4, and 6% WSA. A clear increase in sodium sulphate resistance of the concrete was observed with an increasing percentage of ash addition.

3.9. *Bamboo leaf ash as bio-silica*

In countries such as Brazil, significant amounts of bamboo are processed in industrial processes, generating high volumes of solid waste. For example, Brazilian paper production consumes about 0.5 Mt of cultivated bamboo annually, generating 0.19 Mt of organic residues. Bamboo wastes are often burnt in open landfills, negatively impacting the environment (Villar-Cocina, Morales, Santos, Savastano, & Frias, 2010).

Dwivedi, Singh, Das, and Singh (2006) burned bamboo leaves in a muffle furnace at 600 °C for 2 h, which generated ash with 76% SiO_2 (Table 1). Bamboo leaf ash (BLA) contains amorphous bio-silica that has pozzolanic properties. Its pozzolanic activity increased with longer reaction time and increasing temperature (Dwivedi et al., 2006). A biocement with 20% BLA showed compressive strength comparable to Portland cement after 28 days of curing (Singh, Das, Singh, & Dwivedi, 2007).

4. Biocement from sewage sludge

Sewage sludge is an organic residue generated by municipalities following secondary and tertiary treatment of wastewater streams. It is used as a soil amendment and fertiliser to improve the yield of selected crops, as well as a fuel in co-combustion with other fuels or types of waste. Sewage sludge is disposed of by land spreading, burial in landfills, and incineration. Municipalities produce large quantities of sewage sludge each year. The City of Toronto (Ontario, Canada) produced 70,000 t (dry) of sewage sludge in 1999, for a population of about 2.4 million people (Environment Canada, 2001).

Sewage sludge can be used in biocement production via two different processes: (1) by blending its incinerated ash with Portland cement or (2) by co-combustion of sewage sludge with limestone before its addition to Portland cement. Sewage sludge has appreciable quantities of silicon, present mainly in minerals such as sand, so both processes could be followed to replace Portland cement. The added advantage of the co-combustion process is that it would allow for some energy recovery from sewage sludge waste. Energy produced during sewage sludge incineration strongly depends on water content of sludge and furnace performance, although its calorific value is close to fossil fuel (Table 3) (Rulkens, 2008). Thus, sewage sludge can be considered as raw material and an energy source for biocement production, an environmentally friendly alternative to Portland cement.

Sewage sludge ash (SSA) produced from incineration at 700 °C for 3 h, contains 50.6% SiO_2, 12.8% Al_2O_3, and 7.21% Fe_2O_3 (Table 1). SSA contained amorphous SiO_2 particles with diameters between 0.1 and 1 μm (Pan & Tseng, 2001). However, the chemical properties of SSA are expected to be highly variable, depending on what materials enter the waste stream and the wastewater treatment process. Pan, Tseng, Lee, and Lee (2003) showed that finer SSA particles increased the comprehensive strength of mortar at a replacement ratio of 20% SSA. Monzó, Payá, Borrachero, and Girbés (2003) reported that mortar containing high replacement level of 30% SSA had decreased workability. This could be due to irregular morphology of SSA particles and high water absorption on SSA particle surfaces. Cement blends of 15 or 30% SSA by mass did not affect the strength of mortars for 3–28 day curing periods (Monzo, Paya, Borrachero, & Peris-Mora, 1999). Trace metals in sewage sludge represent an environmental concern due to their potential toxicity to humans and other organisms. However, the environmental impact of biocement containing SSA was the same as Portland cement because trace metals from sewage sludge were immobilised in the cement at high processing temperature (Cyr, Coutand, & Clastres, 2007).

The direct use of sewage sludge in biocement production was examined by Tay and Show (1994a) and Tay and Show (1994b). As a silica replacement material, dry sewage sludge was mixed with limestone in ratios of 25, 40, 50, 60, and 75%, by weight, and fired 1000, 1100, 1200 °C for in different times duration. The mixtures were then blended with Portland cement at levels of 5, 10, 20, 30, 40, and 50%. Cement with equal amount of sludge and limestone by weight, fired at 1000 °C for 4 h exhibited the highest comprehensive strength (Tay & Show, 1994a). However, the water demand of biocements made from sewage sludge, limestone, and Portland cement increased with greater sewage sludge content (Tay & Show, 1994b). This suggests that biocement producers need to consider limestone-sewage sludge mixtures that optimise the mechanical strength of concrete while conserving water, particularly in regions where water shortages could occur.

Table 4 – Criteria for Si-accumulating plants (adapted from Ma & Takahashi, 2002).

Parameter	Type		
	Si-accumulator	Intermediate	Si-excluder
Si content (%)	>1.0	0.5–1	<0.5
Si/Ca ratio	>1.0	0.5–1	<0.5
Degree of Si accumulation	+	+	−

Table 5 – Silicon accumulator plants adapted to temperate and cold temperate regions of North America. Production values (yield and organic residues) are from Canada only.

No.	Species	Common name	Life cycle	Average Si content, %	Climate	Annual Canadian production, [a] kt	Harvest Index	Annual Canadian organic residue production, kt	Used as fuel	Used as raw material for cement
Cultivated plants										
1	*Zizania latifolia*	Wild rice	Annual	4.40	Temperate	0.7701 (in 2003)	ND[b]	ND	No	No
	Zizania aquatic			4.20	Temperate					
	Zizania palustris			ND	Cold temperate					
2	*Avena sativa*	Oat	Annual	2.08	Cold temperate	2798.2 (in 2009)	0.52[e]	2582.9	Fuel alcohol	No
3	*Hordeum vulgare*	Barley	Annual	1.53–2.71	Temperate	9517.2 (in 2009)	0.50[e]	9517.2	Fuel alcohol	No
	Zea mays	Corn	Annual	1.23	Temperate	10592 (in 2008)	0.53[e]	9392.9	Fuel alcohol	Yes[c]
4	*Helianthus annuus*	Sunflower	Annual	1.38	Wide range	101.9 (in 2009)	0.27[e]	275.5	Oil fuel	No
5	*Secale cereal*	Rye	Annual	1.04	Cold temperate	280.5 (in 2009)	0.27[f]	758.4	Fuel alcohol	No
6	*Triticum aestivum*	Bread wheat	Annual	1.44	Cold temperate	26514.6 (in 2009)	0.39[e]	41471.5	Fuel alcohol	Yes[d]
7	*Linum usitatissimum*	Flax	Annual	High silica in ash shives	Temperate	930.1 (in 2009)	0.34[g]	1805.5	Fuel pellet	No
8	*Panicum virgatum*	Switchgrass	Perennial	1.79	Wide range	ND	ND	ND	Fuel pellet	No
Native plants										
9	*Panicum bisulcatum*	ND	Annual	2.16	Temperate	ND	ND	ND	No	No
10	*Andropogon virgincus*	Chalky bluestem	ND	1.48	Temperate	ND	ND	ND	No	No
11	*Festuca rubra*	Red fescue	Perennial	1.40	Temperate	ND	ND	ND	No	No
12	*Leersia oryzoides*	Rice cutgrass	Perennial	1.20	Cold temperate	ND	ND	ND	No	No
13	*Agrostis clavata*	Clavate bent	Annual	6.97	Cold temperate	ND	ND	ND	No	No
14	*Glyceria acutiflora*	Mannagrass	Perennial	2.53	Temperate	ND	ND	ND	No	No
15	*Miscanthus sinensis*	Chinese silver grass	Perennial	2.96	Cold temperate	ND	ND	ND	Biomass fuel	No
				3.20	Temperate	ND	ND	ND		
16	*Aegilops squarrosa*	ND	Annual	2.11	Temperate	ND	ND	ND	No	No
17	*Lolium perenne*	Ryegrass	Perennial	1.15	Cold temperate	ND	ND	ND	No	No

a Food and Agriculture Organization of the United Nations (2011).
b ND, no data.
c Adesanya and Raheem (2009a).
d Biricik et al. (1999).
e Whalen and Sampedro (2010).
f Singh and Stoskopf (1971).
g Malhi, Johnston, Schoenau, Wang, and Vera (2007).

5. Canadian plants with potential for biocement production

A variety of plant residues contain sufficient Si to generate amorphous bio-silica for biocement production. Much of the research to date has focused on crops grown in the tropics and sub-tropics. In those areas, the plant residue is incinerated, then the ash is blended with conventional cement, effectively replacing up to 40% of the Portland cement in the mixture. Concrete strength, durability and resistance to acidity/humidity were generally optimal in blended cement with 10–20% ash from organic residues. Due care is needed in the combustion process to ensure the maximum ash recovery, and pozzolanic content of at least 70% of SiO_2, Al_2O_3 and Fe_2O_3 in an amorphous form. Additionally, grinding the ash can optimise pozzolanic reaction. These considerations could be helpful as a starting point in generating bio-silica from temperate plant species and subsequently producing biocement.

The challenge ahead is to adapt practices that work in the tropics/sub-tropics to the Canadian context, and to optimise the efficiency of the biocement production process. One major gap in the research is how to utilise the calorific value of organic residues in the preparation of bio-silica for biocement. The best scenario is that organic residues are first used as biofuel in an industry process and the remaining ash is then collected for further processing and incorporation into biocement. The key parameter is the combustion temperature in this secondary process. When organic residues are used as bio-fuels, ash is produced by self-combustion, but the combustion temperature might not be high enough to oxidise silicon sufficiently into amorphous bio-silica with the desired pozzolanic reactivity. Therefore, heat treatment of organic residue ash is necessary. The energy required in this process is much lower than in clinker production. If successful, the entire process produces zero waste and emits much less CO_2. Organic residues are utilised to their greatest potential when exploited for both energy production and biocement production. The following discussion considers both aspects in selection of Canadian plants.

Selecting Canadian plants with a potential for biocement production is a necessary first step. To produce bio-silica from plant residues, it would be best to first select silicon accumulator species, and then devise methods to increase their Si content by increasing plant transpiration and the Si content of soil. The silicon content of soil can be increased by application of silicate fertiliser (Jones & Handreck, 1967).

Silicon-accumulating plants can be discriminated from non-accumulating plants by the Si content and the Si/Ca ratio (Ma & Takahashi, 2002). Based on these physiological relationships, we categorised plants according to their potential to acquire Si, as silicon accumulators, intermediate, or silicon excluders, using the criteria stated in Table 4. Plant species with Si content $>$ 1% and Si/Ca ratio $>$ 1 were selected, as they warrant further investigation regarding their use for biocement production in Canada. Although most Si-accumulating plants grow in tropical regions (e.g., rice), a few plants adapted to temperate and cold temperate regions are Si accumulators (Table 5). Among the 17 plant species listed in Table 5 are cultivated and non-cultivated (indigenous) species that grow well in North America. Cultivated plants yield high amounts of residues each year in Canada. Corn is an example of a cultivated plant that produced 10.6 Mt of aboveground biomass in 2008, of which 50% was left in the field after grain was harvested (Table 5). Plant residues left in the field provides benefits such as soil erosion control, maintenance of soil structure and soil organic matter content, improving water retention, providing energy for microbial processes, increasing cation exchange capacity, and enhancing agronomic productivity. Plant residues in excess of these requirements can be considered for biomaterial production (e.g., biofuel and other bioproducts).

In Table 5, we present the harvest index and the amount of residues produced in Canada as two main factors of cultivated plants that might be important from an economic and practical perspective. Natural grasses, such as switchgrass, Chinese silver grass, red fescue, and ryegrass may also be considered for both bio-silica and biofuel in biocement production. Switchgrass is one of three dominant native grasses found in North American and has potential as a biomass crop even in areas with a short growing season. Switchgrass is inexpensive to produce because of its perennial nature and stand longevity, adaptation to marginal farmlands (i.e. low land rents), low input requirements, and moderate to high productivity on marginal soils. Variable costs to grow and harvest switchgrass in Canada are approximately \$40–\$50 t^{-1}. Switchgrass has a Si content of about 2%. It can produce 185 GJ ha^{-1} of energy, reducing greenhouse gas emissions by about 90% when compared to an equivalent fossil fuel (Samson, 2007). These characteristics make switchgrass a suitable candidate for biocement production.

Crops used to produce energy in North America are categorised into three groups: oil crops, alcohol crops, and biomass energy crops. The third group is the suitable option as fuel in cement production, because biomass energy crops produce heat and ash at the same time. Within this group, we targeted crops that are appropriate for large scale production in view of their biomass, silicon uptake capability, silicon content, growth cost, and production volume. Cultivated plants such as oat, barley, and sunflower, which have more than 1% Si content and produce large amounts of residues each year, are also good candidates for biocement manufacturing. To date, there has been no research on switchgrass, barley, oat, and sunflower as a source of bio-silica and energy for biocement production. These topics warrant further investigation.

6. Conclusion and future research directions

There is enormous global demand for cement. The industry is looking for ways to reduce CO_2 emissions from limestone decomposition and fossil fuel combustion. In the tropics, ash from combusted plant residues that contains sufficient reactive bio-silica can be blended with Portland cement to produce biocement without compromising concrete strength and durability. To date, there is virtually no research on biocement production in Canada. There are several reasons for this knowledge gap: (1) temperate plants are relatively “silicon poor”, with less than 2% Si in most cultivated crop plants, compared to rice (about 10% Si content). Yet, the crop acreages are large and would generate substantial quantities of residues; (2) agricultural producers often leave crop residues in the field to conserve soil organic matter and prevent soil erosion, thus would need economic incentives to collect part or all of their residues and transport it to a processing facility for biocement production and energy generation; and (3) technical specifications are lacking regarding the optimal conditions for combustion of temperate plant residues to generate amorphous silica and energy. Consequently, the Canadian cement industry does not have sufficient information to judge the potential of biocement as an alternative to conventional cement production.

We identified switchgrass, barley, oat and sunflower as plants that have the potential to simultaneously generate energy and produce bio-silica for biocement, and therefore would be the best candidates for further research in Canada. The technical feasibility of the process and resulting biocement still needs to be fully evaluated.

This review serves as a case study for other temperate regions. Since the availability of crop residues suitable for biocement is controlled by environment (adapted cultivars, climate and soil conditions) and economic factors (i.e., farmer's decisions based on crop market prices), knowledge of crop acreages is helpful. A survey of the Si content and calorific value of the major crops and native plant species is an important first step in developing a local research program for biocement.

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