POZZOLANIC ACTIVITY OF INDUSTRIAL SUGAR CANE BAGASSE ASH

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Abstract

With an annual production of 4 million tons, sugar cane bagasse ash (SCBA) has potential to be used as an alternative supplementary cementitious material (SCM) for Thailand. Prior research has reported satisfactory improvements in compressive strength when SCBA was used to partially replace cement. Such improvements partly result from the filler effect and the pozzolanic reaction between reactive SiO_2 from the SCBA and $Ca(OH)_2$ from cement hydration. Four samplings of SCBAs obtained from a sugar factory (Dan Chang Bio-Energy Co., Ltd., Suphanburi, Thailand) were analyzed for their pozzolanic activities using various methods in this work. The SCBAs were each ground to two different finenesses such that the filler and pozzolanic effects can be elucidated. From chemical extraction, the amorphous (or reactive) SiO_2 contents of the SCBAs were found to be in the range of 42-49 and 34-43 wt% for fine and coarse SCBAs, respectively. These are considered low compared with typical rice husk ash (> 85%). Nevertheless, the agreements between the amorphous SiO_2 content, the $\Delta\sigma_{2\ \mathrm{min}}$ from the conductometric method of Luxán *et al.* (1989), and the 28-day strength activity index (SAI) suggest that the former two methods can potentially be used to predict the pozzolanic effect on the SAI. Despite the low amorphous SiO_2 contents, cement mortars made with 10% SCBA replacement still show satisfactory gains in compressive strength, suggesting that the amorphous SiO_2 content is not a primary factor contributing to strength in this system. The results should help promote the use of industrial SCBAs as an SCM, given that their particle sizes are reduced prior to use, to increase *both* the filler and the pozzolanic effects and to make the effect of the amorphous SiO_2 content on the compressive strength gain less discriminating.

Keywords: Bagasse ash, pozzolanic activity, supplementary cementitious materials

Introduction

Sugar cane bagasse, the fibrous residue after crushing and juice extraction of sugar cane, is a major industrial waste product from the sugar industry in Thailand. Nowadays, it is commonplace to reutilize sugar cane bagasse as a biomass fuel in boilers for vapor and power generation in sugar factories. Depending on the incinerating conditions, the resulting sugar

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cane bagasse ash (SCBA) may contain high levels of SiO_2 and $Al2O_3$, enabling its use as a supplementary cementitious material (SCM) in blended cement systems. The use of SCBA as an SCM to partially replace ordinary Portland cement not only helps reduce methane emissions from disposal of the organic waste and reduce the production of cement, which is infamous for its high energy consumption and CO_2 emission, but also can improve the compressive strength of cement-based materials.

As stated by Cordeiro *et al.* (2008), the improved compressive strength depends on both physical and chemical effects of the SCBA. The physical effect (or the so-called filler effect) is concerned with the packing characteristics of the mixture, which in turn depends on the size, shape, and texture of the SCBA particles. The chemical effect relates to the ability of the SCBA to provide reactive siliceous and/or aluminous compounds to participate in the pozzolanic reaction with calcium hydroxide (an unfavorable product from cement hydration) and water. The product of such reaction is called calcium silicate hydrate, a compound known to be responsible for compressive strength in cement-based materials. Cordeiro (2006) found that the pozzolanic reactivity of SCBA depended strongly on the incinerating temperature; a maximum reactivity occurred at around 500°C. Unfortunately, the SCBA from typical sugar factories in Thailand is burnt at temperatures in the vicinity of 1000°C. The use of such high temperatures causes most amorphous SiO_2, the most reactive form of SiO_2, to phase-transform to its crystalline and less reactive form called cristobalite, thus worsening the pozzolanic activity of the SCBA.

Typical rice husk ash, which has gained a lot of attention as an industrial waste SCM, usually contain more than 85 wt% amorphous SiO_2. Nevertheless, Cordeiro *et al.* (2008) observed improvement in the compressive strength of mortars made with SCBA of low amorphous content (24%). Their SCBA did not exhibit high pozzolanic activity as a result of high quartz contamination and poor incinerating conditions but the compressive strength gain they obtained was similar to that of low-calcium fly ash. Payá *et al.* (2002) also reported SCBA with high pozzolanic activity based on their thermogravimetric studies, despite its high SiO_2 crystallinity and high unburnt carbon content (15.63%).

Based on these previous findings and its great abundance of ~4 million tons annually, industrial SCBA may still serve as an attractive waste material candidate to be used as an SCM for Thailand. This work seeks to explore the use of industrial SCBA as an SCM by measuring its pozzolanic activity. Three methods were adopted, including the strength activity index method according to ASTM C311 (2004), the conductometric method of Luxán *et al.* (1989), and the impedance method, modified from the method of McCarter and Tran (1996). These results were compared with the amorphous SiO_2 content of the ash as determined by chemical extraction following the method of Payá *et al.* (2001) and other physical properties known to influence the pozzolanic activity of the SCBA.

Materials and Experimental Methods

Four samplings of SCBA (denoted SCBA 1, SCBA 2, SCBA 3, and SCBA 4) were tested for their pozzolanic activity. They were obtained as industrial wastes from a sugar factory (Dan Chang Bio-Energy Co., Ltd., Suphanburi, Thailand). Therefore, the incinerating conditions of the SCBA were not controlled variables in this work. After acquisition, the moisture content of the SCBAs was measured according to ASTM C311 (2004). The chemical oxide composition was determined by X-ray fluorescence spectroscopy (XRF, Phillips, PW2404, 4kW, Netherlands) and the loss on ignition (LOI) was measured according to ASTM C311 (2004); both measurements were performed after the as-received SCBAs were milled to an average particle size of approximately 10 μm (denoted by (C) for "coarse" SCBAs). After these measurements, the coarse SCBAs were further milled to obtain a series of "fine" SCBAs (denoted by (F)). All the following analyses were made on fine and coarse SCBA samples after milling.

The physical properties of the SCBA investigated in this work include the particle size distribution, the specific surface area, the unburnt carbon content, and the amorphous SiO_2 content. The particle size distribution was determined by laser diffraction technique (Mastersizer S, Malvern Instruments, UK), while the specific surface area was measured by nitrogen adsorption (Autosorb-1, Quanta Chrome, USA) after the SCBA samples were outgassed at 300°C for 6 h. A CHNS/O analyzer (TruSpec CHN, LECO, UK) was employed to determine the unburnt carbon content. Following the method proposed by Payá *et al.* (2001), the amorphous SiO_2 content was determined from the weight loss of each SCBA sample after being dissolved in a boiling 4 M KOH solution for 3 min.

The following 3 methods were conducted to assess the pozzolanic activity of the SCBA.

The strength activity index (SAI) method compares the compressive strengths of cement mortars with and without SCBA in percentage terms, according to ASTM C311 (2004). The SAIs at 7 and 28 days were obtained from cement mortars made with 10% SCBA replacement (by weight of cement) under a fixed flow (110 ± 5%) condition. The reported SAI is an average of 3 replicates for each cement + SCBA mortar.

The conductometric method of Luxán *et al.* (1989) relies on the conductivity drop due to the consumption of Ca^{2+} and OH^- ions by the pozzolanic reaction; therefore the faster the conductivity drop, the better the pozzolanic activity. The method measures the conductivity change during the first 2 min ($\Delta\sigma_{2\ min}$, in mS/cm) after adding 5 g of pozzolan into 200 ml of saturated $Ca(OH)_2$ solution at 40°C. The measurements were made under continuous stirring using a portable conductivity meter (PC 300 series, Oakton Instruments, Singapore) with a cell constant, k, of 1.0 cm^{-1}. The conductivity values compensated at 25°C (using a temperature coefficient of 0.021/°C) are reported, to eliminate the effect of temperature on conductivity. In their original work with natural rock pozzolans, Luxán *et al.* (1989) broadly classified the pozzolans into 3 groups, including non pozzolanicity ($\Delta\sigma_{2\ min} < 0.4$), variable pozzolanicity ($0.4 \le \Delta\sigma_{2\ min} \le 1.2$), and good pozzolanicity ($\Delta\sigma_{2\ min} > 1.2$).

Lastly, for the impedance method, modified from the method of McCarter and Tran (1996), each SCBA sample was mixed with $Ca(OH)_2$ and water to form a paste using a fixed SCBA:$Ca(OH)_2$ ratio of 9:1 and a water: solid ratio of 9:10 (both by weight). The paste was cast into a cubic mold, and the conductivity change (in alternating-current mode) under room temperature was measured for 24 h, using an Autolab PGSTAT302 (ECO CHEMIE, The Netherlands) with frequency ranging from 1 MHz to 1Hz, a fixed amplitude of 0.35 V, and zero bias. To take into account the conductivity contribution from pre-existing salts and/or the unburnt carbon in the paste, all conductivity values at later times were normalized by the earliest measurement (σ_0).

Results and Discussion

The chemical oxide compositions of the SCBAs are shown in Table 1. It is found that the total amounts of $Si0_2$, Al2O_3, and Fe_2O_3 for all SCBAs are higher than the minimum requirement stated for Class N pozzolan (> 70%) according to ASTM C618 (2003). Moreover, the percentages of SO_3 and the losses on ignition (LOIs) for all SCBAs are well below the maximum requirement of 4% and 10%, respectively, as specified by the same standard. Although the moisture contents for all SCBAs are higher than the maximum requirement of 3%, this poses no serious problem to the use of SCBAs as an SCM, since it can be easily reduced by oven-drying at 105-110°C overnight or by sun-drying, for a more energy-efficient and economical means.

From Figure 1, the fine SCBAs show similar particle size distributions, corresponding to the mean particle size, D[4,3], of 3.0-5.7 μm in Table 2. Likewise, coarse SCBAs show similar particle size distributions in Figure 2, corresponding to the mean particle size, D[4,3], of 8.3-10.4 μm, in Table 3. It should be noted that all SCBAs display a bimodal

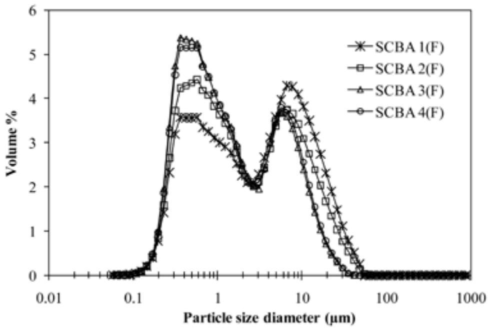

Figure 1. Particle size distribution of the fine SCBAs

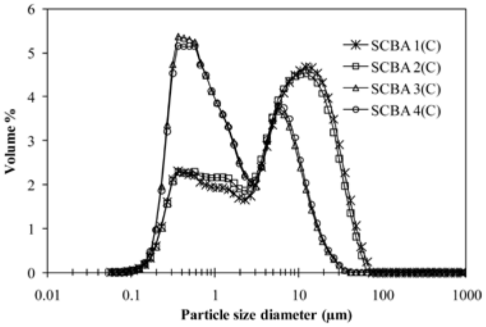

Figure 2. Particle size distribution of the coarse SCBAs

Table 1. Chemical compositions of the SCBAs (measured from the coarse SCBAs)

	SCBA 1	SCBA 2	SCBA 3	SCBA 4
Moisture content (wt%)	55.27	52.56	60.25	61.34
LOI (wt%)	6.58	7.50	7.18	8.58
Chemical oxide composition (wt%)				
SiO_2	75.96	77.21	75.27	74.67
Al_2O_3	5.32	4.69	5.38	4.85
Fe_2O_3	2.22	2.05	2.54	2.12
CaO	3.87	3.30	3.74	3.80
MgO	1.15	0.97	1.15	0.96
SO_3	0.21	0.18	0.12	0.28
Na_2O	0.02	0.02	0.02	0.02
K_2O	3.10	2.56	2.76	2.98
TiO_2	0.36	0.32	0.37	0.32
P_2O_5	0.88	0.84	1.07	1.04

Table 2. Properties of the fine SCBAs investigated

	SCBA 1 (F)	SCBA 2 (F)	SCBA 3 (F)	SCBA 4 (F)
Mean particle size D[4, 3] (μm)	5.7	4.2	3.0	3.1
Specific surface area (m^2/g)	62.7	56.8	59.4	67.6
Unburnt carbon (w%)	5.7	5.1	5.0	6.0
Amorphous SiO_2 (w%)	47.5	41.6	49.4	43.9
Luxán method $\Delta\sigma_{2min}$ (ms/cm)	-0.84	-0.82	-0.97	-0.90
Strength activity index (%)				
7d	104	107	105	104
28d	112	111	112	112

behavior in their particle size distributions. For the fine SCBAs, the first mode occurs around 0.3-0.5 μm, while the second mode occurs around 3.0-5.7 μm. For the coarse SCBAs, the two modes occur around 0.3-0.4 μm and 8.3-10.4 μm, respectively. The appearance of bimodal distributions was also observed by Cordeiro *et al.* (2008) and has been attributed to the tendency of fine particles to agglomerate after milling. The amorphous SiO_2 contents are in the range of 42-49 and 34-43 wt% for the fine and coarse SCBAs, respectively, which are considerably low compared with 85 wt% in typical rice husk ash. It should be noted that the amorphous SiO_2 contents of fine SCBAs are always slightly higher than that of coarse SCBAs. However, the slightly higher amorphous SiO_2 contents in the fine SCBAs cannot be explained by the specific surface area of the two types of SCBAs. As can be seen from Tables 2 and 3, the specific surface areas of the fine SCBAs are even slightly lower (although not significantly) than those of the coarse SCBAs. This can be reasoned by the destruction of internal porosity of the SCBA particles by milling, as suggested by Cordeiro *et al.* (2008), or partly by the fact that the measured specific surface area of agricultural ashes (rice husk ash included), is not a strong function of the particle size, but rather a strong function of the unburnt carbon content, which is a microporous high-surface-area species (~1000 m^2/g), as suggested by Nehdi *et al.* (2003). As shown in Tables 2 and 3, no significant change in the specific surface area is observed between the fine and coarse SCBAs, given that their carbon contents remain unchanged and essentially the same for all four samplings. Beside, the similar unburnt carbon contents (5-6%) for all SCBAs are below 6-8% suggested by Ha *et al.* (2005) to prevent corrosion of steel rebar in ordinary Portland cement mortar containing fly ash.

Using the method of Luxán *et al.* (1989), the conductivity drops of the fine SCBAs are always faster than the coarse SCBAs, as shown in Figure 3. This is in agreement with the trend in amorphous SiO_2 contents obtained by chemical extraction as shown in Figure 4, corresponding to a correlation coefficient of -0.87. Numerically, the values of $\Delta\sigma_{2\ \min}$ are -0.84, -0.82, -0.97, and -0.90 mS/cm for SCBA 1(F), SCBA 2(F), SCBA 3(F), and SCBA 4(F), respectively. At the same time, the values of $\Delta\sigma_{2\ \min}$ are -0.77, -0.64, -0.92, and -0.67 mS/cm for SCBA 1(C), SCBA 2(C), SCBA 3(C), and SCBA 4(C), respectively. These numbers place all SCBAs investigated under the "variable pozzolanicity" category. None of the SCBAs investigated possesses good pozzolanic activity, in agreement with their low amorphous SiO_2 contents.

Figure 5 shows the change in normalized conductivity (σ/σ_0) with time during the first 24 h from the modified impedance method. The corresponding slopes, $d(\sigma/\sigma_0)/dt$, during the first 24 h are also shown in Tables 2 and 3. From these values, it is clear that the slope

Table 3. Properties of the coarse SCBAs investigated

	SCBA 1 (C)	SCBA 2 (C)	SCBA 3 (C)	SCBA 4 (C)
Mean particle size D[4, 3] (μm)	9.7	8.9	8.3	10.4
Specific surface area (m^2/g)	69.4	60.4	66.6	68.1
Unburnt carbon (w%)	5.8	5.1	5.0	6.0
Amorphous SiO_2 (w%)	42.3	33.7	42.7	37.7
Luxán method $\Delta\sigma_{2\ \min}$ (ms/cm)	-0.77	-0.64	-0.92	-0.67
Strength activity index (%)				
7d	97	94	94	90
28d	104	100	105	99

carries no relationship with the amorphous SiO_2 content for all SCBAs investigated, unlike the case of rice husk ashes as studied by Wansom *et al*. (2010). The reason for the inapplicability of the impedance method to SCBAs might be due to their amorphous SiO_2 contents, which are so low that the conductivity drops are no longer a strong function of the amorphous SiO_2 contents, but rather a strong function of the temperature variation in the laboratory (even after temperature correction, according to McCarter and Tran (1996)).

As shown in Figures 6 and 7, at both curing times of 7 and 28 days, all mortars still yield the SAIs well beyond 75%, which is the minimum requirement to classify a material as a Class N pozzolan according to ASTM C618 (2003), in spite of the meager amorphous SiO_2 contents of the SCBAs. At both curing times, the higher SAIs is observed for the fine SCBAs, in agreements with the trends in the amorphous SiO_2 content (higher for the fine SCBAs) and the $\Delta\sigma_{2\ \min}$ (faster for the fine SCBAs). The agreements are further shown in Figures 8 and 9, where the SAIs at 28 days show satisfactory correlation coefficients of 0.83 and -0.80 with the amorphous SiO_2 content and the $\Delta\sigma_{2\ \min}$, respectively. The high correlation between the amorphous SiO_2 content and the $\Delta\sigma_{2\ \min}$, and the agreement between each of these variables and the SAIs at 28 days, suggest that the amorphous SiO_2 content and the conductivity method of Luxán *et al.* (1989) can potentially be used to predict the pozzolanic effect on the SAI. However, the fact that the SCBAs can still exhibit high

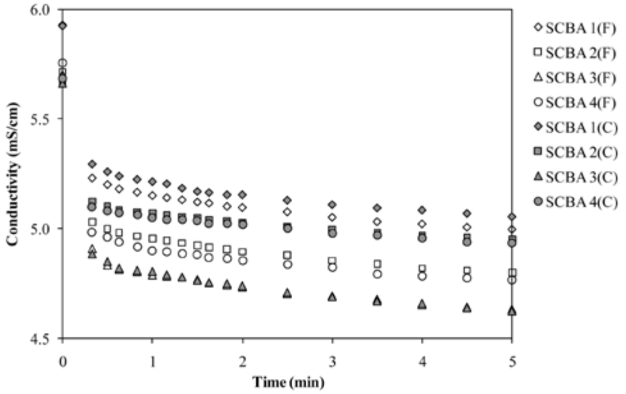

Figure 3. Conductivity vs. time following the method of Luxán *et al.* (1989)

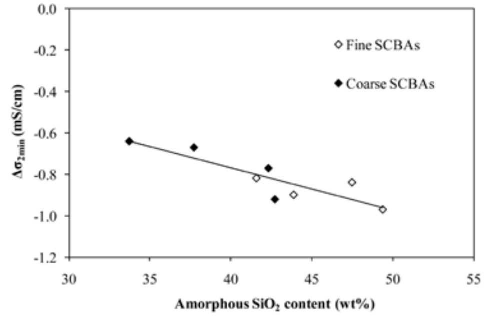

Figure 4. Relationship between amorphous SiO_2 content vs. $\Delta\sigma_{2\min}$

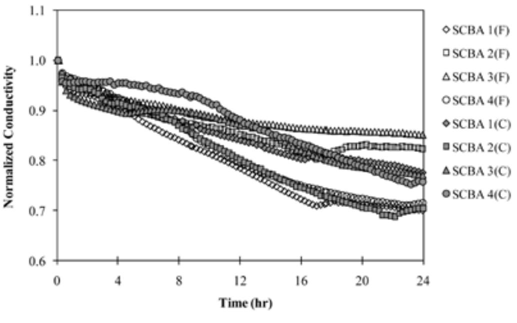

Figure 5. Normalized conductivity vs. time for the modified impedance method

SAIs despite the low amorphous SiO_2 contents suggests that the amorphous SiO_2 content is not the only primary factor contributing to compressive strength gain in this system. In fact, the filler effect might even play a more vital role than the amorphous SiO_2 content in determining the SAIS. As seen from Table 3, with the coarse SCBAs (whose particle sizes are not much smaller than the median cement particle size of 10 μm), a greater variability in the 28-day SAIs is observed, reflecting the role of the amorphous SiO_2 content. However, when the SCBAs were milled more finely, the resulting 28-day SAIs in Table 2 are essentially the same, regardless of the amorphous SiO_2 content. It is, therefore, recommended that the industrial SCBAs be milled as finely as possible prior to use as an SCM, since this would increase both the filler effect (through better packing characteristics of the smaller particles) and the pozzolanic effect (through the greater reactivity of the smaller particles), and thus making the effect of the amorphous SiO_2 content on the compressive strength gain less discriminating.

Conclusions

The amorphous SiO_2 contents are found to be in the range 42-49 and 34-43 wt% for the fine and coarse SCBAs, respectively, which are still considered low compared with typical

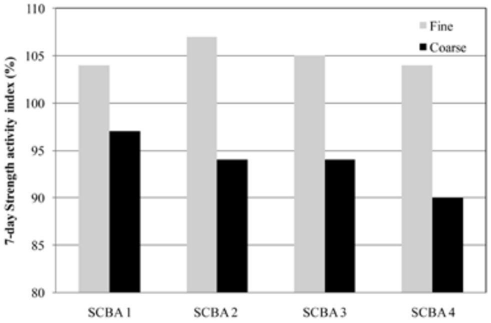

Figure 6. Strength activity index of the mortars made with 10% SCBA replacement at 7 days

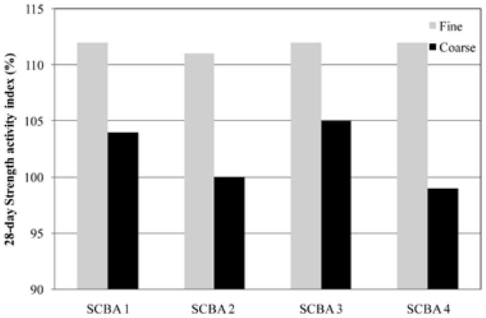

Figure 7. Strength activity index of the mortars made with 10% SCBA replacement at 28 days

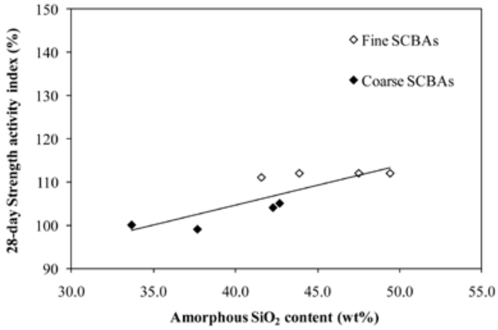

Figure 8. Relationship between the amorphous SiO_2 content vs. 28-day strength activity index

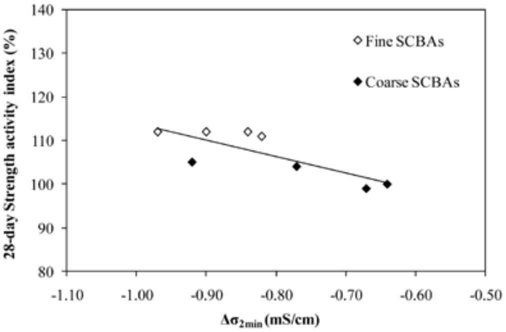

Figure 9. Relationship between the $\Delta\sigma_{2min}$ vs. 28-day strength activity index

rice husk ash. Such low amorphous SiO_2 contents were in agreement with the conductometric method of Luxán *et al.* (1989) which ranks all the investigated SCBAs under the "variable pozzolanicity" category. The linear relationships between the amorphous SiO_2 content, the $\Delta\sigma_{2\,min}$, and the 28-day SAIs suggest that the a morphous SiO_2 content and the conductivity method of Luxán *et al.* (1989) can potentially be used to predict the pozzolanic effect on the SAIs. However, despite the low amorphous SiO_2 contents, the SCBAs can still exhibit high SAIs, suggesting that the amorphous SiO_2 content is not the only primary factor contributing to compressive strength gain in this system. A more vital role of the filler effect may be realized when considering the variability in the 28-day SAIs with respect to the particle sizes and the amorphous SiO_2 contents of the SCBAs. The results should help promote the use of industrial SCBAs as an SCM, given that their particle sizes are reduced prior to use, to increase both the filler and the pozzolanic effects and to make the effect of the amorphous SiO_2 content on the compressive strength gain less discriminating.

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