

EVALUATION OF BIOMASS FIRED AND CO-FIRED FLY ASH FOR ALKALI-SILICA REACTION MITIGATION IN CONCRETE

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Abstract

Biomass and co-fired fly ash, an emerging class of renewable energy by-products, are not recognized for use in concrete under current U.S. standards; however, recent European standards have permitted co-fired fly ash use with certain restrictions including a limit on total soda equivalent content for alkali-silica reaction (ASR) considerations. In this study, the ability of binary blends utilizing a sampling of these fly ashes, with a wide range of chemical and physical properties, to mitigate ASR expansion are assessed using the accelerated mortar bar test (AMBT). Binary blends with co-fired fly ash replacement of 25% the mass of cement significantly reduced expansion compared to the cement control after 14-days accelerated mortar bar testing. Overall, the data suggest that co-fired fly ash of an appropriate composition can be as effective in mitigating ASR as other low-calcium fly ashes.

Keywords: fly ash, biomass, cement, alkali-silica reaction

1 INTRODUCTION

New federal legislation imposing renewable energy requirements and greenhouse gas emission limits is expected to increase the practice of firing biomass and co-firing biomass with coal, which can be sustainable energy sources when the consumption of the biomass is less than its rate of growth [1]. The by-product of these processes (biomass and co-fired fly ash, respectively) can have unique engineering properties compared to coal fly ash. Limited research on pathways for utilization of these by-products has been conducted; however recent studies have begun to examine their reuse in concrete [2-4]. Yet, these sources of ash are not addressed in the U.S. standard for fly ash use in concrete, ASTM C 618 [5]. The current European standard for fly ash use in concrete (EN450-1) permits ashes that are “produced when small quantities of secondary materials are combusted with at least 80% of coal by dry mass in a power station with a maximum ash content of 10% being derived from the secondary material” [6]. Additional requirements for co-fired ashes in EN-450-1 include limits on soluble phosphate, initial setting time, reactive SiO₂ and MgO for various durability and strength concerns in addition to a maximum of 5% total soda equivalent content for alkali-silica reaction (ASR) considerations.

The influence of biomass and co-fired ash sources on ASR expansion is not well-understood. Wang et al. [2] found that ashes derived from co-firing coal with switchgrass and sawdust were able to substantially reduce expansion compared to a cement control, however available alkali contents were increased. Another recent study [7] found that ternary blends of treated biomass ashes and metakaolin significantly improved ASR expansion mitigation, however binary blends with treated biomass ashes only provided a small improvement over the cement control. These mixed results suggest that the regional

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variation in biomass sources and subsequent differences in their ash structure and composition can significantly alter the performance of biomass and co-fired ash in concrete especially with regards to ASR mitigation. Thus more research is needed on this topic. In this study, the ability of binary blends utilizing a sampling of biomass and co-fired fly ashes, with a wide range of chemical and physical properties, to mitigate ASR expansion with a highly reactive fine aggregate are assessed using the accelerated mortar bar test (AMBT). Trends between ash composition and expansion data are examined and linked to possible mechanisms in an attempt to better understand the effect of this emerging class of by-products on concrete durability properties.

2 MATERIALS AND METHODS

2.1 Materials and mixture proportions

A standard mortar expansion test method, ASTM C 1260 [8] and its companion ASTM C 1567 [9], was used to assess binary blends of coal fly ash, co-fired fly ash, and biomass ash. Seven ash samples with varying chemical and physical characteristics were investigated. Co-fired ashes were produced by full-scale co-combustion tests in which bituminous coal was fired with a range of wood types varying in weight percentage replacement of coal, energy content, and moisture content (see Table 1). Companion coal samples produced at the same facilities under similar processing conditions were also included in the testing matrix. Co-fired and coal ash samples were provided by the Ernest C. Gaston Electric Generating Plant in Wilsonville, AL (EC) and the Gadsden Electric Generating Plant in Gadsden, AL (GA). A commercially available coal Class F fly ash (CA) was used as a benchmark comparison. Additionally, biomass ash (BA) derived from firing a mixture of waste wood including tree limbs and sawdust at McNeil Generating Station in Burlington, VT was also assessed for potential mitigation of ASR. Two ash blends were also created from the coal (CA) and biomass (BA) ashes to determine if such laboratory blends could effectively simulate co-fired ash produced at biomass co-firing percentages higher than is capable with current facilities in the Southeast. Co-firing tests have revealed that the ash contents of local wood range from 0.25-1% while the ash contents of local coal range from 5-15%. Ash mixes were produced using the assumption that 100 kg of wood will produce 1 kg of wood ash, and 100 kg of coal will produce 10 kg of coal ash as seen in Table 2. All mortars were prepared with commercially available Type I portland cement [10].

The expansion behavior of ten mortar mix designs including an ordinary portland cement (OPC) control and binary blends of 25% ash (as a weight percent replacement of cement) were analyzed using the accelerated mortar bar test (AMBT). Mix designs consisted of 60.5 wt% sand, 26.9 wt% cementitious materials and 12.6 wt% water. Water to cementitious materials ratio was equal to 0.47 by weight for all mixes. Mortars were prepared using a very reactive sand from Texas primarily composed of chert, quartz and feldspar. The sand was sieved to accommodate grading requirements specified in ASTM C 1260 [8]. Deionized water (17.1 M Ω -cm) was used in making the mortar specimens. All ash and cement samples were passed through a No. 30 sieve (0.6mm opening) to remove large clumps. Furthermore, the BA sample was oven-dried for 24 hours at 100°C to evaporate its high (i.e., nearly 50%) in situ moisture content to values similar to the other ash samples used in this experiment. Mortars were produced in a power-driven mixer with a total mixing time of 4 minutes as described in ASTM C 305 [11]. Water was first placed in the bowl, followed by the cement and ash, and finally the slow addition of the fine aggregate. Mortars were moist cured for 24 hours at 23°C before demolding for testing.

2.2 Methods for assessment and analysis

Chemical analysis of bulk concrete (XRF)

Fly ash and cement samples were digested in Li-borate (mixed $\text{LiBO}_2 + \text{Li}_2\text{B}_4\text{O}_7$) at $>1020^\circ\text{C}$. The resulting fused beads were analyzed by X-ray fluorescence for SiO_2 , Al_2O_3 , Fe_2O_3 , CaO , MgO , SO_3 , Na_2O , K_2O , P_2O_5 , TiO_2 , Mn_2O_3 , Cr_2O_3 , and ZnO . Operating conditions of the Philips PW-2400 XRF instrument were set at 24-60kV and 50-125mA depending on the measured element. Loss on ignition (LOI) was determined gravimetrically using a LECO TGA 601. Samples were held to a constant weight at 107°C to determine free moisture content, and then weighed before and after ignition at 950°C to determine LOI, which comprises both CO_2 and H_2O . Raw sum totals of analytical results are within 100.0 ± 1.3 wt% (Table 3).

Particle Size Analysis

Fly ash and cement particle size distributions were measured by a Sympatec RODOS T4.1 Particle Size Analyzer using laser diffraction. The particles were dry dispersed through a compressed air cyclone separator. The R3 lens was used for all samples, which accommodates particles from $1\text{-}175\mu\text{m}$ in diameter.

Scanning Electron Microscopy (SEM)

Unprocessed co-fired and biomass ash samples were placed on sample holders and sputtered with gold in a Quorum Q150R Rotary-Pumped Sputter Coater device. The prepared samples were then analyzed in a LEO 1530 Thermally-Assisted Field Emission Scanning Electron Microscope. Operating conditions were set at an acceleration voltage of 8kV and varying magnifications under high vacuum.

Accelerated Mortar Bar Test (AMBT)

The procedures described in the standard accelerated mortar bar test (AMBT) ASTM C 1260 [8] and in the similar standard for mortars containing pozzolans ASTM C 1567 [9] were used to perform expansion measurements on all mixes. Three mortar bars ($25 \times 25 \times 286\text{mm}$) were prepared for each mix. Stainless steel gage studs were embedded at the ends of all mortar bars. To improve the accuracy of expansion measurements, a rigid plastic rod cut to 250mm in length was inserted into the molds prior to casting to ensure the correct distance between the gage studs. Following the initial moist curing period, specimens were demolded and placed in water maintained at 80°C for 24 hours. Immediately afterwards, the specimens were submerged in 1 N NaOH solution at 80°C for the duration of the testing period. A length comparator with an accuracy of $1\mu\text{m}$ was used to measure expansion every two days until 14 days, and approximately every five days thereafter until 28 days (note that measurements were taken for twice the standard AMBT time length). ASTM C 1260 [8] describes that expansion measurements from the AMBT can be interpreted such that: (1) any value less than 0.1% at 14 days indicates a nonreactive aggregate; (2) any value greater than 0.2% at 14 days indicates an aggregate that is potentially susceptible to ASR damage; and (3) any value between 0.1-0.2% may be an innocuous or deleterious aggregate and should be subjected to further testing.

Quantitative Elemental Analysis

To determine if ash samples with relatively higher carbon contents (as expressed through LOI values) have the ability to adsorb alkalis from the pore solution, a preliminary set of experiments were performed. Quantitative elemental analysis using inductively coupled plasma optical emission spectroscopy (ICP-OES) measured the sodium uptake capacity of each ash sample when stirred in a sodium hydroxide solution. Mixtures were prepared by adding 12 g of 0.7M NaOH solution—

representing the pore solution of a typical concrete—to 1.2 g of ash in a polypropylene vial. These slurries were then agitated on a suspension mixer for 24 h before being vacuum filtered through a 0.70 μm glass fiber filter. The filtrate solutions were then diluted 25X and stored in sealed polypropylene vials until analysis by ICP-OES. The ICP-OES Perkin Elmer Spectrometer Optima 7300DV used to analyze the diluted sorbate has a dual plasma view that offers both a radial mode (to detect elements of larger quantities) and an axial mode (to detect trace elements). Three characteristic wavelengths to detect Na (330.237 nm, 588.995 nm and 589.592 nm) were selected to produce the most accurate measurements. The instrument was calibrated using Na standard stock solution in a nitric acid matrix diluted to 2000, 1000, 100, 10 and 1 ppm. Measurements were performed in triplicate for each sample.

3 RESULTS

3.1 Fly Ash Samples

The oxide analysis performed on the ashes (shown in Table 3) reveals that all of the coal and co-fired samples have primary oxide contents (the summation of SiO_2 , Al_2O_3 and Fe_2O_3) greater than 70% and total calcium contents expressed as calcium oxide lower than 10%. Thus, the co-fired ashes would be categorized as Class F under ASTM C 618 [5]. While the alumina and silica contents for co-fired ashes are slightly elevated and iron contents are lower compared to their companion coal sample (i.e., GA 2 and companion GA1 and EC 2 and EC2 and their companions EC1), these values are within the range expected for ordinary fly ash. There was no strong correlation observed between biomass co-firing and change in calcium. Alkali contents, expressed as total soda equivalent, for co-fired ashes also are within the range of values found for typical coal fly ashes [12] and also below levels found in the high-quality commercial coal fly ash (CA). Some co-fired fly ash has been shown to be more alkaline compared to coal fly ash [13], however no correlation was detected with these samples. Yet co-firing does appear to potentially increase phosphate levels in the ash, with 0.05% and 0.19% by mass increases evident among the companion samples for EC and GA, respectively. Biomass co-firing resulted in lower LOI in the EC-series and higher LOI in the GA-series compared to companion coal samples demonstrating no relationship between increased biomass to an increase in carbon content with these samples. However, the EC and GA samples do have high LOI values in general. The co-fired ashes in the EC-series meet all of the chemical requirements for a Class F fly ash stipulated in ASTM C 618 [5] (i.e., (1) primary oxides greater than 70%; (2) sulfur trioxide levels less than 5%; (3) moisture contents less than 3%; and (4) LOI less than 6% by weight), while GA-series meet all requirements but the LOI limit.

Conversely, the only pure biomass sample examined (BA) satisfies only the sulfur trioxide limit. The BA has a low primary oxide content, making its contribution to pozzolanic activity questionable. Consequently, its total calcium content is increased. Furthermore, it has a high alkali content especially with regards to potassium levels. Phosphate concentrations are also elevated similar to the co-fired ashes. Lastly, a large percentage of volatile matter is present in the BA after firing as indicated by its high LOI. It should be noted that the composition of biomass ashes are highly variable and results in this study only represent one source.

The median particle size of the ashes measured by particle size distribution can also be seen in Table 3. Results are not shown for the BA samples because the agglomeration and angular shape of its particles prohibited its use in the laser analyzer. The cement particles are finer than all measureable ash samples. The GA-series ashes are finer than the EC-series ashes, with GA2 being the finest ash. Within each series co-firing appears to decrease the median particle size. The angular morphology of the BA can be observed in the scanning electron microscopy (SEM) image shown in Figure 1a. The fibrous wood

particles seem to retain much of their original structure and shape even after firing. The high micro-porosity of the BA particles indicate that the sample has a high surface area. Similar fibrous particles were also observed in the co-fired ashes mixed with the more typical spherical particles (shown in Figure 1b). These images demonstrate that co-firing can alter the physical characteristics of the resulting ash.

3.2 Accelerated Mortar Bar Test

The AMBT expansion plots for the control and binary blends are shown in Figures 2 and 3. The standard 14-day AMBT period is indicated by the vertical dotted line and the limits on expansion at that age shown as horizontal dashed lines. 14 and 28-day AMBT expansion data is reported in Table 4. Ordinary portland cement control mortars experienced rapid expansion reaching 0.66% during the first 14 days, with expansion values similar to those previously reported using the same aggregate source [14]. Binary blends with coal and co-fired fly ash reduced expansion by 78-94% at 14 days and by 68-85% at 28-days compared to the control. The incorporation of the GA-series ashes resulted in the largest reduction in expansion compared to the control at both ages, with the co-fired ash GA2 being the most effective additive. Within the EC-series a co-fired ash (EC-5) also produced the lowest expansion. The binary blend with the baseline coal ash (CA) performed well with low expansion at all ages compared to the control.

The use of biomass ash (BA) in a binary blend was ineffective in controlling expansion as indicated by the AMBT, with its expansion being nearly 85% of the control at 14 days. Yet, the biomass ash became slightly more effective in mitigating expansion during the second half of the measurement duration. Binary blends utilizing the 25% and 50% simulated co-fired ash both reduced expansion compared to the control at all ages. The replacement of coal ash (CA) with biomass ash (as a simulation of firing 25% biomass by weight with coal) resulted in similar expansion values to CA alone. However, its replacement with a larger quantity of biomass ash (as a simulation of firing 50% biomass by weight with coal) resulted in a slight increase in expansion compared to CA alone. Both sets of mortars containing simulated ashes expanded faster than the CA binary blend mortars during the first 8 days.

The rate of expansion of the biomass ash mortars peaked on the second day before leveling out around day 8, a trend echoed by the simulated ashes. The early-age expansion of the biomass ash binary blend was greater than the OPC control until day 6 when the control surpassed all mixes (note that the OPC control experienced its highest rate of expansion on day 4). All other binary blends exhibited slowly increasing, although variable, rates of expansion for the first 14 days. At 14 days of exposure all of the mortars with coal and co-fired ashes had attained 35-57% of their total expansion (with an average of 46%). After 14 days the rates of expansion were more uniform and remained steady before noticeably decreasing after 24 days. No significant trends between expansion rates of co-fired ashes in both the EC and GA series compared to their companion coal samples were observed.

3.3 Quantitative Elemental Analysis

Prior research [15,16] has suggested that alkali ions may be sorbed by carbon in the ashes. For ASR mitigation, the ability of the carbon in the ash to potentially act as an alkali sink could be viewed as beneficial. This capacity was analyzed by measuring the change in concentration of sodium in solution after mixing with each of the ash samples. Results from the ash sorption test can be found in Table 5 and can be compared to the solution concentration itself, which when diluted 25x, measured 708ppm. The ICP results presented are averages of the concentrations measured in triplicate at two wavelengths (588.995 nm and 589.592 nm) in radial mode. Concentrations detected from the third wavelength

(330.24nm) followed similar trends, but interference from other elements at this wavelength can affect results and therefore they are not included in this paper. For all coal and co-fired ash samples sodium concentrations of the sorbate (i.e., the filtered solution after mixing) remain in the range of error of the control indicating no sorption by the carbon has occurred. Even the GA-series ashes, which have high carbon contents, did not lower sodium concentrations. However, the biomass ash did reduce the sodium concentration to 663ppm—a 6.4% decrease from the control NaOH solution.

4 DISCUSSION

4.1 Influence of Co-fired Ash on ASR Expansion

As demonstrated by the AMBT results, the replacement of cement with either coal or co-fired ash substantially reduced expansion during accelerated testing with an alkali-reactive aggregate. All coal and co-fired fly ash binary blends reduced expansion to improved aggregate reactivity classifications. Most effective were the GA-series ashes (both coal and co-fired) and the CA, which decreased expansion to the “innocuous” category. Further research is necessary to better understand the mechanism(s) by which the co-fired ashes reduce expansion. However, given their similar composition and particle size to the coal-derived ashes examined, it is likely that the mechanisms of ASR mitigation are similar.

For example, it seems that particle size may play a role. That is, AMBT expansion values for all coal and co-fired ashes are strongly correlated to particle size. Finer fly ash samples produced less expansion potentially due to their greater pozzolanic reactivity, but given the short curing time the effect of particle packing on matrix densification also likely plays a role. Co-fired samples had smaller median particle sizes than their companion coal sample, and thus in general had lower expansion values at 14 and 28 days (EC2 was the only sample to have a slightly higher expansion compared to its companion coal sample EC1 at 28 days).

Increasing mortar expansion values may also be correlated to coal and co-fired ashes with higher calcium contents. It is well known that Class C fly ash containing high amounts of CaO do not effectively mitigate ASR expansion [17]. Although the EC-series ashes have low enough CaO (and high enough primary oxides) to still be classified as Class F, these ashes still exhibited greater expansion compared to the lower calcium CA and GA-series ashes especially after 6 days. Yet, it is difficult to conclusively determine which ash characteristic (i.e., particle size or calcium content) has the greater influence on ASR expansion and mitigation in these samples. Likewise, the influence of permeability on the mortar expansion for these blends may not be captured by use of the AMBT—the only measureable changes may stem from chemical interactions [14]. Further experimentation using the concrete prism test [18] may clarify these issues and provide a better understanding of the behavior of these ashes.

4.2 Influence of Biomass Ash on ASR Expansion

The pure biomass ash (BA) utilized as a replacement for cement provided only a small reduction in expansion at later ages compared to the control. Yet, the BA binary blend exhibited higher expansion at early ages (<6 days) compared to the control before its rate of expansion decelerated to levels below the cement mortars. After day 12, rates of expansion for the BA blends were within the range of the coal and co-fired ashes. The high volatile content of this BA is most likely a result of poor firing conditions. The high moisture content of the raw biomass can reduce the maximum firing temperature resulting in incomplete combustion. The high LOI represents not only the burning of organic carbon but also the decomposition of carbonates which occurs over the same temperature range. X-ray diffraction (XRD) results presented in a previous publication by this author [19] reveal that calcite is the only calcium-

containing crystalline component in this particular ash—a finding similar to other wood ash analyses for certain species [20]. Therefore, the calcium content of this ash measured as CaO from the oxide analysis presumably has little, if any, hydraulic properties. The low silica content and lack of an amorphous hump on its diffraction pattern indicates that the ash has negligible glassy phases and accordingly no discernable pozzolanic properties. Consequently, the biomass ash should behave similar to an inert filler such as limestone. However, there are some key differences between this ash and an inert filler that may explain its non-inert expansion performance.

The high alkali content of the ash (principally high potassium levels) is one factor that could have contributed to the higher early age expansion. Fly ashes that reduce pore solution alkalinity have been found to be most effective in controlling ASR expansion [17]. Also, the high water absorption capacity of the BA may have made the matrix more brittle and crack-prone through absorbing mix water, which could have contributed to early expansion due to greater availability of moisture (swelling) and alkalis (ASR). At later ages, the expansion may have decreased as a result of a dilution of available calcium compared to the control. Calcium carbonate is not soluble in basic conditions and thus there is less free calcium in the pore solution needed for expansive reactions to occur.

The simulated mixes, which may be considered as a ternary blend of CA and BA, performed significantly better at ASR mitigation compared to the BA alone. In fact, the 25% simulated blend had lower expansive values at some ages compared the CA only blend. Yet the same effect observed in the BA samples at early ages was also identified in these blends but to a much lesser degree. The potential effects are complex, but include alkali binding both during the initial and later stages of the test and water absorption. More research on the influence of biomass carbon on alkali adsorption will be necessary to confirm these results and to better understand the multiple potential physical, chemical, and mechanical interactions and their influence on expansion.

5 CONCLUSIONS

The performance of binary blends composed of biomass and co-fired fly ashes were compared to both ordinary portland cement and typical Class F coal-derived ash mortars prepared with the same highly reactive aggregate to assess their potential to mitigate ASR-induced expansion during the AMBT. Key findings include:

- Despite co-firing with biomass, the summation of SiO_2 , Al_2O_3 and Fe_2O_3 was greater than 70% and total calcium contents expressed as calcium oxide were lower than 10% for each of the co-fired ashes examined.
- With regard to ash composition, no trend was observed between co-firing and measured calcium, alkali or LOI. However, co-firing did impact ash morphology and resulted in finer ashes.
- Mortar bar expansion was significantly decreased compared to the control with the addition of all coal and co-fired fly ashes. Ashes with finer median particle sizes and lower CaO contents performed better. This could be attributable to their greater pozzolanic reactivity and improved particle packing, producing densification in the mortar matrix.
- The use of this particular biomass ash, with its low primary oxide content, was ineffective as a mitigation technique and actually increased early age expansion compared to the control, potentially due to its high alkali content and/or matrix embrittlement due to mix water absorption. However, expansion was significantly reduced when used in combination with Class F coal ash. Further analysis showed that the biomass ash carbon can adsorb alkalis from solution, which could have beneficial applications if properly used.

Overall, the ASR mitigation potential of an ash is linked to its chemical and physical properties rather than to its source (i.e., from coal or co-firing). Therefore, co-firing can actually improve ASR mitigation as seen in this study if the composition of the ash resulting from co-firing has beneficial attributes.

6 REFERENCES

- [1] Baxter, L (2005): Biomass-coal co-combustion: opportunity for affordable renewable energy. *Fuel* (84): 1295-1302.
- [2] Wang, S, and Baxter, L (2007): Comprehensive study of biomass fly ash in concrete: Strength, microscopy, kinetics, and durability. *Fuel* (88): 1165-1170.
- [3] Rajamma, R, Ball RJ, Tarelho, LAC, Allen, GC, Labrincha, JA, and Ferreira, VM (2009): Characterisation and use of biomass fly ash in cement-based materials. *Journal of Hazardous Material* (172): 1049-1060.
- [4] Johnson, A, Catalan, LJJ, and Kinrade, SD (2010): Characterization and evaluation of fly-ash from co-combustion of lignite and wood pellets for use as cement admixture. *Fuel* (89): 3042-3050.
- [5] ASTM C 618 (2008): Standard specification for fly ash and raw or calcined natural pozzolan for use in concrete. American Society for Testing & Materials, West Conshohocken, PA.
- [6] EN-450 (2005): Fly ash for concrete - Part 1: Definition, specifications and conformity criteria. European Standard. Brussels, Belgium.
- [7] Esteves, TC, Rajamma, R, Soares, D, Silva, AS, Ferreira, VM, and Labrincha, JA (2011): Use of biomass fly ash for mitigation of alkali-silica reaction of cement mortars. *Construction and Building Materials* (in press).
- [8] ASTM C 1260 (2007): Standard test method for potential alkali reactivity of aggregates (mortar-bar method). American Society for Testing & Materials, West Conshohocken, PA.
- [9] ASTM C 1567 (2008): Standard test method for determining the potential alkali-silica reactivity of combinations of cementitious materials and aggregate (accelerated mortar-bar method). American Society for Testing & Materials, West Conshohocken, PA.
- [10] ASTM C 150 (2009): Standard specification for portland cement. American Society for Testing & Materials, West Conshohocken, PA.
- [11] ASTM C 305 (2006): Standard practice for mechanical mixing of hydraulic cement pastes and mortars of plastic consistency. American Society for Testing & Materials, West Conshohocken, PA.
- [12] Malvar, JL and Lenke, LR (2006): Efficiency of fly ash in mitigating alkali-silica reaction based on chemical composition. *ACI Materials Journal* (103-5): 319-326.
- [13] Demirbas, A (2003): Sustainable cofiring of biomass with coal. *Energy Conversion and Management* (44): 1645-1479.
- [14] Moser, RD, Jayapalan, AR, Garas, VY, and Kurtis, KE (2010): Assessment of binary and ternary blends of metakaolin and class C fly ash for alkali-silica reaction mitigation in concrete. *Cement and Concrete Research* (40): 1664-1672.
- [15] Puri, BR and Bansal, RC (1964): Studies in surface chemistry of carbon blacks, Part II. Surface acidity in relation to chemisorbed oxygen. *Carbon* (1): 457-464.
- [16] Ishizuka, M and Atsumu, O (1974): Activation of hydrogen by active carbon with adsorbed alkali metal. *Journal of Catalysis* (35): 320-324.
- [17] Shehata, MH and Thomas, MDA (2000): The effect of fly ash composition on the expansion of concrete due to alkali-silica reaction. *Cement and Concrete Research* (30): 1063-1072.
- [18] ASTM C 1293 (2008): Standard test method for determination of length change of concrete due to alkali-silica reaction. American Society for Testing & Materials, West Conshohocken, PA.
- [19] Shearer, CR, Yeboah, N, Kurtis, KE, and Burns, SE (2011): The early age behavior of biomass fired and co-fired fly ash in concrete. *Proceedings of World of Coal Ash*, May 9-12, 2011, Denver, CO.
- [20] Misra, MK, Ragland, KW, and Baker, AJ (1993): Wood ash composition as a function of furnace temperature. *Biomass and Bioenergy* (4-2): 103-116.

Sample	Type	Co-fired Material	Wood Properties, %		
			Weight	Energy ^a	Moisture ^b
GA1	Coal Only	-	-	-	-
GA2	Co-Fire	Coarse Dry Hardwood	15.00	6.20	31.00
EC1	Coal Only	-	-	-	-
EC2	Co-Fire	10 mm Pine Chips	4.00	1.14	49.20
EC3	Co-Fire	10 mm Pine Chips	8.20	3.17	48.06

^aAs percent of total BTUs produced during co-combustion with coal
^bMoisture content before co-combustion with coal

Mix	Wood Ash Yield ^a , kg	Coal Ash Yield ^a , kg	Wood Ash %	Coal Ash %
25% Wood Blend (BL1)	0.25	7.5	3.23	96.77
50% Wood Blend (BL2)	0.5	5	9.09	90.91

^aAssuming 100 kg. of combined total fuel is fired

Measured Components, %	CA	GA1	GA2	EC1	EC2	EC3	BA	Cement ^a
LOI	1.39	14.99	15.03	5.87	5.47	5.23	47.96	1.27
SiO ₂	55.28	46.95	47.06	42.77	42.84	43.95	7.38	20.45
Al ₂ O ₃	27.21	22.90	23.08	25.62	26.21	26.45	1.16	4.70
Fe ₂ O ₃	7.98	9.82	8.66	14.67	13.87	13.18	0.57	3.32
Σ(SiO ₂ +Al ₂ O ₃ +Fe ₂ O ₃)	90.47	79.67	78.80	83.07	82.92	83.58	9.11	28.47
CaO	1.26	0.49	0.77	3.83	4.01	3.76	28.29	63.06
MgO	1.23	0.71	0.76	1.27	1.25	1.25	2.89	3.27
SO ₃	0.07	0.04	0.08	0.48	0.44	0.52	1.92	2.80
Na ₂ O	0.47	0.19	0.26	0.51	0.52	0.53	0.48	0.07
K ₂ O	3.02	2.13	2.24	2.13	2.08	2.09	5.86	0.53
Na ₂ O _{eq}	2.46	1.58	1.74	1.91	1.89	1.91	4.34	0.42
P ₂ O ₅	0.19	0.34	0.53	0.60	0.65	0.65	2.18	0.06
TiO ₂	1.41	1.36	1.43	1.26	1.31	1.31	0.09	0.25
Mn ₂ O ₃	0.06	0.03	0.03	0.06	0.06	0.06	1.03	0.16
Cr ₂ O ₃	0.05	-	-	0.07	0.06	0.06	0.00	0.02
ZnO	0.01	-	-	0.01	0.01	0.01	0.10	0.06
SUM Total	99.64	99.94	99.94	99.14	98.78	99.04	99.92	100.02
Median Particle Size (µm)	16.15	17.33	11.39	29.91	26.88	23.26	-	10.08

^aBogue Potential Composition: 54.00% C₃S, 15.82% C₂S, 6.84% C₃A, 10.10% C₄AF

Mix	Cement Only	CA	EC1	EC2	EC3	GA1	GA2	BL1	BL2	BA
14-day	0.658	0.086	0.149	0.147	0.101	0.085	0.043	0.078	0.101	0.560
(st dev)	(0.021)	(0.013)	(0.009)	(0.004)	(0.011)	(0.005)	(0.008)	(0.008)	(0.005)	(0.016)
28-day	0.819	0.195	0.262	0.266	0.208	0.195	0.121	0.193	0.226	0.685
(st dev)	(0.033)	(0.056)	(0.018)	(0.033)	(0.041)	(0.030)	(0.022)	(0.025)	(0.027)	(0.007)

Sample	0.7 M NaOH	CA	GA1	GA2	EC1	EC2	EC3	BA
Sodium Concentration, ppm	708.33	718.95	726.64	711.20	706.18	711.00	706.94	663.25
(st dev, ppm)	(10.26)	(5.70)	(5.58)	(10.72)	(7.67)	(6.61)	(15.15)	(8.86)

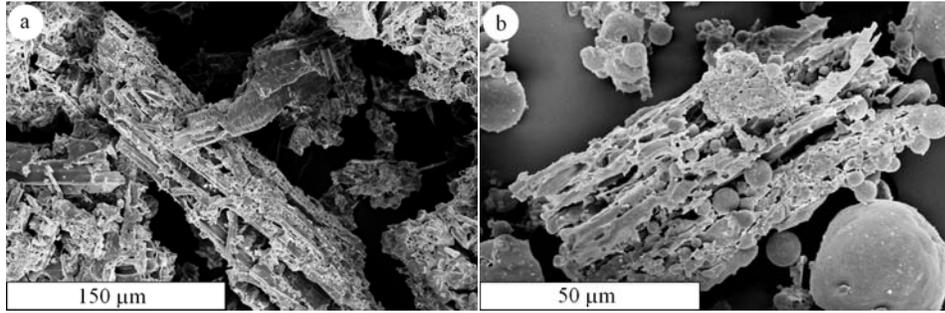


FIGURE 1: SEM micrograph of (a) biomass ash (BA) and (b) co-fired ash (EC2)

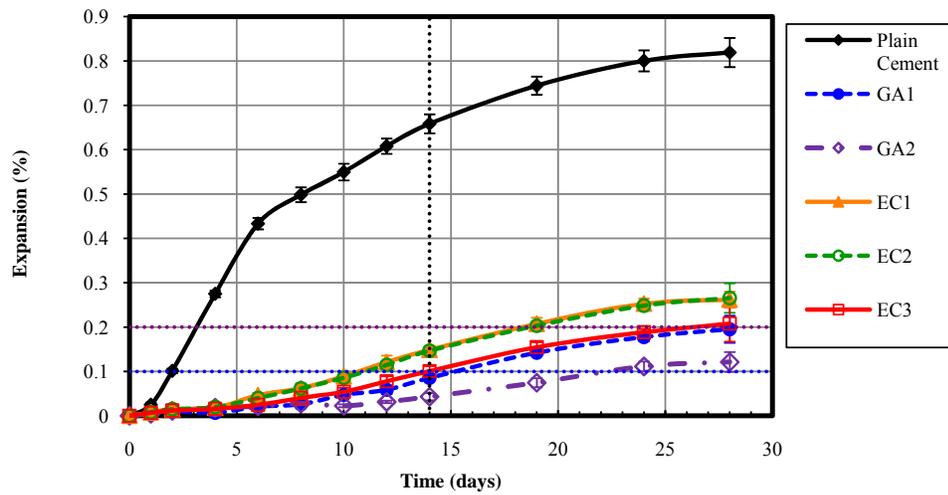


FIGURE 2: AMBT expansion plots for co-fired blend, their companion coal blends and the control

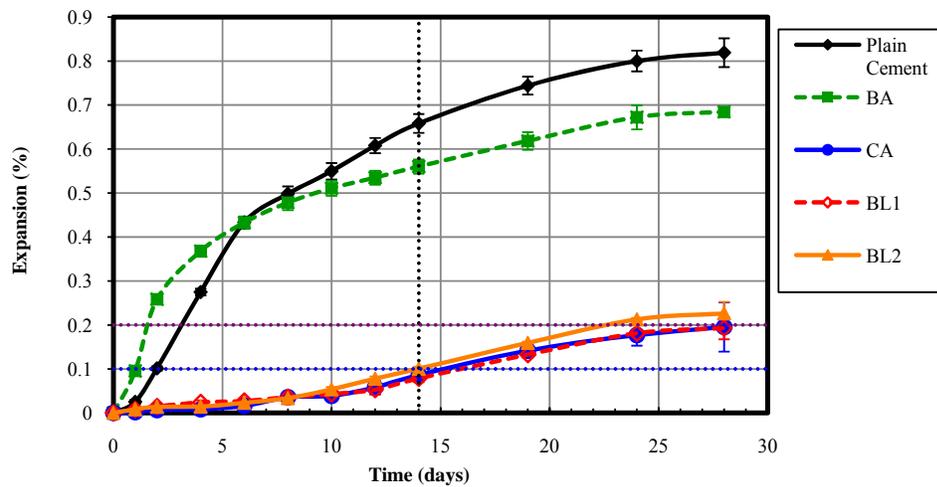


FIGURE 3: AMBT expansion plots for biomass ash blend, coal blend, simulated ash blends and the control