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Thermochemical Pretreatments for Agricultural Residue Ash Production for Concrete

Feraidon F. Ataie[1] and Kyle A. Riding[1]

Abstract:

Agricultural residue ash is known to be a very reactive source of supplementary cementitious material (SCM) for use in concrete. The influence of thermochemical pretreatments on the reactivity of agricultural residue ash (ARA) for use as an SCM was studied. It was shown that pretreatments are effective in partial removal of alkali metals and other impurities out of both wheat straw and rice straw leading to ARA with lower loss on ignition (LOI), higher internal surface area, and higher amorphous silica content than that of unpretreated ARA. It was shown that the ash alkali content correlated with the ash LOI and amorphous silica content. When used at a cement replacement rate of 20% by mass, pretreated ARA accelerated the hydration of cement paste samples while unpretreated ARA retarded the cement hydration. Pretreatments were found to increase ARA reactivity as measured by calcium hydroxide content reduction with time. ARA increased compressive strength of mortar samples by 25% when used as 20% replacement of cement in the samples. It was found that the calcium hydroxide content of paste samples and mortar compressive strength were correlated to the amorphous silica content of the ash.

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Introduction:

The use of supplementary cementitious material (SCM) can reduce the energy and CO_2 intensity of concrete. Natural SCMs have received increasing interest because of their high reactivity, low cost, and availability in some regions where other SCMs are not available. Agricultural residue ash (ARA) such as rice husk ash (RHA) and sugarcane bagasse ash have been championed as SCMs that can greatly enhance strength and durability of concrete (Salas, et al. 2009; Feng, et al. 2004; Nair, et al. 2006; Cordeiro, et al. 2006; Agarwal 2006; Tuan, et al. 2011; Sales and Sofia 2010). Other agro-biomass such as wheat straw (WS) and rice straw (RS) could be a potential source for SCMs with similar pozzolanic reactivity to RHA. 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(Wanson, et al. 2009).

$$CH + S + H \rightarrow CSH \qquad \text{Eq. 1}$$

Note: Oxide notation is used throughout this paper, C = CaO, S = SiO_2, H=H_2O, A = Al_2O_3, F=Fe_2O_3.

The pozzolanic reaction kinetics is known to be affected by many factors such as ash mineralogy, surface area, and carbon content of the pozzolanic materials (Feng, et al. 2004; Wanson, et al. 2010).

Agro-biomass pretreatment processes can enhance ARA reactivity for use in concrete. Thermochemical pretreatment techniques, such as dilute acid, have been shown to improve pozzolanic reactivity by increasing surface area and amorphous silica content and decreasing carbon content of RHA (Feng, et al. 2004; Wanson, et al. 2009; Chandrasekhar, et al. 2006). In the biofuel industry, thermochemical pretreatment of lignocellulosic biomass has proven to be very effective hydrolysis process for ethanol production (Zheng, et al. 2009; Saha, et al. 2005; Kristensen, et al. 2008; Mosier, et al. 2005). The dilute acid pretreatments are effective in

removal of some hemicellulose; breakdown, re-localization, and structure change of lignin; and defibration/decrystallization of cellulose of the biomass cell wall. Pretreatment of agro-biomass has been shown to improve combustion properties of biomass for use as a fuel as a result of leaching impurities such as Na, K, Ca, and Mg (Jenkins, et al. 2003). These metals decrease the biomass melting temperature and promote the release of unwanted byproducts during combustion (Jenkins, et al. 2003).

The pozzolanic properties of rice straw ash (RSA) and wheat straw ash (WSA) have been examined by only a few researchers. WSA that has not been pretreated has been found to be pozzolanically reactive when burned at 570 ^{o}C and 670 ^{o}C for 5 hours (Biricik et al. 1999). Al-Akhras and Abu-Alfoul (2002) have reported that mechanical properties of autoclaved mortar specimens were improved with by WSA made by burning wheat straw at 650 ^{o}C for 20 hrs. RSA has been shown to improve mechanical properties of mortar and concrete specimens through a pozzolanic reaction (Francisco et al. 2008). One study showed that rice straw pretreated with hydrolysis could produce good quality ash for use in concrete, however no comparison with unpretreated rice straw ash was made to quantify the benefits of pretreatment (El-Damatty and Hussain 2007). The impact of thermochemical pretreatments on the RSA and WSA sensitivity to burning conditions and subsequent reactivity in a cementitious system has not been studied. Additionally, the mechanism by which pretreatments improve ARA pozzolanicity has not been fully established.

This paper documents the effects of thermochemical pretreatments on the physical properties, chemical properties, and reactivity of WSA and RSA in a cementitious system. Employing several pretreatments techniques and burning conditions, this study attempts to examines the mechanism(s) by which pretreatments enhance ARA reactivity. Distilled water (DW) and 0.1 N

hydrochloric acid (HCl) were used to pretreat the biomass at 23^{o}C, 50^{o}C and 80^{o}C for several soaking durations followed by burning at 500^{o}C, 650^{o}C, 700^{o}C, and 800^{o}C. Loss on ignition (LOI), internal surface area, and amorphous silica content of ARA were measured for these ashes. Isothermal calorimetry, thermogravimetric analysis, electrical conductivity measurements, and mortar compressive strength were used to quantify the ARA reactivity.

Materials:

An ASTM C 150 (2009) Type I/II portland cement was used for this study with the cement properties shown in Table 1. Standard graded sand (ASTM 2006) was used for the mortar experiments. Wheat straw (WS) was purchased from Britt's farm in Manhattan, KS and Rice straw (RS) was obtained from Missouri Rice Research Farm, Glennonville, Missouri. Reagent grade HCl was obtained and diluted to 0.1 N for use in the study.

Experimental methods:

Hydrothermal and thermochemical pretreatment methods were performed on the WS and RS using distilled water (DW) and 0.1 N HCl. To pretreat the biomass, 250 g of biomass was immersed in 3100±100 mL of the solution in a 4000 mL glass jar. The sample was stored undisturbed at a constant temperature for the immersion period of interest. Three different temperatures, 23^{o}C, 50^{o}C, and 80^{o}C, were used to make ash for each pretreatment method which will be referred to as DW23^{o}C, DW50^{o}C, and DW80^{o}C for the distilled water pretreatment at 23^{o}C, 50^{o}C, and 80^{o}C and HCl23 ^{o}C, HCl50^{o}C, and HCl80^{o}C for the 0.1 N HCl pretreatment at 23^{o}C, 50^{o}C, and 80^{o}C, respectively. AR samples were immersed for 0.5, 1, 2, 4, 8, and 24 hrs before burning. Leachate samples were collected from two separate containers of pretreated AR for each time and temperature. The Mg, Ca, K, and Na concentration was measured using atomic absorption spectroscopy (AAS) for each container. The Mg, Ca, K, and Na concentration

was reported as the average concentration of the two containers. After pretreatment, the biomass was rinsed twice with distilled water and dried at 80^{o}C for storage until burning. 200 g of biomass was burned in each ARA batch made. A stainless steel cage with two wire mesh shelves was used to hold the biomass during burning. A stainless steel pan was placed below the cage to catch any ash that fell through the mesh. A programmable electric muffle furnace was used to heat the samples to a predetermined temperature and hold time. Samples were heated to 500^{o}C, 650^{o}C, 700^{o}C, or 800^{o}C using 1, 2, or 3 hr soak times. Finally, the ash was ground for one hour at 85 revolutions per minute (rpm) in a laboratory ball mill.

Particle-size distribution and internal surface area of the ground ARA were determined using a laser diffractometer and BET nitrogen adsorption respectively. LOI of ARA was determined by measuring the mass loss after heating one gram of dry ARA (WSA or RSA) to 800^{o}C for 3 hrs. LOI was calculated as the percentage mass loss during firing.

To measure the amorphous silica content of ARA, the ash impurities and soluble material content were measured (Nair, et al. 2006). The impurities content was measured by first boiling 0.5 g of ARA after the LOI test in 25 mL of 10% nitric acid. After boiling in acid the sample was filtered through a glass microfiber filter paper with 1.1 µm openings and rinsed with deionized water. The sample was then dried at 90±10 ^{o}C and weighed. To measure the ash soluble material content, 3 g of ARA was boiled in 200 mL of 10% sodium hydroxide solution (2.5 N NaOH) for 5 minutes. After boiling, the sample was cooled to room temperature, filtered through a 1.1 µm glass microfiber filter paper, and washed with deionized water. The residue and filter paper was then heated to 800 ^{o}C for 3 hrs. The ash weight change after boiling in the sodium hydroxide and heating was recorded. The ARA amorphous silica content was then calculated using Eq. 2 :

$$Si_{am} = w_{sol} - LOI - w_{im} \qquad \text{Eq. 2}$$

where Si_{am} is the amorphous silica content of the ash (%), w_{sol} is the ash weight loss after boiling in sodium hydroxide and heating (%), LOI is the ash loss on ignition (%), and w_{im} is the weight of impurities (%).

The decrease in electrical conductivity of a calcium hydroxide solution mixed with SCMs has been used by other researchers as a simple reactivity index for pozzolanic behavior of SCMs (Sinthaworn and Nimityongskul 2009; Paya, et al. 2001) and was used in this study. One gram of ARA was mixed with 100 mL of saturated calcium hydroxide solution at 23±2 °C. The solution's electrical conductivity was then measured for 7 days.

For the cement paste experiments, ARA was used at a 20% replacement level by mass of cement when used. A water-cementitious materials ratio (w/cm) of 0.5 was used for all paste samples. The paste samples were mixed using a procedure previously used (Riding, et al. 2010). Distilled water was added to the cementitious material and mixed using a vertical laboratory mixer at 500 rpm for 90 seconds, followed by a 120 second rest period, and finally mixed at 2000 rpm for 120 seconds.

Isothermal calorimetry was used to study the reaction rate of ARA in a cementitious system. An eight-channel isothermal calorimeter was used in this study at 23°C. Paste samples of approximately 30 g each were used. The calcium hydroxide (CH) content of cement paste samples was measured by thermogravimetric analysis to study the pozzolanic consumption of CH by ARA. Samples were wet cured starting at 24 hrs after casting at 23 ^{o}C. Cement paste hydration was stopped at 7, 28, and 90 days after mixing by means of solvent exchange with isopropanol. 3-5mm thick samples were cut and placed in isopropanol for 7 days. After 7 days in isopropanol, the samples were dried in a vacuum for at least 3 days. For thermogrametric analysis, samples were heated at 20°C/min up to 900 ^{o}C in a nitrogen environment.

Mortar cube compressive strength was measured according to ASTM C 109 (2008) with a sand to cementitious material ratio of 2.75. A w/cm of 0.55 was used for all mortar samples because of the decreased workability of systems with ARA. ARA was used at a 20% replacement level by mass of cement when used. Mortar cube compressive strength was tested at 7 and 28 days with the results reported as the average of the compressive strength of three mortar cubes.

Results and discussion:

Pretreatments and alkali leaching

Pretreatments were very effective in altering the chemical and physical structure of the straw and removing K, Ca, and Mg. Figure 1 shows the leachate K concentrations for different pretreatments used for WS. The sodium concentrations were found to be much lower than K, and varied only slightly by pretreatment method. Figure 2 shows the calcium (Ca) and magnesium (Mg) leachate concentration for WS. HCl and higher temperatures increased the leaching rates of K, Ca, and Mg. A much larger difference between HCl and DW pretreatments was seen however with Ca and Mg removal from WS than K and Na. Similar trends were observed for RS. The temperature sensitivity of K removal during pretreatments was quantified by calculating the dissolution activation energy. First, the leachate K concentration with time for a given pretreatment temperature was fit to Eq. 3 (ASTM, 2010):

$$C(t) = C_{ult}\frac{K \cdot (t)}{1 + K \cdot (t)} \qquad \text{Eq. 3}$$

where *C(t)* is the potassium concentration as a function of soaking duration (ppm), t is the time passed after starting the pretreatment (days), C_{ult} is the ultimate potassium concentration assumed

to be equal to the concentration measured at 24 hr of treatment (ppm), and K is the rate constant of potassium dissolution. The Arrhenius plot was made by plotting the natural log of the rate constant K against the reciprocal of the pretreatment temperature in Kelvins. Figure 3 shows the Arrhenius plot for the rate constants calculated for the leachate K concentration for wheat straw. The activation energy was calculated as the slope of the fit line on the Arrhenius plot multiplied by the universal gas constant R (8.314 J/mol/K). The activation energy for leaching K with 0.1 N HCl was found to be 32.2 KJ/mol, versus 13.3 KJ/mol with DW pretreatments. This shows that the higher the acid concentration the more effectively heat can be used to remove K from the AR with high acid concentrations.

Surface area, LOI and amorphous silica content of ARA

Pretreatments were effective in reducing the carbon content in the ARA, increasing the internal surface area, and increasing the percentage of amorphous silica in the ash. Figure 4 shows the amorphous silica content of ARA. For a given burning temperature, pretreatments increased the amorphous silica content. Pretreated ARA burned at 500°C for 2 hrs had a similar amorphous silica content as the one burned at 650°C for 1 hr. The unpretreated WSA had 21% crystalline silica and unpretreated RSA had 19% crystalline silica when burned at 650°C for 1 hour as calculated from the ash total silica content shown in Table 2 and the ash amorphous silica content shown in Figure 4. The ash pretreated with 0.1N HCl at 80°C showed little if any crystalline silica while the WSA pretreated with DW at 80°C had 8% crystalline silica. The increase in amorphous silica content of the pretreated ARA correlated with the removal of Ca, Mg, and K out of the biomass by pretreatments. Figure 5 shows the amorphous silica content of ARA versus the CaO, MgO, and K_2O content. The amorphous silica content of the ARA corresponded with a decrease in the CaO, MgO, and K_2O content, with the MgO showing a

slightly better correlation. Figure 6 shows the LOI measured for WSA and RSA. The ARA LOI decreases as the burning temperature increases regardless of the pretreatment type. At a given burning temperature, pretreated ARA had a lower LOI than that of the unpretreated control ash. Figure 7 shows the metal impurity (Ca, Mg, and K) content of the ash for the WSA and RSA was also correlated to the ARA LOI. The RSA had a lower LOI than the corresponding WSA, possibly because of the lower alkali content of the RSA before pretreatment than the WSA. Even though distilled water pretreatments were not as effective as the more acidic pretreatments, when burned at 650°C for 1hr the WSA pretreated with DW23/24 still had 52% lower LOI and 15% higher amorphous silica than that of unpretreated WSA. RSA pretreated with DW23/24 had 55% lower LOI and 17% higher amorphous silica than that of unpretreated RSA.

Another important impact of the pretreatments is the decrease in temperature sensitivity of the biomass. Sensitivity reduction is vital for low cost ARA production in using simple kilns or large scale applications where it may be more difficult to control the temperature. The pretreatments were very effective in reducing the sensitivity to burning temperatures. The HCl80/24 WSA burned at 800 ^{o}C had a higher amorphous SiO_2 content than that of the control burned at 500°C as shown in Figure 4.

LOI and amorphous silica content of ARA was shown to be affected by the duration of burning. Table 4 shows the LOI and amorphous silica content for WSA pretreated with 0.1N HCl at 80°C for 24 hours and then burned at different temperatures and holding durations. There appears to be an optimum burning time for each temperature which appeared to coincide with the removal of most of the carbon. At 500°C, the optimum burning time was found to be between one and two hours whereas at 600°C it was found to be less than or equal to one hour. Burning

periods longer than the optimum time did not appear to improve amorphous silica content or LOI.

The pretreatment changed the color of the ash, mainly because of the decrease in carbon content. Figure 8A shows WSA pretreated with 0.1N HCl at 80°C for 24 hrs, while Figure 8B shows control WSA samples ashed at four different temperatures. The WSA-HCL80/24 ash was much lighter in color than that of control WSA ashes regardless of the burning condition. Even though it had a low LOI, the WSA pretreated with HCl at 80°C for 24 hrs and burned at 800°C for one hr had a slightly darker color than the pretreated ashes made at lower temperatures (Figure 8A). Although the color of the ash is largely related to carbon content of the ash, impurities such as alkali metals can change the ash color. At higher temperatures these metals react with silicon (Si) to produce crystalline phases that may combined with carbon or contain iron giving the ash a darker color (Muthadhi and Kothandaraman 2010; Genieva, et al. 2011). It was also observed that washing the biomass after pretreatments is very important in removing alkalis from surface of biomass and reducing LOI of the resulted ash. This could be because when the straw was not washed after the pretreatment, potassium and other impurities in solution would precipitate on to the surface of the straw during drying. These precipitates could trap carbon during ashing, leading to higher ash LOI. Even though pretreatments remove metal impurities out of the biomass cell wall, it is beneficial to wash the biomass after pretreatment to limit the impurities that would precipitate on the biomass surface. For a given burning condition, pretreated but unwashed biomass resulted in ARA with darker color and higher LOI compared to the ash obtained from pretreated and washed biomass. This could be attributed alkalis on the surface melting at lower temperature and trapping carbon.

Table 3 presents the ARA surface area determined by BET nitrogen adsorption while Figure 9 shows the particle-size distribution for some selected ARAs. For a given pretreatment, ashes burned at 500°C for 2 hrs had higher surface area than those burned at higher temperatures. This is probably because at higher temperatures melting of some material may occur eliminating pores inside of the ash. The particle-size distribution was not significantly affected by pretreatments. Although the surface area of unpretreated RSA and WSA were similar, pretreated RSA had a larger surface area than that of pretreated WSA.

Conductivity measurements

Figure 10 shows the normalized conductivity (the measured conductivity divided by the initial conductivity of the solution) data for WSA pretreated with 0.1N HCl at 23°C, 50°C, and 80°C and burned at 500°C for 2 hours and 650°C for 1 hour. The normalized conductivity for unpretreated WSA and WSA pretreated with DW and 0.1 N HCl is given in Figure 11. The pretreatment temperature did not significantly affect the measured conductivity change. WSA burned at 500^{o}C for 2 hrs shows a more rapid drop in conductivity than WSA burned at 650^{o}C for 1 hour indicating a higher reactivity consistent with the higher surface ash measured in the samples burned at 500°C. Very little difference was seen between different pretreatments in the conductivity experiments. Similar behavior was seen for RSA conductivity experiments. The initial increase in the electrical conductivity from the control sample is likely the result of dissolution of metal impurities such as Na, K, Ca, and Mg in the solution (Sinthaworn, et al. 2011).

Isothermal Heat of Hydration

Figure 12 compares the heat of hydration for WSA burned at 650^{o}C for 1 hour with and without thermochemical pretreatments. Large differences in hydration behavior were seen

between the pretreated and control WSA. Figure 13 shows the total heat of hydration of cement paste samples containing WSA. The pretreated ashes show similar total heat of hydration during the first 120 hours, indicating a similar degree of cement hydration at 120 hours. Figure 14 shows the heat flow rate for paste samples containing RSA. The hydration rate of pretreated ARA was accelerated compared to the control samples, whereas the samples with ARA that were not pretreated were retarded as seen in Figure 12 and Figure 14. The hydration acceleration is most likely caused by increased nucleation because of the very high ARA surface area (Bullard, et al. 2011; Scrivener and Nonat 2011). Also, the samples containing pretreated ARA (WSA and RSA) showed much more similar behavior to each other during the first 120 hours after mixing than the non-pretreated ARA.

Pozzolanic Reactivity

The decrease in CH content of cement paste samples containing ARA is a measure of the ARA pozzolanic reaction. The CH content for cement paste samples with and without ARA was measured using TGA at 7, 28, and 90 days of hydration as shown in Figure 15 and 16 for WSA and RSA, respectively. For a given pretreatment type and age, samples containing ARA (WSA or RSA) burned at 500^{o}C for 2 hr had a lower CH content than those burned at higher temperatures. This can be attributed to the higher surface area of ARA burned at 500^{o}C for 2 hr. At a given burning condition, samples containing ARA pretreated with 0.1N HCl at 80^{o}C for 24 hrs had a lower CH content than any other pretreatment type. At a given age, samples containing WSA at burned at 500°C showed lower CH content than those containing RSA burned at 500°C.

Figure 17 shows the compressive strength development for mortar with and without 20% cement replaced by ARA. The WSA and RSA pretreated with HCl at 80°C for 24 hours showed the highest compressive strength development, with a 25% increase in strength over the ordinary

portland cement (OPC) mixture at 28 days of age. The increased strength seen with pretreated ashes confirms the increased pozzolanic reaction seen with the reduction of CH content with time in samples containing the pretreated ARA.

A comparison of the ARA material characteristic improvement from the pretreatments (amorphous silica and surface area) and CH content at 90 days is shown in Figure 18. The increase in amorphous silica content of ARA and surface area correlated with a decrease in the CH content of paste samples containing ARA and increases compressive strength of mortar samples containing ARA. The isothermal calorimetry results did not show a reduced hydration development with the use of ARA indicating that the decrease in CH content seen with the ARA is likely from the pozzolanic reaction and not a lower cement degree of hydration. Additionally the OPC mixture showed an increase in CH content while the mixtures with ARA showed a decrease in CH between 7 and 28 days.

Conclusions:

The material physical and pozzolanic properties of wheat straw ash (WSA) and rice straw ash (RSA) were studied. From this study, the following conclusions can be made:

1- Pretreatments are effective in partial removal of Ca, K, and Mg out of the biomass. The activation energy for K leaching was higher for dilute acid pretreatment than distilled water pretreatment. This shows that heating samples during pretreatment even more effective for the more acidic pretreatments.

2- Pretreatments increased the amorphous silica content and surface area and decreased the LOI of ARA at a given burning temperature. It was shown that amorphous silica content inversely correlated with the Ca, K, and Mg content of the ash while LOI of ARA is directly correlated with the Ca, K, and Mg content of the ash. Alkalis seemed to encase or

combine with carbon during burning. Pretreatments reduced the sensitivity of the ash to the burning temperature, showing less of a decrease in amorphous silica content than the non-pretreated ash at 700°C and 800°C.

3- Pretreatments improved the system hydration kinetics. Non-pretreated ARA retarded the cement hydration, whereas pretreated WSA and RSA accelerated the cement hydration. The acceleration may be from increased nucleation from the increased material surface area.

4- Cement paste sample containing ARA burned at 500°C for 2 hrs contained lower CH than those samples containing ARA burned at 650°C for 1 hr. This was attributed to the higher surface area of the ash burned at 500°C for 2 hrs. It was shown that CH content of the paste after 90 days of hydration was inversely correlated with amorphous silica content and surface area of the ash used in the paste. Samples containing WSA showed lower CH content at 90 days than the RSA with similar surface area and amorphous silica content.

5- When used as 20% replacement of cement in mortar samples, pretreated ARA increased compressive strength of mortar samples at 28 days by 25% compared to the OPC sample. Mortar samples containing pretreated ARA showed a 32% increase in 28 day compressive strength compared to samples containing unpretreated ARA. It was also shown that mortar compressive strength correlated well with the ash amorphous silica content.

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429 **Table 1: ASTM C 150 Type I/II ordinary portland cement (OPC) Composition**

Chemical Composition (wt%)	
SiO_2	21.85
Fe_2O_3	3.4
Al_2O_3	4.35
CaO	64.19
MgO	1.79
K_2O	0.52
Na_2O	0.17
SO_3	2.77
LOI	0.89
Blaine Surface area= 362 m^2/kg	

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Table 2: Oxide composition of selected ARA

Ash Type	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	K_2O	Na_2O
WSA-Cont-650/1	66.3	0.26	1.12	14.3	3.05	14.7	0.15
WSA-DW80-650/1	78.8	0.12	1.05	13.2	2.61	4.4	0.12
WSA-HCl80-650/1	86.5	0.28	1.13	9.73	0.78	1.54	0.1
WSA-HCl80-500/2	87.9	0.05	1.07	9.63	0.63	0.7	0.08
RSA-Cont-650/1	79.1	0.34	0.82	11.6	2.54	5.18	0.5
RSA-DW80-650/1	85.4	0.45	0.92	10.69	1.36	0.96	0.26
RSA-HCl80-650/1	88.2	0.47	0.74	9.48	0.56	0.31	0.17
RSA-HCl80-500/2	85.7	1.4	1.02	10.73	0.6	0.34	0.23

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437 **Table 3: BET data for WSA and RSA under different burning conditions**

Ash type	BET surface area (m^2/g)
WSA-Cont-500/2	27.6
WSA-Cont-650/1	8.3
WSA-HCl80/24-500/2	168
WSA-HCl80/24-650/1	65
WSA-HCl80/24-700/1	39.7
RSA-Cont-500/2	16.9
RSA-Cont-650/1	9.6
RSA-HCl80/24-500/2	200
RSA-HCl80/24-650/1	134.5
RSA-DW80/24-650/1	58.94

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441 **Table 4: Effect of holding time on LOI and amorphous silica content**

WSA type	Amorphous Silica (%)	LOI (%)
HCl80/24-500/1	72.70	17.58
HCl80/24-500/2	88.65	2.76
HCl80/24-500/3	88.7	2.62
HCl80/24-650/1	89.14	1.18
HCl80/24-650/2	88.99	1.1

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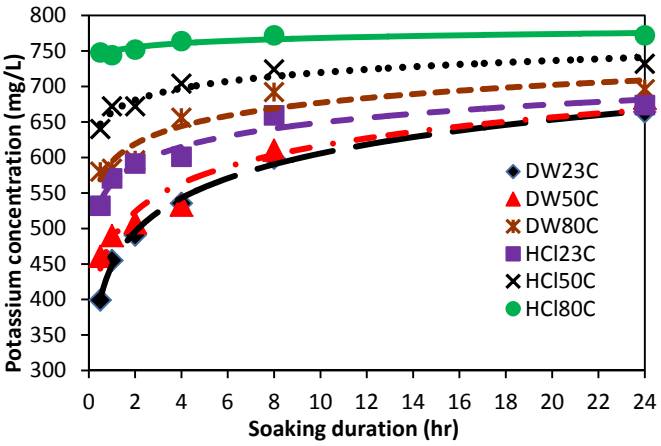
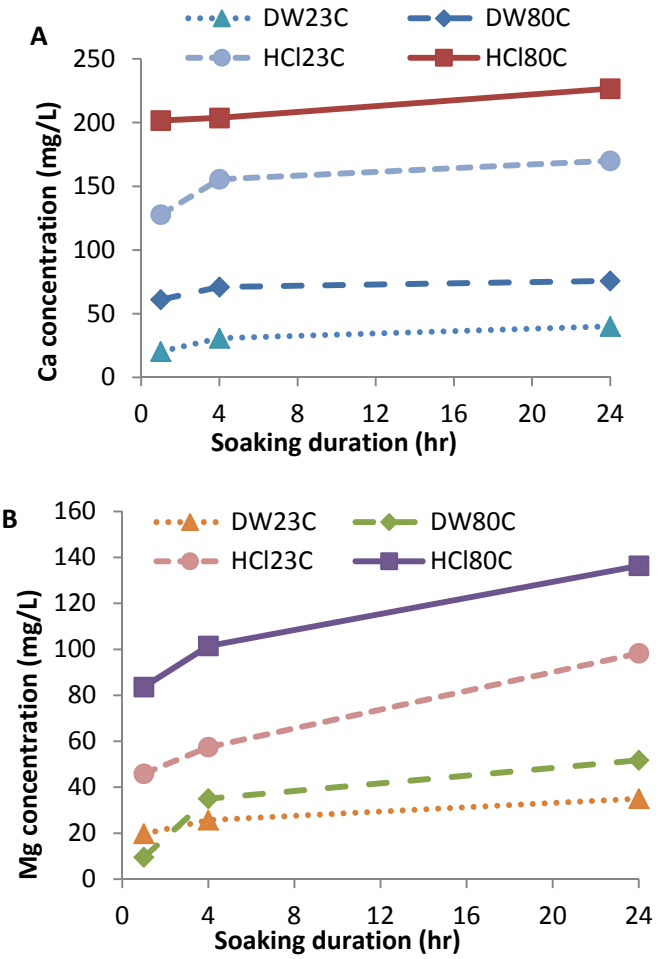


445

446 **Figure 1: Potassium (K) concentration for wheat straw**



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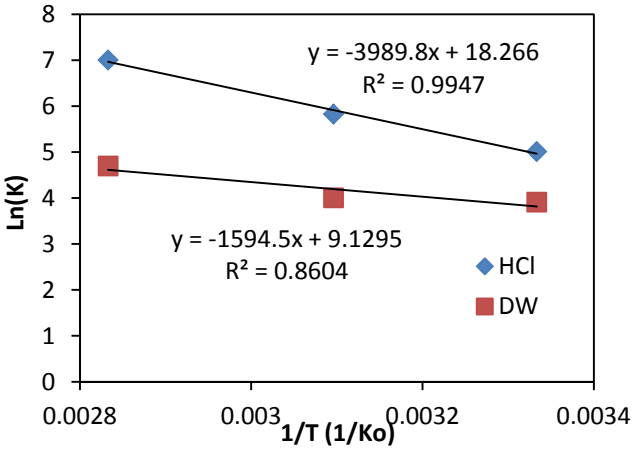
449 **Figure 2: Ca (a) and (b) Mg concentration for wheat straw**



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451 **Figure 3: Arrhenius Plot for wheat straw**

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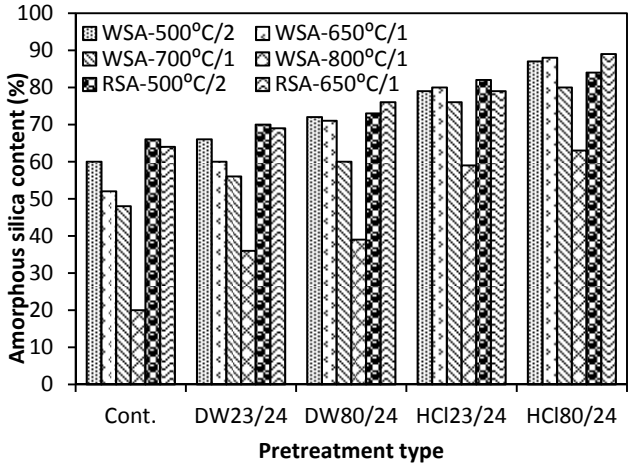

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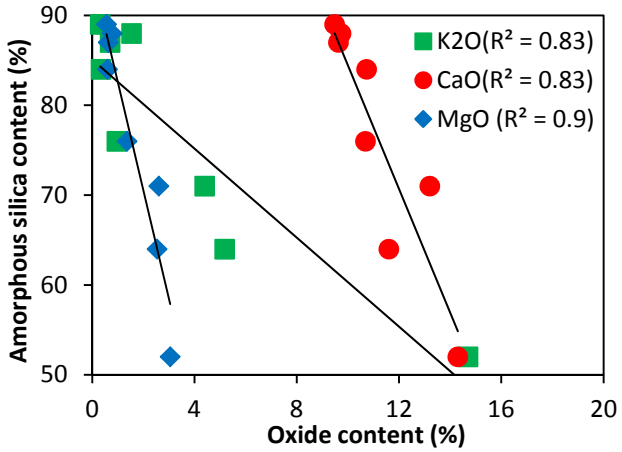
454 **Figure 4: Amorphous silica content of pretreated and unpretreated ARA**



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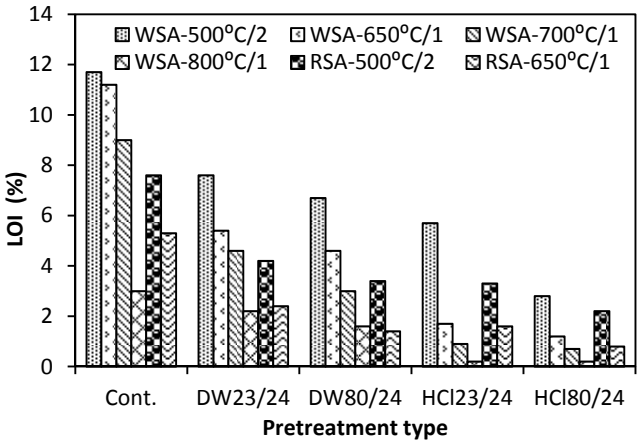
456 **Figure 5: ARA amorphous silica vs ARA (WSA and RSA) oxide content**



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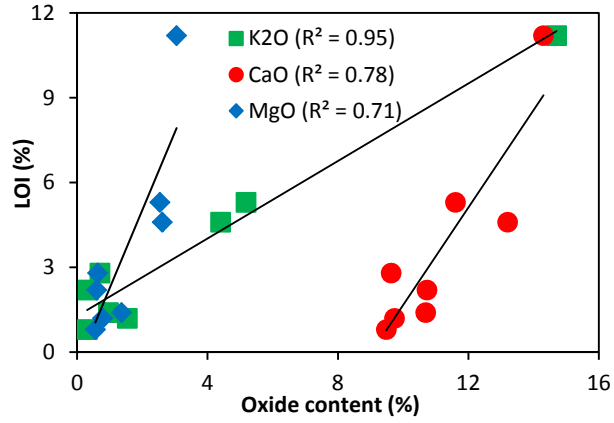
458 **Figure 6: LOI of pretreated and unpretreated ARA**



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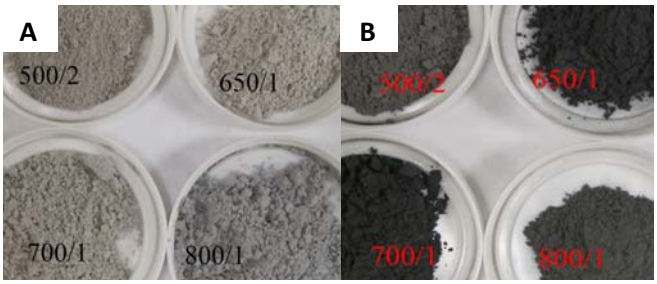
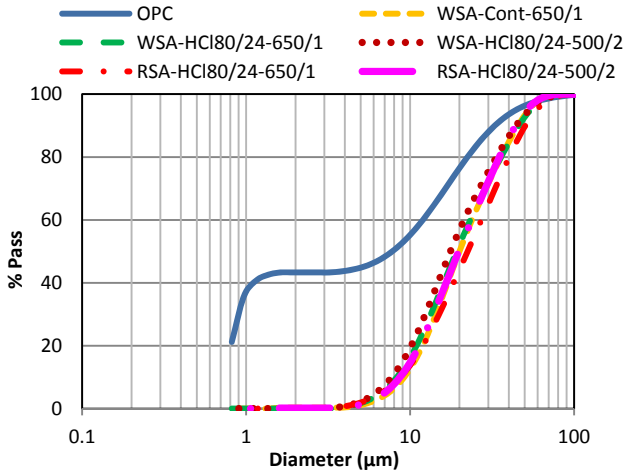
460 **Figure 7: ARA LOI V vs ash K_2O, CaO and MgO content**



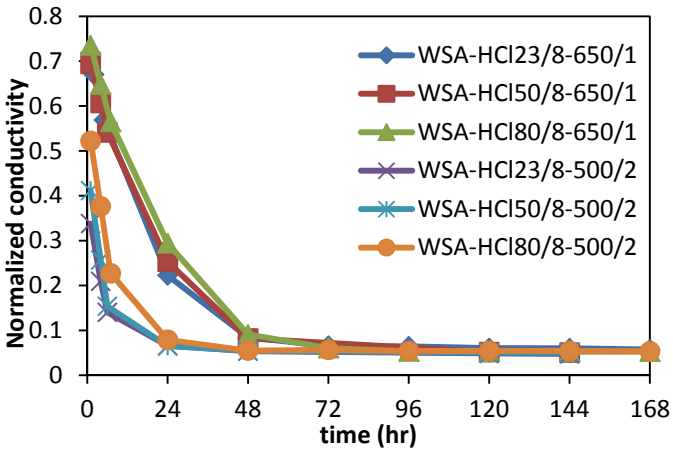
461

462 **Figure 8: Color of wheat straw ash, a) HCl80/24 pretreated and b) unpretreated**



463

464 **Figure 9: Particle size distribution of OPC and ARAs**



465

466 **Figure 10: Electrical conductivity change of HCl pretreated wheat straw ash**

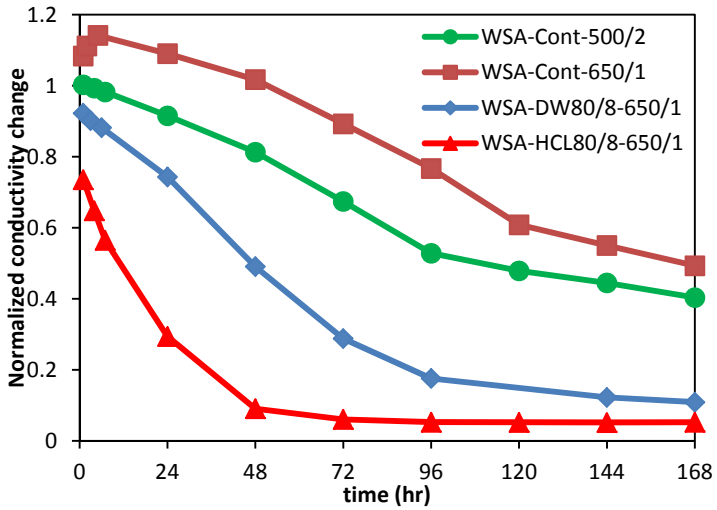


Figure 11: Electrical conductivity change wheat straw ash with different pretreatments

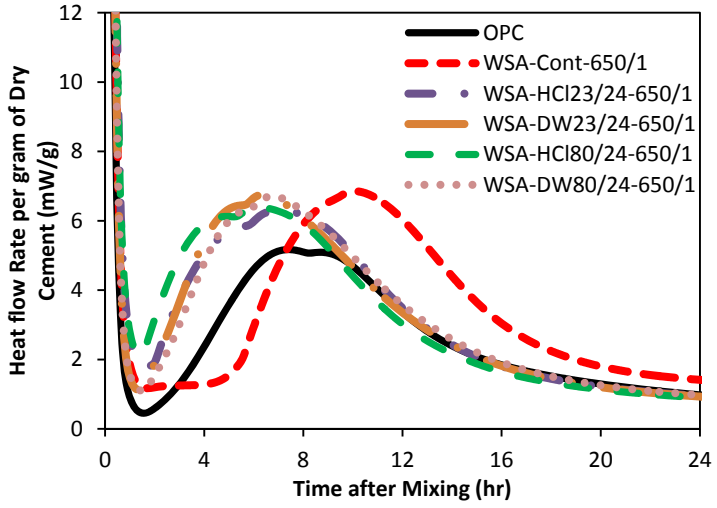
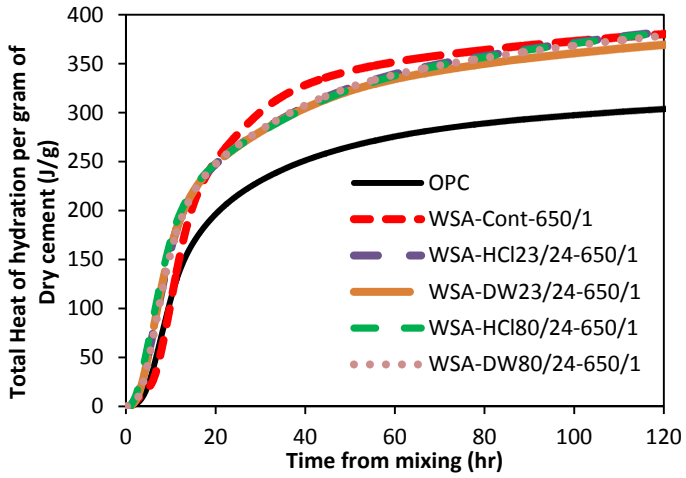


Figure 12: Heat flow rate of paste samples containing different wheat straw ash



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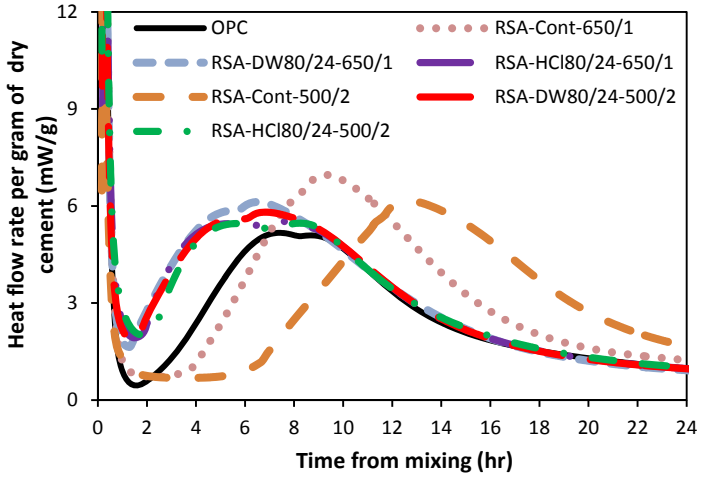
472 **Figure 13: Total heat of hydration of paste samples containing different wheat straw ash**



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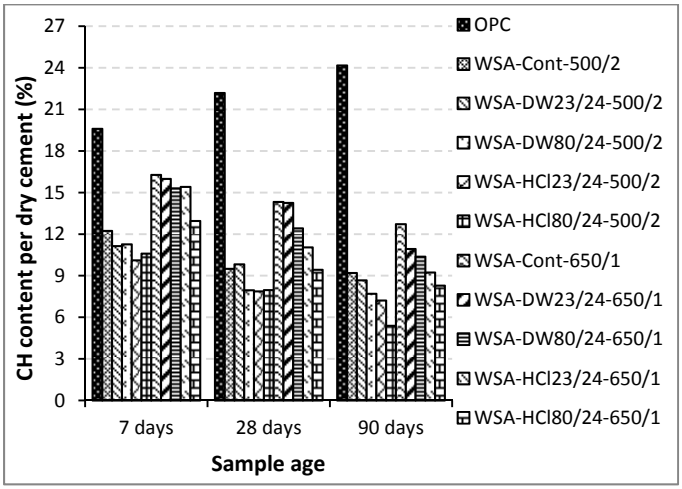
474 **Figure 14: Heat evolution rate of paste samples with and without rice straw ash**



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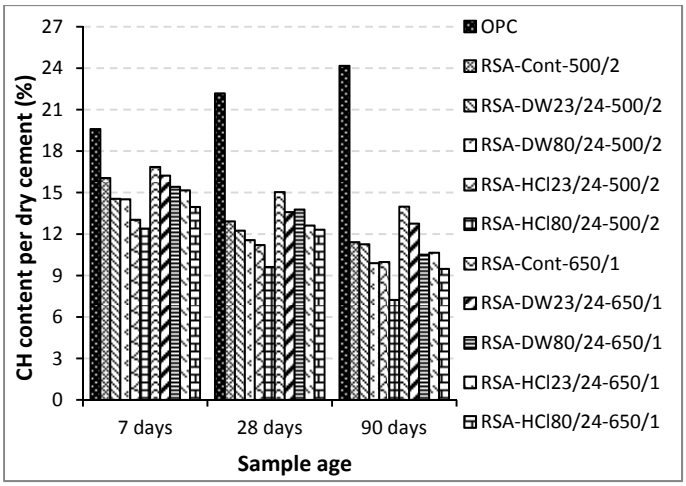
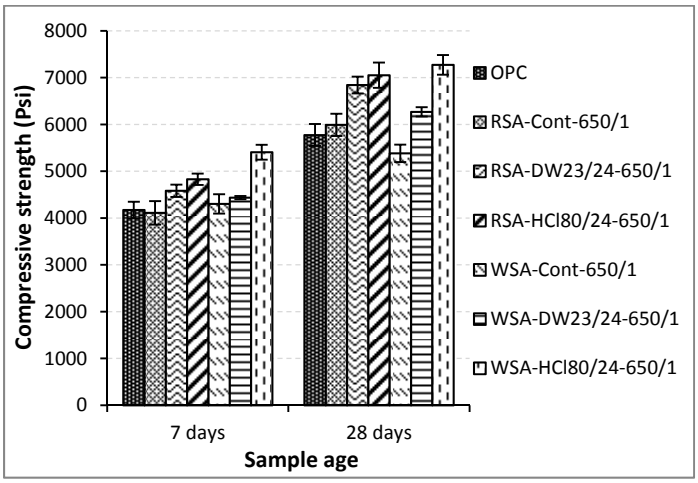
476 **Figure 15: CH content of cement paste containing wheat straw ash**



477

478 **Figure 16: CH content of cement paste containing rice straw ash**



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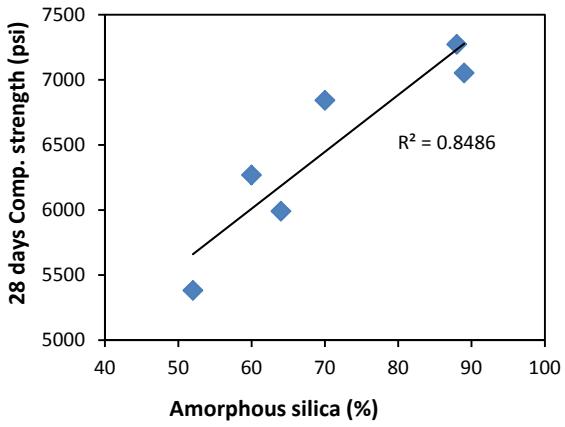
480 **Figure 17: Mortar cube compressive strength data**

a)



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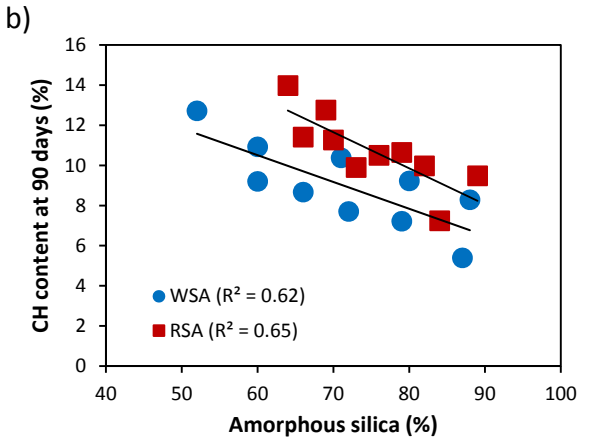

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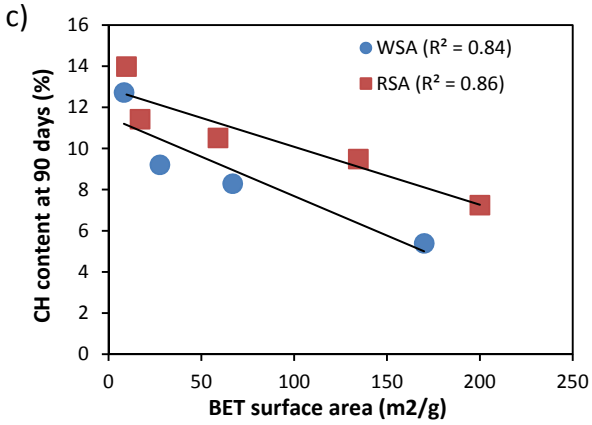

483

484 **Figure 18: Relation between material characteristics and performance a) amorphous silica**

485 **content vs 28 days mortar cub strength, b) amorphous silica content vs CH content of paste**

486 **after 90 days c) Surface area of ash vs CH content of paste after 90 days**