Influence of Agricultural Residue Ash on Early Cement Hydration and Chemical Admixtures Adsorption

Feraidon F. Ataie and Kyle A. Riding

Corresponding author's email: fataie@csuchico.edu

Abstract:

This study investigated impacts of internal surface area of wheat straw ash (WSA) and rice straw ash (RSA) on cement early hydration as well as on chemical admixture adsorption in cementitious systems. Results were compared to those of silica fume. Hydration kinetics and mortar strength experiments showed RSA and WSA to have similar reactivity to silica fume. High surface areas of WSA and RSA did not increase early hydration as compared to silica fume. However, high surface areas of WSA and RSA dramatically increased their adsorption capacity of air entraining agents and retarders compared to silica fume.

1. Introduction:

Supplementary cementitious materials (SCMs) particularly industrial by-products such as fly ash, silica fume, and slag, are widely used to partially replace portland cement in concrete to reduce carbon footprint and increase quality of concrete. However, these materials are not available in large quantities at a low cost uniformly around the world. Natural SCMs such as agricultural residue ash (ARA) are gaining more attention for use as SCMs because of their low cost, wide availability, and excellent reactivity in concrete. Every year, millions of tonnes of agricultural residues such as corn stover, wheat straw, and rice straw are produced worldwide [1]. Some biofuel plants are beginning to produce thousand tonnes of biomass waste material that would otherwise be landfilled. After burning, the ash is very friable and requires only minimal energy to grind [2]. Therefore, agricultural residues are renewable and sustainable resources for ARA production for concrete use. Because ARAs, such as Rice Straw Ash (RSA) and Wheat Straw Ash (WSA), can be produced at low cost, they are of great interest to the concrete industry, especially in developing regions.

Chemical and physical properties of ARA depend on the type of agricultural residue. This is because each of agricultural residues, such as rice straw, wheat straw, and corn stover, has different composition. The composition of agricultural residues greatly affects the burning sensitivity of ARA, and influences the suitability of ARA for use in concrete [2] [3] [4]. However, variability of ARAs and their sensitivity to burning conditions can greatly be reduced by using pretreatment techniques, such as dilute acid pretreatment [2] [3]. Using pretreatment methods, ARA can be made with a high surface area and high amorphous silica content, making them highly reactive pozzolanic materials [2] [5] [3] [6] [7]. More research is needed to study whether pretreatment techniques are economically as well as environmentally feasible for SCMs

production or not. However, biofuel industry produces a lignocellulosic waste product that is equivalent to pretreated agricultural residues; authors have shown that the waste product could be used to produce highly reactive SCMs without any pretreatment [2].

It has been shown that pretreated WSA and RSA have enhanced pozzolanic reaction [3]. The pozzolanic reaction is the reaction between a siliceous material and calcium hydroxide (CH) under water to form a cementitious material, as shown in Eq. 1 ([8])

Note: Oxide notation is used throughout this paper, C = CaO, S = SiO₂, H=H₂O, A = Al₂O₃, F=Fe₂O₃.

The pozzolanic reaction is known to be affected by many factors such as mineralogy, surface area, and carbon content of the pozzolanic materials. Being one of the most reactive pozzolanic materials, silica fume has high amorphous silica content and relatively high surface area. Surface area and amorphous silica content are the two most influential factors in pozzolanic reaction. Surface area of SCMs has a major impact on the reaction rate. Surface area provides nucleation sites for calcium silicate hydrate (C-S-H) precipitation which plays an essential role in the hydration process of cementitious systems [9]. However, an increase in surface area of SCMs could increase adsorption of chemical admixtures, such as air entraining agents (AEAs) and superplasticizers [10] [11] [12]. Using foam index method, Ley et al. [10] suggested that as the surface area of fly ash samples increases the demand of concrete containing fly ash to AEA becomes higher.

Authors have published other publications focusing on methods and techniques to enhanced pozzolanic reactivity of ARAs, namely WSA, and RSA [2, 3, 4]. This study, however, emphasizes on the impact(s) of ARAs properties, particularly their surface area, on concrete chemical admixtures. Although ARAs, particularly WSA and RSA, can have similar chemical

compositions to those of the silica fume, they can have higher surface area than silica fume [3]. Contrarily to the relatively spherical particle shapes found with silica fume, ARAs contain porous and irregularly shaped particles. The high surface area of ARAs has been attributed to their internal porosity [7]. Because most of the ARAs surface area is attributed to their internal porosity, the ability of ARAs in adsorbing chemical admixtures in cementitious systems has not been established yet. Furthermore, the impact of internal surface area on the early cement hydration has not been investigated yet. The impact of internal surface area on the cement hydration and adsorption could be different than that of the external surface area. Internal porosities of ARAs, as reactive pozzolanic materials with high amorphous silica content, could be blocked by hydration products. It is also possible that dissolution of ARAs in cementitious system will rapidly reduce their surface area. Both of these phenomena, blockage and dissolution of surface area, could reduce ARAs pozzolanic reaction rate and ability to adsorb chemical admixtures in cementitious systems.

This study aimed to investigate the impact of ARA surface area on the early cement hydration and on the adsorption of chemical admixtures in cementitious systems. WSA and RSA with high surface area and amorphous content was produced. Additionally, because WSA and RSA had similar chemical compositions to that of silica fume, an undensified silica fume sample was selected for comparison. Undensified silica fume rather than densified silica fume was selected to provide improved dispersion. Pozzolanic behavior of WSA, RSA, and silica fume was determined by measuring the impact of each material on heat of hydration, calcium hydroxide (CH) consumption, and chemical shrinkage of paste samples, and compressive strength of mortar cubes. The Chappelle test [13] was also used as an index test for material

pozzolanic reactivity with calcium hydroxide solution. WSA and RSA adsorption capacity of chemical admixtures was tested on air entraining agents and cement hydration retarders.

2. Materials and methods:

2.1. Materials:

An ASTM C 150 [14] Type I portland cement and undensified silica fume were used in this study. Cement and silica fume chemical and physical properties are shown in Table 1 and Table 2, respectively. Standard graded sand [15] was used for the mortar experiments. Wheat straw (WS) was purchased from a local farm in Manhattan, Kansas, and rice straw (RS) was obtained from Missouri Rice Research Farm, Glennonville, Missouri. A reagent grade HCl was obtained and diluted to 0.1 N for use in the study. Reagent grade calcium oxide (CaO) and ACS grade zinc oxide were used for Chappelle test and Rietveld analysis, respectively. A high-grade saponified rosin air entraining admixture was used. An aqueous solution of hydroxylated organic compounds was employed as cement hydration retarder.

2.2. Methods:

2.2.1. Biomass ash preparation:

It has been shown that removal of alkalis and organic compounds from biomass prior to burning (ashing) can dramatically enhance pozzolanic properties of biomass ash [2] [3]. In this study, the biomass (wheat straw and rice straw) was pretreated with 0.1N HCl at 80°C to remove impurities from biomass in order to produce WSA and RSA with high amorphous content, high surface area, and low loss on ignition (LOI). To pretreat the biomass, 250 g of biomass (rice straw or wheat straw) was immersed in 3100±100 mL of 0.1N HCl solution in a 4000 mL glass jar. The sample was stored undisturbed at a constant temperature of 80°C for 24 hrs. The biomass was then rinsed twice, each time with 2500 mL of distilled water, and dried at 80°C in an oven.

To prepare the ash (WSA or RSA), a programmable electric muffle furnace was used to heat the biomass. 200 g of dried biomass was ashed in each batch. A stainless steel cage with two wire mesh shelves was used to hold the biomass during burning, and a stainless steel pan was placed below the cage to catch any ash that fell through the mesh. It took the furnace an hour to reach to 650°C and almost 6 hours to cool down to room temperature. It is worth mentioning that the biomass was first placed in the furnace and then the furnace was turned on. Finally, the ash was ground for one hour at 85 revolutions per minute (rpm) in a laboratory ball mill. WSA was prepared by burning the pretreated wheat straw at 650°C for one hour and was called (WSA650). Two types of RSA were prepared. (RSA650) was obtained by burning pretreated rice straw at 650°C for one hour, and (RSA500) was prepared by burning pretreated rice straw at 500°C for two hours. Properties of WSA and RSA are shown in Table 2.

2.2.2. Silica fume and biomass ash characterization:

Physical and chemical characteristics (such as particle size, surface area, and amorphous content) of SCMs affect their behavior in cementitious systems. Particle size and surface area are influential factors on early pozzolanic reaction of SCMs [9]. Beside packing effect, particle size distribution influences the pozzolanic reaction; the finer the particle size of SCMs, the faster their pozzolanic reaction [16]. Surface area has been shown to largely impact the pozzolanic reaction of SCMs. An increase in surface area could enhance the pozzolanic reaction; it also increases the potential of chemical admixture absorption [10]. It is also well established that an increase in amorphous silica content is associated with an increase in pozzolanic reaction.

In this study, particle-size distribution silica fume, WSA, and RSA samples were determined using a laser diffractometer. Ultrasonic waves were used to disperse the particles in an isopropanol suspension during the laser diffraction particle size measurements. Surface area

was measured using BET nitrogen adsorption. LOI was determined by measuring mass loss after heating one gram of dry materials (SF, WSA or RSA) to 900°C for three hrs. Chemical composition of ash samples and silica fume was determined using x-ray fluorescence (XRF). Secondary electron images of selected ash samples were taken using Scanning Electron Microscopy (SEM). Ash samples were carbon coated to reduce surface charging during imaging process to improve quality of images.

To determine crystalline phases of the materials, x-ray diffraction (XRD) analysis was performed (Cu K α radiation with $\lambda=1.5046\text{\AA}$). A step size of $0.02^\circ 2\theta /4\text{s}$ and a scan range of $5^\circ-70^\circ 2\theta$ was used. The Rietveld analysis [17] [18] [19] was performed to obtain the amorphous content of the WSA, RSA, and silica fume. Sample preparation for Rietveld refinement analysis included mixing 1.8g of SCM with 0.2 g of zinc oxide as an internal standard in ethanol to create a slurry. This was followed by hand grinding in a ceramic mortar for approximately two min., followed by drying in a fume hood for 20 min. The Rietveld algorithm optimizes the model function by minimizing the weighted sum of squared difference between observed and computed intensity values [20]. The refinement process of each SCM sample was evaluated with R-factor refinement criteria, including R-pattern (Rp), R-weighted pattern (Rwp) and R-expected (Rexp) [21]. A commercial software was used to perform the Rietveld refinement until the best fit was obtained.

2.2.3. Pozzolanic reactivity measurements:

Several experimental procedures, such as heat of hydration, chemical shrinkage, and calcium hydroxide consumption measurements, have been used to determine the pozzolanicity of SCMs [9] [22] [23]. Reactive SCMs when added to cementitious systems increase heat of hydration and chemical shrinkage of cementitious systems [24]. However, pozzolanic reaction

between SCMs and cementitious systems reduces the CH content of the system based on Eq.1. In this study pozzolanic reactivity of WSA, RSA, and silica fume was measured by several experimental methods.

Chapelle test [13] was used to determine pozzolanic reactivity of the SCMs by measuring the calcium hydroxide consumption by SCMs in a calcium hydroxide solution. The Chapelle test is a French standard (NF P18-513) [13] and has been used to measure pozzolanic properties of SCMs [22] [25] [26]. In this test, 2 g of calcium oxide was mixed with 1 g of SCM sample in 250 mL of deionized water in a 500 mL Erlenmeyer glass flask. The flask was placed on a stirring–heating plate for 16 hrs at 90°C. At the end of 16 hrs, the slurry was cooled to 23°C by placing the flask in cold water. 60 g of sucrose was mixed with 250 ml of deionized water, added to the slurry, and stirred for 15 min. The resulting solution was filtered through a 1.1 µm diameter filter paper. Five drops of 0.1% phenolphthalein and 25 mL of filtrate were then titrated with 0.1N HCl. The total volume of 0.1N HCl solution needed for titration was recorded as V_b for the blank sample (no WSA, RSA, or silica fume added) and V_m for samples containing SCMs (WSA, RSA, and silica fume). Titration results were then used to determine the amount of calcium hydroxide (mg) fixed by the pozzolanic materials using Equation 1:

$$Ca(OH)_2 \text{ fixed} = 2 \frac{(V_b - V_m)}{V_b} \frac{74}{56} 1000 \quad \text{Eq. 1}$$

Pozzolanic reactivity was also determined by measuring the heat of hydration of cement paste samples containing SCM (WSA, RSA, or silica fume). 10% cement by weight was replaced with WSA, RSA, or silica fume when used. A 0.45 water-cementitious material ratio (w/cm) was used. Paste samples were mixed with a vertical laboratory mixer [27]. Distilled water was added to the cementitious material and mixed at 500 rpm for 90 seconds, followed by

a 120 second rest period, and then mixed at 2000 rpm for 120 seconds. Paste samples of approximately 30 g each were used in an eight-channel isothermal calorimeter at 23°C.

Calcium hydroxide (CH) content of paste samples was measured at various ages to determine CH reduction by the pozzolanic reaction. To obtain CH content of paste samples, samples were cast in 11 ml polystyrene vials. Hydration was stopped at 7, 28, and 90 days of hydration by means of solvent exchange with isopropanol. Samples approximately 2mm thick were cut and placed in isopropanol for seven days. After this period, the samples were dried in a vacuum for at least three days. CH content was measured using a thermogravimetric analyzer (TGA) to heat the dried samples at 20°C/min up to 800°C in a nitrogen environment [28].

Chemical shrinkage has also been used to determine the pozzolanicity of SCMs [24]. The chemical shrinkage is the total shrinkage resulting from hydration process in paste sample. The chemical shrinkage happens because the volume of reactants (cement and water) is less than the volume occupied by the hydration products [24]. The chemical shrinkage of paste samples were measured in accordance with procedure A of ASTM C1608. Approximately 6 g of paste sample was cast in a 26 ml polystyrene vial. The vial was then filled with water. A capillary tube was inserted through the center of a rubber stopper, and the stopper was then inserted into the vial. The capillary tube was partially filled by distilled water, and a few drops of red oil were added in the tube. The decrease in water level in the tube was monitored by taking pictures with an automatic webcam. The images taken were then analyzed using Shrinkage Suite developed by Bishnoi [29]. The average of three replicate samples was used for chemical shrinkage results.

Mortar cube compressive strength was also measured to determine the impact of SCMs on compressive strength. This test was performed according to ASTM C 109 [30] with a sand to cementitious material ratio of 2.75. To keep the w/cm of paste and mortar samples identical,

w/cm for all mortar samples was also 0.45. WSA, RSA, or silica fume was used at 10% replacement level by mass of cement. Mortar cube compressive strength was tested at 7, 28, and 91 days with results reported as the average of three mortar cubes.

2.2.4. Foam Index (FI) test:

The foam index test has been used to determine AEA adsorption by fly ash and other supplementary cementitious materials (SCMs) in cementitious systems [10] [31]. The test measures AEA adsorption in cementitious slurry and determines the amount of AEA needed to stabilize the foam layer at the top surface of the slurry. In this study, an ASTM sand equivalent shaker was used to ensure consistent shaking from sample to sample [32]. Ten gram of SCM (ash or silica fume) was mixed in 20 mL of deionized water in a 50 mL plastic centrifuge tube. The tube had a height of 115 mm and a diameter of 27 mm. The tube was shaken for 30 sec, followed by a 30-second rest period. Twenty μ l of 5% air-entraining agent solution was added to the mixture, and the mixture was shaken for 10 sec. The tube was left undisturbed for 15 seconds. A shaking speed of 172 cycles per min was used. At this time, if a stable foam layer at the water-air interface was observed, the volume of AEA was recorded as the foam index. If, however, a stable foam layer was absent, another 20 μ l of 5% AEA solution was added and the procedure continued until a stable foam layer was reached and recorded. To determine the impact of ash samples on the foam index, 5%, 10%, or 20%, of the cement was replaced by the ash with a constant water volume.

2.2.5. Retardation measurements:

Calorimetry experiments were conducted to see the potential impact of nucleation site seeding from the high surface area SCMs on retardation effects from retarder use. To measure the impact of WSA, RSA, and silica fume on retardation, two different cement replacement

levels of 5% and 10% were used. Paste samples of approximately 30 g each were used in an eight-channel isothermal calorimeter at 23°C to measure heat of hydration. An aqueous solution of hydroxylated organic compounds was used as the retarder with a dosage of 200ml/100 kg of cement.

3. Results and Discussion:

3.1. Materials characteristics:

Particle size distribution of cement (OPC), WSA, RSA, and silica fume samples is shown in Fig. 1. In spite of the use of undensified silica fume and ultrasonic dispersion, large particle sizes were seen in the particle size distribution. This could be because of agglomeration of silica fume particles or because the majority of silica fume particles were smaller than the size detectable by the instrument. Chemical and physical properties of WSA-650, RSA-650, RSA-500, and silica fume are shown in Table 2. All ash samples (WSA-650, RSA-650, and RSA-500) had similar chemical composition. Silica (SiO_2) content of silica fume was approximately 10% higher compared to ash samples; however, CaO content of ash samples was approximately 9% higher than that of silica fume which contains very little CaO. The ash samples had much higher surface area than silica fume. Among the ash samples, WSA-650 had the lowest ($65 \text{ m}^2/\text{g}$) surface area, and RSA-500 had the highest ($200 \text{ m}^2/\text{g}$) surface area which was more than 20 times larger than that of the silica fume. This could be attributed to the internal porosity of ash samples as shown in Fig. 2.

The XRD data for WSA-650, RSA-650, RSA-500, and silica fume samples are shown in Fig. 3. WSA-650 showed very low crystalline phases, similar to silica fume. RSA-650- and RSA-500 showed some crystalline quartz. Table 3 shows Rietveld refinement results. The RSA

samples had the lowest amorphous content, whereas the WSA sample was made up of over 99% amorphous content, practically like silica fume.

3.2. Chappelle test:

Results from the Chappelle test showed that SCMs used were pozzolanic because the amount of CH fixed by each SCM was higher than 800 mg [25]. Silica fume fixed/consumed more CH than ash samples, as shown in Fig. 4. Silica fume fixed 18.8% more CH than what was fixed by the RSA-650 sample. The high surface area of ash samples did not appear to increase CH fixation during the Chappelle test. This result is in agreement with what Cordeiro and Sales [25] have shown. This is most likely because the high temperature and alkalinity in the Chappelle test provides only an index of the total potential reactive material in the SCM rather than the reactivity kinetics of the SCM. The accuracy of the Chappelle test in determining the pozzolanic reactivity of materials is also limited because of the extreme conditions in the test and because the pozzolanic reaction in cementitious systems is more complex than that provided by the test solution. This is evidenced by the crystalline quartz results which fixed 202 mg of CH in the Chappelle test.

3.3. Reaction Kinetics

Silica fume and ash samples increased the heat of hydration produced by cement, as illustrated in Fig. 5. Ash samples (WSA-650, RSA-650 and RSA-500) and silica fume shortened the induction period, possibly because of the high surface area of samples that can act as nucleation sites, thus accelerating the hydration [9] [33]. Peaks from silicate and aluminate hydration were slightly larger for samples containing silica fume than those containing ash samples. However, cement paste samples containing WSA or RSA showed similar total heat of hydration to silica fume containing sample.

Chemical shrinkage per gram of dry cement is also a measure of the paste reaction kinetics complementary to isothermal calorimetry, shown for the paste samples experiments in Fig. 6. Samples containing SCMs (RSA-650, RSA-500, WSA-650, and silica fume) had higher chemical shrinkage, per gram of dry cement, as compared to control (OPC) samples. However, paste samples containing SCMs showed similar chemical shrinkage to each other.

Calcium hydroxide (CH) of cement paste samples at different ages is shown in Fig. 7. The OPC mixture has the highest CH content as expected. At three and seven days, the CH content of paste samples containing ash samples (OPC+WSA650, OPC+RSA650, and OPC+RSA500) was slightly lower than those containing silica fume, whereas for the rest of the hydration period (28, 91, and 180 days) the CH content of silica fume containing paste samples was lower than those containing ash samples.

3.4. Compressive strength:

Compressive strength data for mortar samples is shown in Fig. 8. At a given age, samples containing either RSA or silica fume had higher compressive strength than control (OPC) samples. At a given age, compressive strength of samples containing RSA was similar to those containing silica fume. High surface area of RSA samples did not significantly increase early compressive strength of mortar samples containing RSA since the compressive strength result differences were within the margin of error.

3.5. Adsorption of air entraining agents:

Results of foam index test are shown in Fig. 9. Results are shown based on non-diluted AEA. As it can be seen, RSA and WSA samples had higher foam index values compared to that of silica fume. At a 5% replacement level, sample containing RSA-500 required 2.75 μl of AEA whereas the sample containing silica fume needed 1.5 μl of AEA to form a stable foam layer.

The increased AEA adsorption by WSA and RSA samples could be associated to their higher surface areas than that of the silica fume. As it can be seen in Fig. 2, the high surface area of ash samples is because of their internal porosities. However, AEA requirements of SCMs not only depend on the surface area but also on the amount of SCMs used (Fig. 9). The higher the amount of SCMs, the lower is the AEA requirement per gram of SCMs. Therefore, the surface area of SCM is not the only factor that affects AEA dosage requirement. The extent of pozzolanic reaction could also affect the AEA adsorption in cementitious systems.

3.6. Impact of ash samples on retarders:

Isothermal heat of hydration of cement paste showed that for the retarder dosage used, samples containing WSA, RSA, or silica fume reduced retardation compared to control samples (OPC). Retarded samples containing 10% RSA (RSA650 or RSA500) showed similar induction period to the control sample without retarder, as it can be seen in Fig. 10a. Comparing Fig. 10a and Fig. 10b, it can be said that a reduction in SCM content was associated with an increase in retardation. Samples containing 5% of RSA650 showed a 2.75 hr. retardation while samples without SCM had 5.32 hr. retardation. At the retarder dosage used (200ml/100 kg of cement), samples containing silica fume showed higher retardation compared to those containing either WSA650 or RSA (RSA500 and RSA650). This could be attributed to lower surface area of silica fume compared to that of the ash samples.

3.7. Final Discussion:

WSA and RSA showed similar pozzolanic behavior to that of the silica fume. Although SCMs with high surface area are believed to increase early reaction of cementitious systems, the higher surface area of WSA and RSA did not increase the early hydration because paste samples containing WSA and RSA revealed similar induction periods and total heat of hydration when

316 compared to silica fume. This result could be because surface area of WSA and RSA was not
317 available for C-S-H precipitation. Availability of surface area of ash in cement hydration could
318 be limited by various factors. Ash samples are not spherical and have complex shape and
319 structure [7]. Consequently, dissolution of small amounts of silica from ash may dramatically
320 reduce the surface area. This could mean that the very high surface area provided by RSA and
321 WSA could affect setting by providing additional nucleation sites, but may decrease in
322 effectiveness in increasing hydration with time. It is also possible that availability of surface area
323 is less in WSA and RSA because internal pores can be diffusion controlled. Pozzolanic reactivity
324 of WSA and RSA will also be affected by reactivity of their silica phase. In addition, if carbon
325 and potassium or other impurities precipitate on the surface of ash [3], it could prevent the
326 surface area from participating in the nucleation process of calcium silicate hydrate. Besides
327 limited surface area availability of ash samples for pozzolanic reaction, silica fume could provide
328 enough surface area for the nucleation process. These factors effectively result in similar strength
329 performance for ash samples to silica fume, even though the ash samples have higher surface
330 areas. The surface area did seem to increase the pozzolanic reactivity of the WSA and RSA
331 before 7 days as measured by CH consumption. The silica fume showed however lower CH
332 content at later ages, possibly owing to the higher amorphous silica content of the silica fume.
333 This higher CH consumption of the silica fume than the RSA and WSA was not reflected in later
334 age strengths. It is possible that the higher CH consumption could reduce water absorption or
335 other transport properties, however these measurements were beyond the scope of this study.

336 It was noticed in the mortar experiments that the workability of the mixtures containing
337 RSA and WSA was reduced substantially. This is because of the angular particles and high

internal surface area of the particles that would trap water. Detailed measurements of the workability were however beyond the scope of this study.

Larger silicate and aluminate hydration peaks and higher early age (3 and 7 days) CH content of paste samples containing silica fume, as compared to those containing WSA or RSA could be attributed to water sorption by ash samples. WSA and RSA could have higher sorption capacity than silica fume because of higher internal porosity and surface area. Sorption of water by WSA and RSA reduces available water for cement reaction, thus reducing CH content of paste samples. Water encased in pores within ash samples is available for hydration once a demand is presented. Availability of water at later ages could be the cause of high CH content of samples containing WSA and RSA after 28 days of hydration, as shown in Fig. 7.

The analogy of water sorption by WSA and RSA samples could also be applied to chemical admixtures or dissolved Ca. The increase in foam index for samples containing WSA or RSA, as shown in Fig. 9, could be because of adsorption of AEA on the surfaces of WSA and RSA. Besides surface area, it has been postulated that unburned carbon content of SCM can also impact AEA adsorption [10]. However, results revealed that there is no correlation between LOI and foam index, as shown in Fig. 11. The ash sample with the highest surface area had the highest foam index while the silica fume mixture had the lowest surface area and the lowest foam index (Fig. 11). At 10% cement replacement level, there was a good correlation between surface area and foam index (Fig. 11a). However, at 20% cement replacement level, the correlation between surface area and foam index became poor (Fig. 11b). Therefore, it can be said that AEA adsorption capacity of SCMs not only depends on their surface areas and LOI, but also on the type of surface area, surface charging, and availability of the surface area for AEA adsorption.

Several mechanisms have been proposed on the influence of retarders on cement hydration [34]. One mechanism, though, is the adsorption of retarders onto the unhydrated silicates and aluminates surfaces. This reduces the dissolution of silicates and aluminates and lowering nucleation sites for calcium-silicate-hydrate (C-S-H) precipitation. Therefore it can be said that the dramatic reduction in retardation in samples containing WSA or RSA, as shown in Fig. 10, is because of adsorption of retarders onto the surface area of ash samples. A small increase in slow-reaction period for samples containing WSA or RSA can be attributed to the adsorption of small amount of chemicals onto the surface of cement grains. Thus, for concrete containing SCM with high surface area, such as WSA and RSA, it is important to adjust the AEA dosage accordingly.

4. Conclusions:

Influences of dilute acid pretreated wheat straw ash (WSA) and rice straw ash (RSA) prepared at either 650°C or 500°C in the laboratory on early hydration behavior as well as on chemical admixtures were studied. Results were compared to those of silica fume. Results showed that although WSA and RSA samples had much higher surface area than silica fume, pozzolanic reactivity of all samples was similar. Cement paste samples containing 10% silica fume showed similar heat of hydration, chemical shrinkage, and calcium hydroxide (CH) content to those containing 10% WSA or RSA. Additionally, at a given age of hydration, mortar samples containing 10% silica fume and those containing 10% RSA had similar compressive strength, showing that the high surface area of WSA and RSA samples had negligible influence on the early pozzolanic reactivity. This shows that it is not just the surface area of amorphous silica but also availability of surface area that can be affected by shape and composition of SCMs that controls early cement reaction. Results suggested that WSA and RSA samples had much higher

adsorption capacity of air entraining agents and retarders compared to silica fume. This was mainly because of high surface area of WSA and RSA. Thus, WSA and RSA could dramatically reduce the effectiveness of these chemical admixtures in concrete.

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Table 1: Cement properties

Chemical Composition (%)		Bogue compounds (%)	
SiO ₂	19.36	C3S	62.76
Al ₂ O ₃	5.13	C2S	8.16
Fe ₂ O ₃	2.53	C3A	9.31
CaO	63.17	C4AF	7.70
MgO	1.03		
K ₂ O	0.88		
Na ₂ O	0.086		
SO ₃	3.22		

Table 2: SCM properties

Sample ID	Chemical compositions (%)							BET surface area (m ² /g)	LOI (%)
	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	K ₂ O	Na ₂ O		
WSA650	86.5	0.28	1.13	9.73	0.78	1.54	0.1	65	1.2
RSA650	88.2	0.47	0.74	9.48	0.56	0.31	0.17	134	0.8
RSA500	85.7	1.4	1.02	10.73	0.6	0.34	0.23	200	2.2
Silica Fume (SF)	96.96	0.13	0.05	0.43	0.96	0.38	0.08	8.9	1.6

Table 3: Rietveld refinement data

Minerals	RSA-650	RSA-500	WSA-650	SF
Quartz (mass %)	4.2	11.8	0.7	0.1
Amorphous (mass %)	95.8	88.2	99.3	99.9

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