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Research Article

Evaluating the Effect of Calcination and Grinding of Corn Stalk Ash on Pozzolanic Potential for Sustainable Cement-Based Materials

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In developing countries, one of the usual practices is the uncontrolled, open burning of corn stalk (CS) or its utilization as a fuel. It is known that the ash obtained under uncontrolled burning conditions constitutes blackish and unburnt carbon particles as well as whitish and grayish particles (representing crystallization of silica) due to over burning. However, controlling the burning process can improve the quality of ash produced to effectively use it in cement-based materials. Hence, this research was aimed at exploring the pozzolanic properties of corn stalk ash upon calcination and grinding, for it to be used in the manufacturing of sustainable cement-based materials. In order to obtain a suitable corn stalk ash (CSA), which can be used in cement/concrete, a research investigation consisted of two phases. In the first phase, calcination was carried out at 400°C, 500°C, 600°C, 700°C, and 800°C for 2 hours. The tests applied on the resulting ashes were weight loss, XRD, pozzolanic activity index (PAI), Chapelle, Fratini, and consistency. From XRD spectra, it was found that, at lower temperatures, silica remained amorphous, while it crystallized at higher temperature. Ash combusted at a temperature of 500°C possessed largest pozzolanic activity of 96.8%, had a Fratini CaO reduction of 93.2%, and Chapelle activity of 856.3 mg/g. Thus, 500°C was chosen as an optimum calcination temperature. In the second phase, the ash produced at 500°C was grinded for durations of 30, 60, 120, and 240 minutes to ascertain the optimum grinding times. Resulting ashes were examined for hydrometer analysis, Blaine fineness, Chapelle activity, and pozzolanic activity. Experiment outcomes revealed a direct relationship between values of Blaine fineness, surface area, Chapelle activity, PAI, and grinding duration. It was concluded that CSA can be used as a pozzolan, and thus, its utilization in cement/concrete would solve ash disposal problems and aid in production of eco-friendly cement/concrete.

1. Introduction

Engineering, economic, and ecological benefits of by-products of industry as well as agriculture, including sugar cane bagasse ash (SCBA), blast furnace slag, fly ash, and rice husk ash (RHA), have made a common practice of using them in production of cement-based materials [1, 2]. Moreover, their use is growing at a faster rate for the development of sustainable cement-based materials [3, 4]. Comprehensive analysis has been conducted on these ashes by a variety of investigators to assess their pozzolanic activity [5–8]. These researches proved that calcination temperature not only affects the pozzolanic activity, but can be used to optimize amorphous silica. Furthermore, strength and durability properties were not adversely affected when ash burnt at optimum burning conditions was partially replaced with cement [9, 10].

Corn stalk (CS), by-product of an agricultural activity, is the stem of maize plant and constitutes roughly 50% of a net grain production [11]. In developing countries, when CS cannot be utilized as an animal food, it is incinerated openly in a nonmanageable way or utilized as a fuel in cogeneration process. It is known that blackish particles might exist in the ash obtained under uncontrolled burning conditions because of the presence of unburnt carbon. Aside from that, whitish and grayish particles also exist which indicate over burning, and hence, the crystallization of silica. However, controlling the parameters like temperature, heating rate, soaking time, and atmosphere, the quality of ash can be improved, as reported in the literature, for highly pozzolanic material such as RHA [12–14] to use it efficiently in cement-based composites.

The crop yield of maize must be evaluated to examine the CSA production capability. In 2013, world quantities of corn stalk produced constituted 509.05 million tons [11, 15]. According to Morissette et al. [16], 6% of ash can be obtained from corn stalk. Hence, with 509.05 million tons of corn stalk generated, the world has the total ash production potential of 30.5 million tons (Table 1). This data further implies the significance of evaluating the practice of CSA application in cement-based materials. Moreover, the ash resulting from burning a huge amount of corn stalk provides no significance in terms of further application and that is why an elimination of it has recently become an extensive issue.

When ashes obtained from agricultural by-products are used in cement-based materials, they resolve the matters of sustainability as well as create more durable concrete by acting as pozzolans [17, 18]. Research studies that have been conducted on bagasse ash and RHA have shown significantly viable results. [6, 19–21]. A few notable studies evaluating the effect of calcination and grinding of agriculture-based materials are mentioned here. Mehta [22] concluded that amorphous silica ash was received by the controlled burning of rice husk ash, which was highly reactive. The burning temperature, time, and rate controlled the crystallization of silica, as per the author's opinion. Cook et al. [19] observed the formation of highly amorphous silica in ash burnt at 450°C for 4 hours. However, the silica could crystallize under 15 hours exposure to a temperature as low as 350°C [23]. The effect of incineration duration of calcination of rice husk was investigated by James and Subba Rao [20]. For this purpose, the soil and rice husk were separated by being washed with water, followed by drying at room temperature. Subsequently, it was burnt at different temperature values, ranging from 300°C to 900°C during the time period from one to thirty hours. According to the test results, the samples burnt at 500°C showed the highest reactivity, while having different durations of burning. Hence, it was concluded that the incineration temperature, compared to the duration of burning, is a critical factor in the crystallization of silica. The evaluation of effects of RHA incineration on mechanical properties of cement paste and the mineralogy was carried out by Bie et al. [5] who burnt the rice husk samples in a muffled furnace at a heating rate of 5°C/minute for 1 and 2 hours. 600°C was found out to be the optimum combustion temperature for the purpose of achieving high reactivity RHA, as shown by the compressive strength and mineralogical analysis of cement mortar samples. Xu et al. [24] conducted microlevel and nanolevel investigation of the RHA structure to establish the link between its high specific surface area and its high pozzolanic activity. Heat treating of the RHA was carried out at 20°C/minute heating rate in an electric oven. The samples were kept at different temperatures ranging from 500°C to 800°C for 2 hrs. Test results from XRD analysis and compressive strength test demonstrated that the highest reactivity of the RHA was achieved during its incineration at 600°C. Furthermore, images from SEM and TEM analysis showed that the structure of RHA contains three layers, i.e., inner, outer, and interfacial layer as well as two type of pores, interstitial (less than 50 nm) and honeycombed (10 μm). These pores contribute to the RHA's high chemical reactivity and very large specific surface area. Ramadhansyah [25] evaluated how the mineralogical composition and the RHA's PAI was influenced by variation in temperature and grinding. RHA samples were calcinated at 700°C for 6 hours at 10°C/minute heating rate. The process was followed by grinding in a ball mill for a period of 30 to 300 minutes with a successive increment interval of 30 minutes, having pozzolanic activity analyzed by TGA and PAI. The conclusions drawn by the authors, which were built upon test results, explained that the highest pozzolanic index was found under a condition of 90 minutes grinding. Moreover, in accordance with authors' observation, calcination modified the mineralogy of RHA, while PAI was affected by grinding; however, no change in chemical composition was detected. Givi et al. [26] examined the influence of grinding RHA for 30 and 180 minutes on cement-based composites' water permeability and compressive strength. It was found out that with the decrease in particle size, compressive strength increased and the porosity of the cement-based composite reduced. Xu et al. [27] considered the mechanical properties of cement-based composites and the effect of RHA grinding for different duration on them. The authors found out that grinding RHA for 30 minutes produced maximum compressive strength.

Even though extensive research has been accomplished on a various secondary raw materials, such as SCBA and RHA, to measure the impact of calcination on the pozzolanic performance of these ashes, organized and systematic study evaluating the influence of calcination of CSA on the pozzolanic properties of CSA has not been carried out yet. Therefore, in this research, the evaluation of effects of variation in temperature and grinding duration on the pozzolanic properties of CSA is carried out. Moreover, on the basis of the above-mentioned literature, it can be concluded that incineration temperature and grinding time are the key factors affecting pozzolanic activity. Optimum incineration temperature was usually established around 500–600°C, but it was directly dependent upon the incineration time and rate. Thus, with an increase in incineration duration and decrease in incineration rate, optimum temperature decreased. Furthermore, optimum grinding time was found above 60 minutes, but it was also dependent upon the speed of revolution and type of mill used in grinding.

Table 1: Corn, corn stalk, and potential corn stalk ash production for top 25 countries of the world.

S #	Country	Corn production (mt)	Corn stalk production (50% of corn production [11]) (mt)	Corn stalk ash (6% of corn stalk [16]) production (mt)
1	USA	353,699,441	176,849,721	10610983
2	China mainland	218,489,000	109,244,500	6554670
3	Brazil	80,273,172	401,365,86	2408195
4	Argentina	32,119,211	160,596,06	963576.3
5	Ukraine	30,949,550	154,747,75	928486.5
6	India	23,290,000	116,450,00	698700
7	Mexico	22,663,953	113,319,77	679918.6
8	Indonesia	18,511,853	925,592,6.5	555355.6
9	France	15,053,000	752,6500	451590
10	Canada	14,193,800	709,6900	425814
11	South Africa	12,486,000	624,3000	374580
12	Russia Federation	11,634,943	581,7471.5	349048.3
13	Romania	11,347,637	567,3818.5	340429.1
14	Nigeria	10,400,000	520,0000	312000
15	Italy	7,899,617	394,9808.5	236988.5
16	Philippines	7,377,076	368,8538	221312.3
17	Hungry	6,724,800	336,2400	201744
18	Ethiopia	6,674,048	333,7024	200221.4
19	Turkey	5,900,000	295,0000	177000
20	Serbia	5,864,419	293,2209.5	175932.6
21	United Republic of Tanzania	5,356,350	267,8175	160690.5
22	Thailand	5,062,828	253,1414	151884.8
23	Pakistan	4,944,210	247,2105	148326.3
24	Germany	4,387,300	219,3650	131619
25	Paraguay	4,120,000	206,0000	123600
	Rest of the world	98,689,750	493,44875	2960693
	Total	1,018,111,958	509,055,979	30543359

Based on the literature review, an incineration temperature range of 400–800°C and grinding time range from 30 to 240 minutes was chosen. All described inferences from the reviewed literature are taken into account for conducting experiments.

2. Experimental Investigation

2.1. Materials

2.1.1. Cement. Standard Portland cement, meeting requirement of ASTM C150 [28], was utilized. Specific gravity and fineness of cement were 3.15 and 2750 cm^2/g, correspondingly.

2.1.2. Corn Stalk. The samples were crushed into pieces of 1-inch length (Figure 1) to maintain homogeneous calcination and achieve lowest carbon concentration. The selected crop was maize crop from the district Abbottabad, Pakistan.

Figure 1: Corn stalk after crushing.

2.1.3. Corn Stalk Ash (CSA). In phase I, corn stalk was combusted in a muffle furnace at 10°C/minute for 2 hours at different temperatures ranging from 400°C to 800°C. The corn stalk ash samples burnt at these temperatures were accordingly marked as CS400, CS500, CS600, CS700, and CS800. For incineration, the sample was retained up to 1-inch height in a ceramic bowl and then grinded for 30 ± 5 minutes in a ceramic ball mill at a speed of 100 rpm with grinding media to a CSA ratio of 21 weight.

In phase II, CSA burnt at an optimum temperature was grinded for intervals of 30, 60, 120, and 240 minutes in a ball mill at a speed of 100 rpm with grinding media to CSA ratio of 21 weight. CSA samples grinded for 30, 60, 120, and 240 minutes were described as G30, GS60, G120, and G240, correspondingly.

2.1.4. Water. The experimental work was carried out using distilled water.

2.2. Testing Program

2.2.1. Phase I. The diffractometer model JDX-3532 JEOL, Japan, was used to study the mineralogical features of the corn stalk ash. The operation was carried out with a 2θ scan at temperature interval between 20° and 80° and CuKα radiation (1.5418 Å) functioning at 40 kV and 25 mA [29]. The chemical phases of the samples were identified by the pattern defined by ICDD using "MATCH Phase Identification from Powder v3.1" software.

Scanning electron microscopy (SEM), that has an acceleration voltage value of 20 kV with secondary electrons, was used to study the morphology of the CSA as well as the corn stalk. To identify the chemical composition of CSA, XRF was performed, while the loss on ignition was performed as per ASTM C311 and C114.

PAI was found by replacing 20% of cement by weight of ash prepared at different temperatures (from 400°C to 800°C). It was estimated by using ASTM C311 [30] as per the following formula:

$$\text{PAI} = \left(\frac{\sigma_{\text{ash blended}}}{\sigma_{\text{control mix}}}\right) \times 100, \quad (1)$$

$\sigma_{\text{ash blended}}$ = mean compressive strength of the ash blended cubes, MPa (psi), and $\sigma_{\text{control mix}}$ = mean compressive strength of the control mix cubes, MPa (psi).

The Fratini and Chapelle tests were used additionally to check the CSA pozzolanic activity [2, 17] in accordance with British Standard BS EN 196(5) [31] and as per procedure mentioned in [32, 33]. Finally, the consistency test was performed according to ASTM C187 [34] on cement paste prepared with WSA incinerated at 400, 500, 600, 700, and 800°C.

2.2.2. Phase II. In the second phase of study, the effects of grinding on CSA obtained at an optimum calcination temperature (phase I) were analyzed. The ash was grounded in a ball mill with a speed of 100 rpm. The grinding media to CSA ratio was maintained at 21 [35]. Different CSA samples were obtained at a duration of 30, 60, and 120 minutes of grinding and were denoted by G30, G60, G120, and G240, while ungrounded CSA was donated by G0. Blaine fineness values were determined according to ASTM C204 [36] in order to ascertain the effect of grinding on particle size. Hydrometer analysis was performed to analyze the particle size distribution of grounded ashes. The morphology of CSA-grounded samples was evaluated using SEM with the same specification as mentioned in phase I. Other important tests such as the Chapelle test, Fratini test, and pozzolanic activity were performed again using the procedures as mentioned in phase I of the testing program.

3. Results and Discussions

3.1. Morphology of Corn Stalk. The images of corn stalk (stripped of its leaves), crushed corn stalk, outer corn stalk covering, and inner core are depicted in Figure 2. The typical internode length in the corn stalk varied from 0.5 to 1 ft. The outer layer of corn stalk contains green or golden brown longitudinally knitted dense and compacted fibers, while inner core has longitudinal fibers, off-white color, and is less dense.

SEM image of inner core of corn stalk represented by Figure 3 displays different textures (foliated, fibrous, and layered). The longitudinal section (Figure 3(a)) shows fibers with large aspect ratios, while relatively thick fibers can be observed in internodal cross section (Figure 3(b)). Moreover, the size of pores ranged from less than 1 μm to higher than 5 μm (Figures 3(a)–3(c)).

3.2. Calcination at Different Temperatures (Phase I)

3.2.1. Color Alteration of Corn Stalk at Various Calcination Temperatures. Color of ash can be considered as the indirect presence indicator of the unburnt carbon. The unburnt carbon is signified by the presence of darker colored ash [37]. Its presence decreases the pozzolanic activity of ash [38]. Figure 4 shows modifications in the color of ash at distinctive calcination temperatures. The raw corn stalk is brown in color (Figure 4(a)), while its ash is mostly grey and black (Figure 4(b)–4(f)). The sample calcined at 400°C (CS400) exhibited a blackish color, due to the presence of unburnt carbon, demonstrating partial calcination of the ash. The extent of blackish color was considerably reduced in CS500 and CS600; however, some blackish color could be observed in the outer portion, while CS700 and CS800 did not show any blackish-colored fibers. It was also observed that from CS500 onwards, different color contrasts started to appear: pure whitish, grayish, and faintly brownish color. Furthermore, CS700 and CS800 comprised only of these three before-mentioned colors. During testing, inner portion displayed pure white color, while grayish color was exhibited by reasonably burnt outer portion, at the same time nodes signified the brownish color. As stated in the available literature, crystallized ash appeared to be of pure white color while the presence of basic oxides demonstrated brownish color [39–41]. Thus, the calcined ashes of corn stalk displayed different colors and properties at the same temperature, due to the diversity of physical properties of corn stalk ash.

3.2.2. Weight Loss of Corn Stalk Ash at Various Calcination Temperatures. Due to the decomposition of organic matter occurring at a higher temperature with the release of CO_2, more weight loss was observed at higher temperatures, as it is evident from Figure 5. Moreover, carbon is more efficiently oxidized at higher temperatures [24]. The sample calcined at 400°C showed least weight loss (92.2%), which can be explained in terms of the presence of large concentration of unburnt carbon, as evident from its dark color.

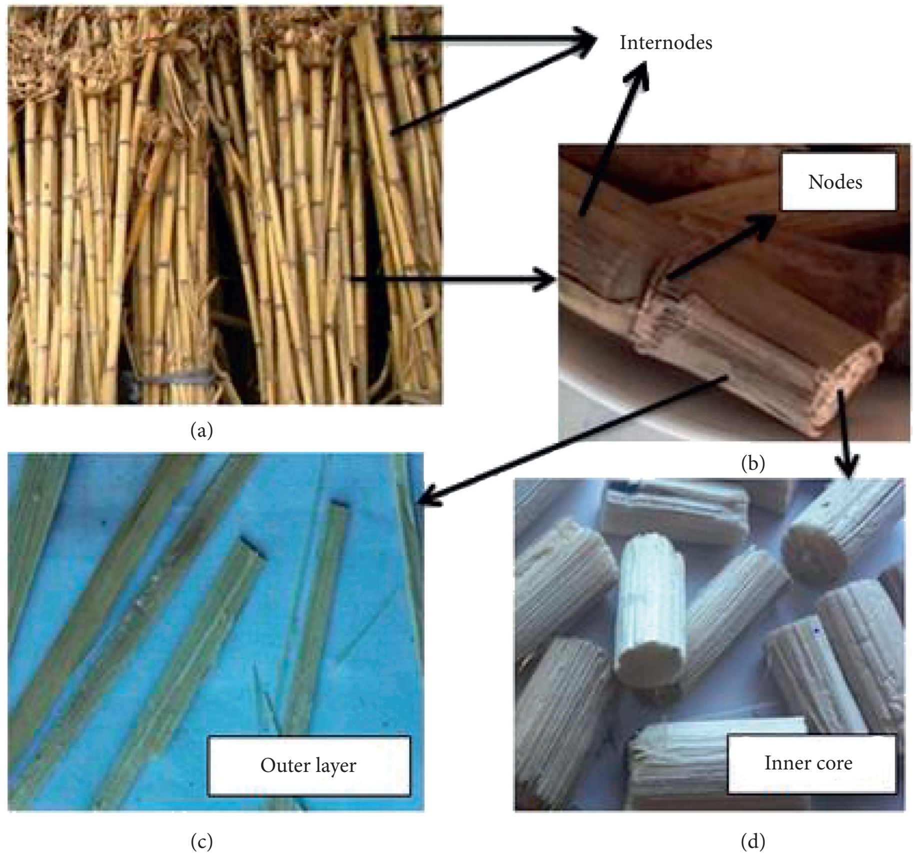


Figure 2: (a) Corn stalk. (b) Crushed corn stalk. (c) Outer layer of corn stalk. (d) Inner core of corn stalk.

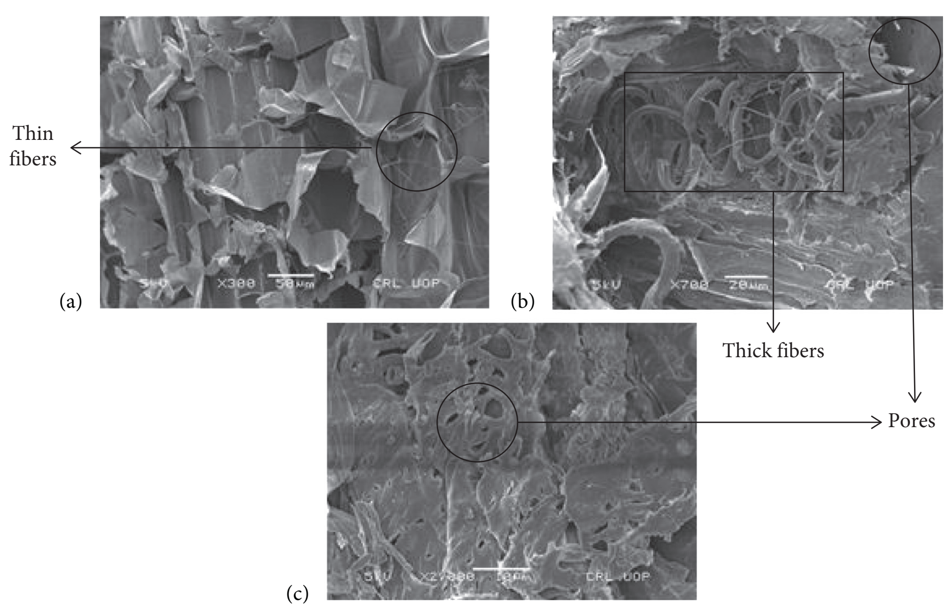


Figure 3: SEM of inner core of corn stalk: (a) Longitudinal section (foliated texture). (b) X-section at internodes (fibrous texture). (c) X-section near nodes (layered texture).

The maximum observed weight loss values were found to be 96.02% and 96.44% for CS700 and CS800 samples, respectively. This was possibly due to combustion of most of the organic compounds at this temperature. The literature [5, 24] points out that generally a weight loss at 700°C decreased when compared to that at 600°C, due of

FIGURE 4: (a) Corn stalk. Color change at different temperatures: (b) CS400, (c) CS500, (d) CS600, (e) CS700, and (f) CS800.

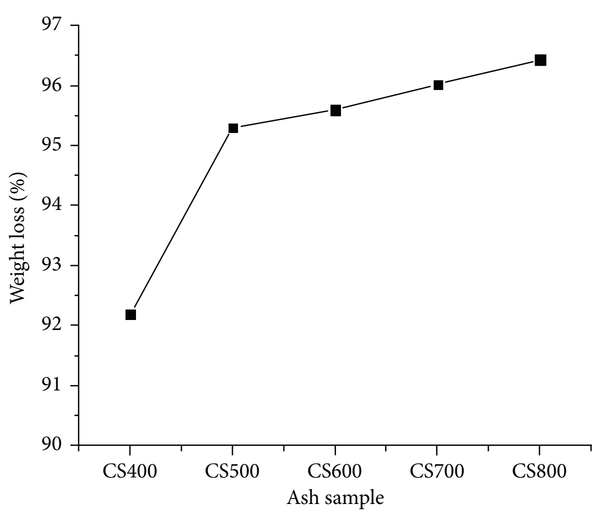


FIGURE 5: Weight loss of corn stalk ash at different temperatures.

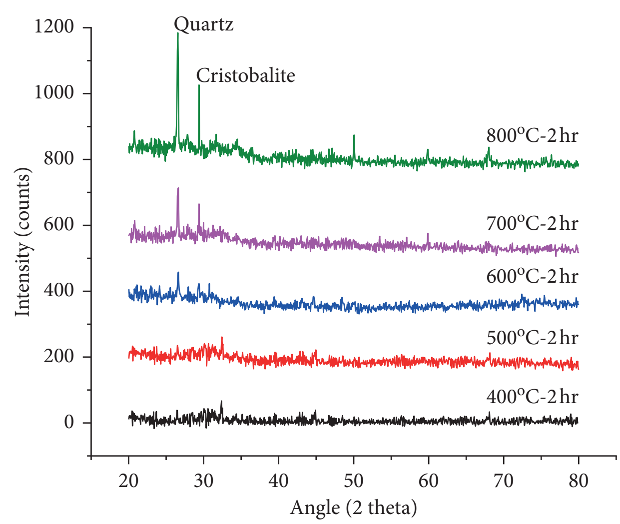


FIGURE 6: XRD of corn stalk at different temperatures.

fragmentation of K_2O into elemental potassium that catches organic material; however, in the framework of this research, the contrary was valid. One of the reasons for such change was a gradual pace of calcination (adopted in this research) as the carbon is oxidized before K_2O decomposes; hence, avoiding any entrapment of carbon [42].

3.2.3. X-Ray Diffraction of Corn Stalk Ash at Various Calcination Temperatures. The XRD spectra of ashes calcined at different temperatures showed intense sharp peaks after 600°C as depicted in Figure 6. These sharp peaks represented crystalline structures (at specific 2θ orientation) since such structures tend to cause more X-rays to diffract. No peaks were observed at the temperatures of 400°C and 500°C, indicating the presence of amorphous silica in ashes. At a calcination temperature of 600°C and $2\theta = 26.51°$ ($d = 3.1545$ Å), a slightly sharp peak of quartz appeared displaying trigonal hexagonal crystal structure. This became more prominent with further increase in temperature. Similarly, another sharp peak of cristobalite ($d = 3.0379$ Å related with $2\theta = 29.38°$) was observed at 700°C, where it became remarkable with monoclinic crystal structure. At 800°C, both peaks appeared to be relatively sharper because

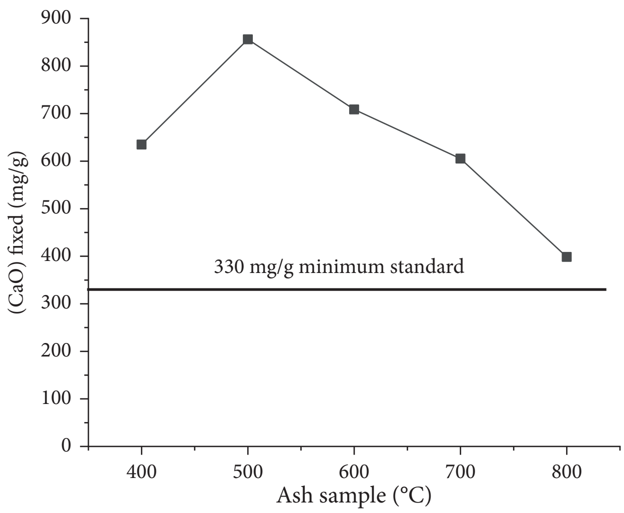


Figure 7: Chapelle activity at different temperatures.

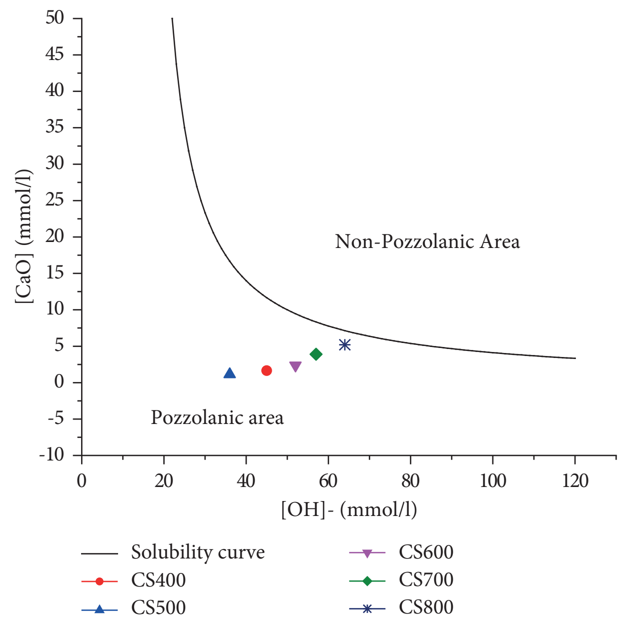


Figure 8: Fratini solubility cure for corn stalk ash samples.

of high crystallization of silica in ash samples. The XRD spectra showed the presence of amorphous silica in CSA400 and CSA500.

3.2.4. Chapelle Activity Test of Corn Stalk Ash at Various Calcination Temperatures. Figure 7 shows the results of the Chapelle test according to which, the minimum requirement for the pozzolanic activity (330 mg of CaO/g of pozzolan) [43] was satisfied by all the tested samples. However, CS500 demonstrated the highest lime consumption (856.3 mg/g), which was 159.5% more than the required standard (330 mg of CaO/g of pozzolan) [43]. Furthermore, increase in calcination temperature decreased the Chapelle activity to 708.7 mg/g, 605.3 mg/g, and 398.6 mg/g for CSA600, CSA700, and CSA800, respectively. CS400 displayed Chapelle activity of 634.9 mg/g, which is less than the Chapelle activity for samples calcined at 700°C and 800°C, respectively, indicating that the negative effects of crystalline silica affected the Chapelle activity more than unburnt carbon content. The results from the Chapelle activity shows that all samples of CSA displayed varying degrees of reactivity, depending on the calcination temperature. However, CSA500 depicted highest reactivity.

3.2.5. Fratini Test of Corn Stalk Ash at Various Calcination Temperatures. The Fratini test results depicted that each sample was situated under the solubility curve signifying more pozzolanic activity, according to Figure 8. Table 2 quantitatively shows the arrangement with regards to lime reduced by ash sample (in percentage) (CS500 > CS400 > CS600 > CS700 > CS800). As expected, the highest pozzolanic activity was demonstrated by CS500, where the percentage of CaO was reduced by 93.2% (Table 2). This can be attributed to the high amorphous silica, and less unburnt carbon at CS500, in comparison to other ashes. The percentage decrease in CaO at higher temperature was caused by the conversion of silica from amorphous to crystalline nature at higher temperatures. Furthermore, the impact of extreme carbon content on pozzolanic activity was adversely affected by the absorption of calcium ions [44]. So, all the samples may be classified as pozzolans by both the chemical tests; however, the results of XRD and weight loss were more closely validated by the Fratini test rather than the Chapelle test.

3.2.6. PAI of Corn Stalk Ash at Various Calcination Temperatures. The results of compressive strength and PAI of calcined ashes are represented in Table 3. Results clearly demonstrated the dependence of PAI on the temperature of incineration. The pozzolanic activity at 28 days exhibited by CS400 was 76.3% and was above the minimum ASTM milestone of 75% [45]. The amorphous silica presence yielded notable compressive strength even though it contained unburnt particles. CSA at 500°C had lesser quantity of unburnt particles and more amorphous silica in comparison to CS400. The XRD results confirmed the presence of crystalline silica contributing to the reduced value of PAI above 500°C; however, the CSA ash incinerated at 600°C had PAI value that meets the ASTM requirement. The negative influence of crystalline silica on the compressive strength was a lot more than that of unburnt carbon. Therefore, silica obtained at 500°C was found to be the most reactive.

The 7- and 28-day compressive strengths (Figure 9) displayed greater difference between the control mix and CS400 and CS500, while the difference was less for CS700 and CS800. The highest difference (11.2 MPa) signified the maximum rate of strength gain in the mix CS500. This is believed to be due to the pozzolanic activity, causing an increase in strength with the passage of time due to the production of more calcium silicate hydrate (CSH) gel by the reaction of $Ca(OH)_2$ with ash [46]. The CS700 and CS800

Table 2: Fratini test results.

Ash sample	[OH] mmol/l	[CaO] mmol/l	Theoretical max [CaO] = (350/[OH] − 15) mmol/l	[CaO] reduction %
CS400	45.5	1.64	11.5	85.7
CS500	36.0	1.13	16.7	93.2
CS600	52.0	2.37	9.5	75.0
CS700	57.2	3.91	8.3	52.9
CS800	64.4	5.20	7.1	26.6

Table 3: Mix proportion and compressive strength of CSA-blended cement cubes.

Mix designation	(%), CSA	7 days compressive strength (MPa)	PAI	28 days compressive strength (MPa)	PAI
M0	0	35.25	100.0	39	100.0
CS400	10	21.75	61.7	29.75	76.3
CS500	10	26.51	75.2	37.75	96.8
CS600	10	29.5	83.7	33.25	85.3
CS700	10	18	51.1	20	51.3
CS800	10	17.25	48.9	18.75	48.1

*Water/binder = 0.4.

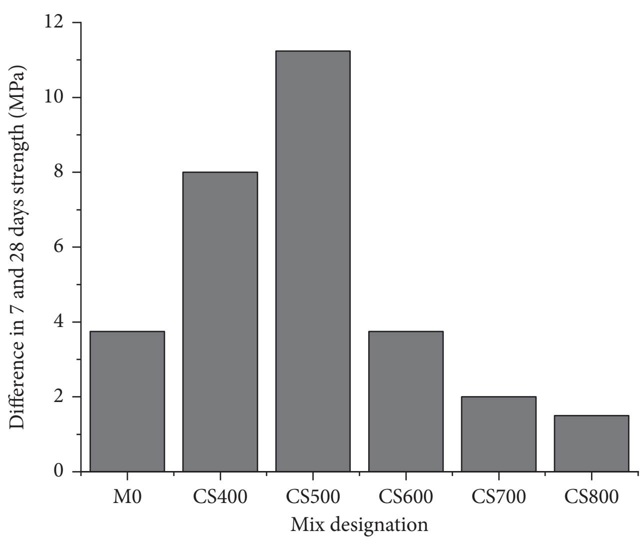


Figure 9: Difference in compressive strength at 7 and 28 days.

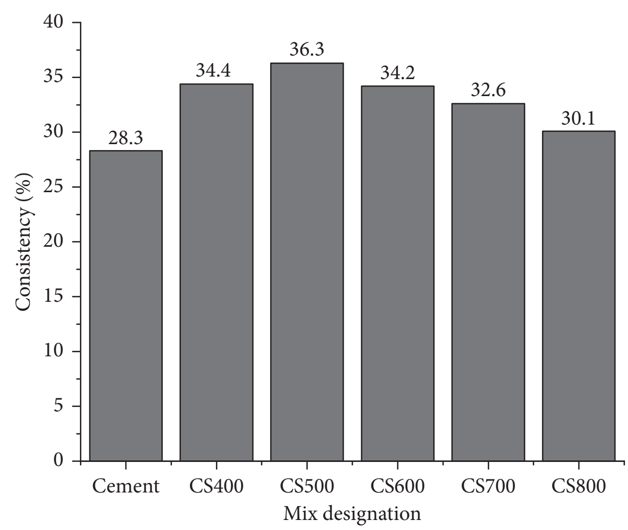


Figure 10: Consistency of control mix and ash-blended mixes at different temperatures.

samples did not strengthen much because of the presence of inactive crystals, which was also verified by the XRD results.

3.2.7. Consistency of Corn Stalk Ash at Various Calcination Temperatures. Blended mixes of ashes are more consistent in comparison to that of control mix as is evident from Figure 10. Also, the consistency of all samples decreased with the rise in incineration temperature, except for CS500. At higher temperatures, the crystallization smoothens the internal surfaces resulting in the reduction of water absorption capacity [47] (Figure 11(a)). Besides, the ash has a specific gravity value less than cement (Table 4), so, the amount of ash required by weight is more for a specific volume, resulting in an increased water demand for same consistency. Finally, the anomalous behavior exhibited by CS500 is because of the removal of outer layers from ash particles causing exposure of the inner surface. This results in an increased surface area as well as porosity of the whole ash as compared to CS400 (Figures 11(b)and 11(c)).

3.2.8. XRF of Ash Calcined at 500°C. XRF performed on ash sample calcined at 500°C to observe its oxide configuration (Table 4) represented the sum of ferric oxides, alumina, and silica to be 82.4 %, which satisfied the criteria of ASTM C618 [48], i.e. the sum of SiO_2, Al_2O_3, and Fe_2O_3 should be greater than 70%, for the material to be classified as pozzolan. The amount of K_2O and P_2O_5 depends upon quantity and fertilizer class utilized at the time of growth period [49]. The presence of K_2O 2.46% and P_2O_5 3% can be accredited to the use of manure, sulphate of potash (SOP), and diammonium phosphate (DAP) fertilizers. It is known that SOP and DAP contain 46% of P_2O_5 and 50% of K_2O, respectively [50]. Finally, the loss on ignition (LOI) was 4.9%, which did not cross the maximum specified limit set by ASTM C618 i.e. 6% [48].

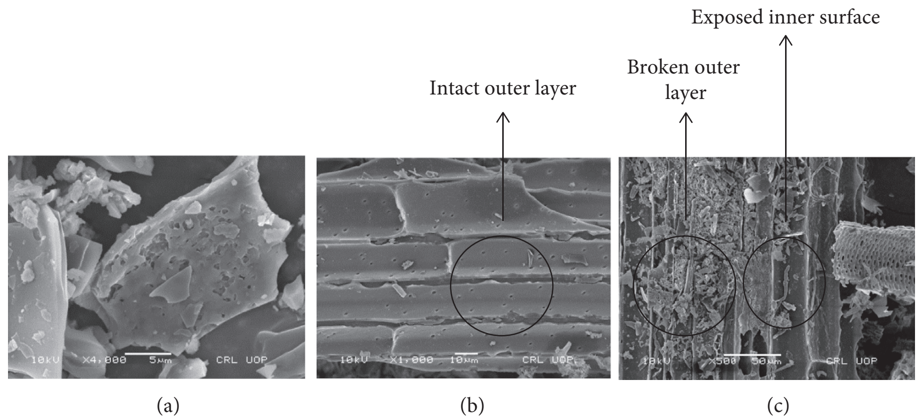


Figure 11: (a) Smooth surface at 800°C. (b) CS400 showing outer layer. (c) CS500 (outer layers blot out).

Table 4: Physical and chemical properties of CSA incinerated at 500°C.

Physical and chemical properties of CS500	
SiO_2	78.4
Fe_2O_3	3.1
Al_2O_3	0.8
K_2O	2.4
CaO	4.8
MgO	5.4
SO_3	1.5
Na_2O	0.2
TiO_2	0.02
P_2O_5	3.00
LOI	4.9
Specific gravity (after 2 hours of grinding)	2.26

The discussion given above concludes that the ash sample calcined for 2 hours at 500°C, i.e., CS500, displayed the best pozzolanic activity, since minimum amount of unburnt carbon was obtained along with high-amorphous silica at this calcination temperature.

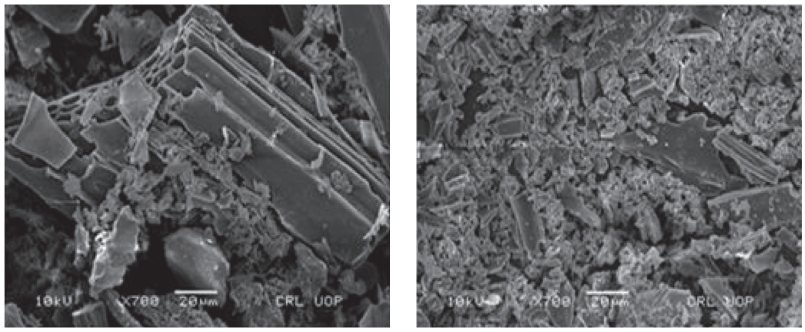
3.3. Grinding of CSA for Different Duration (Phase II): On the basis of above discussion, it was concluded that CS ash produced at 500°C had the best pozzolanic properties. In this phase, the effect of fineness and particles size on pozzolanic activity of CSA was analyzed. CSA 500 was grinded for durations as mentioned in Section 2.2.

3.3.1. SEM Analysis of Grinded CSA. SEM images of grinded ashes are presented in Figure 12. As expected, increasing grinding time increases particles' fineness. When the ashes were grinded for a duration of 30 minutes, particles size was in the range of 1 μm to 200 μm, while 240 minutes of grinding yielded a particle size of less than 40 μm. Furthermore, different type of structures could be observed like cellular, prismatic spherical, and flaky as shown in Figures 12 and 13. It can also be observed that when particles were large, channels of 1–15 μm were present. These channels occupied with finer particles formed at higher grinding time periods (Figure 13(b)). In addition, minute pores having a size from 0.5 μm to 2 μm spaced at >5 μm were visible in cellular and prismatic particles (Figures 13(c) and 13(d)).

3.3.2. Blaine Fineness of Grinded CSA. In order to identify a connection between grinding time and particle size, Blaine fineness test was carried out. Figure 14 represents the results of the test. It can be observed that as grinding duration increases, so does the value of Blaine fineness, indicating an increased particle size. Prior to grinding (G0), the surface area of ash was 2620 cm^2/g, smaller than that of cement (2750 cm^2/g). Subsequently, grinding for 30 minutes, the surface area of G30 increased to 3880 cm^2/g, and this constituted a rise in value on 48% with respect to G0. G60 had a surface area of 4960 cm^2/g showing a growth of 89% with respect to G0. G120 and G240 had a surface area of 5610 cm^2/g and 5860 cm^2/g, correspondingly. However, this increase was less than that observed for G30 and G60. One of the possible reasons for this discrepancy may be because of the fact that pores were now filled by smaller particles.

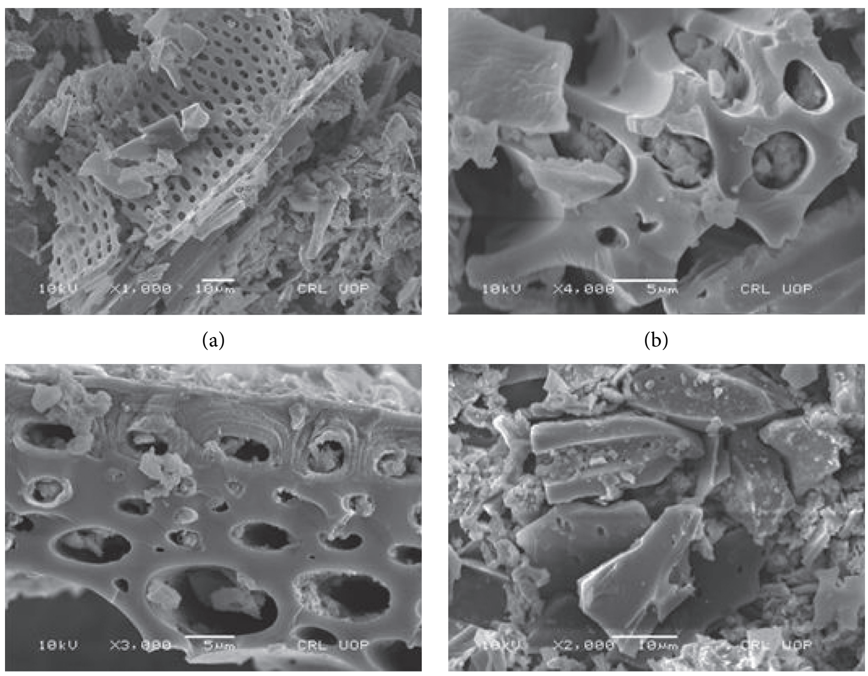
3.3.3. Particle Size Distribution of Grinded CSA. Particle size distribution of ashes grinded at various durations (30, 60, 120, and 240 minutes) is shown in the Figure 15. The average particle size denoted by D_{50} was in the range from 56.8 to 7.75 μm for grinding durations of 30 to 240 minutes, respectively. In addition, it was examined that two other particle size representatives of D_{10} (particle size at 10% finer) and D_{90} (particle size at 90% finer) had a value from 9.8 μm to <1 μm and 156.8 μm to 22 μm, respectively. From Figure 15, it can also be noted that most of the breaking of coarser particles occurred from G60 to G120 as evident from values of D_{90}, which vary from 46.4 μm to 116.5 μm. The ashes G60, G120, and G240 satisfied the physical requirement of ASTM, i.e., 66%, finer than 45 μm as per particle size distribution results.

3.3.4. Chapelle Activity of Grinded CSA. To evaluate the impact of grinding on chemical characteristics, the Chapelle test was conducted. As expected, the result of increasing grinding duration was an increased Chapelle activity (Figure 16). Ungrounded CSA had a Chapelle activity of 531 CaO



(a) (b)

Figure 12: SEM of corn stalk ash at different grinding times: (a) 30 minutes and (b) 240 minutes.



(a) (b) (c) (d)

Figure 13: SEM of corn stalk ash: (a) Mesh sheets particle, (b) filling of pores by smaller particles at higher grinding duration, (c) pores in cellular particles, and (d) pores in prismatic particles.

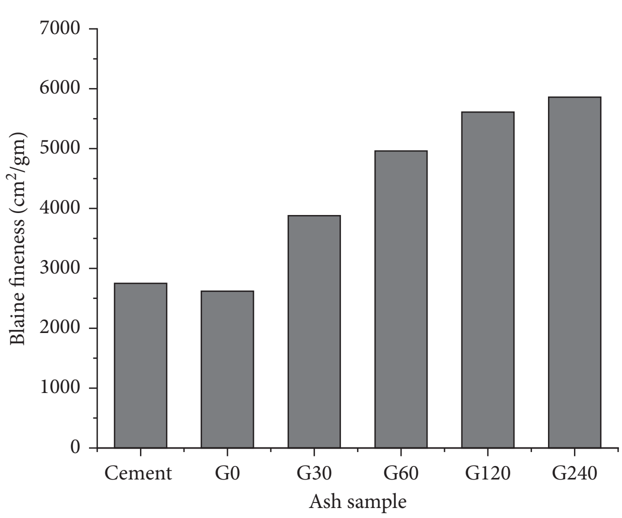


Figure 14: Specific surface areas at different grinding times.

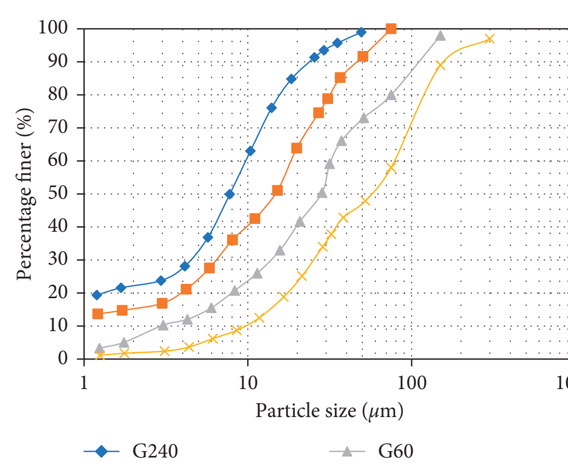


Figure 15: Particle size distribution of mix ash at different grinding times.

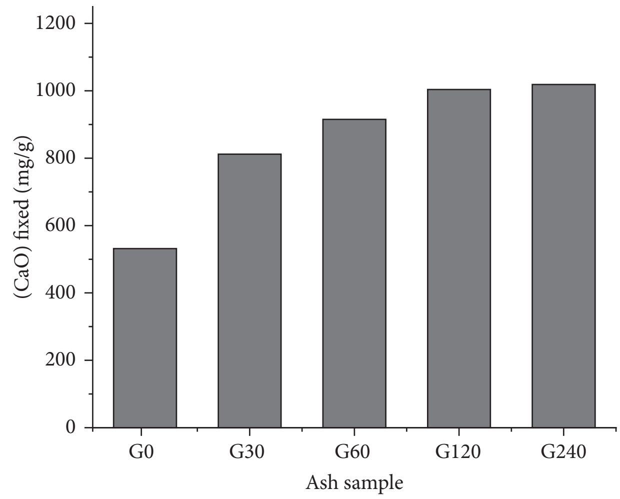


Figure 16: Chapelle test at different grinding times.

Table 5: Mix proportion and compressive strength of corn stalk ash at different grinding times (w/*c* ratio = 0.4).

s	(%), CSA	7 days compressive strength (MPa)	PAI	28 days compressive strength (MPa)	PAI
M0	0	35.25	100.0	39	100.0
G0	10	11	31.2	25.2	64.6
G30	10	25.51	75.2	37.5	96.8
G60	10	26.93	76.4	38.25	98.1
G120	10	27.25	77.3	42.25	108.3
G240	10	30.5	86.5	42.75	109.6

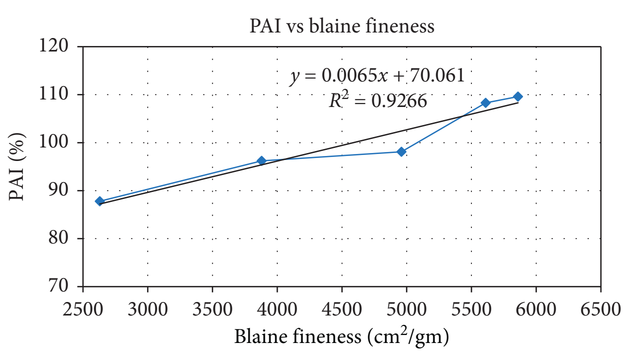


Figure 17: Relationship between PAI and Blaine fineness.

mg/g. G30 showed a percent increase of 53% as compared to nongrounded ash, while G60 indicated an increase of 72%. A similar trend was observed for G60 and G120 with an increase of 89% and 92%, respectively. These results are in line with Blaine fineness results showing a direct proportionality of specific surface area and Chapelle activity.

3.3.5. Pozzolanic Activity Index (PAI) of Grinded CSA. Results of pozzolanic activity index and compressive strength for grinded ashes are shown in Figure 16 and Table 5. Results provided a clear proof that except G0, all the CSA-blended samples complied with minimum PAI criteria of 75% as per ASTM at the age of 28 days. Increase in grinding time resulted in an increased surface area, which in turn increased the PAI value. G0 had a PAI value of 64.6%, which increased to 96.8% after 30 minutes of grinding (G30). This significant increase can be explained in terms of large particle size and substantially small surface area of particles in G0, whereby considerable breakage occurred initially. Between 30 minutes and 60 minutes, a small increase of PAI was observed with G60, having a PAI of 98.1%. After 120 minutes, an increase of around 10% in PAI values was observed, while only 2% increase was observed for G240 with a PAI of 109.6. Considering the energy requirement for grinding, 120 minutes was selected as the optimum grinding time for CSA, as beyond that very little increase in PAI was achieved. There also existed a strong correlation between the value of Blaine fineness and PAI with an R^2 value of 0.93, as shown in Figure 17.

4. Conclusions

This study was directed at examining the influence of calcination and grinding duration on pozzolanic properties of CSA, so as to acquire sustainable cement-based materials for optimum calcination and grinding condition. The conclusions deduced from this research are as follows:

(i) CS400 and CS500 retained the maximum amount of amorphous silica evident from its XRD pattern, but the dark color and low weight loss (92.2%) of CS400 was due to its high organic content. Upon increasing the temperature (beyond 500°C), the ash samples showed brighter color and increased weight loss; however, nonreactive crystalline silica was formed. It needs to be noted here that the desired properties were lower organic content and higher amorphous silica.

(ii) The results of Chapelle and Fratini tests concluded all the samples of corn stalk to be chemically reactive. The CS500 possessed a Chapelle activity having a value of 856.3 mg/g, which is 159.5% higher than the minimum prescribed standard (330 mg/g), while in the Fratini test, 93.2% of CaO was fixed in comparison with theoretical maximum CaO. The most chemically reactive sample was obtained at 500°C.

(iii) The blended mix showed higher consistency, which was more than that of the control mix, but increasing the incineration temperature caused consistency values of ash-blended mixes to decrease because of shiny texture of the internal ash surface. The behavior of CS500 (with consistency of 36.3%) showed abnormality due to the removal of outer covering when ash was incinerated at 500°C. This exposed the inner layers causing an increase in the surface area and porosity of the ash when contrasted with CS400.

(iv) The minimum PAI of 75% for CS500 and CS600 was visible by the results of compressive strength, which was within the limits set by ASTM. The crystallized silica in CS700 and CS800 rendered it inert resulting into less PAI: 51.3 and 48.1, respectively, at 28 days.

(v) SEM analysis showed that 240 minutes of grinding yields a particle size of less than 40 μm. Different variety of shapes like mesh sheets, rounded, prismatic, flaky, and cellular and small pores of 0.5 μm to 2 μm spaced at >5 μm was observed. G120 and G240 showed a Blaine fineness value of 5610 and 5860 cm^2/g, respectively, almost twice as that of a standard cement (2750 cm^2/g). An increase of 53%, 72%, and 89% of the Chapelle activity was observed for G30, G60, G120, and G240 with respect to G0. A directly proportional relationship between values of Blaine fineness, particles size, Chapelle activity, PAI, and grinding duration was observed.

(vi) As per the results of PAI, all the grounded ashes qualified for ATSM pozzolanic activity criteria for a minimum PAI of 75%. A small difference of PAI for G120 and G240 was observed; hence, grinding of CSA for 120 minutes was considered optimum, as it was less energy intensive.

(vii) From the above discussion and results, it was concluded that CS500 grinded for 120 minutes satisfy the physical, mechanical, and chemical requirements of ASTM for pozzolanic materials; and thus, is deemed to be applied as pozzolan in sustainable cement-based materials.

Data Availability

The data used to support the findings of this study are included within the article

Conflicts of Interest

The authors declare that they have no conflicts of interest.

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References

[1] V.M. Malhotra and P.K. Mehta, *Pozzolanic and Cementitious Materials*, Vol. 1, Taylor & Francis, Abingdon, UK, 1996.

[2] H.A. Mboya, K. K. Cecil, N. N. Karoli, and L. M. Alex, "Measurement of pozzolanic activity index of scoria, pumice, and rice husk ash as potential supplementary cementitious materials for Portland cement," *Advances in Civil Engineering*, vol. 2017, Article ID 6952645, 13 pages, 2017.

[3] P.K. Mehta, *Role of Pozzolanic and Cementious Material in Sustainable Development of the Concrete Industry*, vol. 178, pp. 1–20, Special Publication, Thousand Oaks, CA, USA, 1998.

[4] I.A. Smith, *The Design of Fly-Ash Concretes*, Institution of Civil Engineers, London, UK, 1967.

[5] R.-S. Bie, X.-F. Song, Q.-Q. Liu, X.-Y. Ji, and P. Chen, "Studies on effects of burning conditions and rice husk ash (RHA) blending amount on the mechanical behavior of cement," *Cement and Concrete Composites*, vol. 55, pp. 162–168, 2015.

[6] G. C. Cordeiro, R. D. Toledo Filho, and E. M. R. Fairbairn, "Effect of calcination temperature on the pozzolanic activity of sugar cane bagasse ash," *Construction and Building Materials*, vol. 23, no. 10, pp. 3301–3303, 2009.

[7] C.-L. Hwang and T.-P. Huynh, "Evaluation of the performance and microstructure of ecofriendly construction bricks made with fly ash and residual rice husk ash," *Advances in Materials Science and Engineering*, vol. 2015, Article ID 891412, 11 pages, 2015.

[8] J. Feng, J. Sun, and P. Yan, "The influence of ground fly ash on cement hydration and mechanical property of mortar," *Advances in Civil Engineering*, vol. 2018, Article ID 4023178, 7 pages, 2018.

[9] J. H. S. Rêgo, A. A. Nepomuceno, E. P. Figueiredo, and N. P. Hasparyk, "Microstructure of cement pastes with residual rice husk ash of low amorphous silica content," *Construction and Building Materials*, vol. 80, pp. 56–68, 2015.

[10] H. Chao-Lung, B. L. Anh-Tuan, and C. Chun-Tsun, "Effect of rice husk ash on the strength and durability characteristics of concrete," *Construction and Building Materials*, vol. 25, no. 9, pp. 3768–3772, 2011.

[11] Z. YaNing, A. Ghaly, and L. BingXi, "Physical properties of corn residues," *American Journal of Biochemistry and Biotechnology*, vol. 8, no. 2, pp. 44–53, 2012.

[12] S. Sugita, "On the burning principle and the furnace design based on the principle for producing highly active rice husk ash," in *Proceedings of 3rd International Conference on the Concrete Future*, Kuala Lumpur, Malaysia, 1994.

[13] P.K. Mehta, "Properties of blended cements made from rice husk ash," *ACI Journal Proceedings*, vol. 74, no. 9, 1977.

[14] V. P. Della, I. Kühn, and D. Hotza, "Rice husk ash as an alternate source for active silica production," *Materials Letters*, vol. 57, no. 4, pp. 818–821, 2002.

[15] Faostat, ," 2013, http://faostat3.fao.org/browse/rankings/commoditirs-by-region/E.2013.

[16] R. Morissette, P. Savoie, and J. Villeneuve, "Combustion of corn stover bales in a small 146-kW boiler," *Energies*, vol. 4, no. 7, pp. 1102–1111, 2011.

[17] S. Munshi and R.P. Sharma, "Experimental investigation on strength and water permeability of mortar incorporate with rice straw ash," *Advances in Materials Science and Engineering*, vol. 2016, Article ID 9696505, 7 pages, 2016.

[18] S. A. Memon, W. Israr, K. Muhammad, T. Muhammad, and B. Madina, "Environmentally friendly utilization of wheat straw ash in cement-based composites," *Sustainability*, vol. 10, no. 5, 2018.

[19] D. Cook, R. Pama, and S. Damer, "The behaviour of concrete and cement paste containing rice husk ash," in *Proceedings of the Conference of Hydraulic Cement Pastes, Their Structure and Properties*, University of Sheffield, Sheffield, UK, 1976.

[20] J. James and M. Subba Rao, "Reactivity of rice husk ash," *Cement and Concrete Research*, vol. 16, no. 3, pp. 296–302, 1986.

[21] S. Rukzon and P. Chindaprasirt, "Utilization of bagasse ash in high-strength concrete," *Materials & Design*, vol. 34, pp. 45–50, 2012.

[22] P. Mehta, *Rice hull Ash Cement High quality, Acid-Resisting*, Vol. 72, American Concrete Institute, Farmington Hills, MI, USA, 1975.

[23] D.D. Bui, *Rice Husk Ash a Mineral Admixture for High Performance Concrete*, TU Delft University of Technology, CD Delft, Netherlands, 2001.

[24] W. Xu, T. Y. Lo, and S. A. Memon, "Microstructure and reactivity of rich husk ash," *Construction and Building Materials*, vol. 29, pp. 541–547, 2012.

[25] P.J. Ramadhansyah, "Thermal analysis and pozzolanic index of rice husk ash at different grinding time," *Procedia Engineering*, vol. 50, pp. 101–109, 2012.

[26] A. N. Givi, S. A. Rashid, F. N. A. Aziz, and M. A. M. Salleh, "Assessment of the effects of rice husk ash particle size on strength, water permeability and workability of binary blended concrete," *Construction and Building Materials*, vol. 24, no. 11, pp. 2145–2150, 2010.

[27] W. Xu, Y. T. Lo, D. Ouyang et al., "Effect of rice husk ash fineness on porosity and hydration reaction of blended cement paste," *Construction and Building Materials*, vol. 89, pp. 90–101, 2015.

[28] ASTM, *C150: Standard Specification for Portland Cement*, ASTM International, West Conshohocken, PA, USA, 2001.

[29] R. C. Kanning, K. F. Portella, M. O. G. P. Bragança, M. M. Bonato, and J. C. M. dos Santos, "Banana leaves ashes as pozzolan for concrete and mortar of Portland cement," *Construction and Building Materials*, vol. 54, pp. 460–465, 2014.

[30] ASTMC311M-13, *Standard Test Methods for Sampling and Testing Fly Ash or Natural Pozzolans for Use in Portland-Cement Concrete*, ASTM International, West Conshohocken, PA, USA, 2013.

[31] BSI, *Indoor Environmental Input Parameters for Design and Assessment of Energy Performance of Buildings- Addressing Indoor Air Quality, Thermal Environment, Lighting and Acoustics Contents*, BSI, London, UK, 2007.

[32] G. C. Cordeiro, R. D. Toledo Filho, and E. de Moraes Rego Fairbairn, "Use of ultrafine rice husk ash with high-carbon content as pozzolan in high performance concrete," *Materials and Structures*, vol. 42, no. 7, pp. 983–992, 2009.

[33] Metakaolin.info, ," 2015, http://www.metakaolin.info/quality-criteria/chapelle-test.html.

[34] ASTMC187-98, *A Standard test method for normal consistency of hydraulic cement*, ASTM International, West Conshohocken, PA, USA, 1998.

[35] S. A. Memon and M. K. Khan, "Ash blended cement composites: eco-friendly and sustainable option for utilization of corncob ash," *Journal of Cleaner Production*, vol. 175, pp. 442–455, 2018.

[36] ASTM, *Standard Test Method for Fineness of Hydraulic Cement by Air-Permeability Apparatus*, ASTM Internationals: United States of America, West Conshohocken, PA, USA, 2000.

[37] R. M. Ferraro, A. Nanni, R. K. Vempati, and F. Matta, "Carbon neutral off-white rice husk ash as a partial white cement replacement," *Journal of Materials in Civil Engineering*, vol. 22, no. 10, pp. 1078–1083, 2010.

[38] M. Nehdi, J. Duquette, and A. El Damatty, "Performance of rice husk ash produced using a new technology as a mineral admixture in concrete," *Cement and Concrete Research*, vol. 33, no. 8, pp. 1203–1210, 2003.

[39] S. Peterson and J. Peterson, *The Craft and Art of Clay: A Complete Potter's Handbook*, Laurence King Publishing, London, UK, 2003.

[40] ceramicartsdaily, ," 2016, http://ceramicartsdaily.org/wp-content/uploads/2013/05/Coloring-Oxides-Basic-Percentages.pdf.

[41] A. Bahurudeen and M. Santhanam, "Influence of different processing methods on the pozzolanic performance of sugarcane bagasse ash," *Cement and Concrete Composites*, vol. 56, pp. 32–45, 2015.

[42] R. V. Krishnarao, J. Subrahmanyam, and T. Jagadish Kumar, "Studies on the formation of black particles in rice husk silica ash," *Journal of the European Ceramic Society*, vol. 21, no. 1, pp. 99–104, 2001.

[43] E. Vázquez, C.F. Hendriks, and G.M. Janssen, *PRO 40: International RILEM Conference on the Use of Recycled Materials in Buildings and Structures*, Vol. 1, RILEM Publications, Paris, France, 2004.

[44] F.G. Bell, *Foundation Engineering in Difficult Ground*, Elsevier, Amsterdam, Netherlands, 2013.

[45] ASTM-C608, *Standard Specification for Coal Fly Ash and Raw or Calcined Natural Pozzolan for Use in Concrete*, ASTM International, West Conshohocken, PA, USA, 2010.

[46] J. Young, *Reaction Mechanism of Organic Admixtures with Hydrating Cement Compounds*, Transportation Research Record, Arlington, TX, USA, 1976.

[47] B. González-Corrochano, J. Alonso-Azcárate, M. Rodas, F. J. Luque, and J. F. Barrenechea, "Microstructure and mineralogy of lightweight aggregates produced from washing aggregate sludge, fly ash and used motor oil," *Cement and Concrete Composites*, vol. 32, no. 9, pp. 694–707, 2010.

[48] C. ASTM, *Coal Fly Ash and Raw or Calcined Natural Pozzolan for Use in Concrete*, American Society for Testing Materials, West Conshohocken, PA, USA, 2003.

[49] M. F. M. Zain, M. N. Islam, F. Mahmud, and M. Jamil, "Production of rice husk ash for use in concrete as a supplementary cementitious material," *Construction and Building Materials*, vol. 25, no. 2, pp. 798–805, 2011.

[50] EngroZarai, ," 2016, http://engro.pakissan.com/fertilizer/fertilizer.available.pakistan.shtml.