

PRODUCTION OF SODIUM SILICATE FROM BAMBOO LEAF ASH FOR ALKALI ACTIVATION OF BINDERS

R. VINAI, F. NTIMUGURA, W. CUTBILL, R. EVANS

** College of Engineering, Mathematics and Physical Sciences, University of Exeter, Exeter EX4 4QF, UK*

SUMMARY: The use of biomass ash for the development of bio-derived activators or precursors of alkali-activated materials has revitalized the search for sustainable source of initial silica materials for alkali-activated cements. In this study, a simple process to produce a one-part sodium silicate activating powder from bamboo leaf ash (BLA) is presented. Bamboo leaves were calcined at 550 °C and 800 °C and combined with NaOH pellets to produce a reactive sodium silicate powder. The thermochemical reaction with NaOH converted the amorphous silicates from BLA into a crystalline sodium silicate powder with mineral phases of various Na₂O/SiO₂ ratios. Na₂SiO₃ was the main phase identified. The effectiveness of the produced powder was assessed through mechanical compression tests comparing mortars made from commercially available sodium silicate and sodium hydroxide activating solutions. The strength of mortars activated with BLA-based sodium silicate showed lower early strength, but fully comparable 28-day strengths. These initial results confirmed that the reactivity of BLA-silicate powder was similar to that of commercial sodium silicate solutions. The results show the potential valorisation of future biomass renewable energy waste in the production of low carbon, alkali-activated concretes.

1. INTRODUCTION

The concerns about relatively high environmental impacts of cement in concrete have spurred the search for more environmentally friendly binders including supplementary cementitious materials such as fly ash (FA), ground granulated blast furnace (GGBS), silica fume (SF) and metakaolin (MK), but these materials can provide only a partial replacement of Portland cement in concrete mixes. Instead, the alkali activation of aluminosilicate materials allows the full replacement of Portland Cement in concrete and produces a low carbon geopolymer concrete with low embodied energy [1,2]. Fly ash and GGBS remain the most common precursors, typically used with a range of liquid/solid mixes of activators. These activators provide silica to form ortho-silicate ions (SiO₄)⁴⁻, the backbone of alkali-activated materials (AAMs). However, sodium silicate (SS) used in combination with sodium hydroxide as a blended alkaline activator for AAMs remains expensive and carbon-intensive [3]. Hence, finding new sources of silica to produce sustainable alkali-activators for AAMs can represent a booster in the alkali activation technology take-up.

The current shift and advances in biofuels suggest high availability of biomass ash in the UK. Some of the conventional biomass ash (BMA) valorisation strategies in a range of industrial applications include its use as cementitious materials, mainly due to the high content of reactive silica.

BMA were investigated for the partial substitution of Portland cement for their pozzolanic potential [4-6]. Most of the studies on the incorporation of biomass ash in geopolymer concrete or alkali-activated composites cover the partial substitution of the traditional precursors (such as FA, GGBS or MK). The potential use of non-wood biomass ash in alkali-activated concrete as a source of silica and alkalis when combined with coal fly ash and activated with $\text{Na}_2\text{SiO}_3 + \text{NaOH}$ to produce binders based on alumino-silicate hydrates has been reported [7, 8].

Despite the high silica content of non-wood BMA suggests its potential use in the production of alkali silicate for the activation step, the use of BMA in the production of activators (sodium or potassium silicates in conjunction with alkali hydroxides) has not been extensively investigated yet. Significant research has been carried out only on the use of rice husk ash (RHA) as ingredient for the silicate activation of AAM, with most of the available literature proposing hydrothermal dissolution of RHA in sodium hydroxide solutions varying concentration, temperature, and process time [9]. Few other BMA materials have been studied to date. Moraes et al. investigated the use of sugar cane straw ash (SCSA) as a silica source for the production of alkaline activating suspensions [10]. The authors used a simple dissolution thermal bottle and various parameters were investigated including dissolution time, and water/NaOH/ash ratios in mixes. Results suggested that, even if SCSA compressive strength was marginally (20 - 25%) lower than that of commercial SS + NaOH activated mortars, from the microstructural standpoint, SCSA based systems exhibited reaction products similar to those observed in matrices of commercially available SS activated mortars. Among the Si-rich biomass by-products, bamboo leaves are of particular interest due to their silica content and to their significant availability after the harvest of culms. Bamboo Leaf Ash (BLA) has been investigated as a pozzolanic material for partial Portland cement substitution [11-13]. Kow et al. investigated the hydrothermal extraction of silica from BLA in NaOH solution for the production of waterglass, aiming at the development of BLA-based aerogel materials [14].

In addition to the search for alternative silica sources for activators, practicalities of handling large amounts of highly corrosive liquid activating solutions have motivated the development of solid-based ‘one-part’ activators [15]. The development of alternative ‘one-part’ silicate activators seems to be the next direction for sustainable geopolymer binders for application in mortars and concrete.

The main objective of this study was to assess the potential of using BLA for the production of an alkaline activating powder for the production of alkali-activated mortars. BLA was added to sodium hydroxide pellets and heated to a moderate temperature to allow a thermo-chemical reaction that transformed amorphous BLA in a crystalline sodium silicate powder, according to the method proposed by Vinai and Soutsos [16]. The effectiveness of the produced BLA-silicate powder was assessed through a comparison against mortars produced using commercial chemicals.

2. Materials and experimental methods

2.1. Materials

Stems from bamboo species *Arundinaria japonica* were locally sources, chopped down and stripped off their leaves. Leaves were oven-dried at 50-70°C for 48 to 72 h. Dried bamboo leaves (BL) were milled into fine powder and tested with Thermo-Gravimetric Analysis (TGA), Scanning Electron Microscopy (SEM) coupled with Energy Dispersive X-ray Spectroscopy (EDS) and X-ray Diffraction (XRD). Informed by the results from TGA, the calcination of BL was carried out in two batches: at 550°C for 4 hours (batch 1), and at 800°C for 2h (batch 2). The ash was allowed to cool down at room temperature. The bamboo leaves ash (BLA) was subsequently ground using a pestle and mortar to a fine powder that was stored in airtight sealed bags. In order to check the effect of the quality of the milling step, the BLA produced with batch 2 was ground in a ball mill prior to its

utilisation for the production of activator. Fly ash (FA) and ground granulated blast furnace slag (GGBS) were used as precursors. Fly ash was obtained from a coal fired power plant in UK (Drax Power plant) and GGBS was sourced from Ecocem, Ireland. The standard activator chemical was a mixture of sodium silicate ‘water glass’ (12.8% wt.% Na₂O, 25.5 wt.%SiO₂ and 61.7 wt.% water) sourced from Fisher Scientific and 30% NaOH solution obtained from NaOH solid pellets dissolved in water.

2.2. Preparation of BLA activator powder and alkali activated mortars

The production of sodium silicate activator from BLA and NaOH powders was obtained in three steps: a) the amount of SiO₂ from BLA was assessed either interpreting SEM/EDX results (batch 1) or with X-Ray Fluorescence (XRF) method (batch 2); b) the amount of NaOH powder required was calculated considering a molar ratio equal to 1 in Na₂O + SiO₂ → Na₂SiO₃ and considering that Na₂O content in NaOH powder is 77.5%; c) following the method proposed by Vinai and Soutsos [16], BLA and NaOH powders were mixed with enough water to reach an homogeneous paste-like consistency and then heated to 300-330°C for 1h. The resulting paste was greenish in colour possibly due to the presence of reduced sulfur species, particularly trisulfur radical anions S₃⁻ [17]. The obtained hardened paste was subsequently crushed down for its use in producing alkali activated mortars (AAM). A FA/GGBS blend with mass ratio 60%/40% was used as binder precursor. Silica sand proportioned with a sand:binder ratio of 2.75 was added to the mixes. Activation parameters Alkali Dosage (M⁺), i.e. the mass ratio Na₂O/dry precursor blend, and Alkali Modulus (AM), i.e. the mass ratio Na₂O/SiO₂, were chosen equal to 7.5% and 1 respectively for the mixes with BLA-based activator as well as with commercially available solutions. A mix with AM = ∞ (i.e., no SiO₂) was also prepared using NaOH solution as the only chemical in order to provide a benchmark for the absence of silicate in the activator. The amount of BLA-based activating powder was calculated according to its assumed chemical composition, which was estimated from the quantity of SiO₂ identified in the two ash batches. Table 1 shows the mix proportioning details of the produced mortars, cast in 50-mm cubic PVC moulds and cured at room temperature and 50% RH. Mixes were labelled after the following sequence: batch – activator – w/s ratio.

Table 1. Mix proportions of produced mortars. BLAA: Bamboo leaves ash-based activator, SS: Commercial sodium silicate solution, SH: Commercial sodium hydroxide solution. Quantities in g.

Mix	FA	GGBS	Sand	SS	SH	BLAA	Water
1-BLAA-0.49	300	200	1375	-	-	130	282
1-SSSH-0.49	300	200	1375	147	80	-	135
1-SH-0.49	300	200	1375	-	161	-	151
2-BLAA-0.39	300	200	1375	-	-	90	187
2-SSSH-0.39	300	200	1375	147	80	-	77
2-SH-0.39	300	200	1375	-	161	-	97
2-BLAA-0.43	300	200	1375	-	-	90	206
2-SSSH-0.43	300	200	1375	147	80	-	100
2-SH-0.43	300	200	1375	-	161	-	118

2.3. Characterization techniques

The x-ray diffraction of powders (XRD) was carried out on the Bruker D8 Advance diffractometer with a Cu K α of a wavelength 1.5418 Å. The generator was calibrated to a voltage of 40kV and a current of 40 mA and a goniometer speed of 0.017 to 0.031° 2 θ /s over the range 5 – 80° 2 θ . Each spectrum was processed through the MAUD (Materials Analysis Using Diffraction) software with

the crystallographic information files from the crystallography open database (COD.cif files). The chemical composition of raw materials (FA, GGBS and BLA) was determined by X-ray fluorescence (XRF) using a Bruker-AXS S4 Pioneer X-Ray Fluorescence Spectrometer (WDS XRF). Thermogravimetric analysis was performed with a Mettler Toledo TGA/DSC1 STARE system on a temperature range 25 – 800 °C. The microstructure of ash and raw materials was observed under Tescan Vega 3 scanning electron microscope (SEM) using secondary electron mode. The electron beam was set at 20.0 kV, the emission at 22 μ A and the 1.10-10 mbar low vacuum was used for all samples. Compressive strength was assessed with a MCC8 multi-test hydraulic system under load/stress control with a pre-load of \sim 10 kN and a loading rate 250-500 N/s.

3. RESULTS AND DISCUSSION

3.1. Chemical composition and microstructure of raw materials

The oxide composition of raw materials is shown in Table 2. The main source of alumina is fly ash, whereas the highest content in silica is from BLA. The microstructure of raw materials obtained using SEM is shown in Figure 1 for FA, GGBS and BLA, respectively. FA is made of rounded particles of \sim 4-8 μ m, while GGBS has octahedral particles that are larger than FA, with a width of 10-15 μ m. BLA micrograph (obtained from batch 1) shows typical interior and exterior parts of calcined BL. The XRD pattern of FA shows the main identified phases are quartz (SiO_2), mullite and hematite ($\alpha\text{-Fe}_2\text{O}_3$).

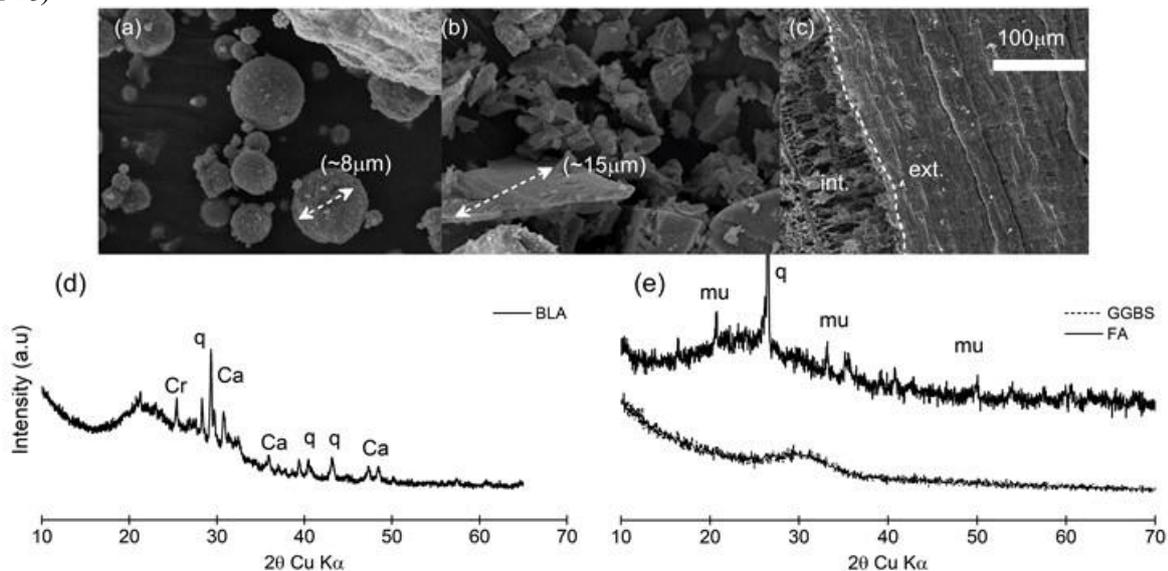


Fig. 1. SEM micrographs and XRD diffractograms of raw materials: (a) SEM of FA, (b) SEM of GGBS, (c) SEM of BLA (d) XRD patterns of BLA and (e) XRD patterns of FA and GGBS. Cr: cristobalite, q: quartz, Ca: calcite, mu: mullite.

Table 2. Oxide composition of BLA, Fly ash and GGBS.

Element	SiO_2	Al_2O_3	Fe_2O_3	MgO	CaO	Na_2O	K_2O	P_2O_5	MnO	SO_3	LOI
BLA	53.50	0.28	12.05	1.23	5.99	0.31	14.48	3.94	1.88	/	0.40
Fly ash	46.78	22.52	9.15	1.33	2.24	0.89	4.09	0.17	0.05	0.90	3.57
GGBS	36.50	10.40	0.70	8.10	42.40	0.50	0.20	0.00	0.40	0.30	/

The XRD patterns of the biomass ash BLA (obtained from batch 1) shows small diffraction peaks matching calcium carbonate (as the furnace temperature was lower than the calcite decarbonation

threshold), and silicon dioxide in the form of quartz and Cristobalite. The XRD patterns of BLA and its phases' identification are shown in Fig. 1.d as well as in Fig. 4. A large broad hump between 18 and 30 °2θ centred at 25 °2θ, is a typical characteristic of the amorphous nature of BLA. Fig. 1.e. shows the amorphous nature of XRD diffraction patterns of FA and GGBS.

3.2. Microstructure and mineralogical composition of BLA activator powder

Thermo-gravimetric analysis suggested that thermal decomposition of organic material was completed at about 550°C (i.e. where the plateau in the derivative curve started, see Fig. 2). The calcination of batch 1 was therefore carried out at 550°C, whereas batch 2 was produced at 800°C for ruling out the possible presence of carbon in the ash. The two peaks in the derivative curve (283°C and 330°C) were attributed to the pyrolysis of hemicellulose and cellulose respectively [18].

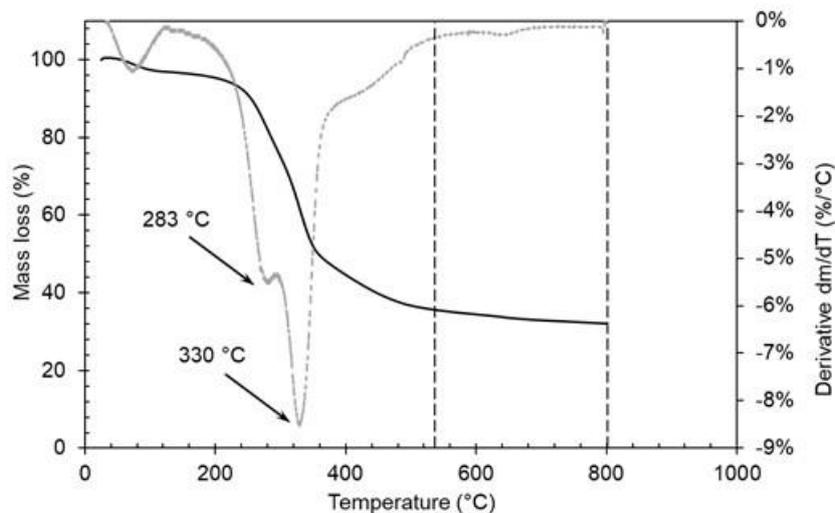


Fig. 2. Thermo-gravimetric test curves.

The microstructural analysis was performed using SEM-EDS on BLA-based sodium silicate (SS) powder to assess the effectiveness of reaction between BLA and NaOH (Fig. 3). The texture of reacted SS powder appears to be made of large round granules of a porous structure (Fig.3.a). The pores were identified to be of a width 20-50 µm (Fig 3.b and c). The EDS analysis on the powder found a molar content of major elements with a Na/Si ratio in the range of 1.16 to 2.25. The mineralogical analysis of BLA – SS powder was further investigated using XRD to confirm the crystallinity of SS powder from amorphous raw BLA. The XRD pattern of the produced powder shown in Fig. 4 confirmed the success of the thermochemical reaction from an amorphous BLA into a crystalline powder with distinguishable peaks of sodium silicates with dominant peaks of Na₂SiO₃.

3.3. Compressive strength of mortar cubes

The compressive strength of mortar activated using BLA sodium silicate powder was compared to that of control mortar activated by commercial SS + NaOH and a mortar activated by NaOH only for both BLA-based activators produced from batch 1 and 2. Results seem to suggest that BLA-based activator had a slower reaction kinetics, as strengths at 1 day and 7 days of curing in standard indoor curing conditions (SIC) were lower than these of mortars activated with commercially available sodium silicate (Fig. 5.a). However, at 28 days the BLA-based mortar provided comparable strength, suggesting that the reaction was fully developed. The comparison between batch 1 and 2, carried out on 7-day strength, indicated no significant difference between the two calcination temperatures, as well as among different w/s ratios.

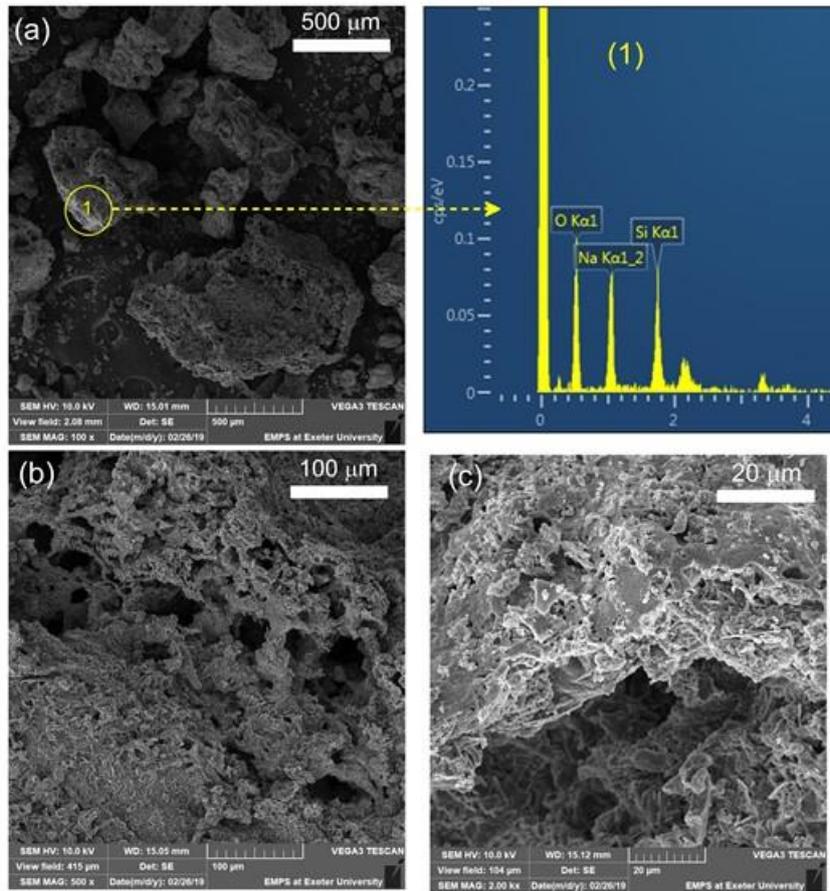


Fig. 3. SEM micrographs and EDS analysis of sodium silicate activator powder: (a), (b) and (c) SEM of sodium silicate activator powder at 100x, 500x and 2.0kx Mag. (1) EDS analysis, Na/Si = 1.157.

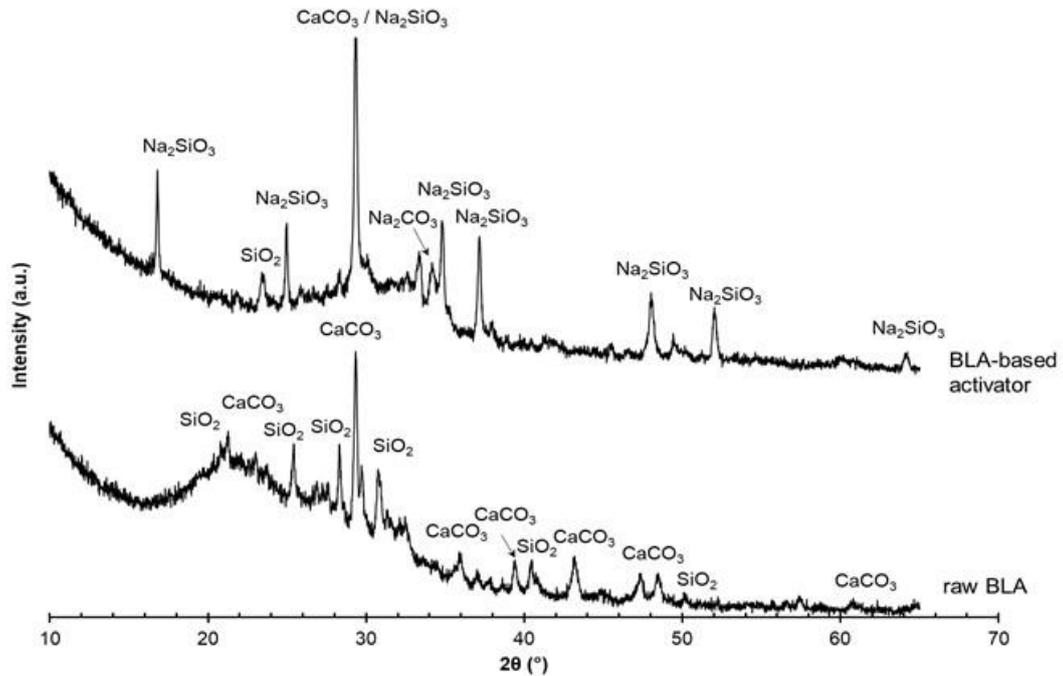


Fig. 4. XRD patterns of processed powder activator and raw BLA powder.

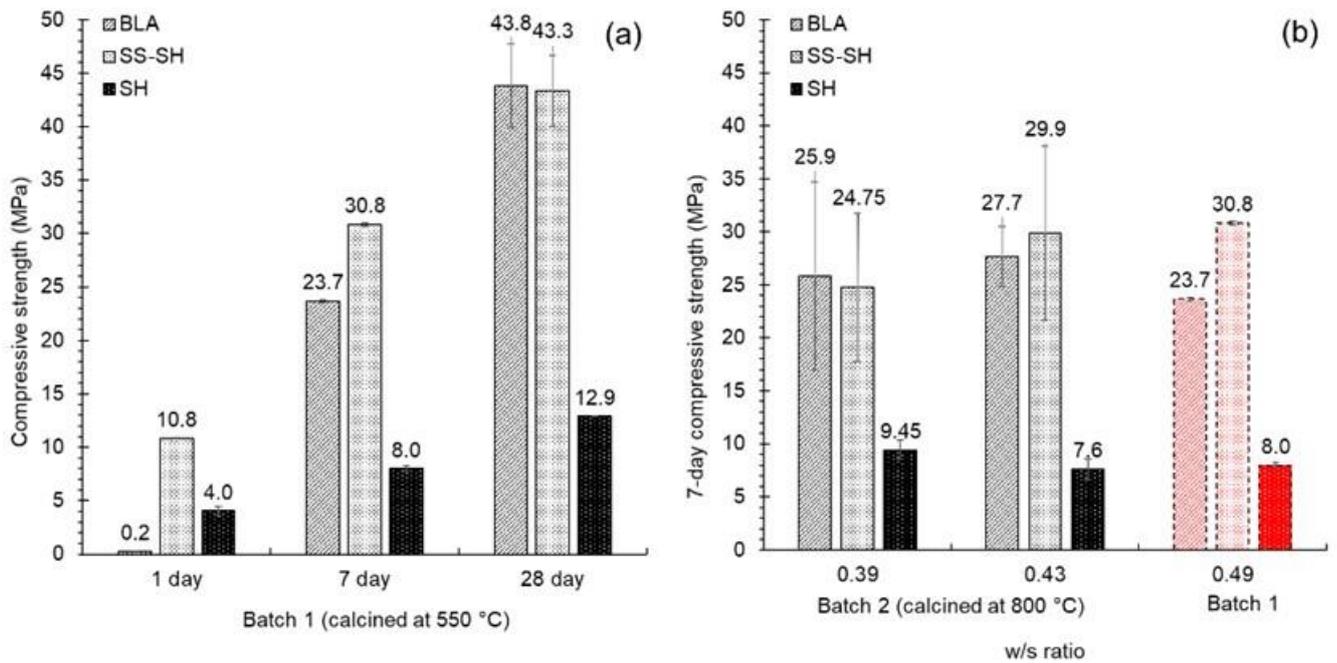


Fig. 5. (a) Compressive strengths of mortars produced with BLA-based SS, commercial SS and NaOH and NaOH only with w/s 0.49. (b) Comparison of 7-day strength of samples produced with BLA from batches 1 (in red) and 2 and control alkali activators at different w/s ratios.

4. CONCLUSIONS

This paper discusses the results from a preliminary investigation on the production of a bio-derived sodium silicate powder from bamboo leaves ash. This study confirms the use of biomass ash as an alternative silica source for alkali activated concrete. It can be concluded that:

- Bamboo leaves ash is a suitable silica source for the development of sodium silicate powdered activator. The production process involves the combination of bamboo leaves ash, sodium hydroxide pellets and water, the resulting paste being processed in oven at about 300°C for 1h. Main reaction product was sodium metasilicate (i.e. $\text{SiO}_2/\text{Na}_2\text{O} = 1$).
- Calcination temperatures in the range 550 to 800 °C were suitable for the production of BLA.
- The reaction of BLA-based activator in AAB showed a slower kinetics, with very limited 1-day strength obtained on mortar cube samples. However, the same strength of control samples produced with commercially available sodium silicate was achieved at 28 days of curing.
- Increasing the w/s ratio in the range 0.39 to 0.49 did not seem to affect negatively the mixes.

Further investigation will determine the effect of the variability of biomass ash chemical composition on the performance of the activator powder. In addition, the microstructural characterisation of pastes developed using the developed powder in comparison with pastes from the commercial activating solutions will confirm the nature of reaction products.

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