



ORIGINAL ARTICLE

The effect of including biomass on the rheological and pozzolanic properties of Portland limestone cement- case study

Olaniyi Arowojolu^{a,b}, Ahmed Ibrahim^{b*}, Armando McDonald^c

^aTexas Department of Transportation (Bridge Division), 6230 E Stassney Ln, Austin 78744, USA

^bDepartment of Civil & Environmental Engineering, University of Idaho, Moscow 83844, USA

^cDepartment of Forest, Rangeland and Fire Sciences, University of Idaho, Moscow 83844, USA

*Corresponding author: Ahmed Ibrahim. Email: aibrahim@uidaho.edu

Abstract: Various investigations have been presented on the possibility of using agro-allied industry waste in concrete, with the goal of achieving a cleaner environment and environmentally friendly construction. Biomass fly ash (BFA) and limestone clinker are waste from steam/power plants and the cement industry, respectively, and are of high relevance to economic and environmental problems. The effect of including biomass on the rheological and pozzolanic properties of Portland limestone cement (PLC) pastes are presented. The BFA was used as partial replacement for PLC as supplementary cementitious materials (SCMs). The rheological properties (yield stress, viscosity and thixotropy) of the cement paste were determined using a parallel-plate rotational rheometer. The pozzolanic properties were determined using thermogravimetric analysis (TGA) by measuring the amount of calcium hydroxide (CH), and calcium silicate hydrate (CSH) of the hydrated paste, as well as the reaction kinetics. Different characterization techniques including X-ray diffraction (XRD), X-ray fluorescence spectroscopy (XRF), and scanning electron microscopy (SEM) were used to study the microstructure and mineralogy of the BFA. It was observed that the mineral composition of the biomass fly ash is like class C fly ash. At 15% of cement replacement the paste exhibits better rheological properties: lower yield stress and lower viscosity up till 120 min after mixing, which is an important factor in ready-mix concrete plants. However, a better pozzolanic behavior was observed at 20% cement replacement. From the results obtained, the properties of the paste containing BFA is very sensitive to water/binder ratio (w/b). Above 20% cement replacement, it is suggested to use viscosity modifying agent (VMA) to get a better rheology and pozzolanic behavior.

Keywords: Portland limestone cement; biomass fly ash; sustainability; rheology; pozzolanic.

1 Introduction

The last two decades have witnessed increased pressures to cut down carbon emission for cleaner environment and energy security. This has led to the diversification of energy sources from fossil fuels into renewable and sustainable sources. Scientists around the globe have reacted to this pressure by focusing on waste recycling and reuse. To this end, the European Union (EU) prioritizes research based on European sustainable development policies (European Directive 2008/98/EC) [1] on the use of biomass for heating and cooling, and generating electricity, towards waste reduction, recycling, and



reuse (3Rs). In a broader view, the research is to consider the availability, conversion techniques/efficiencies, and emission abatement of biomass [1]. Solid biomass conversion is one of the major technologies that has been implemented in many steam and power plants [2], however, one of the problems associated with this technology is the disposal and management of the ash generated during biomass combustion.

There are various sources of solid biomass including agriculture wastes, wood or bark, and wastewater treatment plants. It has been reported that agroindustry waste accounts for about 140 billion metric tons annually generated around the world [3]. In the last few years, biomass combustion majorly focuses on the combustion of rice husk ash, and sometimes bamboo ash [4-5]. In more recent times, focus has shifted to biomass waste from power and steam plants that run on wood fuels. The quality and quantity of ashes depend on the biomass source in addition to the combustion technology. In a fluidized bed technology, the combustion usually takes place at a temperature below 900 °C, while in the grate furnace technology, the combustion temperature could be as high as 1200 °C. This combustion temperature influences the quality, amount of organic and volatile compounds in the BFA [6]. At a combustion temperature above 1200 °C, the biomass ash from sugar cane bagasse was reported to contain crystalline quartz, and cristobalite, with less volatile compounds. At a lower temperature, the ash contained high amorphous silica [6].

In the last two decades, fly ash obtained from the combustion of coal-fired plants have been used in concrete as a supplementary cementitious material to modify and improve the strength and durability of the concrete. In addition, the partial replacement of cement with fly ash yields a reduction in the quantity of cement required for concrete thereby reducing the amount of global carbon emission from cement-based industry. On the other hand, most of the coal-fired power plants are closing due to the inherent carbon emission from coal burning. The shortage in supply of fly ash caused by the closure of the coal powered plant would lead to shortage in fly ash and therefore less durable and sustainable concrete. The need to find alternative sources of fly ash has led to research the feasibility of using sustainable and environmentally friendly ash in concrete [7]. This sustainable ash is termed BFA.

Past research findings have shown that these ashes are rich in silica and alumina, and they can contribute to the pozzolanicity of cement-based material in the presence of calcium hydroxide (CH) [8-10]. However, the source, combustion temperature and type of the BFA influences the properties of the cement paste or concrete. As an instance, Van Tuan et al. [11] reported a higher compressive strength when rice husk ash (RHA) was used as partial replacement of cement at 20 % by weight; Feng et al. [12] reported higher amount of heat of hydration and reduced setting time. On the contrary, Ganesan [13] and Berodier [14] reported that at 0-30% by weight of RHA as replacement for cement, the rheology of concrete was affected, but at 20% replacement, a 20% increase in compressive strength was observed in addition to improved chloride resistance. The change in rheology was caused by the high internal porosity of RHA. Cabrera et al. [15] suggested a reduction in the level of organic content in BFA by combusting the ash at a temperature above 1050 °C prior to its use in concrete.

Limestone being a technical and economic superior material, when interground with normal cement would improve workability and reduced bleeding of fresh concrete [16]. The intergrinding of limestone powder with ordinary Portland cement (OPC) as a replacement material for cement clinker during the production of cement at a certain proportion has led to the production of Portland limestone cement (PLC). The European standards includes provisions for cements containing limestone in amounts up to 35%. The behavior of concrete made with PLC widely differs from that made with OPC. Some researchers [17,18] have reported poor workability in concrete made with PLC, evidence by higher yield stress and plastic viscosity. While others [19] reported that the addition of limestone to cement reduced the yield stress and plastic viscosity of the concrete. Bentz et al. [20] reported a higher early strength for concrete incorporating PLC. Lower capillary porosity and higher compressive strengths were observed when PLC was used in concrete [21]. The intergrinding of cement clinker with limestone, with fineness modulus higher than normal cement have both physical and chemical effects on the PLC. These effects influence the kinetics of the cement hydration and the pore structure of the cement paste that may reduce the concrete's ability to resist salt crystallization damage [22].

When non-sulfate resisting Portland limestone cement was used in concrete exposed to sulfates at low temperature, the severity of the Thaumasite form of Sulfate Attack (TSA) increased and it was

therefore recommended that PLC cement should not be used in sulfate environment with SCMs [23]. The parallel-plate geometry rheometer has been extensively used in the study of cement paste rheology. The roughness and the gap distance are two major parameters that control the rheometer tests. On one hand, rough plates tend to increase the Bingham yield stress when compared to the smooth plates; on the other hand, the plastic viscosity decreases with increasing plate roughness [24]. From the foregoing, it is required to add SCMs to PLC to produce durable concrete; however, there is a shortage of SCMs due to environmental protection policies. There is a potential of using BFA as SCMs for sustainability. Therefore, the purpose of this study is to understand the pozzolanicity and the rheology of the paste made from BFA and PLC. The outcome of this study will assist the research community in developing and updating existing design guides on the application of BFA in PLC.

2 Experimental Program

2.1 Materials

The cement used in this study is the PLC type IL (15) (shown in **Fig. 1**) corresponds to ASTM C595-17. The notation implies Portland cement clinker intergrinded with 15 % limestone. At this level of replacement, CO₂ emission is reduced by 10 % [22]. The oxide contents of the cement determined using the X-ray fluorescence spectroscopy (XRF) are listed in Tab. 1. The Hitachi S2300 SEM with EDX25KV was used to determine the morphology of the PLC as shown in **Fig. 2**.



Fig. 1. Samples

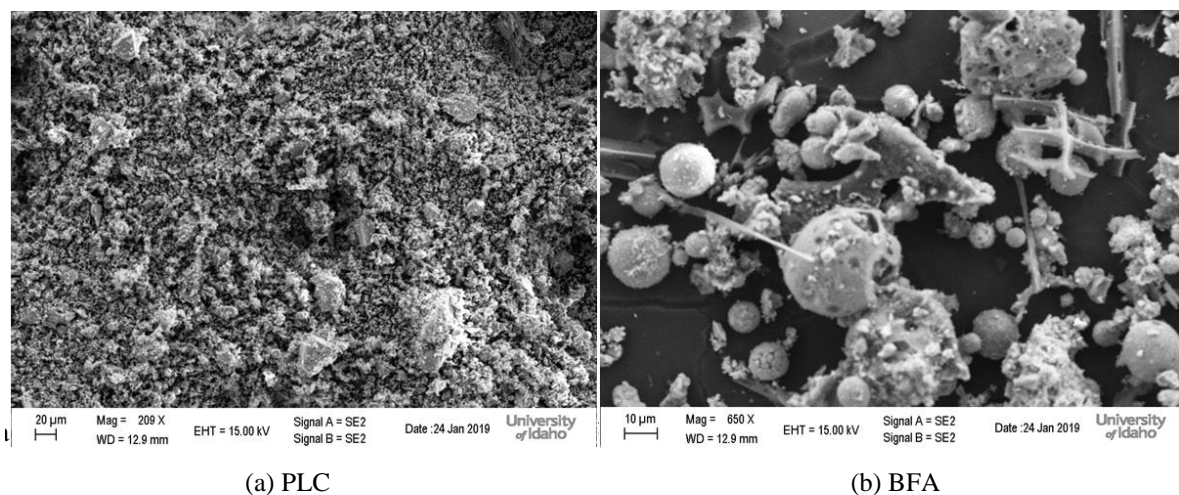


Fig. 2. SEM images

The BFA used in this study was collected from the precipitator of a biomass steam plant located at the Moscow campus of the University of Idaho. The plant runs on forest wastes as its main fuel. Most of the forest waste (mainly *Cedrus atlantica* Manetti (cedar) – Pinaceae (pine) waste) come from lumber

mills around Idaho. The fuel is burnt in a boiler with fluidized bed technology around 950-1050 °C. This biomass fly ash was medium dark in color (as shown in **Fig. 1**). The fly ash collected from the plant was dried in a laboratory oven at 120 °C to remove excess moisture and then sieved through a 75 µm mesh. The relative density of the fly ash particles was determined using a Helium pycnometer and the surface area by the BET (Brunauer, Emmett, and Teller) method, while the particle size was analyzed using a Coulter LS particle size analyzer (LS230FM). The microstructure of the BFA and PLC (shown in **Fig. 2**) were studied using Hitachi S2300 SEM with EDX25KV.

Distilled water obtained from the laboratory was used for preparing the cement paste while mixing the BFA and the PLC.

2.2 Specimen Preparation

The cement pastes were prepared by replacing PLC with varying amounts of biomass fly ash (5%, 10%, 20%, 25% and 30% by weight of Portland limestone cement) in dry condition, as summarized in **Tab. 2**. The cement pastes were prepared with 0.3 and 0.5 water/binder (w/b) ratios (by weight). The cementitious materials were batched by weight and mixed thoroughly in an automatic laboratory mixer. The mixing procedure involved charging the mixing drum with PLC and then adding the BFA. The BFA was gently added to the PLC because of its density. The two cementitious materials were then mixed for 1 min at a low rotation speed of about 60-70 rpm. After dry mixing, the mixing water was discharged into the mixer and then mixed again for 2 min at a higher rotation speed of about 120 rpm. No viscosity modifying agent (VMA), nor plasticizer was used in the pastes.

Table 1. Chemical and Physical Properties of cementitious materials

Chemical compositions (%)	Portland limestone cement	Biomass fly ash
CaO	63.30	13.00
SiO ₂	18.40	48.60
Al ₂ O ₃	4.40	16.70
Fe ₂ O ₃	3.20	6.30
MgO	0.80	5.60
SO ₃	2.80	0.90
MnO	4.40	0.34
P ₂ O ₅	-	3.19
Cl	-	0.68
TiO ₂	-	0.94
LOI	4.40	2.34
NaEq (Alkali)	0.45	0.18
Insoluble Residue	0.18	1.23
Phase Composition		
C ₃ S	50.00	
C ₂ S	15.0	
C ₃ A	6.00	
C ₄ AF	10.0	
Physical Properties		
Specific gravity	3.09	2.70
Fineness retained on 45 µm (%)	98.70	15.00

2.3 Testing Methods

2.3.1 Characterization of BFA

As previously described, the particle size distribution, density, organic matter content and mineralogical composition of the fly ash as collected from the steam plant were determined. The particle size distribution was analyzed using a Coulter size analyzer. The sizes were measured using AeroS dry powder disperser using 850 mg of BFA under 4-bar air pressure at a feeding rate of 30%.

The chemical and mineral composition of the BFA was determined using X-ray fluorescence. A 0.5 g of the oven dried BFA was mixed with 5 g of lithium tetraborate flux in a ratio of 1 to 10, in a ceramic crucible and then fused into a glass bead at a temperature of about 1100 °C. The glass bead was

analyzed using the XRF equipment.

Table 2. Mix proportion and setting time of formulated pastes

Mixture ID	PLC (%)	BFA (%)	w/b ratio	Initial setting time (min)	Final setting time (min)
M1	100	-	0.3	88.0	146.0
M2	95	5	0.3	93.0	155.0
M3	90	10	0.3	96.0	157.0
M4	80	20	0.3	105.0	165.0
M5	75	25	0.3	115.0	170.0
M6	100	-	0.5	90.0	150.0
M7	95	5	0.5	97.0	156.0
M8	90	10	0.5	102.0	162.0
M9	80	20	0.5	108.0	170.0
M10	75	25	0.5	116.0	189.0

The microstructure of the PLC and the BFA were analyzed using the scanning electron microscopy (SEM). A disposable pipette was used to disperse a portion of the BFA on a carbon tape-coated copper sample holder. After blowing off excess samples from the sample mount, the mount was loaded onto the SEM machine and the imaging was conducted in a secondary electron mode of 15 kV. The crystalline phase of the BFA was done using X-ray diffraction (XRD) and the XRD patterns were analyzed using the Bruker EVA 4.3 software.

2.3.2 Consistency Test

The amount of water required for normal consistency and setting time of the cement pastes were determined by Vicat apparatus according to [25], and the amount of water required for this consistency was used as the basis for the w/b ratio adopted in this study.

2.3.3 Isothermal calorimetry and thermogravimetric analysis of cement pastes

The evolution of heat is a measure of the hydration progress in the cement paste. Thermally isolated boxes were used for the quasi-adiabatic calorimeter to study the evolution of heat of hydration of the cement paste. Thermocouples were installed in the boxes to continuously monitor the temperature with the aid of an automatic data acquisition system. A 5 mg sample of the freshly mixed cement paste was placed in a glass holder and placed in the calorimeter at a temperature of 23 ± 0.01 °C and the hydration kinetics measured for the first 7 days until a steady state of temperature change was reached. The data from the calorimeter was collected using an automatic data acquisition system. The heat released for the first 30 minutes was discarded to allow for stability in the sensors' signal.

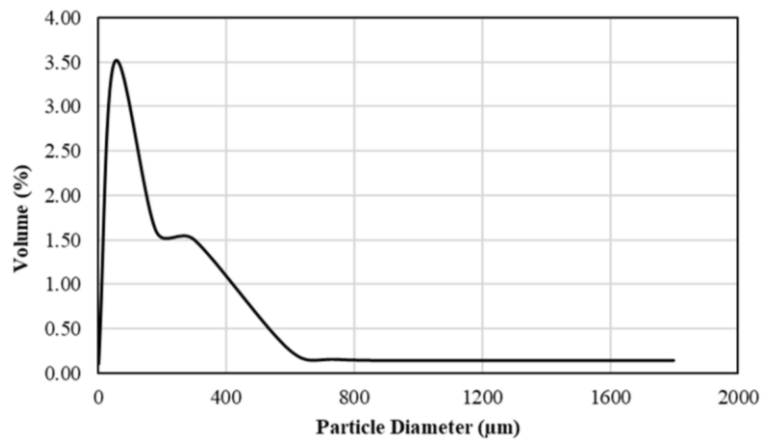
The TGA (TGA 55, TA instruments) was conducted simultaneously with the isothermal calorimetry because they are both dependent on the age of the pastes. The TGA temperature was ramped at 10 °C/ min from 25 °C to 600 °C in an inert Nitrogen environment. The mixed pastes were cast into 50 x 50 x 50 mm cubes and cured according to recommendations [26]. The TGA was done at different ages (1 day, 7 days, 14 days, 28 days, and 90 days) by taking a 5 mg sample from the hardened cement pastes to evaluate the degree of hydration at these ages. The amount of CH consumed during the hydration process was calculated by taking the difference between the initial and final amount of CH in the paste.

2.3.4 Rheology Test

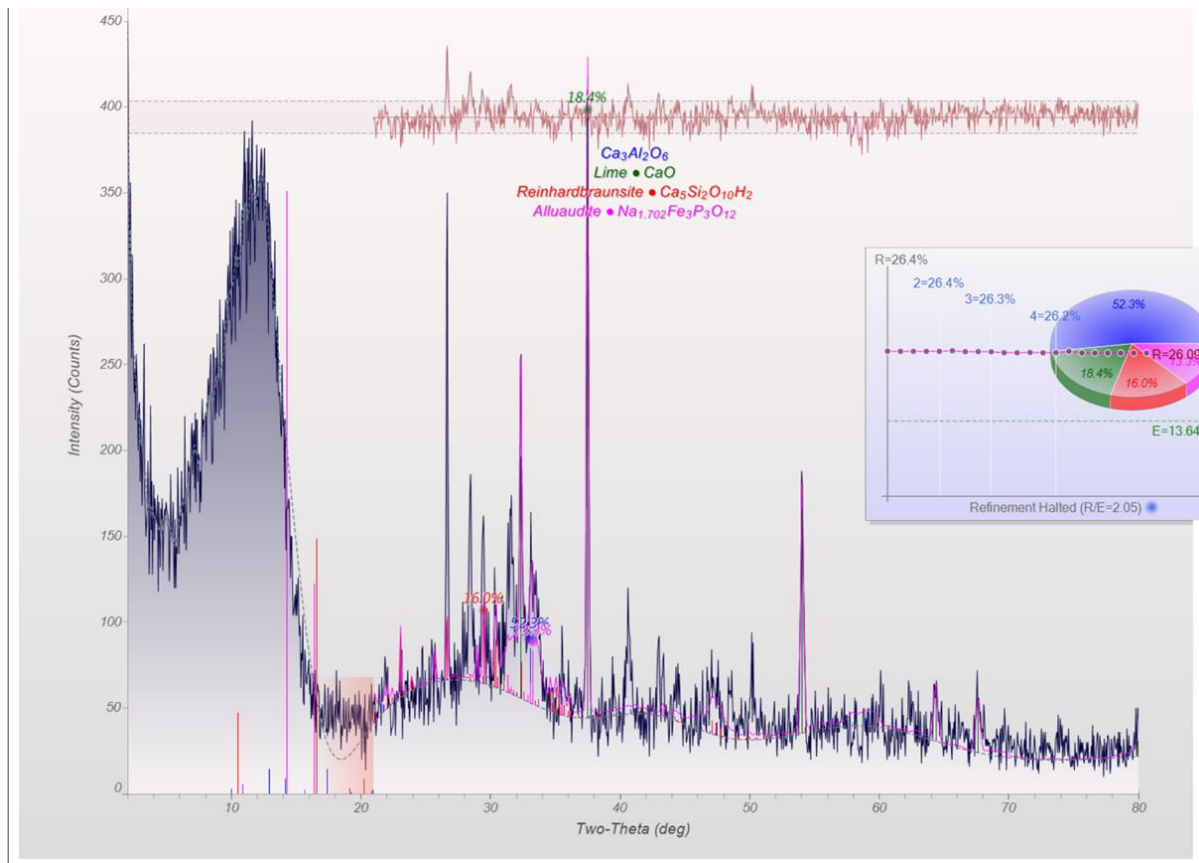
The rheology of the cement pastes was measured using a shear rheometer (Bohlin instruments C-VOR shear rheometer) with stainless parallel plate geometry 25 mm diameter and crosshatched surfaces. Since the rheological properties of the cement paste are sensitive to temperature, the Peltier plate of the rheometer was used to maintain the temperature of the lower plate at room temperature of (25 °C) during the tests.

To ensure the same thickness of specimen was used in all the test, the cement paste was placed in a ring mold of 25 mm diameter and 2.8 mm height, and the ring placed on the lower plate of the rheometer, and the ring was removed. After the removal of the ring, the upper plate of the rheometer

was lowered at a gap distance of about 2800 μm , until it gently touched the surface of the plate. The gap positioning was then set to 1050 μm , in which excess paste would be squeezed out and cleaned. The final gap position was set at 1000 μm and the test was initiated. After reaching a 1000 μm gap, no further adjustment was done to the gap setting and the instrument was ready to run.



(a) Particle size distribution



(b) XRD diffractogram of BFA

Fig. 3. Particle size distribution and XRD diffractogram of BFA

The shear cycles used in this test consisted of two consecutive cycles without rotational pre-shear step. In the first cycle, the shear rate was ramped from 0 to 300 s^{-1} within 60 s, and it was ramped back to 0 in 60 s in the second cycle. In all tests, the gap position was kept constant, and each test was conducted three times, but with different mixing batch and different times after mixing: 0 min., 30 min., 60 min., and 120 min. The flow curves obtained from the test was analyzed using the Bingham rheological model: $\tau = \tau_0 + \eta \nu$; where τ_0 is the yield stress, η is the viscosity, ν is the shear rate

and τ is the shear stress. The thixotropy of the cement paste was calculated by the reduction of shear stress during the constant shear rate as given by:

$$T = \left(\frac{\tau_1 - \tau_2}{\tau_1} \right) \quad (1)$$

Where T is the thixotropy, τ_1 is the shear stress at 300 s^{-1} before retention and τ_2 is the shear stress at 300 s^{-1} after retention.

3 Results and Discussion

3.1 Characterization of biomass fly ash

The density of the biomass fly ash was determined to be 2.70 g/cm^3 with a standard deviation of 0.0017 g/cm^3 while that of the PLC was 3.09 g/cm^3 . These values showed that BFA is significantly lighter than the PLC, but its density is well within the values specified for conventional fly ash. Its specific surface area was $3483 \text{ cm}^2/\text{g}$. The particle size distribution (as shown in **Fig. 3**) of the BFA showed that its average particle sizes are typically below $50 \text{ }\mu\text{m}$. Although, it should be noted that the BFA was sieved to remove particles larger than $75 \text{ }\mu\text{m}$ before adding it to the PLC.

The mineral composition and loss on ignition of the BFA are summarized in Tab. 1. The LOI value of the BFA was 0.34%. This value was low because the BFA is a by-product of high temperature ($1100 \text{ }^\circ\text{C}$) burning of fuel collected over electrostatic precipitator. The constituent's oxide of the BFA obtained from the XRF showed that the BFA could be classified as type C fly ash since the sum of $\text{SiO}_2 + \text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3$ is greater than 50 % but lesser than 70 %.

The XRD diffractogram of the BFA is shown in **Fig. 3**. It can be observed from the XRD peaks, that the main components of the BFA are quartz, alumina, and calcite. The calcite (carbonates) is naturally present in wood; hence it would be available in BFA. Some level of amorphous ash was also observed in the XRD which is likely due to the incomplete combustion of the biomass to ash. Although, the biofuel was burned at a high temperature of $1100 \text{ }^\circ\text{C}$, there is always a level of inefficiency of carbon conversion in the furnace because of mass transfer and reaction kinetic.

From the SEM images of the BFA shown in **Fig. 2**, the particles were spherical in shape, although some level of irregularity could be observed in the BFA particles.

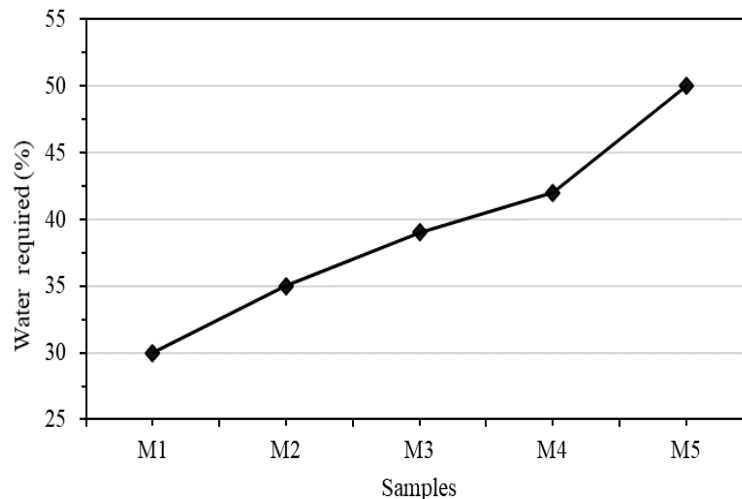


Fig. 4. Water requirement for normal consistency

3.2 Water requirements for normal consistency of the paste

The variation of water requirements for normal consistency of cement pastes is shown in **Fig. 4**. It can be observed that the water requirement increases with the level of cement replacement. When water is added to cementitious materials, part of it was used to fill the pore spaces between the cement particles, another part is adsorbed by the cement and the rest is chemically bonded for hydration process. The

amount of the water used in filling the pore spaces depends on the shape and sizes of the cement particles, and the absorbed water depends on the specific area of the cement particles. Based on this analogy, the water requirement for the first mixture formulation (M1) was the lowest because only one stage of hydration would occur. However, in all other mixtures (M2, M3, M4, M5) containing BFA, because of the secondary hydration involving the BFA and CH from the primary hydration would increase the water demand capacity of the paste. As the amount of BFA increased in the mixtures, more water would be adsorbed by the cement particles thereby reducing available water for hydration. The partially hydrated particles would form a thin film deposit on the un-hydrated particles and make it possible for water to fill the pore spaces within the cement particles. It is difficult to establish a trend between cement replacement and the amount of water required for normal consistency, since the relationship is not linear.

3.3 Setting time

The setting time of concrete is an important parameter in concrete operation to allow for placing, vibrating, and finishing freshly mixed concrete. In some situations, like bridge repair, early setting time would be required to reduce bridge closure duration, and in other situations, delayed setting times would be of interest. The setting time of the paste varied with the w/b ratio, and the level of cement replacement. As an instance, for M4 with 20% BFA and 0.3 w/b ratio, the initial and final setting times were delayed by 17 min and 19 min, respectively. However, for M9 with 20% BFA and 0.5 w/b ratio, the initial and final setting times were delayed by 20 min and 26 minutes, respectively. Therefore, it could be stated that the BFA delayed the setting times. BFA reacts with the C_3A in cement and build up a covering layer on the surfaces of the cement particles and the setting time would be extended. At higher w/b ratio, the extra water would stay in the cement paste, if the water is not used up during hydration. The presence of this water in the paste is dangerous as it could provide a reaction medium for a secondary reaction due to the ingress of deleterious compounds.

3.4 Calorimetric analysis and hydration kinetics

The measured temperature from the calorimeter is shown in **Fig. 5**. The highest temperature of 43°C was observed in the mixture without BFA (M1) after about 13 h when the paste was mixed as the level of replacement of PLC with BFA increased, the heat of hydration reduced. The heat of hydration also reduced with increased in w/b ratio as shown for mixtures M6, M7, M8, M9 and M10. In the same manner, a shift in the peaks of the hydration curve was also observed. The shifts in the peaks have been attributed to the influence of alkalis and chloride presented in the BFA [6, 27].

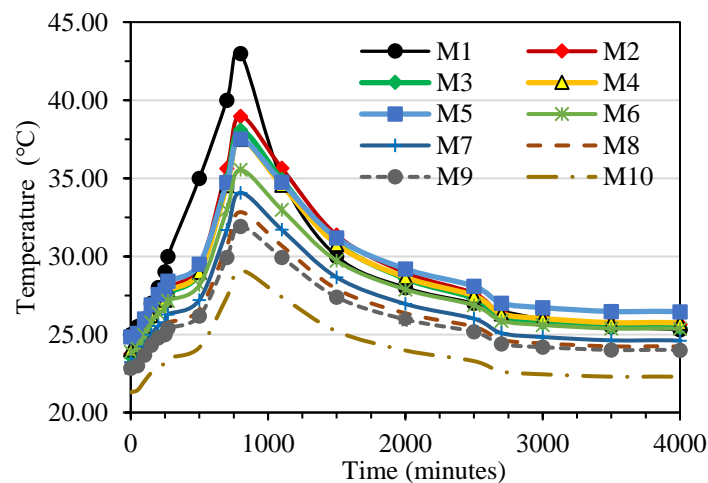


Fig. 5. Heat of hydration curves for cement pastes

The hydration process is a thermodynamic reaction accompanied by the evolution of heat. At the initial stage of hydration, C_3A and C_3S predominantly responsible for the evolution of heat as they react first. From the **Tab. 1**, C_3S occupies about 50 % phase in PLC which explains the rapid evolution of heat in the cement paste, but the secondary hydration of the cement due to the presence of BFA would reduce the amount of heat generated. In mass concrete construction, since low amount of heat is required,

the application of BFA to cement would be beneficial, but a cause for concern would be the delayed hydration that would result in slower rate of strength gain as shown in **Fig. 4**, M10 mixture had the lowest heat of hydration which is caused by the delayed hydration because of the reaction between CH and BFA. When PLC was replaced by 25% of BFA, the heat of hydration has reduced by 67%.

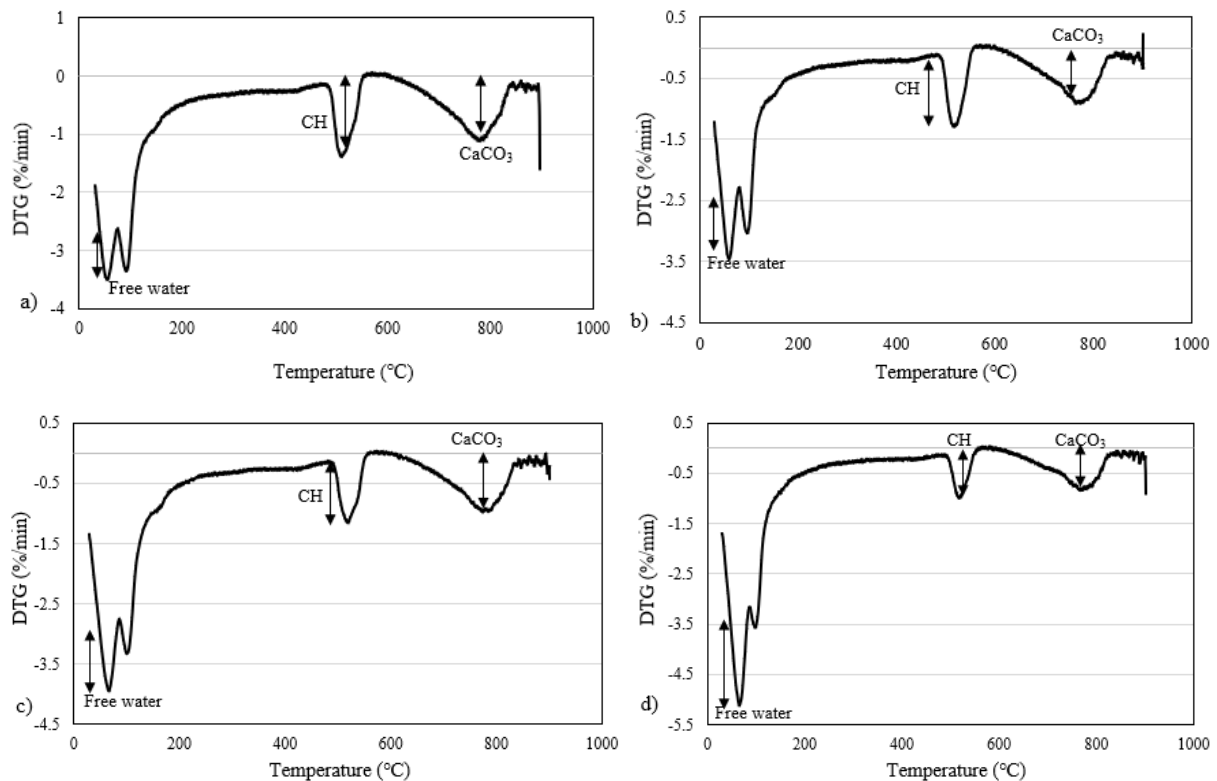


Fig. 6. Typical TGA/DTG thermograms for (a) M1 @ 28-days; (b) M2 @ 28 days (c) M3 @ 28 days (d) M3 @ 90 days

The degree of hydration and hydration products were measured using the TGA/DTG at different ages. Typical TG/DTG thermograms for the cement pastes are shown in Fig. 6. The profiles depict typical hydration reactions occurring in the hydrated pastes when subjected to a temperature increase, by measuring the mass loss for each hydrated product. The two important parameters required to monitor the degree of hydration are the weight loss corresponding to the thermal decomposition of CH and the amount of chemically bound water [28]. In the TGA/DTG thermograms of Fig. 6, the first important peak relates to the loss of free water in the hydrated cement paste which occurs between 0 and 105 °C. At a temperature of 35 °C, the water in large pores get evaporated and above this temperature, the retained water in capillary pores of the paste was released by capillary tension [29]. At temperatures between 150 and 400 °C, a weight reduction was observed which is due to the evaporation of the physically combined water from the calcium silicate hydrate (CSH) gel and the aluminosilicate gel. The loss mass at this temperature range was also reported by [30]. The second most important peak on the TGA/DTG thermogram occurs at a temperature range of 430-510 °C, which corresponds to the dehydroxylation of CH that was formed during the hydration of C_3S and C_2S in the PLC. The amount of CH decomposition is a measure of the pozzolanicity and effectiveness of the hydration. Pozzolanic reaction is the primary reaction between amorphous siliceous materials and CH to form the CSH. The third important peak in the TGA/DTG thermograms occurs at a temperature range of 723 - 835 °C which corresponds to the thermal dissociation of the calcite ($CaCO_3$). The presence of $CaCO_3$ in the paste is related to carbonation process. Carbonation is the reduction of the pH of concrete which destroys the passive film layer that protect embedded steel reinforcement in concrete and makes it susceptible to corrosion.

In all the mixtures, the CH and $CaCO_3$ content were determined at different ages and summarized in **Tab. 3**. The comparison of **Tab. 3** and **Fig. 5** shows that the intensities of the peak corresponding to CH reduced as the BFA content and age of curing increased. The reduction in the CH content indicates

that more CSH gel is being produced because the BFA supplies the amorphous siliceous required for secondary hydration. At age 90 days, a total consumption of CH was not observed. In contrast, the amount of CaCO₃ in the mixture increased with age but decreases with the level of BFA replacement. The increase in the CaCO₃ was because of the longer age of the mixed paste in which the low CO₂ in the atmosphere reacted with the CH left in the paste. This reaction process increases with time, thereby increasing the amount of CaCO₃. However, for the same curing age, higher amount of the BFA in the mixture reduced the amount of CaCO₃ content because of the lower CH content that has been used up during the pozzolanic reaction between the CH and the BFA. Similar results for the CaCO₃ have been reported by [6, 27, 30]. In addition, **Tab. 3** shows the uncombined water at various ages of all specimens. The uncombined water is defined by the unreacted water due to the limited number of pores in the cement gel, which is the major component of the hydration process.

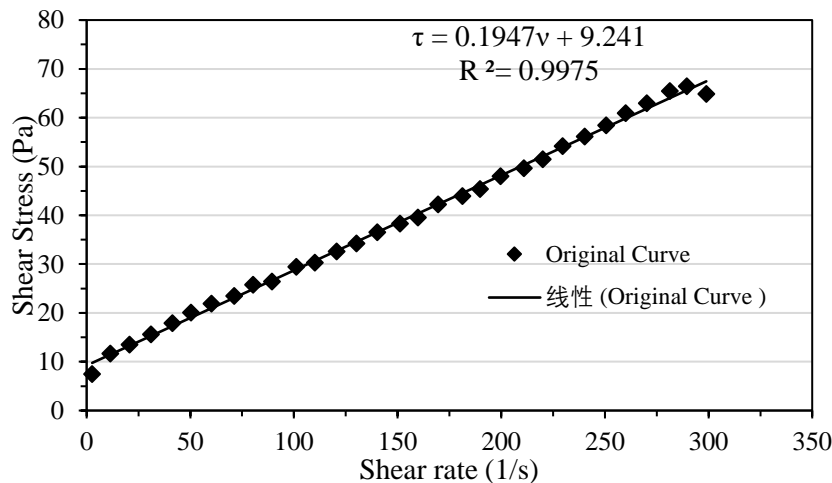
Table 3. Hydration product by weight from TG/DTA

Sample	Uncombined water (%)			CH (%)			CaCO ₃ (%)		
	7 days	28 days	90 days	7 days	28 days	90 days	7 days	28 days	90 days
M1	10.21	11.48	11.96	7.86	7.36	6.98	3.98	4.85	5.89
M2	9.66	10.85	10.93	7.65	7.02	6.53	3.84	4.12	5.36
M3	8.65	10.35	10.87	7.01	6.64	6.24	3.67	4.09	4.98
M4	7.48	9.65	10.02	6.93	5.87	6.01	3.45	4.01	4.89
M5	5.78	8.96	9.97	6.58	5.45	5.89	3.41	4.00	4.78
M6	11.86	12.34	12.91	7.82	7.26	6.87	3.32	3.97	4.38
M7	10.63	11.65	12.30	7.12	6.89	6.58	3.11	3.89	4.02
M8	9.54	10.42	10.88	6.58	6.11	5.88	2.98	3.68	3.99
M9	8.63	9.52	9.98	6.02	5.91	5.15	2.81	3.21	3.68
M10	6.98	7.53	8.32	5.99	5.45	4.92	2.65	3.08	3.45

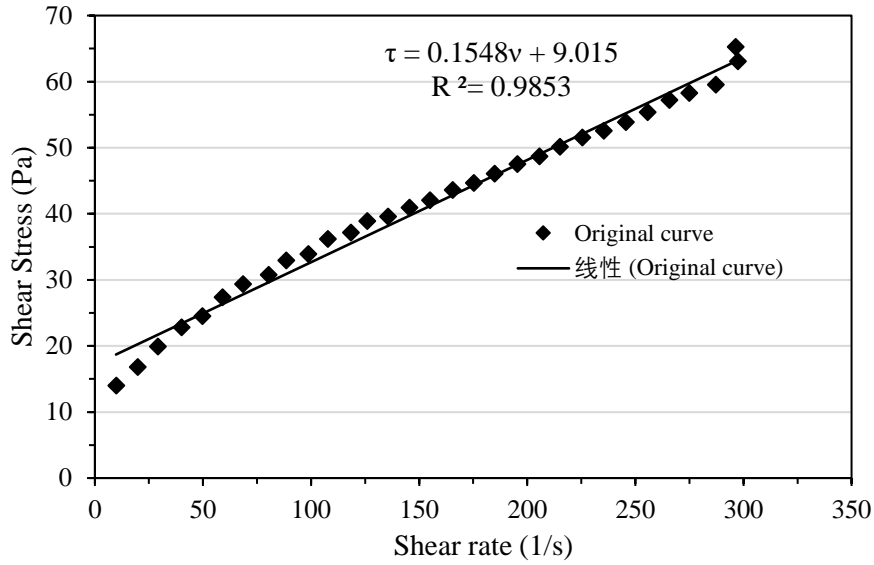
3.5 Rheological parameters

3.5.1 Flow characteristics cement paste

Typical flow curves (shear stress vs shear rate) at 5, 60 and 120 mins after mixing for the cement pastes are shown in **Fig. 7**. From the flow curves, it can be observed the all the mixtures have different rheological properties. The fluidity of the paste increased as the amount of the BFA in the mixture increased. However, lower fluidity was observed in the mixtures containing 20 and 25 % BFA. This is because the BFA particles are finer than PLC, which can effectively fill the pores within the cement particles. As a result, the interstitial pore water between the cement can be released and added to the free water in the paste thereby increasing the flowability of the paste. In contrast, as the amount of BFA increased, more water would be adsorbed because of the large specific area of the BFA and would reduce the water require for the particles to flow easily, resulting in lower fluidity. The above illustration explains the variation observed in the shear stresses relative to the shear rate.



(a) M1 mixtures after 5 min of mixing



(b) M2 mixtures after 5 min of mixing

Fig.7. Typical fitting models

3.5.2 Shear cycles, viscosities, and yield stresses

Fig. 7 shows typical shear cycles for the cement paste loaded in the automatic mode. In **Fig. 6**, it can be observed that there is no major difference between the up and down curves for all cement pastes. Both the up and down assumed the positive slope with almost perfect Bingham linear fluid model. At shear rate between 205 - 220 s⁻¹, the up and down curves intersect because of some structural breakdown in the paste particles. This structural breakdown is also referred to as the thixotropic effect.

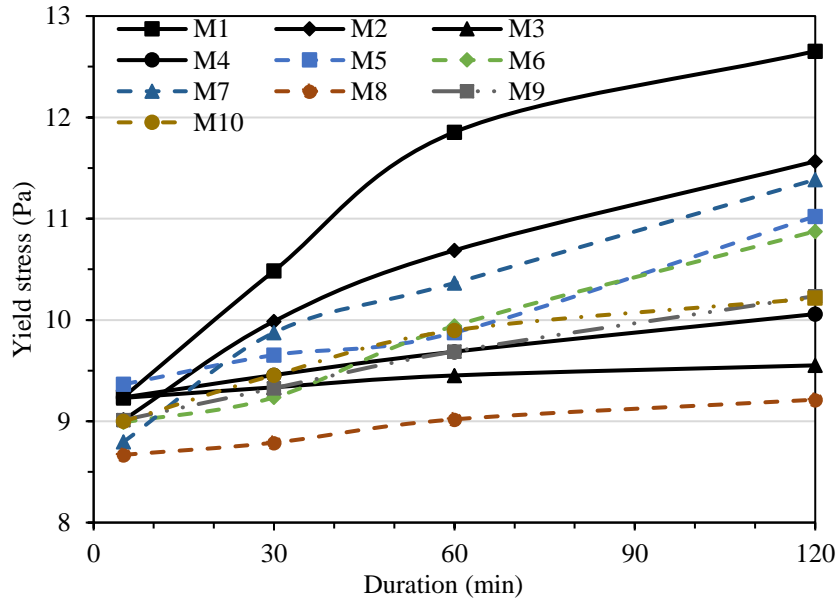


Fig. 8. Yield stress of mixtures within 120 min

The viscosities and the yield stresses are two important parameters used to measure the plasticity of freshly mixed concrete. The shear stresses and viscosities of the pastes were determined by fitting a linear Bingham equation to the shear stress versus shear rate curves and viscosity versus shear rate curves, respectively. Other rheological models like revised Bingham fluid model and Herschel-Bulkey fluid model could be used, but it has been reported that the Bingham fluid model was the best for cement paste containing fly ash [31-32]. Since there is no major difference between the up and down curves, the up curve was used to determine the yield stresses and viscosities. The fitting results and the

rheological properties for all the mixtures are shown in **Fig. 8**. From **Fig. 8**, it can be observed that the yield stress reduced with the addition of BFA. However, when the BFA content was above 20%, the yield stress increased. The trends in the flow parameters observed agree with the results of [33-34]. At higher w/b ratio, the pastes behave in a similar manner like the 0.3 w/b ratio, except that the yield stresses were lower than that of 0.5. Although, mixtures with higher w/b ratio showed better rheological properties, other properties of the mixtures discussed in previous sections are negatively affected by the high w/b ratio.

Fig. 8 shows the variation of the yield stresses with time. From **Fig. 8**, it can be shown that after 120 min of mixing, there was no change in the rheological parameters of the mixtures with 10% BFA. The yield stresses and viscosities for this mixture are almost constant for both 0.3 and 0.5 w/b ratio. These mixtures can be said to retain their plasticizing behavior from mixing until 90 min. The ability of concrete to retain its plasticizing property is highly desirable in premix concrete plants, to allow for handling, transporting, and finishing of the concrete.

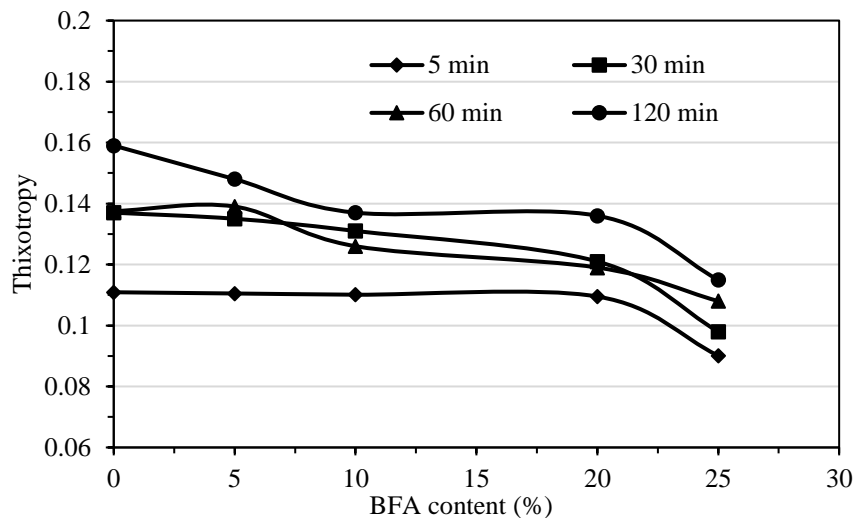


Fig. 9. Thixotropy of cement pastes with 0.3 w/b ratio

3.5.3 Cement paste's thixotropy

The thixotropy of the cement pastes is calculated as described in previous section. **Fig. 9** shows the variation in thixotropy of the paste with BFA content for M1 through M5. It can be observed that the thixotropy reduced with increase in the BFA content.

During the dormant stage of cement hydration, a reversible in the rheological properties of cement paste is usually noticed. This reversibility can be erased when the paste is subjected a strong shearing stress and the paste would regain its original state of stress. Skripkiunas et al [32] reported that the thixotropy of cement paste depends on specific surface area and particle size distribution of the cement particles. Since the BFA is finer than the PLC, the BFA particles would act as lubricant by for the PLC thereby reducing the thixotropy of the cement paste. This better thixotropy properties would make it possible for concrete made with BFA to regain its fluidity when disturbed during concrete placing and finishing.

3.6 Practical applications

In this study, only one source of BFA was studied, but with various replacement level and w/b ratios, and yet significant variation in rheological properties and pozzolanic properties were observed. Also, the cement formulation used in the PLC which has been adopted in many European countries, but the USA is yet to fully adopt it in construction. The mixtures studied did not contain any viscosity modifying agent (VMA). The addition of VMA to the mixtures would totally alter the rheological properties of the mixtures by readjusting the particle agglomeration and dispersal. In a hypothetical situation, there would be a wide variation in the behavior of the mixtures if VMA were added or the

particle size of the cementitious materials changed. Nonetheless, the outcome of this study shows that there is a need for concerted effort on cement chemistry for a better understanding of pozzolanic and behavior of sustainable and environmentally friendly cementitious materials. The practical applications of the BFA might be used in various applications such as concrete sidewalks and concrete pavements. The structural application of BFA concrete needs more in-depth investigation on the long-term behavior under severe loading conditions.

4 Conclusions

In this study, the influence of a specific type of biomass fly ash (*Cedrus atlantica* Manetti – Pinaceae waste) on the rheology and pozzolanic properties of Portland limestone cement pastes were studied. This type was extracted from lumber mills located in the state of Idaho that is being used in power plants in many locations. Variations in pozzolanic behavior and rheological parameters were observed as the BFA content in the cement paste increased. From these outcomes, the following conclusions can be reached:

The BFA (mainly cedar – pine waste) has mineral composition like class C fly ashes based on ASTM standard. As the BFA content in the mixtures increased, the hydration rate reduced, with a lower heat of hydration. This is due to secondary hydration taking place within the paste.

The addition of BFA to the cement paste increased the amount of calcium silicate hydrate formed during the pozzolanic reaction. As the amount of BFA increased, the CH content of the paste decreased, and the CaCO_3 decreased. However, the CaCO_3 content increased with time due to prolong exposure to the atmosphere. At age 90 days, a total consumption of CH was not observed. In contrast, the amount of CaCO_3 in the mixture increased with age but decreases with the level of BFA replacement.

It is suggested to use BFA in mass concrete construction, since low amount of heat is required, however delayed hydration will be observed.

When PLC was replaced by 25% of BFA, the heat of hydration has reduced by 67%.

The flow behavior of the cement pastes fits well with the Bingham linear model. Increasing the amount of BFA in the mixtures does not alter the rheological model of the cement paste. A better rheological property was observed in mixtures containing 10% BFA. However, the rheological properties were greatly affected by higher BFA content. 10% BFA replacement in the cement mixture offers the best rheology.

At 15% of cement replacement the paste exhibits better rheological properties: lower yield stress and lower viscosity up till 120 min after mixing, which is an important factor in ready-mix concrete plants. However, a better pozzolanic behavior was observed at 20% cement replacement. From the results obtained, the properties of the paste containing BFA is very sensitive to water/binder ratio (w/b). Above 20% cement replacement, it is suggested to use viscosity modifying agent (VMA) to get a better rheology and pozzolanic.

Acknowledgements

The authors would like to thank the management of the University of Idaho Steam plant for providing the biomass fly ash used in this study. The Portland limestone cement was supplied by Pre-Mix Inc through the help of Messrs. Jesse. Part of this project was funded by the Idaho Transportation Department (ITD) through RP 262.

CRedit authorship contribution statement

Olaniyi Arowojolu: Investigation, Formal analysis, Writing – original draft. **Ahmed Ibrahim:** Conceptualization, Investigation, Formal analysis, Writing – original draft. **Armando McDonald:** Conceptualization, Supervision.

Conflicts of Interest

The authors declare that they have no conflicts of interest to report regarding the present study.

Disclaimer

The contents of this paper reflect the views of the authors who are solely responsible for the facts and accuracy of the data presented here and do not necessarily reflect the official views or policies of any agency or institute, including the Texas Department of Transportation.

References

- [1] Ericsson K. Co-firing – a strategy for bioenergy in Poland. *Energy* 2007; 32(10): 1838-1847. <https://www.sciencedirect.com/science/article/abs/pii/S036054420700059X>.
- [2] Xiao JZ, Liu HR, Ding T, Ma GW. 3D printed concrete components and structures: an overview. *Sustain Struct* 2021; 1(2): 000006. <https://doi.org/10.54113/j.sust.2021.000006>.
- [3] Martirena F, Monzo J. Vegetable ashes as supplementary cementitious materials. *Cem Concr Res* 2018; 114: 57-64. <https://doi.org/10.1016/j.cemconres.2017.08.015>.
- [4] Cordeiro GC, Kurtis KE. Effect of mechanical processing on sugar cane bagasse ash pozzolanicity. *Cem Concr Res* 2017; 97: 41-49. <https://doi.org/10.1016/j.cemconres.2017.03.008>.
- [5] Frias M, Villar E, Savastano H. Brazilian sugar cane bagasse ashes from the cogeneration industry as active pozzolans for cement manufacture. *Cem Concr Compos* 2011; 33: 490-496. <https://doi.org/10.1016/j.cemconcomp.2011.02.003>.
- [6] Rajamma R, Ball RJ, Tarelho LAC, Allen GC, Labrincha JA, Ferreira VM. Characterization and use of biomass fly ash in cement-based materials. *J Hazard Mater* 2009; 172: 1049-1060. <https://doi.org/10.1016/j.jhazmat.2009.07.109>.
- [7] Shafiq P, Bin Mahmud H, Jumaat MZ, Zargar M. Agricultural wastes as aggregate in concrete mixtures- a review. *Constr Build Mater* 2014; 53: 110-117. <https://doi.org/10.1016/j.conbuildmat.2013.11.074>.
- [8] Cordeiro GC, Kurtis KE. Effect of processing on sugar cane bagasse ash pozzolanicity. *Cem Concr Res* 2017; 97: 41-49. <https://doi.org/10.1016/j.cemconres.2017.03.008>.
- [9] Bahurudeen A, Kanraj D, V.Gokul Dev, Santhanam M. Performance evaluation of sugarcane bagasse ash blended cement in concrete. *Cem Concr Compos* 2015; 59: 77-88. <https://doi.org/10.1016/j.cemconcomp.2015.03.004>.
- [10] Wansom S, Janjaturaphan S, Sinthupinyo S. Characterizing pozzolanic activity of rice husk ash by impedance spectroscopy. *Cem Concr Res* 2010; 40(12): 1714-1722. <https://doi.org/10.1016/j.cemconres.2010.08.013>.
- [11] Tuan NV, Ye G, van Breugel K, Copuroglu O. Hydration and microstructure of ultra-high-performance concrete incorporating rice husk ash. *Cem Concr Res* 2011; 41(11): 1104-1111. <https://doi.org/10.1016/j.cemconres.2011.06.009>.
- [12] Feng QG, Yamamichi H, Shoya M, Sugita S. Study on the pozzolanic properties of rice husk ash by hydrochloric acid pretreatment. *Cem Concr Res* 2004; 34(3): 521-526. <https://doi.org/10.1016/j.cemconres.2003.09.005>.
- [13] Ganesan K, Rajagopal K, Thangavel K. Rice husk ash blended cement: assessment of optimal level of replacement for strength and permeability properties of concrete. *Constr Build Mater* 2008; 22: 1675-1683. <https://doi.org/10.1016/j.conbuildmat.2007.06.011>.
- [14] Berodier E, Scrivener K. Evolution of the pore structure in blended systems. *Cem Concr Res* 2015; 73: 25-35. <https://doi.org/10.1016/j.cemconres.2015.02.025>.
- [15] Cabrera M, Galvin AP, Agrela F, Carvajal MD, Ayuso J. Characterization and technical feasibility of using bottom ash for civil infrastructures. *Constr Build Mater* 2014; 58: 232-244. <https://doi.org/10.1016/j.conbuildmat.2014.01.087>.
- [16] Vance K, Kumar A, Sant G, Neithalath N. The rheological properties of ternary binders containing Portland cement, limestone, and metakaolin or fly ash. *Cem Concr Res* 2013; 52: 196-207. <https://doi.org/10.1016/j.cemconres.2013.07.007>.
- [17] Derabla R, Benmalek M.L. Characterization of heat-treated self-compacting concrete containing mineral admixtures at early age and in the long term. *Constr Build Mater* 2014; 66: 787-794. <https://doi.org/10.1016/j.conbuildmat.2014.06.029>.
- [18] Jiao DW, Shi CJ, Yuan Q, An XP, Liu Y, Li H. Effect of constituents on rheological properties of fresh concrete-a review. *Cem Concr Compos* 2017; 83: 146-159. <https://doi.org/10.1016/j.cemconcomp.2017.07.016>.
- [19] Demirhan S, Turk K, Ulugerger K. Fresh and hardened properties of self-consolidating Portland limestone cement mortars: Effect of high-volume limestone powder replaced by cement. *Constr Build Mater* 2019; 196: 115-125. <https://doi.org/10.1016/j.conbuildmat.2018.11.111>.
- [20] Bentz DP, Irassar EF, Bucher BE, Weiss WJ. Limestone fillers conserve cement; Part 1: an analysis based on Powers' model. *Concr Int* 2009; 31(11): 41-46.
- [21] Gonzalez MA, Irassar EF. Effect of limestone filler on the sulfate resistance of low C3A Portland cement.

- Cem Concr Res 1998; 28(11): 1655-1667. [https://doi.org/10.1016/S0008-8846\(98\)00144-6](https://doi.org/10.1016/S0008-8846(98)00144-6).
- [22] Kurtis KE, Kahn LF, Shalan A, Zaribaf B, Nadelman E. Assessment of Limestone Blended Cements for Transportation Applications. Office of Research 2017; p 265. <https://rosap.nrl.bts.gov/view/dot/32794>.
- [23] Standards of Canada. Cementitious Materials Compendium (CSA A3000-13). Toronto:Canadian Standards Association. 2013.
- [24] Cardoso FA, Fujii A, Pileggi RG, Chaouche M. Parallel-plate rotational rheometry of cement paste: Influence of squeeze velocity during gap positioning. *Cem Concr Res* 2015; 75: 66-74. <https://doi.org/10.1016/j.cemconres.2015.04.010>.
- [25] Standards of PA. Standard Test Method for Amount of Water Required for Normal Consistency of Hydraulic Cement Paste (ASTM C187-16). PA: West Conshohocken: ASTM International. 2016.
- [26] Standards of PA. Standard Practice for Making and Curing Concrete Test Specimens in the Laboratory (ASTM C192 / C192M-19). PA: West Conshohocken: ASTM International. 2019.
- [27] Teixeira ER, Camoes A, Branco FG, Aguiar JB, Fangueiro R. Recycling of biomass and coal fly ash as cement replacement material and its effect on hydration and carbonation of concrete. *J Waste Management* 2019; 94: 39-48. <https://doi.org/10.1016/j.wasman.2019.05.044>.
- [28] Pane I, Hansen W. Investigation of blended cement hydration by isothermal calorimetry and thermal analysis. *Cem and Concr Res* 2005; 35: 1155-1164. <https://doi.org/10.1016/j.cemconres.2004.10.027>.
- [29] Anjos MAS, Reis R, Camoes A, Duarte F, Jesus C. Evaluation of hydration of cement pastes containing high volume of mineral additions. *Eur J Environ Civ Eng* 2019; 23(8): 987-1002. <https://doi.org/10.1080/19648189.2017.1327892>.
- [30] Lee NK, Lee HK. Reactivity and reaction products of alkali-activated, fly ash/slag paste. *Constr Build Mater* 2015; 81: 303-312. <https://doi.org/10.1016/j.conbuildmat.2015.02.022>.
- [31] Zheng DP, Wang DM, Li DL, Ren CF, Tang WC. Study of high volume circulating fluidized bed fly ash on rheological properties of the resulting cement paste. *Constr Build Mater* 2017; 135: 86-93. <https://doi.org/10.1016/j.conbuildmat.2016.12.127>.
- [32] Skripkiunas G, Macijauskas M, Nagrockiene D. The influence of biomass fly ash on the plasticizing effects in cement pastes. *Proc Eng* 2017; 172: 1015-1022. <https://doi.org/10.1016/j.proeng.2017.02.152>.
- [33] Genovese DB. Shear rheology of hard-sphere, dispersed, and aggregated suspensions, and filler-matrix composites. *Adv Colloid Interface Sci* 2012; 171: 1-16. <https://doi.org/10.1016/j.cis.2011.12.005>.
- [34] Li D, Wang D, Ren C, Rui Y. Investigation of rheological properties of fresh cement paste containing ultrafine circulating fluidized bed fly ash. *Constr Build Mater* 2018; 188: 1007-1013. <https://doi.org/10.1016/j.conbuildmat.2018.07.186>.