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Comprehensive study of biomass fly ash in concrete: Strength, microscopy, kinetics and durability

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Abstract

ASTM (American Standard Testing and Materials) C 618 prohibits use of biomass fly ash in concrete. This document systematically investigates the strength, microscopic study and durability (mitigation of Alkali Silica Reaction (ASR) expansion) of biomass fly ash concrete (cement partially replaced by fly ash) and kinetics of the mixture of biomass fly ash and calcium hydroxide. The biomass fly ash in the investigation comes from cofired (herbaceous with coal) fly ash, which includes different kinds of coal and biomass. All the results show that biomass fly ash with cofiring concentration within the interest to commercial coal–biomass cofiring operations at power plants have equal or much better performances than those of coal fly ash; therefore, the exclusion of biomass fly ash in concrete by ASTM C 618 seems inappropriate and more quality research on the applicability of biomass fly ash in concrete should be conducted.

Keywords: Biomass fly ash; Strength; Kinetics and durability

1. Introduction

Coal fly ash is an artificial pozzolan and reacts with calcium hydroxide, the byproduct of cement hydration, to form products similar to cement hydration, Ca–Si gels, which account for main concrete strength [1]. The reactions between fly ash and calcium hydroxide are called pozzolanic reaction. Calcium hydroxide by itself, contributes little to the strength of concrete, and that is the typical case why fly ash addition can increase the strength of concrete.

Biomass–coal cofiring is assumed a sustainable and green energy when the biomass is consumed less than the rate it grows [2] . In this scenario, typically less than 10% biomass by energy content combines with coal in a traditional, large-scale coal combustor. However, the cofired fly ash, which in this paper is one sort of biomass fly ash, is excluded from addition in concrete by ASTM C 618 and other international standards.

Various types of biomass produces ash that has similar pozzolanic activity as coal fly ash, which include rice husk, wheat straw, sugar cane straw and wood [3–6]. Biomass has various ash percentages due to its resources [7], and some of which is quite similar to that of coal as illustrated in Fig. 1 [8]. The cofiring of biomass with coal generally leads to decrease of ash deposition relative to the neat fuels.

The relatively low amounts of biomass in the cofiring process leads to low contents of biomass derived ash. Therefore, European Committee has approved its standard to allow biomass fly ash (up to 25 wt.% straw cofiring with coal) in concrete; however, due to the wide range of biomass resources and combustion conditions, an upper weight limit of alkali content, chloride and unburned carbon is enforced as 5%, 0.1% and 5%, respectively [9]. It is well know in literature that 1) alkali can lead to Alkali Silica Reaction (ASR) expansion, which is called "cancer of concrete" [10]; 2) unburned carbon messes up the air content of concrete, reducing its resistance to freezing and thawing deterioration [11,12,1,] and 3) chloride brings severe corrosion concern for steel bars in concrete [13,14,1].

Concrete strength with partial cement replaced by biomass fly ash results from the combination of cement hydration and pozzolanic reaction. Microscopic study has shown various products of those two types of reactions as well as their similarities by Scanning Electron Microscopy (SEM), Energy Dispersive X-ray analysis (EDX), X-ray Diffraction (XRD), Electron Micro Probe Analysis (EMPA) and X-ray Florescence (XRF) [15–18,1].

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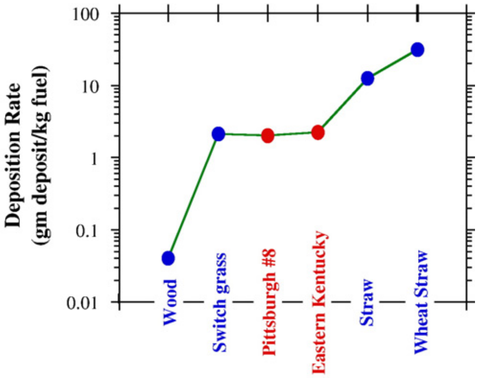

Fig. 1. Ash deposition percentages of different fuels [8].

In order to simplify the kinetics investigation of pozzolanic reaction, a system of fly ash–calcium hydroxide instead of fly ash and cement was applied. In fact, cement used for thousands of years before the invention of modern Portland cement was a mixture of volcanic ash with hydrated lime, the volcanic ash representing a natural pozzolan in a role similar to that of fly ash [19,20].

Kinetic study of pozzolanic reaction were tested either by aqueous solution or solid mixture [21–23], which has all implied a diffusion-controlled mechanism. Calcium hydroxide content can be determined by Thermo Gravimetric Analysis (TGA), organic solvent dissolution or Quantitative X-ray diffraction (QXRD), with TGA representing the most precise and convenient method [24,25].

Besides strength, durability issues play important roles in concrete, among which ASR is the hot topic. ASR was first identified more than sixty years ago [26]. They denote reactions between reactive aggregates and alkali released by cement hydration or from other sources, such as mineral admixtures or aggregates. These reactions lead to concrete expansion, cracks and even failure, which are very detrimental to concrete structures.

Fly ash substitution for cement reduces or eliminates ASR-associated expansion [27]. However, while Class F fly ash is well known to be more efficient in mitigating ASR expansion, Class C fly ash (>1.5% available alkali) has more complicated and less predictable influence. High-calcium material (typically Class C) can increase ASR expansion or less effectively mitigate the expansion, depending on the properties and replacement ratio of fly ash [28].

2. Materials

The main materials used in these experiments include Portland cement I & II, Class C fly ash, cofired fly ash SW1, SW2, 10P and SAW. The sources and inorganic composition of the above materials appear in Table 1 and 2. More specifically, Combustion of Galatia coal by itself produces typical Class F fly ash and combustion of Powder River Basin coal by itself produces Class C fly ash, respectively. Therefore, the four types of cofired biomass fly ash cover two major coal resources, two biomass resources and two combustion mass ratios of coal and biomass, which makes the investigation more representative.

Table 1
Specification of fly ash, cement and aggregate

Materials	Specification
Class C	ASTM C 618
SW 1	Cofired with 20% switch grass and 80% Galatia coal
SW 2	Cofired with 10% switch grass and 90% Galatia coal
10P	Cofired with 10% switch grass and 90% Powder River basin coal
SAW	Cofired with 20% sawdust and 80% Powder River Basin coal
Portland cement I & II	ASTM C 150
High-Alkali Cement	Equivalent Na_2O = 1.15%
Opal	Virgin Valley, Nevada

2.1. Strength of biomass fly ash concrete

In this investigation, Portland cement I & II, three types of fly ash, Class C, SW1 and SW2 and sieved aggregates (sand and rocks) are used.

2.2. Microscopic study of biomass fly ash concrete

In this investigation, small residues or polished sections of biomass fly ash concrete for strength test at certain periods are prepared for microscopic study, either by SEM or ESEM.

2.3. Kinetics of fly ash and calcium hydroxide

This project used calcium hydroxide (regent grade), industrial sand (No. 30 by standard sieve), distilled water and three types of fly ash, Class C, 10P and SAW.

2.4. Mitigation of ASR expansion

High-alkali cement, opal, sieved quartz and three types of fly ash, Class C, 10P and SAW are used in this project.

High alkali and reactive silica are the two requirements for the occurrence of ASR expansion; therefore, cement with alkali content of 1.15% almost doubling the ASTM standard C 114 (maximum 0.6%) and opal, naturally available, the

Table 2
Elemental analysis and LOI (loss of ignition) of fly ash and cement

(Weight %)	Class C	SW1	SW2	10P	SAW	Portland cement I & II
TOTAL	100.66	100.63	99.6	101.51	102.25	99.5
SiO_2	37.26	52.16	53.02	36.22	35.23	21.5
Al_2O_3	19.62	23.55	25.78	20.88	20.87	4.2
Fe_2O_3	6.07	7.57	7.95	6.2	6.22	2.7
CaO	24.18	2.37	1.88	20.78	21.86	64.3
MgO	5.37	1.31	0.91	5.06	5.12	2.2
Na_2O	1.5	0.7	0.26	1.61	1.72	0.51
K_2O	0.43	4.01	2.14	2.01	1.89	
Cr_2O_3	0.01	0.02	0.02	0.01	0.01	0
TiO_2	1.52	1.45	1.65	1.36	1.42	0
MnO	0.01	0.04	0.02	0.06	0.07	0
P_2O_5	1.2	1.04	1.1	1.73	1.73	0
SrO	0.3	0.13	0.2	0.32	0.33	0
BaO	0.66	0.18	0.38	0.59	0.620	
SO_3	1.83	2.25	1.23	3.35	3.87	2.6
LOI	0.7	3.85	3.06	1.33	1.29	1.3
Leachable $Na_2O\%_{Equiv.}$ by ASTM C 33	1.03	–	–	2.46	2.88	–
Insoluble Residue	–	–	–	–	–	0.19

most reactive aggregate involved in ASR and mined from Virgin Valley, Nevada, were applied.

3. Experimental procedures

3.1. Strength of biomass fly ash concrete

The following aspects of mixture proportioning were constant for all concrete mixes: [29] water/(cement+fly ash)=0.5 (mass); (b) fly ash/cement=1/3 (mass); (c) air entrainment of 4–6% measured with ASTM C 231–97; (d) and slump of 7.6–12.7 cm (3–5 inch) measured with ASTM C 143/C 143M-98. All these four parameters are within typical fly ash concrete design.

For compression tests, cylindrical specimens (10.1 cm (4 in) diameter×20.3 cm (8 in) height) were cured in a fog room (ASTM C 192/192 M-98) until their test dates, 7, 28, 91, and 365 days from the mixing date. A 136,080 kg Baldwin Universal Testing Machine from civil engineering at Brigham Young University provided raw data (typically in triplicate) that determined performance statistics (means, pooled error, confidence intervals for the mean, etc.).

3.2. Microscopic study of biomass fly ash concrete

SEM-based images come from either JEOL JSM840a in the BYU Microscopy Lab. EPMA samples (24 mm×46 mm polished thin section with epoxy impregnation, about 30 μm thick) prepared by Wagner Petrographic Company in Provo, UT are analyzed on a Cameca SX50 EMPA in the geology department at BYU.

3.3. Kinetics of fly ash and calcium hydroxide

Fly ash, calcium hydroxide, industrial sand and water are mixed homogeneously to make 5.1 cm (2 in) cubes. An experimental matrix was set up: 1) three fly ashes: Class C, 10P and SAW; 2) three weight ratios of fly ash to calcium hydroxide (80: 20, 70: 30 and 60: 40); 3) three curing temperatures, 23 °C, 43 °C and 63 °C; 4) six testing dates, 1, 2, 3, 6, 9 and 12 month after mixing and 5) two replicates for each above specific situation.

The samples were vacuum and moisture cured in a CO_2 free environment preventing calcium hydroxide from carbonation.

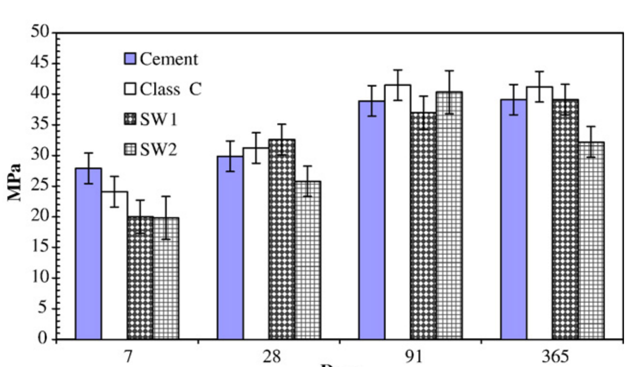

Fig. 2. Compressive strength for each sample material.

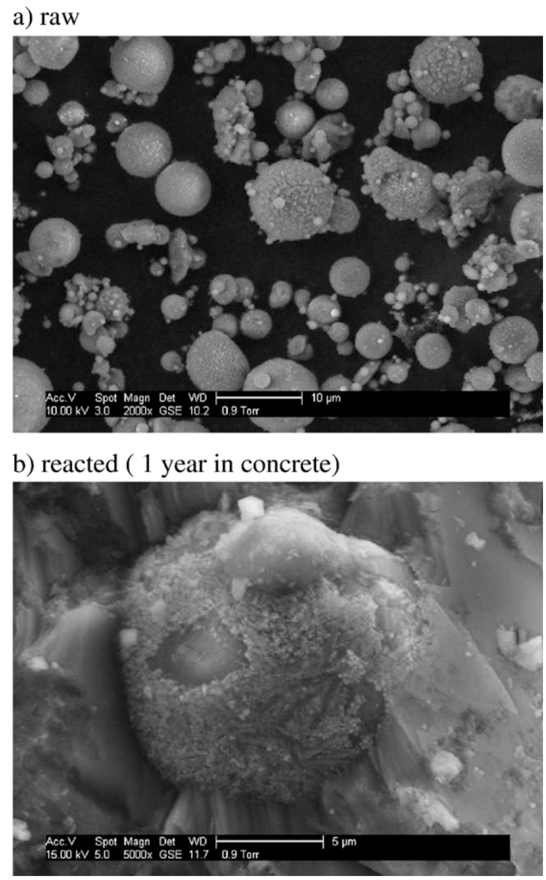

Fig. 3. SW1 fly ash particle: raw versus reacted.

At certain test dates, the sample core was pulverized for reaction extent of calcium hydroxide by TGA. The tests were conducted from 25 to 700 °C at 25 °C/min in an inert N_2 flow environment. The derivative peak in the temperature range of 300–600 °C was integrated by the Pyrex software to determine the available amount of calcium hydroxide [30,31].

3.4. Mitigation of ASR expansion

Four mixes that include control cement and three mixes with cement replaced by Class C, 10P and SAW (35 wt.%) provided the basic data for ASR evaluation.

Steel molds 2.5 cm×2.5 cm×25 cm (ASTM C 490) formed samples from the mortar. The length of the bars was measured by a digital length comparator (ASTM C 490) with a precision of ±1 μm on 1 day, 14 days, 1, 2, 3, 4, 6, 9, and 12 months and compared with the control cement mix.

4. Results and discussions

4.1. Strength of biomass fly ash concrete

Fig. 2 illustrates compression strength with 95% confidence intervals. The cement mix exhibits the highest strength up to 7 days; from 28 days to one year, the compressive strength of all the fly ash mixes become comparable to that of pure cement. Similar results have been found by other workers for coal fly

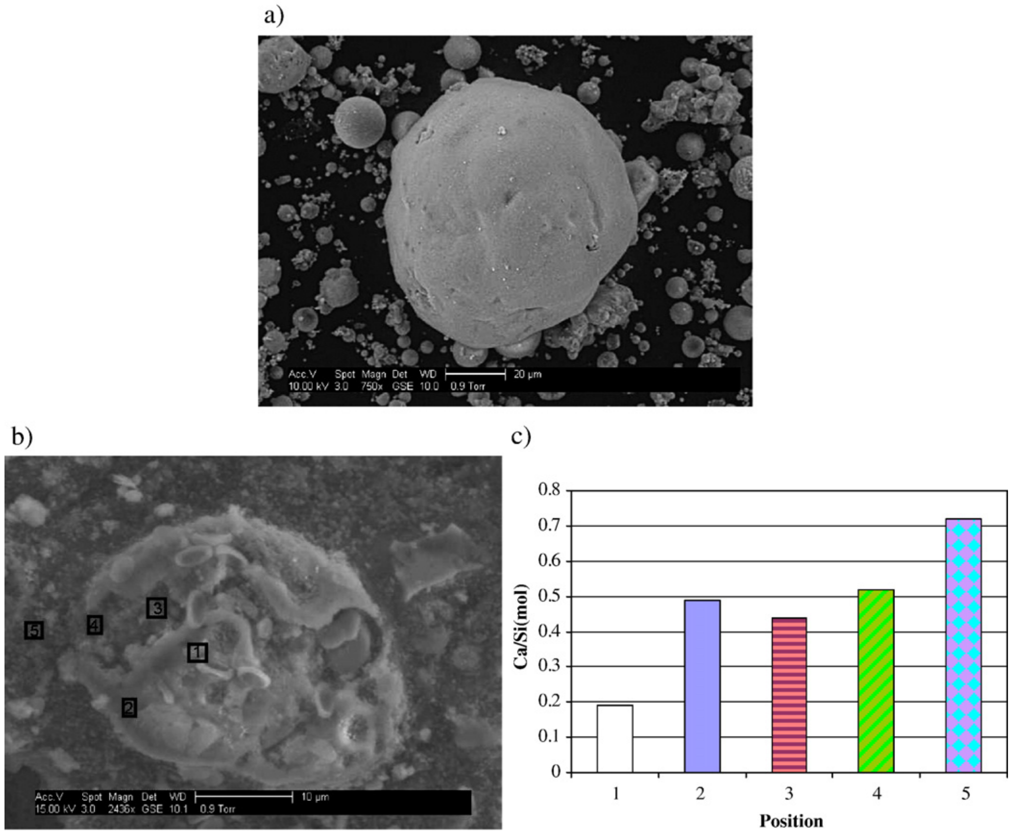

Fig. 4. Reactive fly ash particle (SW2 1-year).

ash [20,1]. The strength of SW1 and SW2 mixes lie within the 95% confident interval of Class fly ash results, indicating that herbaceous-derived biomasses with the reasonable cofiring ratio does not impact strength development.

4.2. Microscopic study of biomass fly ash concrete

Fig. 3 illustrated the comparison of raw and reacted SW1 fly ash particle, with a) showing the relatively smooth surface and sphere of raw particles and b) showing the coated and rough surface of the reacted one. The coated component is crystalline Ca $(OH)_2$, which reacts with fly ash to form Ca–Si gels, the similar products to those of cement hydration. a) raw b) reacted (1 year in concrete).

Fig. 4 shows a raw SW2 fly ash particle in a) and a 1-year-old reacted one by EMPA as well as its chemical analysis in b) and c). The raw particle is smooth and spherical, and the reacted particle is in fragments due to the occurrence of pozzolanic reaction. Positions 1 and 2 are on the main body of the particle, and their Ca/Si (mol) ratios are 0.19 and 0.49, respectively. Positions 3 and 4 are in the broken and eroded area, with Ca/Si (mol) ratios 0.49 and 0.52, respectively. Position 5 is in the cement hydration area and close neighborhood of the fly ash particle, with a Ca/Si (mol) ratio of 0.72. This ash particle has undergone significant

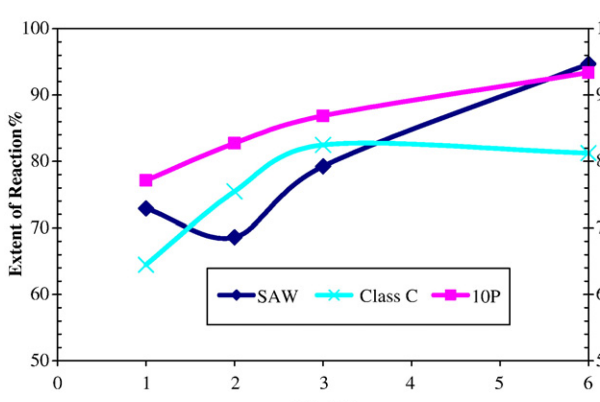

Fig. 5. Extent of reaction of different fly ash mixtures.

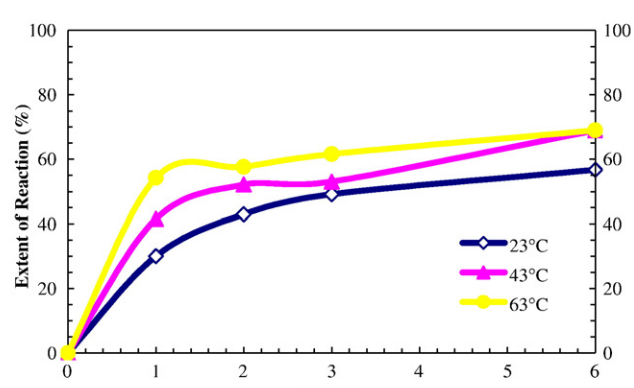

Fig. 6. Dependence of reaction extent on temperature (Class C 60/40).

pozzolanic reaction, with positions 3 and 4 in the reacted area; therefore, they have higher Ca/Si (mol) ratios than positions 1 and 2, which are located on the main body of the particle. Position 1 is in the inner part of the particle's body, and position 2 is on the edge of the particle near the hydrated cement area; therefore, position 1 has a lower Ca/Si ratio (mol) most likely to be inert and position 2 has a higher Ca/Si (mol) ratio most likely to have chemically combined with $Ca(OH)_2$. Position 5 is in hydrated cement area; therefore, it has the highest Ca/Si (mol) ratio in the above five positions detected near and on the ash particle.

4.3. Kinetics of fly ash and calcium hydroxide

Fig. 5 illustrates the extent of reaction as calculated by measuring the amount of calcium hydroxide in the sample at the testing date compared to the initial amount in the fresh mix (mixtures with fly ash: calcium hydroxide = 70: 30 at 43 °C as examples) It is illustrated that within that ratio and at that temperature, all the fly ash mixes have the similar reaction extent from 60–80% at 1 month and increase generally parallel up to 6 month with reaction extent ranging from 80–90%, although some mixtures with lower reaction extent at earlier periods caught up in the later periods.

Actually, almost all the coal and biomass fly ash samples show the similar reaction extent of $Ca(OH)_2$ at the fixed conditions (mixing ratio, curing temperature and testing dates), with the illustration in Fig. 5 as a typical example.

The general trend of reaction extent dependence on temperature shows that a greater reaction extent corresponds to a higher curing temperature, especially in the higher calcium hydroxide ratio (60/40) indicated in Figs. 6 and 7.

4.4. Mitigation of ASR expansion

The ASR expansion results appear in Fig. 8. The pure cement mixes with opal logically and experimentally represents upper limit of ASR expansion, which produces the maximum expansion at all dates from 14 days to 6 months. At 6 month, its expansion is 0.28%, which is about 2.8 times of upper limit of ASTM C 33, 0.1% at 6 month.

Although biomass fly ash 10P and SAW have much higher alkali content than that of Class C (see Table 2), both of them are much better in mitigating ASR expansion than Class C: they can even cut ASR expansion down within 0.1% at 6 month, meeting the requirement of ASTM C 33; while Class C goes beyond that limit at 6 month significantly.

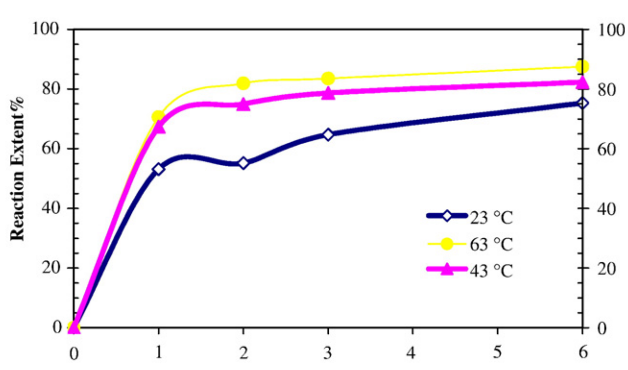

Fig. 7. Dependence of reaction extent on temperature (SAW 60/40).

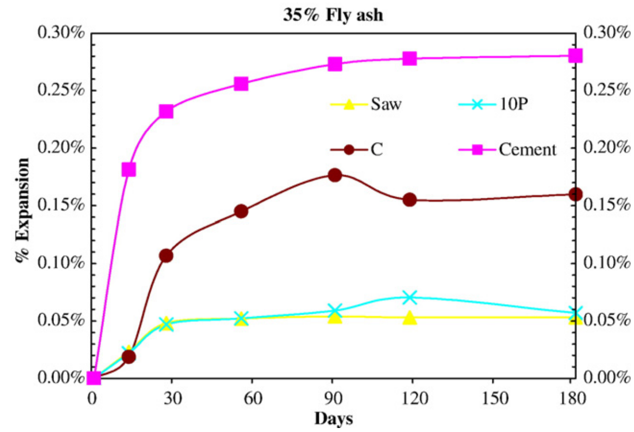

Fig. 8. ASR expansion with 35% fly ash (mass).

5. Conclusions

This comprehensive investigation covers the two key aspects of concrete, strength and durability, and is involved in various tests procedures; the following conclusions regarding coal fly ash in concrete generally and cofired biomass fly ash are listed:

1. With 25% cement replaced by fly ash, biomass fly ash concrete has similar compressive strength to that of coal fly ash from 7 to 365 days, and to that of pure cement concrete from 1 to 12 months.
2. Biomass fly ash has undergone significant pozzolanic reaction at one year in concrete by microscopic study.
3. With respect to calcium hydroxide consumption rate, biomass fly ash is not substantially different from coal fly ash, which indicates that they might have similar kinetics.
4. Two types of biomass fly ash, 10P and SAW, have much better performance than Class C in mitigating ASR expansion despite their much higher alkali content. They can even cut down ASR expansion within 0.1% at 6 month curing.

The overall conclusions are that within this investigation, biomass fly ash has at least equal or much better performances in respect to strength and durability of concrete, which indicates exclusion of biomass fly ash from addition in concrete by ASTM C 618 is inappropriate; instead, it is implied from this work that more quality research should be conducted on the qualification of biomass fly ash in concrete.

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