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The effects of a hydrochloric acid pre-treatment on the physicochemical properties and pozzolanic performance of rice husk ash

A. Gholizadeh Vayghan [a], A.R. Khaloo [b], F. Rajabipour [c,*]

[a] *Faculty member and Director of the Concrete Technology and Construction Materials Laboratories, Alaodoleh Semnani Institute of Higher Education, Garmsar, Iran*
[b] *Faculty of Civil Engineering, Sharif University of Technology, Azadi St., Tehran, Iran*
[c] *Department of Civil & Environmental Engineering, The Pennsylvania State University, 223B Sackett Building, University Park, PA 16802, USA*

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ABSTRACT

This paper investigates the effects of acid normality (0.01–6 N HCl) and combustion retention time (0.25–16 hours) on the pozzolanic properties of pre-combustion acid-treated rice husk ash. The pozzolanic reactivity was quantified by adding ground ash to saturated $Ca(OH)_2$ solutions and monitoring the time-dependent electrical conductivity and pH of the solutions. Also, the strength activity of ashes from different processes was measured by testing the compressive strength of mortars. It was observed that acid treatment results in ashes with higher SiO_2 content, lower alkali and unburned carbon content, better grindability, and smaller particle size, in comparison with ash from non-acid treated husks. Acid leaching increased the lime reactivity of the ashes and decreased their sensitivity to prolonged combustion times. Further, acid treatment with 0.01 N HCl was found to be sufficient, as the use of stronger acids did not considerably improve the pozzolanic reactivity of rice husk ash.

1. Introduction

The growing needs for energy and natural resources, and the resulting environmental pollutions have raised serious concerns in modern and developing countries. An example related to construction industry is the annual production of Portland cement in the world that has reached 3400 Mtons (million tons) (approximately 485 kg per capita) in 2011 [1]. Of this value, a significant portion is contributed by developing countries. For example, in 2011, China produced approximately 2000 Mtons of cement (i.e., ~1480 kg per capita), which accounts for 58.8% of the global production [1]. Manufacturing of Portland cement is energy intensive (embodied energy ≈ 5.3 MJ/kg), and results in a large CO_2 footprint (≈0.97 kg/kg) [2]. In parallel, large quantities of siliceous waste materials (e.g., coal fly ash, blast furnace slag, rice husk ash), are produced by various industries. Some of these waste materials can be used effectively as partial replacement of Portland cement to reduce the environmental impact and the life-cycle cost of concrete structures [3]. In addition, the proper use of such supplementary cementitious materials (SCMs) has been proven to enhance the durability and mechanical properties of concrete [3].

Among agricultural wastes, the best performance as an SCM has been reported for rice husk ash due to a high silica content in the ash (i.e., nearly 90% when burned under optimum conditions); and due to a high percentage of ash that is produced from a unit weight of rice husk [4]. In 2009, over 680 Mtons of rough rice was produced in the world [5]. Since the rice husk (RH) accounts for 20–22% by weight of the harvested rough rice [6], over 140 Mtons of RH is annually produced. The energy density of RH is reported to be approximately 16,720 kJ/kg [7] and, therefore, an annual potential energy of approximately 2.17×10^9 GJ and 26 Mtons of potentially highly reactive pozzolan can be obtained from RH combustion. Research has shown that controlled combustion of RH can result in the formation of silica of amorphous structure, high purity, and very high lime reactivity [8]. However, conventional heap burning and other industrial combustion methods include a steep heating rate, an essentially uncontrolled ultimate temperature and a prolonged retention time. These will result in the formation of ash of high unburned carbon content, partially crystallized silica, and as such, low pozzolanic performance. There is a need for development of successful methods to produce rice husk ash of superior performance at industrial scale.

One of the newer methods to obtain rice husk ash of high silica purity and improved pozzolanic properties is acid leaching pretreatment [9,10]. The method was first proposed by Chakraverty et al. [11]. This process can essentially remove metallic impurities such as Al_2O_3, Fe_2O_3, CaO, MgO and, more importantly, deleterious alkalis like K_2O [7,12,13]. In the case of non-acid leached rice husk, the existing K_2O decomposes during the combustion at 620 K, leaving elemental potassium (whose melting point is 343 K) on the

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* Corresponding author. Tel.: +1 814 863 0601.
E-mail addresses: a.v.gholizadeh@gmail.com (A. Gholizadeh Vayghan), khaloo@sharif.edu (A.R. Khaloo), farshad@psu.edu (F. Rajabipour).

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structure of the burning ash. Potassium element causes surface melting and acts as a crystallization catalyst for silica [13]. When rice husk is heated, the carbonization occurs through decomposition of the organic matter, such as cellulose and lignin to carbon. Further increase in the temperature results in oxidation of the carbon into CO_2, if reasonable oxygen supply is provided [6]. However, the increase in the temperature over the dissociation point of K_2O, is followed by surface melting of the ash which blocks the pathways for transport of oxygen and carbon dioxide. This will result in the entrapment of non-oxidized (i.e., unburned) carbon. Moreover, the surface melting can result in a decrease in the pozzolanic lime reactivity of the ash due to increased crystallization affinity of silica [13]. When an acid leaching pre-treatment is applied, K_2O as the major silica crystallization catalyst is removed from the rice husk, and no surface melting occurs in the silicate structure. Therefore, the carbonized matter in the burning ash is not prevented from volatilizing, which leads to less unburned carbon content in the ash. In addition, the volatiles can escape at lower ultimate temperatures compared to non-acid leached husks [13].

Previous research also indicates that the strength activity of acid leached rice husk ash (ALR) is superior to non-acid treated rice husk ash (NTR). Feng et al. [12] reported 17% and 33% improvements in the 28-day flexural and compressive strengths of mortars incorporating 10 wt.% replacement of Portland cement with NTR. Samples with 10 wt.% of ALR showed 21% and 43% improvements in the 28-day flexural and compressive strengths, respectively. The husks were treated in 1 N HCl acid and combusted at 700 °C for 4 h. Salas et al. [14] used a similar acid treatment, but altered the combustion temperature to be at 600 °C for 3 h. For concrete with 10 wt.% replacement of cement with NTR or ALR, the 28-day compressive strength improved by 5% and 11%, respectively [14].

The majority of the past research has focused on treatment of rice husk using inorganic acids (e.g., HCl, HNO_3 and H_2SO_4) and at relatively high concentrations (1 N up to 18 N) [10–14]. The high volume and acidity of the chemical wastes produced during the treatment and neutralization of the leached husks raise the need to investigate whether treatments using lower acid normality can be also effective in improving the pozzolanic performance of rice husk ash. This is one of the main objectives of the present paper, which uses a much weaker 0.01 N HCl acid. In addition, the effect of combustion retention time (0.25, 1, 4, 8, or 16 h retention at 700 °C) on the properties of the non-treated and acid leached ash is investigated. This is important for minimizing the energy consumption of the process, and to determine the sensitivity of the rice husk ash (both NTR and ALR) to variability in the burning conditions. The pozzolanic performance of the resulting husk ashes is characterized through measurement of the ash reactivity with a saturated $Ca(OH)_2$ solution, as well as measuring the strength improvements in mortars containing partial cement replacement with rice husk ash.

2. Materials and experimental methods

2.1. Materials

The rice husks were provided from a northern state of Iran. In the case of acid leached rice husk ash (ALR), each time 6 kg of the husks were boiled in 60 liters of 0.01 N HCl acid solution for 1 h inside a150-liter stainless steel cylindrical tank. This is consistent with past research which suggested boiling the husks for 1–2 h in the acid solution and, using a husk to solution ratio of 50–100 g/l [10,12,15]. Next, the husks were washed completely with tap water until neutral pH was detected, and then dried in the laboratory air for 3 days. Both types of the husks (ALR and NTR) were burned in a static air muffle furnace under well controlled conditions in small quantities to ensure the accuracy of the applied pyro-processing. Each time, 100 g of the husks were evenly placed in a rectangular stainless steel tray (20 cm × 28 cm × 2 cm), and the pyro-processing was carefully applied as follows. For all samples, the rate of heating was 10 °C/min and the ultimate temperature was 700 °C. In order to investigate the effect of retention time, the ashes were maintained at the ultimate temperature for 15 min, 1, 4, 8, and 16 h. Once the retention time had elapsed, the husks were removed from the furnace and allowed to cool down to the room temperature in 5 min. The husks were then ground in a 5-literporcelain ball mill for 20 min. The type of mill and the grinding time were similar to previous studies [6,12,16–18]. The typical time–temperature variation pattern of the applied pyro-processing is shown in Fig. 1. The rationale behind the rapid cooling of the ashes was to promote the formation of amorphous silicate compounds as opposed to crystalline silicates which are known to be non-reactive. The ashes were named according to their type and retention time. ALR-2 h, for instance, marks the acid leached rice husk ash maintained for 2 h at the ultimate temperature

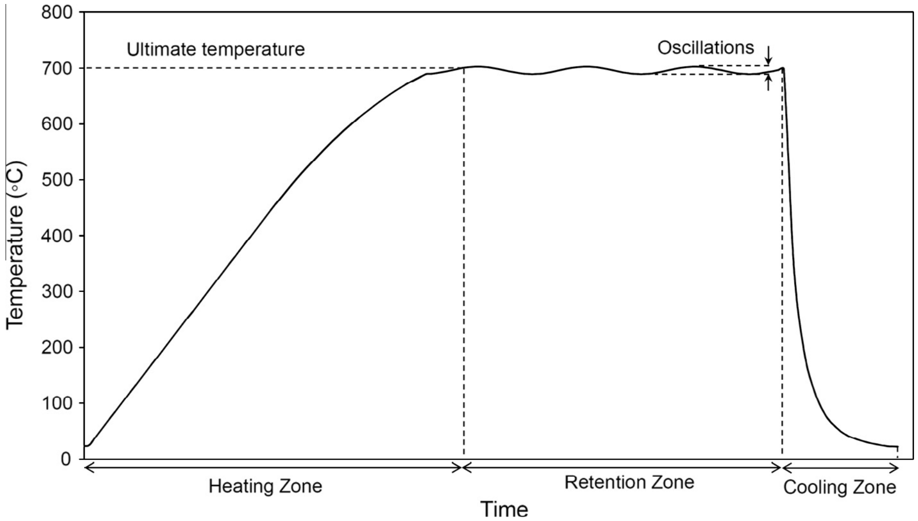

Fig. 1. Typical time–temperature variations of rice husk combustion.

Table 1
Chemical composition[a] and physical properties of materials.

Characteristics	Materials[d]										
	Cement	NTR-1/4h	ALR-1/4h	NTR-1h	ALR-1h	NTR-4h	ALR-4h	NTR-8h	ALR-8h	NTR-16h	ALR-16 h
SiO_2 (%)	21.24	87.14	97.59	94.41	97.89	94.91	97.94	95.22	98.33	95.1	98.51
Al_2O_3 (%)	4.92	0.04	0.03	0.03	0.02	0.05	0.02	0.09	0.02	0.05	0.04
Fe_2O_3 (%)	4.01	0.23	0.11	0.25	0.16	0.25	0.14	0.19	0.26	0.11	0.09
CaO (%)	64.08	1.21	0.22	1.01	0.27	0.98	0.26	1.16	0.32	1.17	0.21
MgO (%)	1.68	0.3	0.13	0.37	0.09	0.44	0.11	0.39	0.04	0.41	0.07
Cl (%)	–	0.09	0.02	0.09	0.02	0.06	0.02	0.07	0.05	0.09	0.03
SO_3 (%)	2.42	–	–	–	–	–	–	–	–	–	–
K_2O (%)	0.64	1.6	0.17	1.69	0.18	1.61	0.2	1.73	0.14	1.66	0.19
Na_2O (%)	0.34	0.06	0.02	0.07	0.03	0.07	0.05	0.06	0.03	0.05	0.03
Equiv. Na_2O (%)	0.761	1.113	0.132	1.182	0.148	1.129	0.182	1.198	0.122	1.142	0.155
P_2O_5 (%)	–	0.31	0.08	0.36	0.13	0.35	0.1	0.29	0.05	0.44	0.06
Loss on drying[b] (%)	1.87	5.64	3.83	4.01	2.66	1.53	2.86	1.12	2.55	1.01	2.57
Loss on ignition (%)-after drying[c]	0.67	9.02	1.63	1.72	1.23	1.28	1.13	0.8	0.76	0.92	0.77
Specific surface, Blaine (m^2/kg)	295	–	–	–	–	–	–	–	–	–	–
BET surface area (m^2/g)	–	–	–	57.1	284.3	–	–	–	–	–	–

[a] Conducted by X-ray fluorescence (normalized values).

[b] The amount of evaporable water absorbed by each ash after 1 week exposure to ambient air (25 ± 2 °C, 50 ± 5%RH, laboratory condition).

[c] The LOI of the ashes was measured according to static method as described by Yalcin and Sevin [15].

[d] ALR and NTR respectively stand for “acid leached rice husk ash (at 0.01 N HCl)” and “non-treated rice husk ash”.

(700 °C), and NTR-1/4 hcorresponds to the non-treated rice husk ash with a 15-min retention time at 700 °C. Table 1 shows the chemical composition and physical properties of the ashes. In addition, a series of ALR ashes were similarly produced by leaching rice husk in HCl solutions of different concentrations: 0.1 N, 1 N, 3 N and 6 N. This was to investigate the effect of acid concentration on the lime reactivity of the resulting rice husk ash. The retention time adopted for this part of the investigation was 1 h. The ashes were named based on the acid normality used for their pretreatment. ALR-1N,for example, refers to the ash leached in 1 N acid.

Type II Portland cement conforming to the specifications of ASTM C 150 was used for this study. The physical and chemical characteristics of the cement are shown in Table 1. Washed manufactured sand conforming to ASTM C 33 specifications, with a fineness modulus of 2.77, and a sand equivalency larger than 97% (measured per ASTM D 2419) was used as mortar aggregates. The superplasticizer (SP) used for this study was a polycarboxylate-based admixture with an allowable dosage of 2 wt.% of cement.

2.2. Experimental methods

2.2.1. Electrical conductivity and pH measurements of lime-pozzolan solutions

When a pozzolanic powder is added to a saturated $Ca(OH)_2$ aqueous solution, the amorphous silicate structure dissolves in the solution, at a rate that is dependent on the pH [19]. These dissolved silicate phases react with the available Ca^{2+} and OH^- ions, and precipitate in the form of calcium–silicate–hydrate (C–S–H) [20]. If no solid $Ca(OH)_2$ is available to replenish the consumed Ca^{2+}, the pH and electrical conductivity (EC) of the solution will drop, proportionally with the formation rate of C–S–H. As such, these measurements can provide useful information for monitoring the reaction rates of pozzolanic materials such as rice husk ash. The faster the drop in the EC and pH of the solution, the higher is the lime reactivity of the ash. It should also be noted that due to the presence of electrostatic forces and the high tendency of ions to be physically adsorbed on surfaces prior to chemical reactions, a sharp drop in the EC of solutions is often observed soon after the pozzolan powder is added to the lime solution. The magnitude of the short-term drop (i.e. within the first 2 min; as suggested by Luxan et al. [21]) is proportional with the surface area of the pozzolan powder. Also, the long-term (i.e. within the first hour) drop in the EC and pH of the solution represents the lime reactivity of the ash.

In this work, for all rice husk ashes, the time dependent variations of the electrical conductivity of saturated lime-pozzolan solutions were recorded at 40 °C, as proposed by Luxan et al. [21], using a portable conductivity meter Model Hach, sensION5. Additionally, the pH variations were measured simultaneously by a portable pH meter Model Hach, sensION1. Analytical grade CaO was used for this investigation. The powdered CaO was used to produce saturated lime solution ($Ca(OH)_2$). According to laboratory measurements, the solubility of CaO in distilled water at 40 °C is approximately 0.124 g/100 ml. The electrical conductivity and pH of saturated lime solution at 40 °C were found to be 7.15 mS/cm and 11.95, respectively. In this work, the exact amount of CaO to produce saturated solution without residual $Ca(OH)_2$ was added. It should be noted that if CaO is added more than needed for saturation, the extra $Ca(OH)_2$ will precipitate as a solid phase and acts as a pH buffer in the solution. This condition should be avoided in this test.

For all ashes, 5.000 g of the ash was uniformly added to 200 ml stirring saturated lime solution in 10 sec and the EC and pH changes were recorded starting 30 sec after NTR/ALR addition. The variations were recorded each 10 sec up to 3 min, and after that, at 1–5 min intervals (depending on the reactivity of the ash) up to 1 h. The tests were performed inside 500 ml beakers covered with paraffin papers in which three holes were punctured for insertion of the sensors and a thermocouple. The temperature of the solution was maintained at 40 ± 1 °C before addition of the ash and during the test, by placing beakers inside a water bath equipped with a PID controller.

2.2.2. Mixture proportions for mortars

Mortar mixtures were prepared to evaluate the strength activity of rice husk ashes. A control mortar mixture with a water to cement mass ratio of 0.45 and a fine aggregate to cement mass ratio of 2.0 were made as reference. For each of the ten different ashes (i.e. both NTR and ALR with 1/4h, 1h, 4h, 8h, and 16h retention times), three mixtures were produced by replacing 5%, 10%, and 15% (mass based) of cement with each of these ashes. In total, 31 mortar mixtures were produced to investigate the effects of acid leaching and retention time on the pozzolanic performance of rice

Table 2
Details of mortars mixture proportioning.

Mixture labels	Materials proportions (kg/m^3)					
	Water	PC	NTR	ALR	Agg.	SP
RT-C	290	644	–	–	1290	–
RT-5-NTR	290	611.8	32.2	–	1290	As appropriate
RT-10-NTR	290	579.6	64.4	–	1290	As appropriate
RT-15-NTR	290	547.4	96.6	–	1290	As appropriate
RT-5-ALR	290	611.8	–	32.2	1290	As appropriate
RT-10-ALR	290	579.6	–	64.4	1290	As appropriate
RT-15-ALR	290	547.4	–	96.6	1290	As appropriate

Keys: PC = Portland cement; Agg. = aggregates; SP = superplasticizer; and RT-*x* = all mortar mixtures in which the cement replacement percent is *x*%.

husk ash. For all mixtures, the water to binder mass ratio (w/b) and aggregate to binder mass ratio (Agg/b) were maintained as 0.45 and 2.0. The flow of each mortar was kept within ± 3 mm of the flow of the control mortar (184 mm or 84%; measured per ASTM C 1437) by adding proper amounts of superplasticizer (SP). This was to ensure that all mortar cubes can be similarly consolidated to the same degree and to prevent variation in compressive strength due to differences in consolidation. This is in accordance with the requirements of ASTM C 311 for measuring the pozzolanic activity. Table 2 shows other details of the mixture proportions. The label of each mixture starts with RT which stands for 'retention time' followed by a number indicating the cement replacement percent by the ash (i.e., 5%, 10%, or 15%). This is followed by the label of the ash used in the mortar (e.g. ALR-2h) as SCM. For example, RT-5-ALR-1/4h corresponds to a mortar in which 5% of cement is replaced with ALR-1/4. Also, RT-C indicates the control mortar mixture (100% PC).

Mixing was performed in a 3-liter Hobart mixer as follows. First, the cementitious materials were dry-mixed for 3 min in a separate bowl, and added to the water–superplasticizer solution weighed in the mixing bowl. The mixing was started at slow speed and continued for 1 min. Then, the mixer was stopped and the materials collected to the side or bottom of the bowl were scraped down into the batch. The paste was then mixed for another 1 min at the same speed. Next, the aggregates were slowly added over a 20 sec period and the mixing was continued for an additional minute. After another scraping, the mortar was mixed for a final 2 min at medium speed. Once the mixing procedure was complete, the flow of the mortar was measured per ASTM C 1437 and, if the mortar did not reach the target flow, a new batch was prepared with a modified SP dosage. For each mixture, three cubic specimens (50 × 50 × 50 mm^3) were cast in accordance with the specifications of ASTM C 109/C 109M. All specimens were kept covered with wet burlaps and plastic sheets for 24 h and then removed from the molds. The cubes were cured in a saturated lime water bath for additional 27 days at 23 ± 2 °C. The cubes were tested according to ASTM C 109 using a loading rate of 0.9 KN/Sec.

2.2.3. X-ray fluorescence (XRF) and X-ray diffraction (XRD) analyses

The XRF analyses were performed for cement and all ashes using a spectrometer model ARL 8410. Powder samples were analyzed for major elements using fused glass disks following methods similar to those of Norrish and Hutton [22]. XRF measurements were performed in a helium (He) atmosphere using a 40 kV, 5 mA X-ray source.

Using a diffractometer model Philips PW 3710, the XRD analyses were performed on 3 g of ALR-4h, ALR-8h, ALR-16h, and ALR-32h and all of the parallel non-treated ashes (i.e. NTR-4h, NTR-8h, NTR-16h, and NTR-32h).The powder was mounted in a sample holder, which was then placed in a goniometer. Using a 40 kV, 30 mA power supply, a copper filament was bombarded by electrons to generate characteristic Cu $K\alpha$ X-rays which, after passing through a beryllium monochromator filter, were radiated towards the sample at incident angles (θ) ranging from 2.5° to 40° ($2\theta = 5$–80°).

3. Results and discussion

3.1. Chemical composition and physical properties of the ashes

The physical and chemical characteristics of NTR and ALR ashes are presented in Table 1. It is observed that the acid leaching leads to higher SiO_2 contents in the yield ashes. It also decreases the

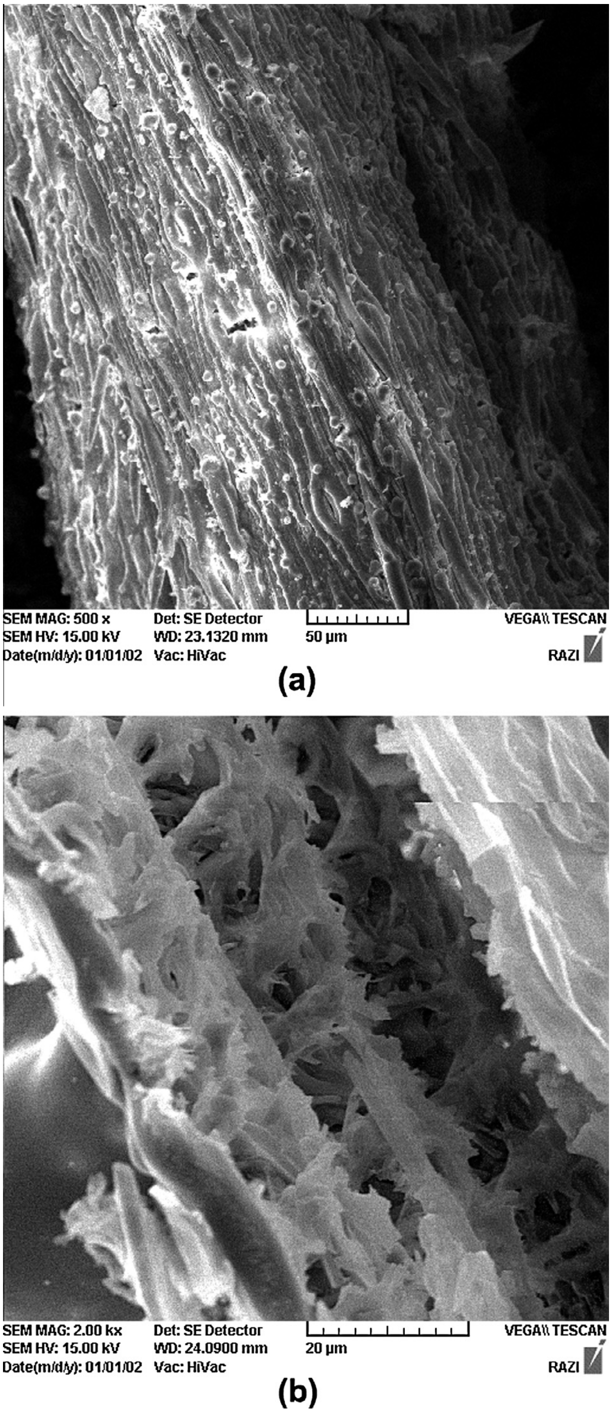

Fig. 2. SEM micrographs of the ashes before grinding: (a) NTR-1 h; (b) ALR-1 h.

amount of alkali contaminants such as K_2O and Na_2O. The presence of these alkalis reduces the melting temperature of silicates in the ash, and also serves as an accelerator for crystallization of SiO_2 during combustion. In addition, the presence of alkalis may increase the alkali-aggregate reaction potential of the mixtures incorporating the ashes. Although past research [23] suggested that rice husk ash can be used to mitigate alkali-silica reaction, caution should be exercised when using rice husk ash with high alkali content along with aggregates containing reactive siliceous minerals.

The substantial decrease in the K_2O content observed in Table 1 for acid leached ashes is expected to make SiO_2 much less prone to crystallization during vigorous and prolonged combustions, which are typical to traditional and heap combustions. Due to their lower K_2O content, and consequently higher melting temperature of SiO_2, surface melting of the silicate skeleton is substantially reduced for the acid leached ashes. As such, the resulting ash preserves its porous microstructure even for prolonged retention times. This is observed in Fig. 2a and b which respectively show the SEM micrographs of NTR-1h and ALR-1h ashes after combustion but before grinding. It is qualitatively observed that while the surface of the NTR ash has melted, the porous microstructure of the ALR ash is better maintained. Consequently, it is expected that under a same grinding energy, the acid leached (ALR) ashes are ground to finer particles with higher surface area compared to NTR ashes. Fig. 3a and b show the SEM micrographs of NTR-1h and ALR-1h ashes after a similar 20-min grinding in the ball mill as described in the materials section. It can be observed that the ALR ash was ground to a smaller particle size.

Using these micrographs, the particle size distribution of the NTR-1h and ALR-1h ashes was quantified using digital image analysis. A thresholding technique was used to create binary images, and particles having dimensions less than 1 μm were considered to be noise, and omitted from the analysis. The pixel size in both images was 0.15 μm. Fig. 4a and b show the histograms of the particle size distribution of the ground NTR-1h and ALR-1h ashes, respectively. The histograms include both the diameter and the maximum dimension of the particles. The diameter of the particles is calculated by dividing four times the surface area to the perimeter. It is observed thatALR-1his ground to a finer particle size, having an average particle diameter of 1.14 μm, compared to that of NTR-1h having an average particle diameter equal to 2.37 μm. Moreover,ALR-1hparticles show less variability in the particle size

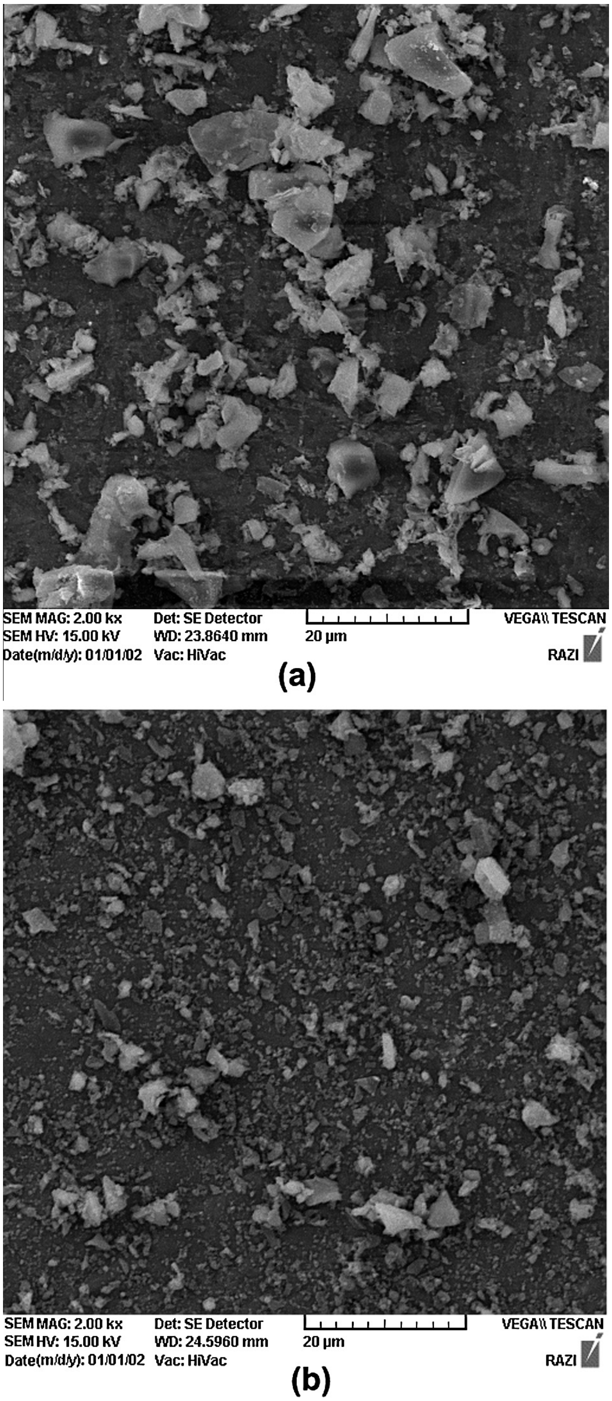

Fig. 3. SEM micrographs of the ashes after 20 min grinding: (a) NTR-1 h; (b) ALR-1 h.

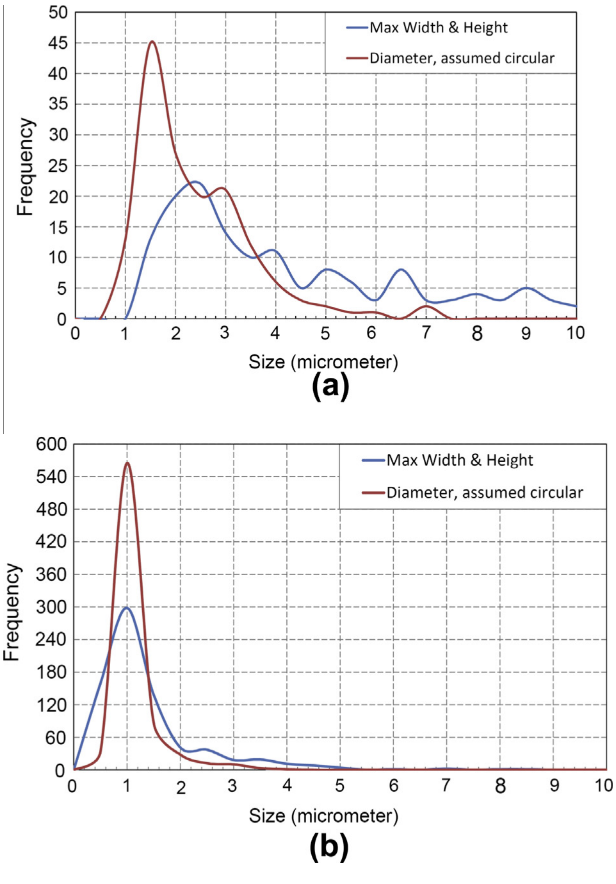

Fig. 4. Particle size distribution histograms of the ashes: (a) NTR-1 h; (b) ALR-1 h.

compared to NTR-1h; the standard deviation of particle diameter for ALR-1h and NTR-1h are measured as 0.43 μm and 1.13 μm, respectively. The resulting coefficient of variation is 37.7% for ALR-1h and 47.7% for NTR-1h.Interestingly, the average roundness factor of the particles of ALR and NTR are almost the same, and equal to 62.1% and 63.8%, respectively. The image analysis data show the same trend observed by nitrogen BET measurements of ALR-1h and NTR-1h ashes (Table 1). The BET specific surface area and the total pore volume ofALR-1hwere found to be 284.3 m^2/g and 0.333 cm^3/g, respectively. The corresponding values for NTR-1h were 57.1 m^2/g and 0.158 cm^3/g. This shows not only an increase in the surface area of the ground ash, but also an increase in its nano-porosity; resulting in the ash's brittleness and better grindability. This further supports the hypothesis that removal of K_2O by acid leaching reduces surface melting and preserves the pore structure and grindability of rice husk ash.

The accelerated surface melting due to the presence of K_2O in NTR, leads to the entrapment of the carbonized organic matter and prevents it from oxidizing. Hence, at any given retention time, the non-acid treated ashes contain higher amount of unburned carbon content compared to acid leached ashes (LOI of NTR and ALR ashes are reported in Table 1); and this could have negative consequences on air entraining of concrete mixtures. Due to the higher porosity of the acid leached ashes, it is expected that the natural moisture content of these ashes would be higher than that of non-acid leached ashes. Therefore, ALRs should have higher loss on drying (LOD) compared to NTRs, which is observed for retention times higher than 4 h. However, an inverse pattern is found in the case of ashes with low retention time. This is probably due to the high carbon content in NTRs of short retention time, whose specific surface area is reported to be about 1000 m^2/g [24] and is highly moisture absorbent.

3.2. Electrical conductivity and pH measurement results

Fig. 5a and b show the electrical conductivity (EC) variations of the saturated lime-NTR and the saturated lime-ALR solutions, respectively. The magnitude of decrease in EC during the test is an indicator of the pozzolanic reactivity of the ashes. For all retention times, it is observed that the drop in the EC of the ALR solutions is much greater than that of NTR solutions; which signifies the higher adsorption potential and reactivity of the acid leached ashes. This is likely due to a higher surface area (lower particle size and higher nano-porosity) of ALR ashes. However, the silica structure of ALRs may also be more disordered (i.e., amorphous) and as such, more reactive. This is discussed further in the XRD section. Considering that the long-term drop in the EC of the solutions represents the pozzolanic lime reactivity of each ash, Fig. 5a shows that an increase in the retention time of NTR ashes (from 15 min to 16 h) results in a decrease in the lime reactivity of these ashes.

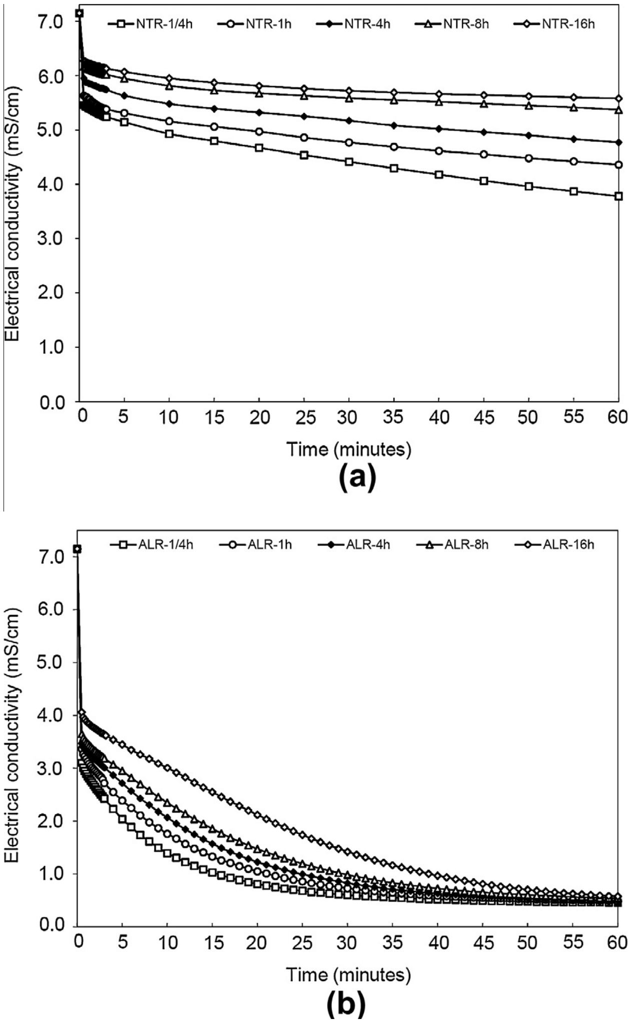

Fig. 5. The time-dependent electrical conductivity (EC) of saturated lime solutions: (a) NTR-added solutions; (b) ALR-added solutions.

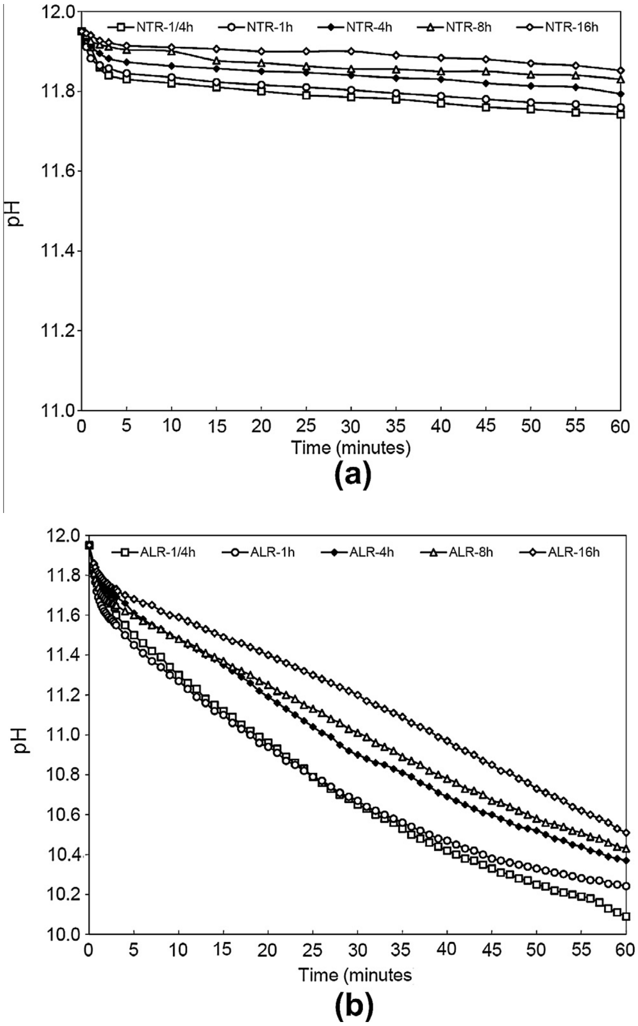

Fig. 6. The time-dependent pH variations of saturated lime solutions: (a) NTR-added solutions; (b) ALR-added solutions.

Table 3
Short-term and long-term variations of the electrical conductivity EC and [OH$^-$] of the NTR/ALR added solutions.

Ash type	Retention time (h)	[OH$^-$] variations ($\times10^{-3}$ mole/l)				EC variations (mS/cm)				Correlation coefficient[b]	
		Short term	Reduction rate (a)[a]	Long term	Reduction rate (b)[a]	Short term	Reduction rate (c)[a]	Long term	Reduction rate (d)[a]	Between a and c	Between b and d
NTR	1/4	1.668	0	3.392	0	1.83	0	3.37	0	0.997	0.983
	1	1.584	5.0	3.158	6.9	1.70	7.3	2.79	17.2		
	4	1.060	36.4	2.699	20.4	1.36	25.8	2.38	29.4		
	8	0.652	60.9	2.152	36.6	1.09	40.5	1.78	47.2		
	16	0.460	72.4	1.800	46.9	0.98	46.5	1.57	53.4		
ALR	1/4	4.015	0	8.789	0	4.5	0	6.69	0	0.540	0.971
	1	4.931	−22.8	8.738	0.6	4.11	8.7	6.67	0.4		
	4	3.664	8.7	8.678	1.3	3.99	11.3	6.65	0.6		
	8	4.235	−5.5	8.643	1.7	3.82	15.1	6.61	1.3		
	16	3.158	21.3	8.589	2.3	3.4	24.4	6.57	1.7		

[a] Expressed in % reduction of [OH$^-$] or EC compared to that of the same type of ash with 1/4 h retention time.
[b] Pearson's linear correlation coefficient.

This may be due to an increased surface melting and reduction in the surface area of the resulting ash, with prolonged retention times. However, given that surface area of NTR ashes other than-NTR-1hwas no measured, this hypothesis cannot be evaluated in the present study. In Fig. 5b, no considerable reduction occurs in the lime reactivity of the acid leached ashes as the retention time is increased; although, lower retention time ashes seem to approach equilibrium quicker (i.e., faster kinetics). The pH variations of the lime-NTR and lime-ALR solutions are shown in Fig. 6a and b, respectively. It is observed that the pozzolanic lime reactivity of ALR is much higher than that of NTR, based on its pH drop. Generally, a good agreement was found between EC and pH drop results. The advantages and disadvantages of EC and pH methods were discussed in a previous work [25].

Short term (i.e., 0–2 min) and long term (i.e., 0–60 min) drop in the electrical conductivity (EC) of solutions containing ALR or NTR

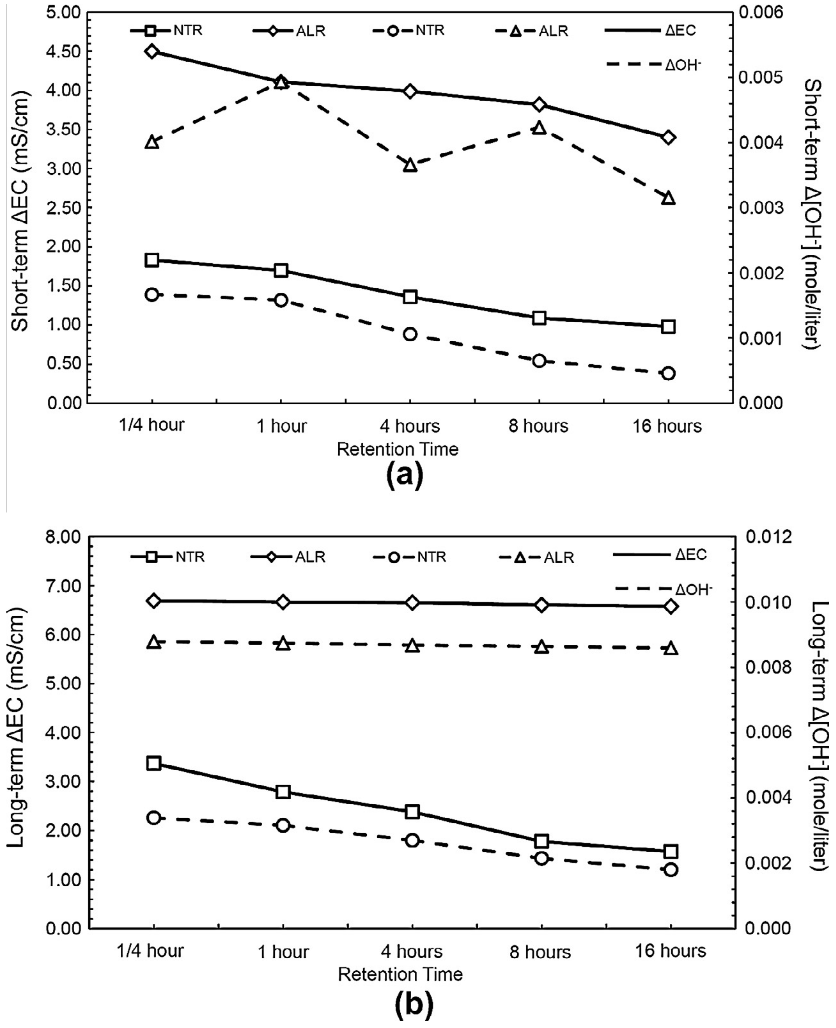

Fig. 7. EC/[OH$^-$] variations versus the retention time: (a) short-term variations; (b) long-term variations.

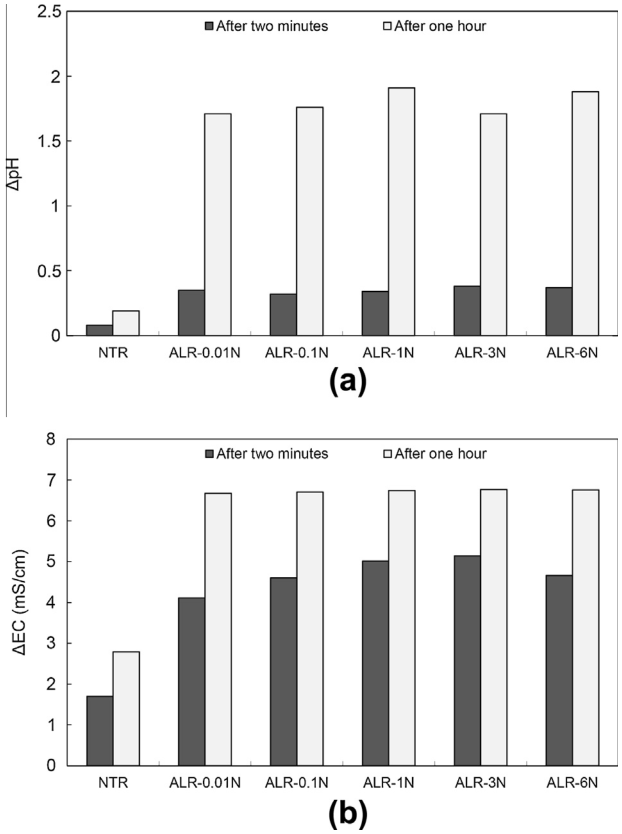

Fig. 8. Short-term and long-term changes in the properties of saturated lime solutions versus acid normality: (a) Electrical conductivity; (b) pH.

ashes were calculated based in Fig. 5a and b, and the values are reported in Table 3. For example, the solution containing NTR-1/4hash lost 1.83 mS/cm of its initial electrical conductivity within the first 2 min of the test and lost 3.37 mS/cm conductivity in the span of 0–60 min. Similar calculations were performed based on the $[OH^-]$ concentration of the solutions (using pH measurements of Fig. 6a and b) and the results are presented in Table 3. The changes in the EC and pH of the solutions are also graphically presented in Fig. 7a and b. A smaller ΔEC or $\Delta[OH^-]$ indicates a weaker pozzolanic reactivity. It is observed that an increase in the retention time decreases the short-term drop in the EC and pH of the solutions for both ALR and NTR ashes (Fig. 7a). Based on the conductivity (EC) results, it is seen that as the retention time increases from 15 min to 16 h, the adsorption potential (i.e., short-term drop in EC) and pozzolanic reactivity (i.e., long-term drop in EC) of NTR are decreased by 46.5% and 53.4%, while there are 24.4% and 1.7% decrease in those values for the acid leached ashes. This is an indicator of the reduction in the sensitivity of acid leached ashes to the prolongation of retention time compared to non-acid leached ashes. More support can be found in the corresponding reduction rates of $[OH^-]$ (i.e. 72.4% and 46.9% for NTR and 21.3% and 2.3% for ALR). In most cases, a good correlation was found between EC and $[OH^-]$ reduction rate results (see correlation coefficients in Table 3).

These observations suggest that acid leached ashes are considerably less susceptible to loss of pozzolanic properties caused by a prolonged combustion. This finding has practical application in that acid leaching is a suitable pre-treatment method for the traditional and heap combustion methods of rice husk where there is little control on the retention time and ultimate temperature. This adds to the findings of Feng et al. [12] who reported that acid leaching reduces the sensitivity of rice husk ash to the ultimate temperature of its combustion.

To study the effect of acid normality on the pozzolanic reactivity of acid leached rice husk ash, a similar series of experiments were performed where the short-term (0–2 min) and the long term (0–60 min) decreases in the EC and pH of saturated $Ca(OH)_2$ solutions were monitored after addition of 5.000 g of rice husk ash to 200 ml of solution. Fig. 8a and b show the results for the pH drop and the EC drop of the saturated lime solutions. For comparison, data for the non-acid treated ash (NTR) is also included. It is observed that acid leaching of rice husk with a dilute 0.01 N HCl acid dramatically increases the reactivity of the resulting husk ash. Higher concentrations of acid did not significantly improve the pozzolanic reactivity of ALR ashes beyond what could be achieved by 0.01 N HCl acid leaching.

3.3. XRD results

Fig. 9 shows the XRD patterns of the ashes. Interestingly, no major crystalline phases are detected in both types of ashes (NTR and ALR) even after 32 h of combustion retention time. This suggests that the presence of higher K_2O content, observed in the case of NTR does not necessarily result in formation of crystalline silica

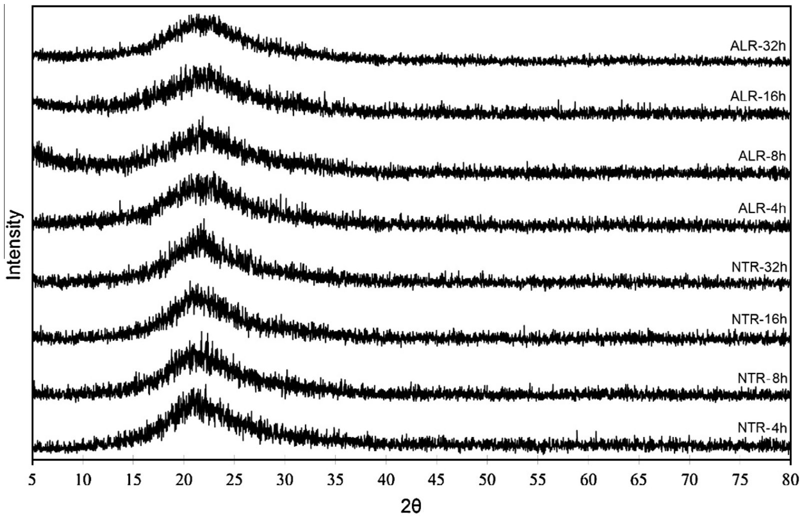

Fig. 9. X-ray diffraction patterns of the ashes.

Table 4
Superplasticizer demand, compressive strength and SDR results for mortar mixtures.

Retention time (h)	Mixture labels	Superplasticizer (l/m^3)	Density[a] (g/cm^3)	28-day Compressive strength (MPa)	Strength to density ratio (m)
–	RT-C	–	2.26	45.81	2027
1/4	RT-5-NTR	1.921	2.25	50.88	2261
	RT-10-NTR	4.153	2.20	54.41	2473
	RT-15-NTR	6.570	2.19	58.27	2661
	RT-5-ALR	3.905	2.23	41.42	1857
	RT-10-ALR	5.702	2.21	57.51	2602
	RT-15-ALR	6.880	2.19	53.26	2432
1	RT-5-NTR	1.921	2.23	51.40	2305
	RT-10-NTR	4.153	2.22	55.17	2485
	RT-15-NTR	6.322	2.20	59.31	2696
	RT-5-ALR	3.892	2.23	43.1	1933
	RT-10-ALR	5.667	2.22	59.68	2689
	RT-15-ALR	6.801	2.19	54.55	2491
4	RT-5-NTR	1.983	2.25	56.25	2500
	RT-10-NTR	4.153	2.23	62.21	2790
	RT-15-NTR	6.446	2.22	65.53	2952
	RT-5-ALR	3.879	2.25	43.69	1942
	RT-10-ALR	5.631	2.22	60.62	2731
	RT-15-ALR	6.667	2.19	55.32	2526
8	RT-5-NTR	2.107	2.25	49.88	2217
	RT-10-NTR	4.339	2.23	52.80	2368
	RT-15-NTR	6.508	2.20	56.91	2587
	RT-5-ALR	3.866	2.23	45.87	2057
	RT-10-ALR	5.633	2.22	65.52	2951
	RT-15-ALR	6.661	2.18	58.72	2693
16	RT-5-NTR	2.169	2.25	46.82	2081
	RT-10-NTR	4.339	2.21	48.65	2201
	RT-15-NTR	6.508	2.20	55.42	2519
	RT-5-ALR	3.862	2.23	51.82	2324
	RT-10-ALR	5.641	2.21	68.87	3116
	RT-15-ALR	6.722	2.18	61.51	2822

[a] The apparent density of the mortars was measured by dividing the SSD weight to the geometric volume of the specimens, immediately after removing the cured specimens from the water bath.

in the ash, if the ash is rapidly cooled from its maximum combustion temperature. It would be interesting to study how the cooling rate affect the formation and concentration of crystalline phases in the NTR and ALR ashes.

3.4. Strength activity of mortars

Table 4 shows the superplasticizer (SP) demand, apparent density, 28-day compressive strength, and the strength to density ratio (SDR) of the NTR and ALR blended mortar mixtures. It is observed that the SP demand of the mortars incorporating ALR is higher than that of the NTR blended mortars, which is probably attributed to the higher fineness and specific surface area of ALR compared to NTR. The 28-day compressive strength results of the mortars are also presented in Fig. 10. The error bars represent ±1 standard deviation. The following observations can be made:

1. For all mortars containing NTR ashes, strength increases consistently with the NTR dosage from 0% to 15%. For the ALR mortars, 10% is the optimum replacement level of cement with rice husk

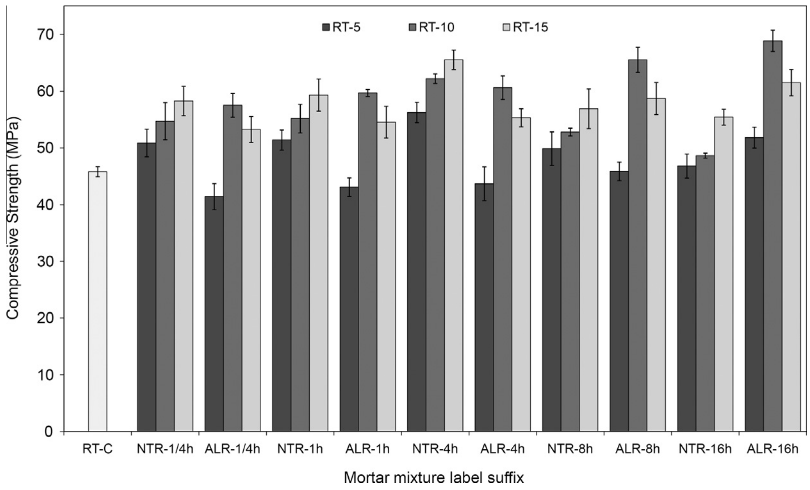

Fig. 10. 28-Day compressive strength results of mortars.

ash. While mortars containing 10% and 15% ALR always show better strength than the control (100%PC) mortar, those containing 5% ALR generally show similar or lower strength than the control mortar.

2. By comparing mortars containing 10% or 15% cement replacement, it is observed that both NTR and ALR ashes show practically similar strength activity in mortars for retention times up to 4 h. Longer retention times resulted in better compressive strengths in ALR mortars in comparison with NTR mortars.
3. In comparison with the control mortar, the highest strength improvement was found in the case of 10% cement replacement withALR-16hash, where 50% increase in the compressive strength, relative to the control mortar, was observed. The second highest increase in strength was found in the case of 15% replacement of cement with the NTR-4h ash, followed by the 10% replacement with theALR-8hash.

4. Conclusions

The following conclusions can be drawn based on the results of this work:

- Acid leaching of rice husks prior to combustion resulted in an ash (ALR) with higher SiO_2 content, lower alkali content, lower unburned carbon content, better grindability, smaller particle size, larger surface area, and larger nano-porosity, in comparison with ash from non-acid treated husks (NTR). These characteristics improve the performance of rice husk ash in concrete mixtures.
- Based on the electrical conductivity (EC) and pH measurement of saturated lime-pozzolan solutions, it was observed that ALR ashes exhibit a higher pozzolanic reactivity than NTR ashes.
- Further, unlike NTR ashes, the pozzolanic reactivity of ALR ashes was not affected by a prolonged combustion retention time. In other words, acid leaching essentially decreases the sensitivity of the ash to the variability in the retention time.
- Acid treatment with 0.01 N HCl was sufficient for improving the reactivity of rice husk ash. The use of higher concentration acids did not considerably improve the reactivity of the ash, according to the saturated lime-pozzolan solution test.
- Both acid-leached and non-acid treated ashes were found to have a highly amorphous structure even for combustion times as long as 32 h. The presence of higher K_2O content in the case of NTR ashes did not result in the formation of crystalline silica, as long as the ash was rapidly cooled to prevent crystallization.
- Based on strength results of mortar cubes containing 10% or 15% rice husk ash as cement replacement, it was observed that, for combustion retention times up to 4 h, both NTR and ALR ashes show similar strength activity. Longer retention times resulted in better compressive strengths in ALR mortars in comparison with NTR mortars.
- In comparison with a control PC mortar, mortars containing 10% or 15% ALR showed an improved 28-day compressive strength by 16–50%. ALR ashes with longer retention times generally resulted in better mortar strengths.
- In comparison with a control PC mortar, mortars containing 5%, 10% or 15% NTR showed an improved 28-day compressive strength by 11–43%. The best mortar strengths were observed for NTR ashes with 4 h retention time.
- The lime reactivity of rice husk ash was not directly correlated with the strength activity of mortars containing the ash.

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