Review

Rice Husk Ash-Based Concrete Composites: A Critical Review of Their Properties and Applications

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Abstract: In the last few decades, the demand for cement production increased and caused a massive ecological issue by emitting 8% of the global CO_2, as the making of 1 ton of ordinary Portland cement (OPC) emits almost a single ton of CO_2. Significant air pollution and damage to human health are associated with the construction and cement industries. Consequently, environmentalists and governments have ordered to strongly control emission rates by using other ecofriendly supplemental cementing materials. Rice husk is a cultivated by-product material, obtained from the rice plant in enormous quantities. With no beneficial use, it is an organic waste material that causes dumping issues. Rice husk has a high silica content that makes it appropriate for use in OPC; burning it generates a high pozzolanic reactive rice husk ash (RHA) for renewable cement-based recyclable material. Using cost-effective and commonly obtainable RHA as mineral fillers in concrete brings plentiful advantages to the technical characteristics of concrete and to ensure a clean environment. With RHA, concrete composites that are robust, highly resistant to aggressive environments, sustainable and economically feasible can be produced. However, the production of sustainable and greener concrete composites also has become a key concern in the construction industries internationally. This article reviews the source, clean production, pozzolanic activity and chemical composition of RHA. This literature review also provides critical reviews on the properties, hardening conditions and behaviors of RHA-based concrete composites, in addition to summarizing the research recent findings, to ultimately produce complete insights into the possible applications of RHA as raw building materials for producing greener concrete composites—all towards industrializing ecofriendly buildings.

Keywords: applications; binders; properties; chemical composition; rice husk ash; RHA-based concretes composites

1. Introduction

One of the most valuable and widespread cultivated cereal plants in the world is rice, which takes the second place after wheat in the total area size of cultivated areas [1–3].

India and China are the largest producers of rice, accounting for about 49% of the total rice harvested worldwide [4]. The statistics of rice harvesting worldwide, from the year 2002 to April 2020, is presented in Table 1.

Table 1. Rice production in different countries (million tons).

| Country	2002	2004	2007	2010	2015	2017	2018	2020
	[5]	[6]	[2]		[5]	[7]	[7]	[8]
India	123	127	133.7	120.6	160	163	167	183
China	177.6	183	196.7	197.2	200	210	216	231
Indonesia	48.7	53.4	64.4	66.4	90	74	77	82
West Africa	10.7	10.9	-	-	13.4	-	16.2	18.3
Vietnam	31.3	37.2	40	40	40	44	56	67
Bangladesh	39	42.3	47.7	49.4	45	53	55	66
Brazil	10.5	11.2	-	-	12.3	11.9	12.4	13.9
Malaysia	2.7	2.9	-	-	3	-	4.6	6.1
Egypt	5.7	5.9	-	-	6.1	6.2	6.5	8.5
Pakistan	5.8	6.1	-	-	9	10.3	10.9	13.1
Europe	1.7	1.9	-	-	2.9	-	3.4	4.9
Thailand	-	29.2	32.1	31.6	-	33	34.5	38.5
Australia	0.9	1.0	-	-	1.2	-	1.55	2.03

Rice grains (paddy grain, Figure 1) are embedded in a natural protective shell, called flower scales by botanical scientists, and commonly known as rice husk (RiH). The RiH comprises of almost 20% of its bulk grain weight [5]. RiH is an agricultural by-product material from the rice plant and constitutes of about one-fifth of the rice weight; its structure consists of lignin (25–30%), cellulose (50%), moisture (10–15%) and silica (15–20%) [3], which upon burning generates a new waste, commonly known as rice husk ash (RHA) (Figure 2) [9]. With the increasing growth rate of rice paddy production, the quantity of RHA is also increasing substantially [7], with 501.96 million metric tons harvested by May, 2020 [8]. Due to the presence of reactive silica, RHA can be utilized for a wide variety of applications [4]. However, the characteristics of the RHA mainly depend on the chemical content of the RiH, as well as both the combustion temperature and time [10]. Due to its high amount of silicon dioxide and high specific surface, RHA is an extremely active pozzolanic technogenic raw material [11].
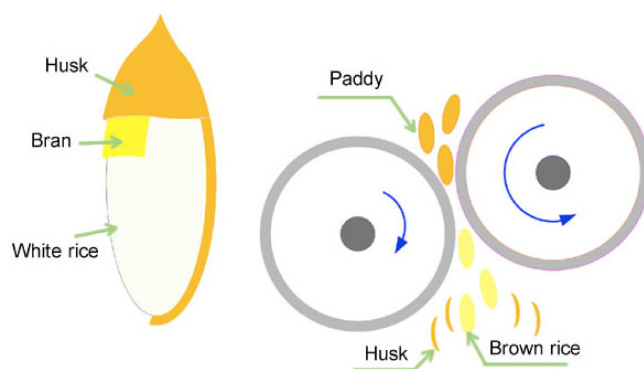
Figure 1. Final products of paddy grain after husking [12].

The utilization of RHA can lower the total porosity of concrete by increasing the packing density and improving the interfacial transition zone (ITZ) between the cement matrix and aggregate [13]. Subsequently, the calcium hydroxide content usually decreases because of the secondary hydration reaction caused by the RHA particles [14].
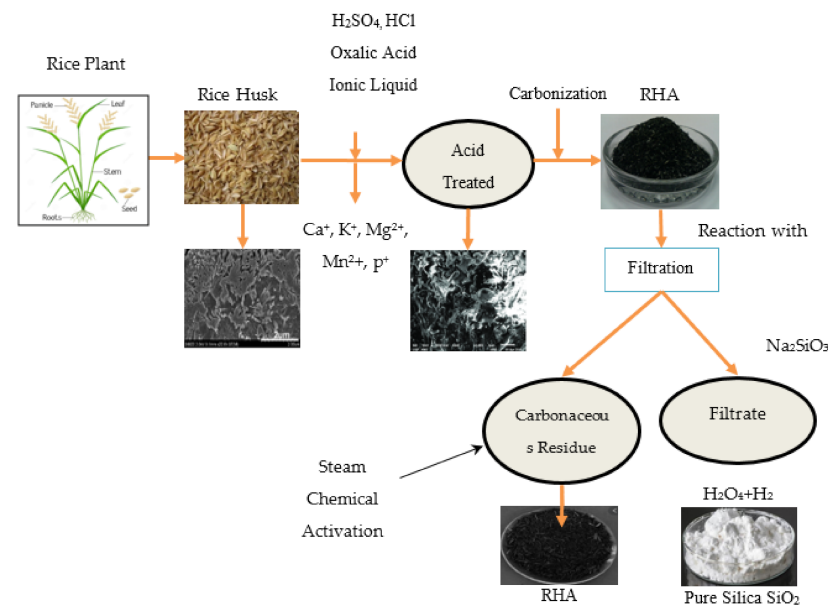
Figure 2. Source of the by-product material and pretreatment of the rice husk (RiH) and rice husk ash (RHA).

To date, RHA has been utilized as an admixture in various components of construction materials due to its good porous structure and excellent insulating behaviors [15,16]. The properties of RHA most often rely on the sort of rice plants, as well as on the process of heat treatment of the RiH. [17]. Besides, the properties of reactive silica present in the RHA may also vary depending on the heat treatment temperature time. The application of RHA in different applications has also been spotlighted, which discusses the role of the reactive silica, derived from RHA, in the technological methods for the creation of various ceramic materials, as well as silica of various dimensions, up to the nano level. [18]. Contrariwise, Liu et al. [19] elaborately identified the reactive and absorbing behaviors of RHA. Thus, the production of reactive silica from RHA is due to its wide range of applications and the solution of the important task of environmental protection and energy conservation [20,21]. However, using cost-effective and commonly obtainable RHA as mineral fillers in concrete brings plentiful advantages to the technical characteristics of concrete and to make a clean environment. The generation of RHA leads to several environmental issues, such as an increase in the disposal landfills and increase in the carbon footprints due to which a proper and safe disposal of RHA is obligatory for proper waste management. Of great importance is also the fact that the utilization of RHA will free ash dumps, which will positively affect environmental protection and improve the micro-filling structure of concrete compared to ordinary Portland cement (OPC) concrete alone [22].

However, with the incorporation of RHA particles, RHA-based concrete composite that are robust, highly resistant to aggressive environments, sustainable and economically feasible can be produced. However, production of sustainable and greener concrete composites has become a key concern in the construction industries globally. Hence, this critical paper reviews the source, clean production, pozzolanic activity and chemical composition of RHA particles. This literature review also aims to provide a critical review of the properties, hardening conditions and behaviors of RHA-based concrete composites. This review also aims to summarize the recent research findings to produce complete insights into the possible applications of RHA as raw building materials, for producing greener concrete composites and in so doing industrialize ecofriendly buildings. It is also anticipated that the conclusions drawn from this review will bridge the gap between researchers and policymakers for a framework of codal provisions regarding the same.

2. Clean Production of RHA

RiH can be used as an alternative fuel; however, a large amount of ash residues in comparison with other types of fuel makes it difficult to use them for energy (Figure 3) [13,23]. Even if burning is taken into account without temperature and time, it is quite easy to obtain 15–20% ash (in terms of dry matter) with a silica content of about 70% [1,24]. Contrariwise, it is known that, sometimes, granules were manufactured on an industrial scale, which is a blend of RiH and the remains of olives. Meanwhile, most often, when rice husk is burned directly near agricultural lands, waste is generated, impacting both the land and atmosphere [4,10,25]. When burning RiH, the organic components (40% cellulose and 30% lignin) are removed, and the target 20% silicon dioxide remains [26]. Depending on time and temperature of the burning, the amorphous or crystalline phases of silicon dioxide are obtained. If RiH is combusted at about 700 °C, then a reactive amorphous RHA is obtained, which is suitable for use as pozzolan in composite binders [27]. It is imperative to closely monitor the burning conditions of RiH; however, this limits the practicality of producing the product in many regions, and particularly in under-developed countries. Nevertheless, despite RHA containing some amount of crystalline silica, at a higher burning temperature, it can still be used as a filler for cementitious compositions, but this requires grinding the resulting ash [28]. Meanwhile, RiH in some cases is used as fuel for small power plants. In this case, RiH combustion occurs at an average temperature of 740 °C [29]. With this combustion technology, ash is abraded simultaneously, resulting in small particles of ash (less than 0.375 mm) [3]. The resultant ash material usually has a SiO_2 content of about 80%, comprising both the amorphous and crystalline silica particles [22]. The average particle size of RHA can be quite high (about 50 μm) while the particle sizes are also extremely low (up to 50–60,000 m^2/kg), owing to its highly porous structure, which makes it highly reactive [30–32]. The activity of RHA can be further increased by milling the particles to a required fineness [33]. Although the high reactivity of RHA particles makes it favorable for utilization in cement mixtures, there are some detrimental issues pertaining to its utilization as well. For example, the introduction of RHA requires increased addition of water to provide the necessary rheological characteristics, owing to the hygroscopic properties of the RHA particles. As a result, this increase in water demand may reduce the final strength of the composite because of the higher ratio of water to cement [26,32]. In addition, the setting time of the binder also increases at an increasing RHA content. However, a substitution of cement with RHA by an amount of 20–30% can increase the physico-mechanical properties and performance characteristics of concrete.
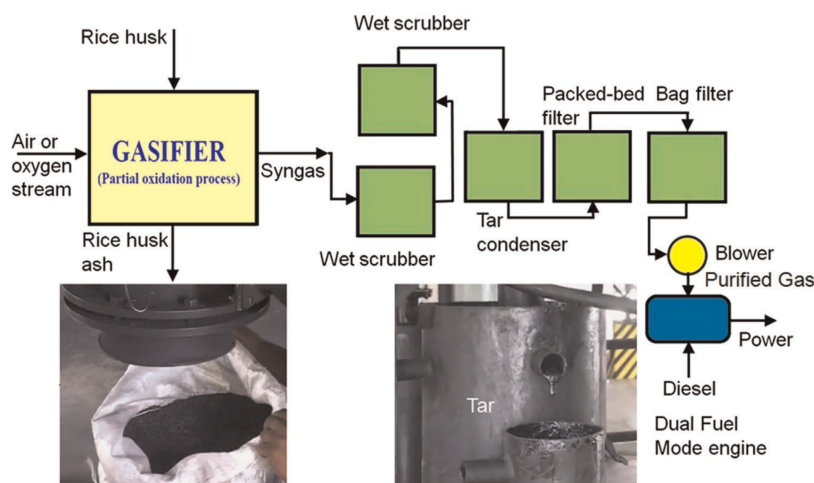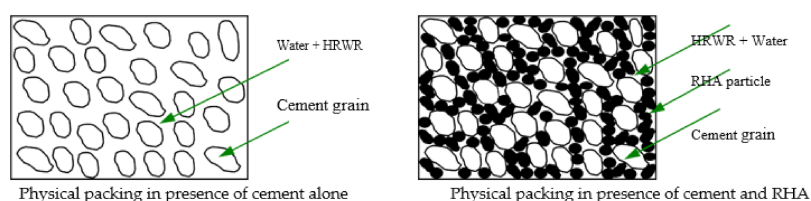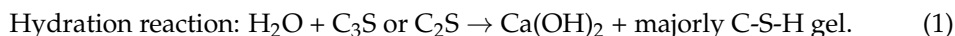

Figure 3. Obtaining of RHA via a gasifier power system [34].

Effect of Production Techniques

Burning of RiH is usually carried out in three ways: (1) open-field burning [3]; (2) fluidized-bed furnace burning [35]; and (3) in an industrial furnace [36]. The lowest quality

ash is formed when burning in an open field and this technology also leads to severe pollution. On the other hand, in controlled combustion of RiH in a fluidized-bed and industrial furnace, high-quality amorphous ash in a highly cellular form is formed [37,38]. The combustion conditions in the industrial furnaces are usually controlled in a controlled environment due to which it produces a high-quality ash with silica [35]. If RiH completely burns out, it has a color from gray to white; partially burnt RiH due to organic residues has a blackish color. Accordingly, there are the two phases that RiH undergoes during heat treatment: carbonization and, conversely, decarbonization [39,40]. RiH of amorphous composition can be obtained by prolonged combustion at temperatures below 500 °C; however, when increased to 680 °C, even 1 min is enough to achieve this goal [41,42]. Similarly, to obtain crystalline silica, it is necessary to raise the temperature to 1000 °C for at least 5 min. For example, even at temperatures up to 900 °C, for an entire hour of burning, the RHA will remain in an amorphous form [19]. The critical temperature is 700 °C, below which the silicon dioxide in the ash remains in amorphous form regardless of the burning time [43]. It was noted that the polysaccharides in the RiH begins depolymerization at 400 °C [3], and the dehydration and decomposition of the sugar units occur at temperatures above 400 °C or at 700 °C, respectively. Moreover, at 700 °C, the unsaturated products react with each other, resulting in a highly reactive carbon residue. RHA containing 95% silica can be obtained after burning the husk at 700 °C for 6 h, which is long and uneconomical [44]. At the same time, the amount of carbon in RHA during combustion decreases almost completely, from 18.6% to 0.14% [45]. The specific surface area of the partly burnt RHA is about 54 m^2/g, but after full firing, it increases to about 81 m^2/g, with a mean particle size usually varying between 3 and 10 µm. Meanwhile, a research study stated that the husk samples that are burnt at temperatures between 500 °C and 700 °C for more than 12 h gives a highly reactive RHA, and burning it in the range of 15–360 min results in a high carbon ash [41]. On the other hand, when RHA is burnt for 2 h, amorphous-phase RHA was observed at combustion temperatures in the range of 500–600 °C, and crystalline new growths began to appear at 700 °C [46]. However, as temperatures exceed 800 °C and after a long burning time, the RHA begins to crystallize into various modifications of quartz, for example, crystobalite [13]. Thus, lower temperatures are needed to obtain the reaction material. The maximum pore diameter characterizing the amorphous structure is observed when RiH is burned at heats between 600 °C and 700 °C. Accordingly, the pozzolanic activity of such an RHA is the highest [36]. In the context of combustion conditions, any changes in the environment in which carbon dioxide predominates in an environment in which oxygen predominates, can lead to growth in the number of crystalline new growths [22]. Reactive SiO_2 in the ash composition fills the pores between the grains of cement and leads to a secondary hydration reaction due to the binding of $Ca(OH)_2$ to calcium hydrosilicates. The positive impacts, micro-filling (Figure 4) [47,48] and pozzolanic effects of ash enrich the pore structure of cement paste and ITZ concrete [49]. The extra CSH gels clogs the pores of the porous ITZ as well as the cement matrix, subsequently improving the intermolecular interaction between the cementitious matrix and aggregate [50,51]. Both reactions, hydration and pozzolanic, occur according to such schemes:

$$\text{Hydration reaction: } H_2O + C_3S \text{ or } C_2S \rightarrow Ca(OH)_2 + \text{majorly C-S-H gel.} \tag{1}$$

$$\text{Pozzolanic reaction: } Ca(OH)_2 + H_2O + RHA (SiO_2) \rightarrow \text{minor C-S-H gel.} \tag{2}$$

Figure 4. The micro-filling effect of RHA [47,48].

3. Pozzolanic Activity

Due to the presence of amorphous silica in RHA, properly burnt and heavily milled RHA particles are a good pozzolanic material that improves the set of physico-mechanical characteristics and performance of cement and concrete mixtures (Figure 5) [23,36,51]. It is the complexity of the technological process for the production of amorphous ash, which consists of the complexity of controlling the conditions for its receipt, which inhibits the large-scale introduction of this supplementary cementitious material [3]. Therefore, a number of methods are used to improve the feedstock, for example, acid leaching [29]. These methods can optimize the pozzolanic properties as well as reduce the influence of the conditions of heat treatment on the husk. In this direction, several scientists studied the influences of RHA in the composition of a composite binder on hydration processes, microstructural features and the composition and microstructure of the ITZ between the cement matrix and aggregate [10,52]. During experimental studies, researchers revealed that the cement paste, including RHA, had a smaller quantity of calcium hydroxide because of the pozzolanic reaction [53]. Accordingly, the porosity and the content of portlandite in the ITZ are reduced in the composite; due to this, the width of this zone between the cement paste and the aggregate is also reduced [54,55]. Reportedly, the improvement in the concrete properties due to the addition of RHA particles has been mainly due to the creation of more C-S-H gels but low portlandite in the composite because of the interaction between the ash and the OH⁻ and Ca⁺ ions, as well as calcium hydroxide [3]. Owing to this, it was evaluated that the pozzolanic reactivity of the RHA particles was primarily due to the increased physico-mechanical properties and operational characteristics of the fine-grained concrete blocks compared to ordinary mortars [56]. Pozzolanic activity can be investigated using three different methods: Firstly, the more the conductivity measurement of a saturated $Ca(OH)_2$ solution changes with the addition of RHA, the more this ash is more active [57]. This method gives adequate results only to define the degree of pozzolanic reactivity of the RHA; secondly, the measurement of the rate of ingesting of the $Ca(OH)_2$ entering into the pozzolanic reaction with RHA [3]; and thirdly, by comparing the strength of a paste using RHA with a control composition on pure Portland cement [36].
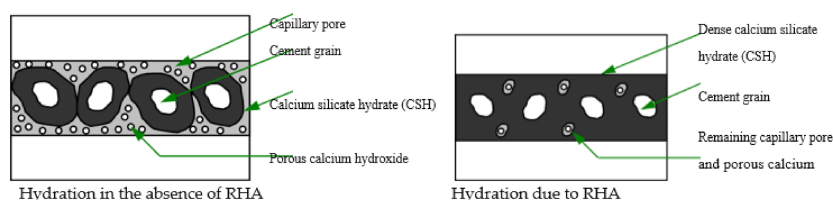

Figure 5. RHA pozzolanic behavior [47,48].

The pozzolanic activity of RHA can be ascertained by the following:

- The pozzolanic activity of RHA can be optimized by a HCl acid pretreatment of the RiH (Table 2) [22,36]. In this case, the heat treatment time is more sensitive for unprocessed rice husk than for that processed in hydrochloric acid.
- RHA shows the same high rate of lime consumption during the initial reaction period [58]. While the reaction pattern corresponded to diffusion control, the RHA had a higher reaction rate with the incorporation of lime [22]; the major product of the hydration reaction is a C-S-H gel.
- During the 12 h, the rate of growth in the hydration heat of the RHA is very alike to the rate of growth for Portland cement [3]. However, the pozzolanic properties of the RHA are much higher than for the other ashes; for example, fly ash.
- As a result of the high content of the silicon dioxide amorphous phase of the RHA with high activity, a sharp rise in the strength of the RHA mortar was observed relative to the mortar made without RHA [13,23,59]. The cement mortar containing RHA particles usually has a lower $Ca(OH)_2$ content after 7 days. Meanwhile, when RHA is added, smaller pores sizes can be formed in the hardened composite [45,60,61].

Table 2. Microanalysis of the RiH.

| Element | Outer Superficial Area | | Inner Superficial Area | | | | References |
| | By Percentage (%) | | | | | | |
	by Weight	by Atomic	by Weight	by Atomic	by Weight	by Atomic	
C	6.91	11.11	62.54	69.54	30.20	40.93	
O	47.93	57.84	35.19	29.38	42.53	43.27	[10,13,36,51]
Si	45.16	31.05	2.27	1.08	27.27	15.80	
Total	100	100	100	100	100	100	

4. Chemical Composition

The chemical composition is the property of a concrete binder that is usually done in a dry process by milling and mixing the dry materials, or in a wet one by using wet grout [62]. RHA particles are very rich in silica content (see Table 3).

Table 3. The oxide content of the RHA by regions of cultivation.

| Chemical Constituents | Countries of Cultivation, % | | | | | | Range (%) | References |
	Vietnam	India	USA	Brazil	Malaysia	Russia		
SiO_2	86.9	90.7	94.5	92.9	93.1	84.3	85–95	
CaO	1.4	0.4	0.25	1.03	0.41	0.5	0.25–1.5	
Fe_2O_3	0.73	0.4	-	0.43	0.21	0.3	0.20–0.75	
Al_2O_3	0.84	0.4	-	0.1	0.21	1.1	0.1–0.9	[6,63,64]
MgO	0.57	0.5	0.23	0.35	1.59	0.9	0.20–1.6	
K_2O	2.46	2.2	1.1	0.72	2.31	3.7	0.7–4.0	
Na_2O	0.1	0.1	0.78	0.02	-	1.0	0–0.8	
SO_3	-	0.1	1.13	0.1	-	0.1	0–0.15	
Loss of ignition	5.14	4.8	-	-	2.36	8.1	-	

Although in some cases the pozzolana activity of the RHA improves with an increase in the particle size, strong grinding of RHA is usually recommended since this material receives its main reactivity from the inner superficial area of its micropores. The mean chemical content distribution of completely burnt ash of rice husk with the right technology of controlled heat treatment is more 90% SiO_2 in the amorphous phase, about 5% carbon and 2% K_2O. Table 4 summarizes the oxide content of RHA by various researchers. In order for the RHA to be used as a cementitious additional material, it should meet the requirements of ASTM C 618 [65]. For example, the total proportion of oxides of Si, Al and Fe should be at least 70%, and the LOI must not exceed 12% [65]. To maintain the required chemical content of RHA, including the phase of SiO_2, it is necessary to carefully control the temperature and duration of the heat treatment [66]. In the case of uncontrolled burning of husks, for example, on open ground or in inappropriate furnaces at temperatures above 800 °C, the unreactive varieties of quartz, such as crystobalite and tridymite, will form in the ash [67]. It is likely that during the structure formation of the cement paste, the crystalline phases will probably act as the centers of crystallization of the new growths; however, it is believed that it is better to use amorphous ash [68]. Methods for increasing the pozzolanic activity of the crystalline sintered particles are known, for example, grinding, but this greatly complicates the process and entails an increase in financial costs [3]. Therefore, the optimal heat treatment of rice husks is to maintain a temperature between 500 to 700 °C for about 1 h. In the case of controlled combustion, an amorphous phase of silica is obtained, which becomes the main component of the ash with a high superficial area due to the developed microporous RHA structure [69].

Table 4. The oxide content of the RHA by various researchers.

| Chemical Composition	[70]	[71]	[72]	[73]	[74]	[75]	[75]	[76]	[77]	[78]
SiO_2	87.2	92.71	86.98	80–95.9	87.3	87.3	86.98	87.96	91.56	87.4
CaO	0.55	1.26	1.40	1.1–1.5	0.55	0.55	1.4	1.14	1.07	0.9
Fe_2O_3	0.16	0.19	0.73	0.2–2.9	0.16	0.16	0.73	0.52	0.17	0.3
Al_2O_3	0.15	0.21	0.84	0.4–0.4	0.15	0.15	0.84	0.30	0.19	0.4
MgO	0.35	0.33	0.57	0.3–0.9	0.35	0.35	0.57	-	0.65	0.6
K_2O	0.24	2.89	-	2.8–6.6	0.24	3.68	2.46	-	3.76	3.39
Na_2O	3.68	0.19	2.46	0.8–2.1	3.68	1.12	0.11	0.3	0.16	0.04
SO_3	1.12	-	0.11	0.7–1.2	1.12	0.24	-	2.4	0.47	0.4
Loss of ignition	8.55	-	5.14	up to 12%	8.55	8.55	5.14	1.3	1.97	0.2

5. Physical properties

5.1. Bulk Density

The density of RiH is typically less than the average density of the concrete mixture, but when RHA is added, the density of the concrete decreases [79] (Table 5). In particular, if the density of traditional concrete is taken as 2430 kg/m^3, then when RiH is introduced into the mixture in amounts of 1.5%, 3% and 5%, the density of the mixture decreases to 2340, 2260 and 2105 kg/m^3, respectively [80]. Meanwhile, it also has been demonstrated that there is a decreasing trend in the effective diffusion coefficient in cement composites when the Portland cement was replaced by 30% of RHA particles [36]. Further incorporation of RHA (>30%) resulted in an increment in the radon diffusion that is principally attributed to the decrease in the density. When the concrete contains 30% RHA, the diffusion coefficient can be reduced by about 69%; it was found that the addition of white RHA particles can have a considerable impact towards reducing the bulk densities of light-weight cement composites.

Table 5. Physical properties of RHA.

Property	Values	References
Dry density, kg/m^3	2060–2160	[81]
Bulk density, kg/m^3	420.0–429.1	
Superficial area, m^2/kg	240–2765	[82]
Pozzolanic activity index, %	81.25–88.90	
Average particle size, μm	5.0–7.41	[6]
Nitrogen adsorption, kg/m^2	24.3–28.8	
Volume of pores, mL/g	0.073	[83]

5.2. Strength Activity Index, Color and Microstructure

RHA is a pozzolanic material possessing extremely high reactivity [6,43]. The use of RHA can lead to a decrease in the portlandite content of the OPC matrix, resulting in the enhancement of the matrix pore structure [3,84]. By comparison with a reference mix without RHA, the ITZ of the coarse aggregates at the binder phase with RHA has less thickness and better performance [2]. The strength activity index is an aspect of calculating the pozzolanic activity indirectly. ASTM C618 recommends that the stated minimum strength activity index of FA should be around 75%. The quality of the generated ash will not vary significantly from region to region, if the burning conditions are properly controlled. The amount of silica and the LOI are the most important aspects of the transformation of RiH into RHA (5-fold increase in amount of silica and almost 10-fold decrease in LOI). The changes in color of the RHA specimens are black with certain gray or white particles at different calcination temperatures (Figure 6) [85]. Meanwhile, the particle shape of the RHA particles is typically irregular, while irregular and strongly cellular particles were found in RHA with micro pores inside its structure (Figure 7) [85]. In general, it is reported that the reactive silica formation in the RiH and the pozzolanic performance of its particles have highly influenced the microstructure of the RHA-based concrete mass.

(a) 500 °C for 2 h　　(b) 600 °C for 2 h　　(c) 700 °C for 2 h　　(d) 800 °C for 2 h
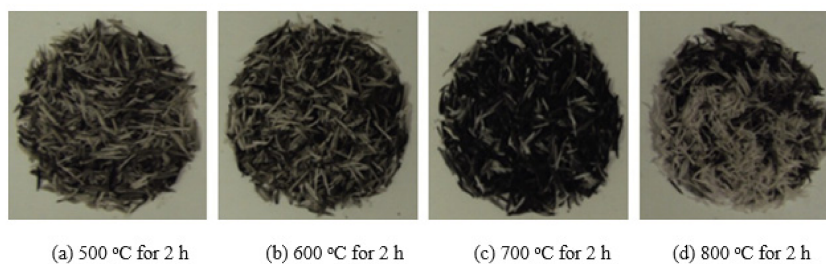
Figure 6. Changes in the RHA color at different calcination temperatures [85].

a　　　　　　　　　　　b　　　　　　　　　　　c
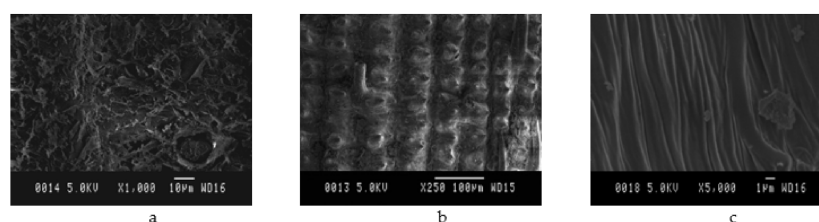
Figure 7. SEM microstructure of RHA [85]: (**a**) SEM of a chip from the RHA interlayer; (**b**) SEM of the outer surface of the RHA at 600 °C; (**c**) SEM of the inner surface of the RHA at 600 °C.

5.3. Particle Size and Distribution

The particle size of RHA is usually below 45 μm (fine substance), with an average particle size of 6–10 μm [86]. These are strongly cellular particles that have a microporous property with a large inner surface and possess a surface area that is 3-fold greater than the particles of a silica fume (SF) [10]. Figure 8 shows a digital image of the (a) RiH; (b) burned RHA; and (c) grinded RHA particles [31]. Since the pozzolanic activity of RHA is obtained from its high internal surface, no benefit will be achieved by grinding the ash to a finer grain size [87]. The dispersed pore sizes in the coarse RHA particles typically ranges between 2 and 40 μm, with the largest recorded actual pore volume of 0.16 cm^3/g. RHA has a poor water absorption due to its high porosity and can severely affect the fresh properties of the RHA concrete or mortar. It was observed that the average particle size (d_{50}) reduces to 0.68 μm (with all particles smaller than 6 μm) when grinding the RHA for about 80 min [45]. Another examination group contemplated the effect of milling time (utilizing a Los Angeles mill) on the RHA's physical attributes and claimed that the crushing time, when increased from 90 to 270 min, brought about a mean grain size (d_{50}) decrease of around 70%, making the RHA particles size practically identical to the mean particle size of OPC [31]. Similarly, findings on the impact of time of grinding on RHA fineness burned at different temperatures for 2h and grinding were made by an improved Los Angeles grinding machine consisting of steel balls and a chain (2 m-long steel chain weighing 450 g/m) [88]. It is also reported that this detrimental behavior in specific surface area (SSA) is proportional to the incineration temperature as well as holding time, as heating at increased temperatures for an extended period of time brings about an agglomeration effect, resulting in lower porosity [10,89]. The actual surface area of RHA can be increased to 81 m^2/g through the employment of wet grinding on the burnt samples for about 80 min. [3]. In conclusion, it is stated that the finer particle size allows the RHA particle size to decrease, which will affect the growth of the cement paste's hydration and microstructure synergistically. Furthermore, reducing the RHA mean particle size negatively affects the slump flow of freshly mixed concrete, while it positively impacts its water permeability as well as compressive strength at its toughened condition.
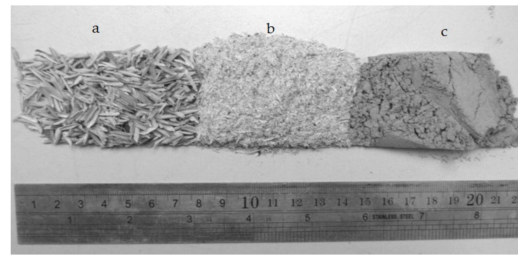
Figure 8. (**a**) RiH; (**b**) burned RHA; (**c**) grinded RHA [31].

6. Fresh Properties

6.1. Workability

The use of water reducing superplasticizers (SP) in RHA concrete was found to show no workability issue at a water-to-cement (w/c) ratio ranging from 0.30 to 0.34, when determined using slump tests (Figure 9) [90]. It was found that the concrete blends become less workable and cohesive by the addition of 15% and 20% RHA, which subsequently requires the use of SP to provide workability to the mix. Generally, the inclusion of any fine mineral admixture in concrete will raise its cohesiveness and make it marginally stiffer due to a large surface area and water demand. Similarly, the addition of RHA in the concrete will decrease the primary slump; thus, the utilization of a greater water content might be required [91]. It might be noticed that, at a specified moisture or water portion, little increments in RHA (below 3% by weight of concrete) would be useful for the workability improvement and compressive strength of concrete by decreasing the inclination to segregation and bleeding [92]. With a higher RHA replacement, the slump and density of the resulting mix reduces; nevertheless, the high-grade RHA (having very fine particles) do not show a huge impact on any of the slump or the density of the concrete [93]. Another research explored the effect of 10, 15 and 20% RHA replacement levels on the workability (slump flow) of concrete mixes. It was observed that the SP dosage continued to stay unaltered, while the workability reduces gradually with expanding RHA replacement levels. An impact on slump at a 20% RHA replacement level exhibited about a 90% slump in the cement-based control concrete [13,30]. When the dosage of SP in concrete is raised from 0.63% (control concrete) to 2%, where the mildly fine RHA was utilized for substituting 20% of the OPC, it was also found that the concrete containing the finer RHA samples obtained a higher density, attributed to finer particle packing [94]; however, due to a high water demand, the workability reduces with increasing percentage of RHA incorporation into concrete. Nonetheless, this may be improved with the adequate dosage of high-range water-reducing agents/supper plasticizers.
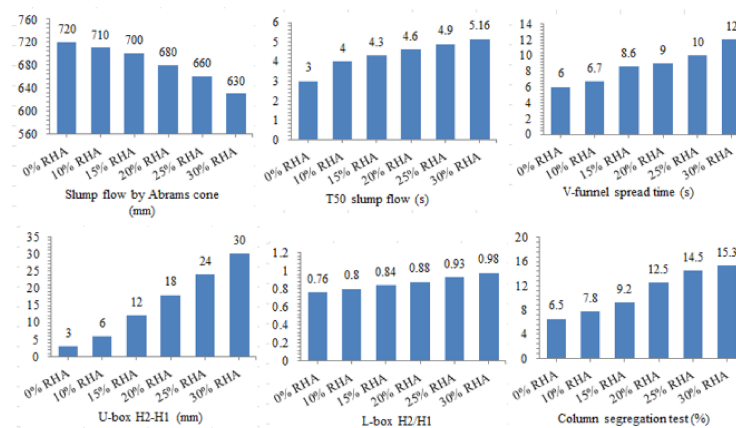

Figure 9. Fresh properties of the RHA-based concrete [90].

6.2. Setting Time

The impact of RHA on the initial and final setting time of the paste is debatable. A few authors [95] reported that, with an increasing percentage of RHA, the setting time of the paste increases, and vice-versa [96]. This has been ascribed to the water assimilation capacity of RHA caused by its micro porous arrangement, because of which the w/c proportion in the encompassing network is decreased. At the 35% RHA replacement level, the standard consistency of the RHA blended cement paste was found to be about 44%, while that of the control paste was about 32% [59,97]. Likewise, it is reported that the expansion of the initial setting time was observed up to the 15% RHA substitution level. Beyond this level, a progressive declining trend in the final setting time was observed with an increase in the level of cement substitution [10,98]. Another examination demonstrated that the strength of cement blended with clay was increased by over 100% at 28 days and this phenomenon was mainly ascribed due to presence of the RHA particles. At curing times of 14 and 28 days, RHA displays greater proficiency on Portland concrete substitution when the cementitious substance is at the very least 20% and 35% [99]. The impact of ligno-sulfonate (LS) and $CaCl_2$ has been examined on the setting times, with the accumulation of 2% of $CaC1_2$, 1% ligno-sulfonate (LS) and 1% ligno-sulfonate (LS) + 2% $CaCl_2$. The consistency and pozzolanic reaction from a 10% RHA and OPC fused cement were examined with RHA pastes [36,100]. In the existence of 1% ligno-sulfonate, the setting time (initial and final) was improved significantly, implying a delay in the setting behavior of the blend [97]. It was observed that 1% ligno-sulfonate acted like a retarder in hydration. On the other hand, the 2% $CaC1_2$ showed that it served as an accelerator in hydration because it shortened both the setting times (initial and final) of the RHA-blended OPC paste [97,101,102]. However, the setting time of the paste containing 2% $CaCl_2$ and 1% LS are greater as compared to paste with 2% $CaCl_2$ and less than 1% LS [59]. That demonstrates that the reduction of water was enhanced when a combination of an accelerator (2% $CaCl_2$) and superplasticizer (1% LS) was used.

6.3. Segregation and Bleeding

In RHA concrete, the sign of segregation has been reported by several researchers while bleeding was minimized significantly [84,86]. It has been observed that the workability as well as segregation decreases when a higher amount of RHA is utilized. Nevertheless, concrete comprising an RHA up to 25–30% upheld an acceptable workability (Figure 9) [90,103]. When RHA is added, it reduces bleeding and the constructor is required to be capable of diligently shielding the concrete surface while the plastic shrinkage cracking factors persist [104]. The pore structure is refined by the pozzolanic action of the RHA; hence, the quantity of drying shrinkage of the concrete with the adding of RHA is slightly greater than that of concrete without RHA at a similar w/b ratio [105]. Concrete produced with RHA usually displays slow permeability and no bleeding. Similarly, to alleviate the autogenous shrinkage of ultra-high-performance concrete (UHPC), RHA was found suitable [13]. The free water from the mix is absorbed by the mesoporous structure of RHA and the w/b is reduced effectively and thus it improves the compressive strength, workability, segregation and bleeding [106]. In terms of fresh properties, the addition of RHA has also other helpful influences: it is found that the efficiency of high-performance, self-compacting concrete could be enhanced by RHA addition, through which bleeding and segregation can be reduced [92]. The physical arrangement of the binders like cement can be improved by the incorporation of RHA and it also increases the plastic viscosity [44], which is distinctly visible at elevated RHA content proportions. The macro-mesoporous structure of RHA might be applied as the viscosity revising agent in concrete because it could induce good intermolecular attraction forces [104]. RHA is a pozzolanic material, and the reaction can take place with $Ca(OH)_2$ while the progress of cement hydration enhances the aggregate–paste connectivity, thus improving the ITZ of the concrete [44]. A research study reported that the use of FA, 7.5% RHA and 1.5% SP increased the workability without raising the w/c ratio and thus raising the cohesiveness, reducing the segregation

or bleeding [107]. In general, the addition of RHA content in fresh mixtures can lead the RHA particles to segment the bleed-water channels and consequently prevent bleeding and segregation, thereby improving the workability.

7. Mechanical Properties

7.1. Compressive Strength

Compressive strength is the utmost significant property for the design of concrete structures. From past experiences, it has been observed that the incorporation of RHA as an SCM in conventional concrete enhances the compressive strength [108] (see Table 6). This enhancement in the compressive strength upon the adding of RHA is mainly as a result of the increased pozzolanic reaction and pore refinement provided by the RHA particles [109]. The addition of RHA particles in concrete causes a reduction in $Ca(OH)_2$ and produces extra C-S-H gels, which refines the pores and improves the strength of the concrete [110]. In case of conventional concrete, the use of RHA up to 15% shows the highest improvement in compressive strength [108]. Whereas, in UHPC, the compressive strength can keep increasing up to the 30% RHA replacement level, as shown in Figure 10. For instance, a compressive strength of about 182 MPa could be achieved at 28 days when 30% of the RHA was incorporated into the UHPC, which is about 51% higher than the 0% RHA concrete [1]. This indicates that the RHA is capable of being utilized as an exceptionally reactive pozzolanic material for the improvement the ITZ and microstructure, and thereby to concrete strength [13]. However, beyond the 30% RHA replacement level, the compressive strength of the UHPC was shown to be reduced, as shown in Figure 10. In terms of strength development, it has been seen that the RHA concrete achieves about a 60% hydration within 7 days [111], but has increased strength development at later curing days (28, 91 and 180 days). This is primarily because of the low reactivity of the RHA at lower curing days and the high reactivity of the RHA particles at longer curing days [39,112]. The use of chemical activators (K_2SO_4, Na_2SO_4 and Na_2SiO_3) at 1% by weight of cement was found to cause a sharp rise in the 7 days compressive strength, at varying w/b ratios [78,113]. It has been observed that a significant quantity of water is soaked up due to the microporosity of the RHA, which serves the dual purpose of preventing bleeding while reducing the trapping of the bleed water beneath the aggregate particles [21]. As a consequence of the enhancement of the aggregate–paste bond, it is recommended to add the appropriate proportion of RHA, as higher doses tend to adversely affect the concrete strength [92]. It has also been identified that the w/b ratio is a deciding factor for the concrete strength at earlier ages, and as far as the ratio is unaltered, the early concrete strength will be unaffected by the existence of pozzolans, except for enhancement of the ultimate strength through the pozzolanic reactions [4]. Conclusively, RHA particles up to the 15 and 30% replacement levels in conventional and ultra-high-performance concrete mixes could improve the compressive strength.
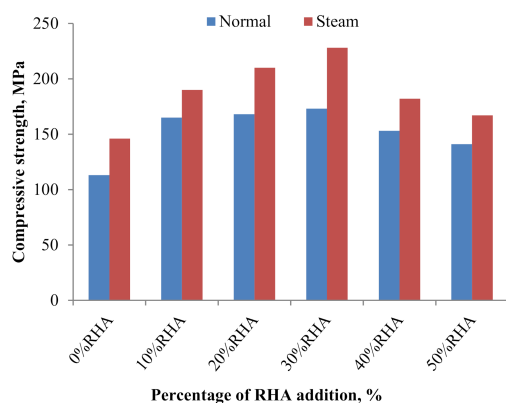

Figure 10. Concrete compressive strength with different levels of RHA replacement [114].

Table 6. Concrete compressive strength of various volume of RHA by various scholars worldwide.

Study	w/b	RHA (%)	Superplasticizer (%)	Concrete Compressive Strength (MPa)				
				7 Day	14 Day	28 Day	56 Day	91 Day
[43]	0.41	0	1	29.0	–	36.7	39.6	–
	0.41	15	1	36.2	–	48.8	53.7	–
	0.41	10	1	32.6	–	41.2	46.4	–
	0.41	20	1	30.4	–	40.2	53.0	–
[115]	0.5	20	3.5	37.2	–	42.9	–	–
	0.38	0	1.8	32.8	–	48.5	–	–
	0.5	40	3.5	28.1	–	33.5	–	–
	0.5	30	3.5	35.1	–	40.9	–	–
[116]	0.31	10	2	48.4	–	54.8	–	72.6
	0.22	0	2	55.9	–	65.0	–	82.8
	0.75	40	2	13.8	–	19.1	–	26.4
	0.46	20	2	21.2	–	28.0	–	39.6
	1.17	60	2	8.3	–	10.4	–	14.8
	2.18	100	2	1.5	–	2.0	–	2.6
	1.80	80	2	2.8	–	4.1	–	5.7
[117]	0.38	5	3.5	25.2	–	38.0	–	–
	0.4	0	3.5	10.5	–	28.4	–	–
	0.36	10	3.5	22.5	–	36.2	–	–
	0.38	5	4	21.4	–	37.8	–	–
	0.4	0	4	6.8	–	18.3	–	–
	0.4	0	45	1.2	–	8.6	–	–
	0.36	10	4	36.8	–	41.4	–	–
	0.36	10	45	38.3	–	48.5	–	–
	0.38	5	45	11.9	–	22.2	–	–
[118]	0.54	15	2.2	22.7	29.6	39.8	–	42.5
	0.39	0	2.2	36.5	37.6	37.8	–	44.7
[96]	0.51	0	0	27.2	37.1	38.3	–	–
	0.58	10	1.2	28.0	41.3	44.8	–	–
	0.57	5	1.2	27.6	40.0	43.3	–	–
	0.66	20	1.2	29.7	42.5	46.0	–	–
	0.6	15	1.2	29.3	41.8	45.7	–	–

7.2. Flexural and Splitting Tensile Strengths

The most fundamental and essential concrete properties after compressive strength is flexural strength and splitting tensile strength [84]. It has been found that the incorporation of RHA particles increases the tensile and flexural strength of the concrete, as revealed in Figure 11 [114,119]. The increase in the tensile and flexural strength was found to be about 4–16% when unground RHA was incorporated; whereas, this improvement was about 15–21% when ground RHA was utilized [94]. The use of RHA in cement mortar was also found to improve its flexural strength [43,59]. The maximum percentage of rise in flexural strength varied from 7 to 28 curing days for the control mortar and slowly decreased with an increase in mortar RHA concentration [3]. For the mortar with the maximum RHA inclusion, the increase in strength within 7 to 120 days was nearly consistent relative to the increase in strength within 7 and 28 days, as witnessed in different mortars [120]. For instance, at a w/b ratio of 0.53, an 20% improvement in the flexural strength was noticed up to the 20% RHA replacement level, beyond which the strength decreases [121]. Contrary to the above findings, Mohseni et al. [54] observed that the use of RHA up to 30% could cause a 2–14% reduction in the flexural strength at 28 days of normal curing. However, the flexural strength was found to be enhanced at longer curing days (90 days), owing to the high reactivity of the RHA particles. The addition of 3% nano-Al_2O_3 was also found to improve the flexural strength of the 10% RHA concrete by 34% and 41% at 28 and 90 days respectively, [107]. Concrete specimens comprising 1% nano-Al_2O_3 and 10% RHA encountered a rise in flexural strength of 18.6% and 23.1% with the corresponding curing

days of 28 and 90, respectively. However, addition of a 0.3% dosage of polypropylene fiber (PF) to the concrete mixtures led to improving the strength properties to some degree [54]. This finding indicates the potential of utilizing RHA (up to 20%) as an SCM to improve the tensile and flexural strength of concrete mixes.
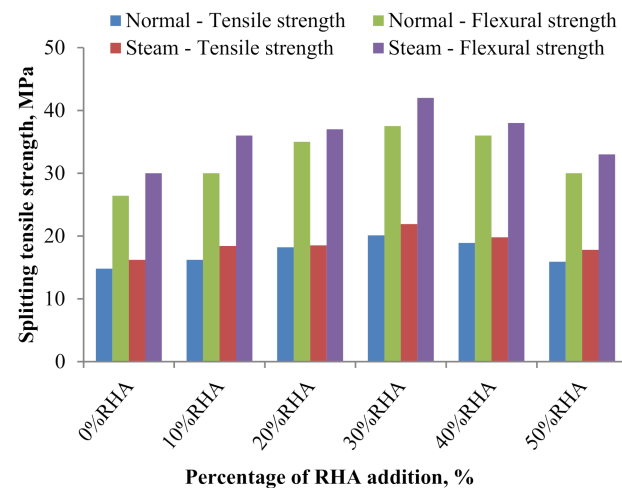

Figure 11. Splitting tensile strength with different levels of RHA replacement [114].

7.3. Modulus of Elasticity

The modulus of elasticity (MOE) of the RHA-based concrete is strongly associated with the compressive strength, thereby indicating that a higher level of geo-polymerization may bring about a denser concrete matrix, which thus adds to a greater MOE (Table 7) [122]. This tendency does not depend solely on the utilized amount of the chemical activator, rather on the quantity of aggregates in the geopolymer concrete mixtures [73,123]. Concrete using RHA as a partial substitution for OPC has been reported to have a higher MOE relative to those without RHA [119,124]. Likewise, the MOE of the blended concrete rises with a rise in the RHA amount of substitution in OPC [125]. An increase in MOE with an increase in OPC substitution with RHA is observed. The increase in MOE with the addition of RHA as a fractional substitution of OPC was attributed to the RHA particles being able to clog the pores throughout the matrix efficiently due to their fineness, thus densifying the gel matrix [11,87,126]. The filling of the pores contributes to further refining of the ITZs between the aggregate and the binder phase. A research study revealed that, with the substitution of cement with 25% RHA, the MOE reduces significantly. According to the investigation on concrete, the modulus of elasticity had an increasing trend with increasing compressive strength [38]. Decreases in the modulus of elasticity are also seen as the substitution of OPC by RHA decreases [127]. The inconsistency in the findings obtained may be due to the difference in the fineness of the RHA used. The trend of a decreasing modulus of elasticity is attributed to the inclusion of more compressible material (amorphous silica), which increases the strain in the concrete [59,128]. An increasing trend in the static modulus of elasticity of concrete was detected through the employment of a larger dose of SP along with a 20% replacement with RHA (Table 7) [30]. Furthermore, the substitution of RHA and FA with cement material has been shown to increase the MOE of the concrete mixtures by various percentages [124]. The best substitution ratios for RHA are 10% and for FA it is 20%. The M16 mixture, comprising 550 kg/m^3 cement-based materials together with a 10% substitution rate of RHS, exhibited a maximum modulus of elasticity of 46.5 GPa. Previous research proved that the optimization of the residual rice husk ash utilization delivers a positive implication for high-strength concretes' properties with a 10% RHA replacement.

Table 7. Elastic modulus of the RHA concrete.

Authors	Mineral Admixture	Content, %	w/c or w/b Ratio	Elastic Modulus (GPa)			Remark
[10,30,36]	Control	0		29.6	30.5	31	—
	RHA	20	0.53	30.1	30.8	31.4	RiH ground for 180 min
		20		30.2	31.4	31.7	RiH ground for 270 min
		20		30.5	32.3	32.9	RiH ground for 360 min
[1,61,129]	Control	0		29.6	—	—	High strength concrete
	RHA	10	0.4	29.6	—	—	

8. Durability Properties

8.1. Drying Shrinkage

Drying shrinkage occurs in concrete when the internal water evaporates from the internal matrix of the hardened concrete [84]. There has been very little research into the drying shrinkage of RHA-containing concrete [3]. It has been observed that RHA-based concrete exhibits drying shrinkage strains identical to those detected in control concrete as well as concrete found in all ages [30,54]. The autogenous deformity assessments of RHA concrete containing 85–90% reactive silica have been investigated. The 0% RHA concrete exhibited deformation around 600 μm/m strain hardening while this value reduced by approximately 50% when 10% of RHA was added [3,10,38]. The influence of RHA fineness (30.4, 29.1 and 27.4 m^2/g) on drying concrete shrinkage at 7, 14, 28, 42, 56, 90 and 180 day hardening was also investigated, wherein it was found that the concrete comprising very fine (30.4 m^2/g) RHA particles showed the peak shrinkage values at all test ages [30,130]. Contradictory views have been observed from the literature, about the pore-refining impact of pozzolanic materials upon the drying of concrete [131]. Likewise, further research into concrete pore-refining additives demonstrates elevated shrinkage as well as creep that describe the findings for the concrete comprising the RHA [30]. Alternatively, some research findings hold [26,29,54,132] the conception of reduction in drying shrinkage through the replacement of cement with pozzolanic materials. One research study indicated that the blend of RHA and SFs along with the average aggregate volume of RHA could enhance the cohesive density [106]. While, the durability of high-strength concrete containing an RHA blend to deliver UHPC has a definitive low quantity of autogenous concrete shrinkage, which has no pozzolanic content or SF concrete mixture [4,78]. Adding 20% of RHA to concrete effectively decreases the autogenous shrinking as the average grain size of the RHA varies from 5.6–9.0 μm [46]. The specimen comprising the tinier part size RHA, i.e., 3.6 μm, displays a greater autogenous shrinkage in comparison with specimens containing an RHA of size 5.6–9.0 μm [91]. Generally, during the early stage of hydration, a certain amount of water is left out in small pores developed though the specific surface area and internal pores of RHA. However, 20% of the RHA content is sufficient enough to soak up adequate water in order to reduce the self-desiccated autogenous shrinkage.

8.2. Permeability

Permeability indicates the extent to which water and other aggressive chemicals can freely penetrate into the concrete matrix and starts to carbonate, induce a chloride-ion attack, and corrode the elements inside the concrete [84]. Concrete permeability is strictly associated to the size of its pores. It was observed that the size of the pores could be considerably reduced when RHA is added in proportions of 10, 20 and 30% at varying w/c proportions of 0.65, 0.75 and 0.80, respectively [133]. It has been observed that the porosity of the concrete reduces by about 25–34% when the RHA was utilized up to 30% [60]. Moreover, OPC specimens containing 10% RHA was very effective in reducing the permeability [134]. Utilization of RHA greatly reduces the permeability of concrete. In fact, it effects the permeability more than the compressive strength [10,44]. It was also noticed that the porosity reduces steadily when the RHA content increases, correlated to a decrease particulate packaging with higher levels of RHA. This may be again accredited to the alteration of the pore structure exercised in the concrete matrix by the RHA grains. Meanwhile, a reduction in the permeability was found only when the average size of

the RHA particles were used but when cured till 90 days only [5,7]. The permeability characteristics (chloride penetration, water absorption and sorptivity) of the RHA-based composites will be further discussed in the subsequent sections.

8.3. Water Absorption and Sorptivity

The penetrability of the concrete needs to be carefully controlled since the ingress of the different ions (SO_4^{2+} and Cl^-) from the outside environment majorly degrade and deteriorate the concrete structures or members [6]. Generally, the porosity of concrete reduces due to the pore refinement ability provided by the RHA particles [43,135]. Moreover, it was also noticed that the water absorption decreases by when the amount of white RHA increases; meanwhile, a drastic increase was observed when beyond the 25% RHA replacement level [136]. Not only this, the capillary rate of absorption was also observed to be much greater beyond a 20% RHA incorporation level and this may be accounted for by the arrangement of the smaller pores upon the utilization of the higher RHA surface area [10]. In contrast, a reduction in the rate of absorption was noticed when RHA was utilized up to a proportion of 15% for the production of SCC mixes [137]. In comparison to the sorptivity estimate of the control specimens, the sorptivity of the mix containing 20% RHA and 20% MK decreased by 19.10% [3]. Furthermore, the water absorption of the mortar specimens decreased by 14.6% when 20% RHA was utilized, whereas this decrease was about 28.1% in the samples made with nano-silica (NS) and 10% RHA [7,83]. Another study observed that the water absorption at 7, 28 and 56 days for the 10% RHA-based mortar was 2.51%, 1.66% and 1.47%, respectively, for three consecutive days of observations [61]. At the time the pores were filled with calcite created by microscopic organisms, and the water absorption of RHA composite was further reduced to 1.86%, 1.03% and 0.80% at 7, 28 and 56 days. In brief, it is possible to conclude that the water absorption in the RHA mixtures mainly decreases due to the improvement of the concrete gel density, reduction in pore sizes and void contents; this behavior continues until the RHA content exceeds 20%.

8.4. Chloride Penetration

The corrosion of reinforced concrete structures has been a significant issue for reinforced concrete used in infrastructure such as seaward and harbor structures and dam and bridge components [84,138]. The rapid chloride penetration test (RPCT) is the most widely used method to measure the electric conductivity of concrete [139,140]. Approximately a 35, 75 and 28% decrement in permeability, chloride permeation and chloride diffusion was observed when 30% RHA was utilized [11,96]. It has been found that the best possible protection against the chloride-ion penetration (dictated by $AgNO_3$ showering test) can be obtained by replacing 15% of cement with RHA particles [82,135]. It was also noticed that the chloride concentration and depth of penetration decreases with a rise in the RHA proportion [13,119]. Furthermore, the total charge decreases by about 52.6% when 10% of the RHA particles were utilized and cured till 56 days [61]. In case of the concrete with bacterial additions, the RHA–bacteria concrete showed 48.4% less charged passed at 56 days with respect to the control bacterial-based concrete. In general, the permeability level was found to be "low to moderate" in the RHA concrete; whereas, "highly low" to "moderate" was found in the bacterial concrete comprising RHA [6]. The addition of 1% K_2SO_4 and 1% Na_2SiO_3 was also found to reduce the total charge passed in RHA concrete by about 71–75%, at varying w/b ratios [6]. The findings from this study indicate that the inclusion of 15% of the RHA particles could considerably improve the chloride-ion penetration resistance by about 4 times greater than the 7 days control mix.

8.5. Resistance to Freezing and Thawing

Selection of materials and mix proportioning plays a crucial role in the concrete making process in places where the structures are more susceptible to external attacks [84]. It has been reported that concrete made with 15% RHA particles exhibited unrivaled freeze–thaw efficiency and was able to withstand 300 cycles without hitting the maximum

durability factor under 60 [3]. Meanwhile, concrete comprising SF in the binary cement blend performed miserably in the freeze–thaw resistivity; this could be due to the high compact gel phase attributed to a densified matrix owing to the developed high-pressure during freezing. Better results for RHA-containing concrete was obtained due to the micro-porous structure of RHA that enables water to expand in the course of freezing, thereby reducing internal stress development [10,23,141]. The finding from this study indicates that the concrete made with 10% SF and 10% RHA has excellent freeze–thaw efficiency over all other mixture compositions. Meanwhile, the specific durability factor of 98.3 for RHA mix shows insignificant variations in weight, density, resonant frequency and pulse velocity even after 300 frequencies [4,142]. Another research stated that RHA concrete resistance to freezing was marginally lower than SF-embedded concrete, after 300 freezing cycles [143]. Greater resistance to freeze–thaw is typically reported with concrete containing acid-leached RHA [141]. In conclusion, concrete using RHA showed development of high compressive strength along with good freeze–thaw resistance, where such rise in compressive strength and freeze–thaw resistance could be attributed to the RHA's pozzolanic action and porous structure, respectively.

8.6. Resistance to Acid and Sulphate Attack

Concrete is extremely basic in nature, and as well as highly susceptible to acid attack. The acids attack concrete by dissolving both the hydrated (gel phases) and unhydrated (free lime) concrete products and the aggregate part (both coarse and fine) [84]. Concrete subjected to acidic condition is inclined to the complex equilibrium of its antacid existence linked to portlandite disintegration, C-S-H gel and alkali extraction from the matrix [13,78]. Concrete exposed to HCl can prompt the generation of dissolvable $CaCl_2$, which greatly affects the concrete porosity and its permeability [36,51]. The SO_4 ions generated from sulphate sources ($MgSO_4/H_2SO_4$) are capable of reacting due to the existence of $Ca(OH)_2$ in the concrete (resulted from gypsum or during hydration), which facilitates the volumetric expansion and separation of the concrete components/ingredients from its original mass [3]. It is reported that the inclusion of RHA in concrete leads to better acid attack resistance in comparison with OPC due to the existence of reactive silica in the RHA particles [144] (Figure 12). Such activity of the RHA concrete was observed as a result of reduced penetrability and a reasonably lower $Ca(OH)_2$ in cement concrete containing RHA, causing improved concrete ITZ and a reduction in porosity [23,145]. However, the compressive strength of the RHA concrete reduces by about 5–16% when the specimens were subjected to a 5% $MgSO_4$ solution [3,22,49,126].
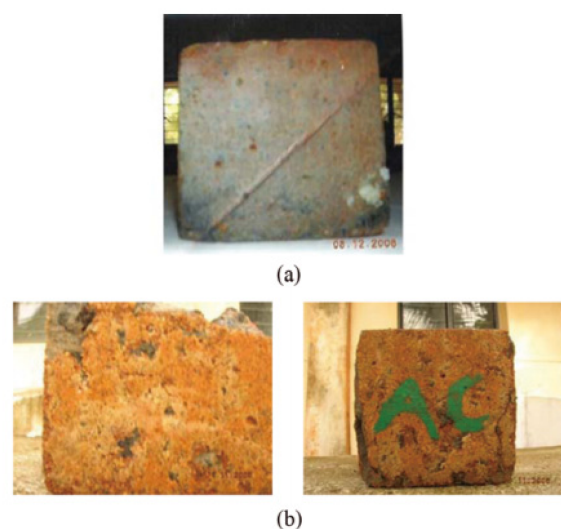
Figure 12. Resistance of (**a**) ordinary concrete and (**b**) RHA-based concrete against acid attack [144].

Contrariwise, the sulphate expansion of the RHA concrete was lesser than the natural concrete noticed when the specimens were engrossed in a 5% Na_2SO_4 solution, resulting in the improvement in the compressive strength due to formation of extra C-S-H gels during the secondary pozzolanic reaction [83,119]. However, this improvement in the compressive strength was noticed till 2 months only, beyond which the strength decreases dramatically due to formation of the gypsum and ettringites [61]. The high pH levels of the Na_2SO_4 solution are noted, and the highest pH observed was 12.5; these observations were made during the initial 7 days of submersion [134]. This finding suggests that during this time a large quantity of $Ca(OH)_2$ was strained and the pH of the solution increases. It was also found that the samples' expansion was very delicate to the solution's pH wherein the lower pH shows the samples as less sensitive to sulphate attack. In general, RHA is very useful as an SCM, which helps to enrich the mortar and concrete quality. The pozzolanic properties of RHA provides additional hydration products that can generate a higher strength and minimize the content of large pores and porosity causing very low permeability, which reduces its susceptibility to attacks by acids and sulphates.

8.7. Alkali–Silica Reaction Resistance

The alkali–silica reaction (ASR), widely recognized as concrete cancer, is an expanding reaction that occurs in the concrete after casting. The reaction often takes place within the exceptionally alkaline cement paste and the sensitive non-crystalline silica contained in aggregates at provided adequate moisture [84,146]. ASR occurs between alkalis (Na_2O and K_2O) and other receptive silica minerals present in the aggregates [147]. The synthetic reaction can cause unusual concrete expansion and splitting. To eradicate this problem, the utilization of low alkali cement is an alternative, or the usage of SCMs is suggested in either case [3]. The alkalis present in the cement paste are capable to react with the grounded RHA to generate alkaline silicates [147]. Such a development would decrease the accessible alkali in the pore structure, reducing the attack on the silica-containing aggregates [111]. ASR would also be smothered in the RHA-containing concretes as these concretes are less porous, thus preventing the entry of moisture into the concrete matrix, hence preventing the occurrence of ASR [148]. Therefore, chances of ASR in concretes containing RHA are comparatively less. The RHA quantity to counteract ASR in concrete would be relative to the quality of the aggregates used in the concrete; therefore it changes from aggregate to aggregate [111]. Estimated expansions at 16 and 30 days due to alkali–silica reactivity showed that RHA incorporation was successful in regulating mortar bar growth at 16 and 30 days of age. Similarly, at 175 days, it was found that the mix containing 7 and 10% RHA showed decreased ASR expansion by approximately 52% and 33% relative to the prisms produced with only OPC [36,149]. In contrast, the specimens comprising 15% RHA exhibited the maximum ASR expansion by approximately 0.045% and showed that the concrete prisms grow up to 175 days. Based on past research, it could be inferred that the use of RHA (10 to 40% by cement weight) will be more effective in reducing ASR expansion; in particular, finer RHA particles can decrease ASR expansion to a larger extent than that of course RHA particles.

8.8. Resistance to Carbonation

The CO_2 present in the atmosphere can penetrate deep within the concrete matrix and react with the basic components, mostly with $Ca(OH)_2$, which may result in deteriorating the concrete structure [150]. This response (carbonation) reduces the pH estimate for the pore solutions to 9 or less [6]. When the alkalinity of the pore system is vanished, the reinforcement steels becomes susceptible to corrosion [61]. Similarly, the transport properties are also significantly affected by carbonation [151,152]. Since RHA is a pozzolanic material, it increases the concrete's impermeability, and is also useful in reducing carbonation. A study found that the carbonation depth, when measured using phenolphthalein ($C_{20}H_{14}O_4$) splashing test procedures, was found to decrease when a chemically treated RHA concrete (containing 20% RHA) was exposed to 5% CO_2, which was measured in a

controlled chamber held at 23 ± 1 °C and 65 ± 1% RH [6,39,113]. In fact, the carbonation depth decreased further when 1% K_2SO_4 was used as an activating agent. Contrariwise, the carbonation depth was found to be increased as the RHA replacement level increases from 20 to 40% and also with an increase in the w/c ratio [6,44,153–155]. The increased value of the carbonation depth is due to the increased porosity and lower cement concentration of the concrete [13]. The beneficial effects of RHA on the mortars were also reported, and it has been demonstrated that RHA is better in enhancing the corrosion resistance compared with FA-blended concrete [61,156]. A point was made that the first crack on the OPC samples was at 89 h from the start of the experiment, but in the case of 10, 20 and 40% RHA-inclusive mortar mixes, this value was 167, 168 and 166 h, respectively [33]. This study shows that increased rates of cement replacement with RHA deleteriously affected the carbonation response in the mortar samples [3,36]. Furthermore, more studies are needed, in particular on concrete containing no RHA, to understand the comprehensive effect of RHA in the carbonation of concrete before its inclusion.

8.9. Electrical and Thermal Conductivity

The electrical resistivity technique is employed for assessing how to control the quality of concrete structures by estimating the particle dispersion in the concrete by means of the pore arrangements [150]. Concrete's electrical resistivity is characterized as its capacity to resist the exchange of ions when exposed to an electric field (Figure 13) [157]. It is influenced by the dispersion and interconnection of pores, the conduction capacity of the pore fluid, temperature and the saturation level [47]. The basic techniques available for such measures are the two- and four-point uniaxial method (Wenner probe). An increase in electrical conduction is seen as the curing time frame has expanded from 3 to 91 days [113]. It was also seen that the electrical conductivity increased by a factor of 2 as the content of RHA increases from 10 to 20%, whereas the electrical resistivity was about 340–404% greater with respect to the control mix. It was also noticed that the true electrical resistivity of the concrete containing 0 to 20% RHA falls between 5 and 10 kΩ cm [47]. With the growing amount of RHA inclusion, the resistivity was noticed to be 52% times greater than the control concrete. Meanwhile, the incorporation of grounded RHA was found to increase the electrical resistivity at 14 days of curing and this was mostly by reason of pozzolanic activity of the RHA that generally fills the pores with additional C-S-H gel [158]. The electrical resistivity of the RHA concrete was also found to be low at 7 days of curing (since the pozzolanic reaction is very slow) and the resistance increases at 28 and 90 days of curing period with respect to the control mixture [159]. Meanwhile, concrete made with RHA and nano-TiO_2 (NT) was found to have an even higher resistivity than the control concrete (within 5 and 10 kΩ cm) [54]. The electrical resistivity of the examples with 5% NT + 10% RHA, 3% NT + 15% RHA and 5% NT + 15% RHA was more than 20 kΩ cm. The ACI 222 [160] recommended limits that the probability of corrosion will be lower if the electrical resistivity exceeds 20 kΩ cm, whereas it will be extremely higher at 5 kΩ cm, higher at 5–10 kΩ cm and low to moderate at 10–20 kΩ cm.
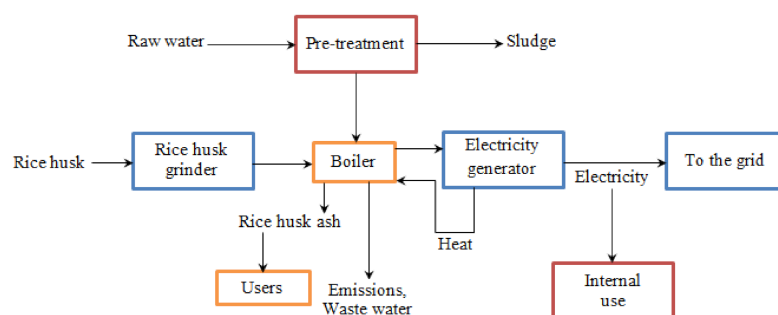
Figure 13. Process diagram for RiH-fueled power generation using a combustion system.

Meanwhile, a study analyzed the thermal conductivity (TC) and water vapor diffusion (WVD) resistance factor of concrete specimens wherein RiH was included at 0, 1.5, 3 and 5% by the mass of the OPC [93]. Reports indicated a decrease in TCC content with an increase in RHA. For instance, the TC of the control mix was 1.88 W/mK, which decreases to 1.85, 1.80 and 1.68 W/mK when RH was used in proportion of 1.5%, 3.0% and 5.0%, respectively [158]. This appears to be the case because the RiH present in the concrete creates empty spaces that minimize heat transfer. Resistance to WPD was measured in line with TS EN 12,086 [161]. The samples were stored in watertight cups with $CaCl_2$ as a sorbent after which the watertight cup was put at a consistent relative humidity and temperature in a controlled environment. The samples were weighed at 24 h to check the amount of moisture diffused [159]. The water vapor diffusion resistance factor was seen to decline in concrete with a higher content of RiH [93]. For the control samples, the water vapor diffusion resistance factor was 41, depreciating to 32, 21 and 18 when the RiH content was utilized in a proportion of 1.5, 3.0 and 5.0%, respectively. Ultimately, an enhanced property will reduce the RHA-based concrete spalling by dropping the WPD within its matrix.

8.10. Fire Resistance

Resistance to fire is regarded as the capacity of the concrete structure to be able to resist against fire without the loss in the load bearing capacity including ability to prevent the spread fire [22,38]. It is known that the concrete expose to high temperatures can affect their strength and durability. It has been established the one of the strategies for improving resistance to fire of concrete is by replacing cement with pozzolanic materials [162]. Another research disclosed that the blended cement concrete is utilized broadly for their great structural and durability performance [20,163]. RHA is one of the typical mineral derived substances that are used in concrete (see Table 8) [13,164]. Similarly, it is known that the increased temperature impact on some of the concrete's mechanical properties [165]. For measurements, three temperature levels of 400, 500 and 700 °C were selected with four separate time intervals, i.e., 30, 60, 90 and 120 min. The samples were heated and cooled under a controlled atmospheric system and tested after different time intervals, at 30, 60 and 90 days [23,50]. Their study found that the concrete's fire resistance was between 70 and 85% at 400 °C, 59 and 78% at 500 °C and 43 and 62% at 700 °C for each specified condition. This result was further endorsed by another study of the mechanical properties and high-performance of concrete exposed to high temperatures [164,166,167]. The samples were exposed to high temperature for a period of 1, 2 and 4 h without loading conditions. The specimens were cooled and tested after the desired time period as per the experimental guidelines. They further expressed that the concrete's fire resistance was between 90 and 106% at 100 °C, 72 and 103% at 300 °C, 55 and 87% at 500 °C and 22 and 66% at 600 to 800 °C. The findings concluded that the residual concrete compressive strength was considerably influenced by exposure for more than 1 h; in any case, the impact was reduced as the temperature further elevated. It also deliberated the impact of fire on concrete building and structures [45,150]. It was also found that water evaporates within 200 °C, whereas the siliceous aggregates starts to deteriorate between 200 and 400 °C. Meanwhile, $Ca(OH)_2$ disintegrates at 400–600 °C and the C-S-H breaks down at 600–800 °C, as a result, the structures' load-bearing ability is lost. The concrete melts over 1000 °C and transforms to a liquid state. Nonetheless, depending on the proposed purpose of the structure, the materials used must meet certain prerequisites for fire resistance, as laid down in the various standard guidelines [13,38,168]. It was also reported that the residual compressive strength could be incidental mainly when combining both a change in color and temperature [77,140,169,170]. Generally, it is reported that mineral admixtures, for example, RHA-based concretes upgrade their mechanical and durability properties, showing that when the pozzolan is mixed with OPC, it helps to structure extra C-S-H gel, thus enhancing the performance of the concrete.

Table 8. Influence of the temperature of burning on the RHA structure.

Temperature	Structure of RHA	Specific Surface Area (m²/g)	References
Up to 500	Particles are globular spherical or in form with permeable structure	0.5 to 2.1	[93,171,172]
500 to 600	Particles are partially crystalline and non-crystalline. It has a fine porous crystalline grain, not more than 1 μm, perhaps establishing the transition between the crystalline and the amorphous state	76 to 122	
600 to 700	Diameter of pores, and amorphous particles is uppermost	100 to 150 at a lower temperature	
700 to 800	Partially crystalline, formulation of coral-formed crystals	6 to 10	
800 to 900	Crystalline	Not more than 5	
900 to and 1000	The formulation of coral-formed crystals augmented, and increasingly finer and molted significantly	-	

9. Applications of RHA

The RHA utilization as a pozzolana in high-performance concrete development helps the construction industry, as a filler, additives, abrasive agent and for energy and non-energy applications (see Figure 14 and Tables 9 and 10) [13,59,99,112,133,137,173,174]. The technological know-how utilized in RiH-fueled power plants influences how the ash could be utilized. Apparently, RHA is effectively utilized in various applications considering its specialized reasonability/viability [171,175]. It is uncovered that RHA created from moving grate technology is appropriate to be used as an adsorbent due to it's the high surface area [75]. Then again, the ash sourced from the fluidized bed may be utilized as filler in polymeric composites and also in innovational ceramics blends [81].
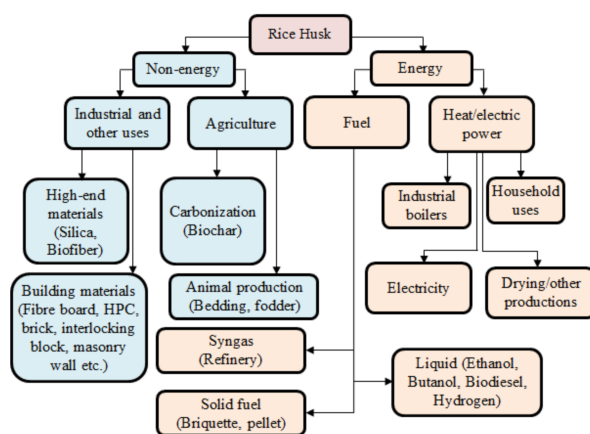
Figure 14. The potential applications of RHA [176].

Meanwhile, the high amorphous silica in RHA is from suspension-fired technology, making it suitable for utilization as a natural pozzolana in the cement industry and to be used in zeolite formulation [13]. It was accounted for that RHA can contribute to diminish the environmental effects when used to substitute cement [38,81]. In view of the discovered technical, environmental, economic and socio performances of the different RHA applications reported, it can be used as a partial or fully substitutional product; its use would support sustainable development in all its three dimensions: environmental, social and economics (Table 9).

Table 9. Some applications of RHA [34].

Silica (Amorphous)	Liquid Sodium Silicate	Activated Carbon
Waterproofing Chemicals	Binders and Ceramics	Water Purification
Ceramic Glaze	Cements and Adhesives	Solvent Recovery
Oil Spill Absorbent	Textile Processing	Air Purification
Catalysts, Coatings	Paper and Pulp Processing	Sweetener
Green Concrete	Cleaning Compounds and Detergents	Pharmaceuticals
Soap And Detergents	Mineral Ana Mining Processing	
Cosmetics, Healthcare, Food,	Petrochemical Processing	
High Performance Concrete	Water Treatment	
Carrier For Pesticides	Coatings And Paints	
Rubber and Plastic Bars		
Bio Fertilizers and Insecticides		
Flame Retardants		
Insulator, Refractory		
Specialty Paints		
Paper and Pulp Processing		
Roofing Shingles		
Solar Panels		

Table 10. Applications of RHA towards sustainability performance.

Type of Application	Year	Rate of Used		Product	Type of Impact				Refs.
		Fully	Partially		Technical	Social	Economic	Environmental	
HPC	2000	-	√	OPC	√	-	√	-	[177]
Heat absorbing	2008	√		Sand	√	-	-	-	[70]
Sand–cement block	2009	√	-	Clay brick	√	-	√	-	[72]
Silica powders	2010	√		Commercial silica	√	-	-	-	[155]
Silica	2011	√	-	Sodium powder and quartz	√	-	-	-	[178]
Epoxy coating		-	√	Epoxy paint	√	-	-	-	[169]
Activated carbon		√		Commercial Activated carbon	√	-	-	-	[178]
Concrete	2012	-	√	OPC	√	-	√	-	[179]
Bio-char		-	√	Charcoal	√	√	√	√	[180]
Soil conditioner	2013	-	√	N fertilizer	-	-	-	√	[175]
Concrete block		-	√		-	-	-	√	
Brick		-	√	OPC	√	-	-	√	[87]
Mortar coating		-	√		√	-	-	-	
Concrete									
Brick		-	√	clay	-	-	-	√	[175]
Pb and Zn stabilization	2014	√	-	Commercial adsorbents	√	-	-	-	[181]
Porous silica		√	-	Water glass	√	-	-	-	[182]
Concrete		-	√	OPC	√	-	-	√	[75]
		-	√		√	-	-	-	[94]
Pure white silica	2015	√	-	Commercial silica	√	-	-	-	[77]
glass		-	√	Natural sand	√	-	-	-	[174]
Insulator		√	-	Commercial insulator	√	-	√	√	[183]
Rice mill wastewater treatment		√	-	Commercial adsorbents	√	-	-	-	[77]
Concrete	2016	-	√	OPC	√	-	-	-	[133] [81]
Ultra-HSC	2019	-	√		√	-	-	√	[13]
Cement-based materials	2020	√	-	Resistant to sulfate attack	√	√	√	√	[184]

10. Conclusions

It is known that the increase in demand for cement production is because of the fast construction techniques, industrial revolution and increase in population worldwide. Due to these factors, cement plants cause massive ecological issues by emitting 8% of

the global CO_2, as the making of 1 ton of ordinary Portland cement (OPC) emits almost 1 ton of CO_2. This significant air pollution could contribute to global warming. Therefore, the search for producing alternative, ecofriendly supplementary cementing materials is highly imperative. Rice husk (RiH) is a cultivated by-product material, obtained from the rice plant in enormous quantities. With no beneficial use, it is an organic waste material that causes dumping issues. Its high silica content marks it appropriate for use in OPC, by burning it to generate a high pozzolanic reactive rice husk ash (RHA) for renewable cement-based recyclable material. Such a huge quantity of RHA generation leads to several environmental issues, such as an increase in the disposal landfills and increases in the carbon footprints due to which a proper and safe disposal of RHA is obligatory for proper waste management. However, due to the shortage of disposal landfills, alternative solutions towards the utilization of RHA in a sustainable manner need to be found.

It is found that the properties of RHA most often rely on the sort of rice plants, the nature and quality of the RHA, the process of heat treatment of the rice husk, method of burning, holding time and temperature of consuming. It also discovered that the utilization of RHA can lead to a safe dumping of these waste products, avoid health issues, decline the ecological contamination caused by the cement processing plants and decrease the emissions of CO_2 to the climate and production cost of cement.

The physiochemical properties of RHA are good for concrete production. The properties of reactive silica present in the RHA may also vary depending on the heat treatment temperature and its time. RHA can be utilized to partially substitute cement. Rice husk ought to be burnt at a controlled temperature of about 500–700 °C in order to obtain the maximum reactive silica. However, the production of silica from RHA is due to a wide range of its application and the solution of the important task of environmental protection and energy conservation. The use of RHA as an SCM can be utilized as an admixture in various components of construction materials due to its significant porous structure, which leads to a decrease in concrete self-weight and excellent insulating behaviors. The inclusion of nano-silica in the RHA concrete would indeed be advantageous, because nano-silica can lead to high early strength and improve the durability of RHA-based concrete composites. It also exhibited high pozzolanic properties and leads to high impermeability and strength of the concrete. Likewise, the blended mixtures made with greater than 20% RHA showed a decrease in porosity, water absorption, the autogenous drying shrinkage, the chloride penetration, carbonation, corrosion potential, acid and sulphate attack and higher electrical resistivity, because of the refinement of the pore structure and high pozzolanic reaction.

Using cost-effective and commonly obtainable RHA as mineral fillers in concrete brings plentiful advantages to the technical characteristics of concrete, and would also help to ensure a clean environment. With RHA, an RHA-based eco-efficient concrete composite that can be robust, highly resistant to aggressive environments, sustainable and economically feasible can be produced. However, production of sustainable and greener concrete composites has become a key concern in the construction industries internationally. This article reviews the source, clean production, pozzolanic activity and chemical composition of RHA. This literature review also provides state-of-the art reviews on the properties, hardening conditions and behaviors of RHA-based concrete composites in addition to overviewing the recent research findings to produce complete insights into the possible applications of RHA as a raw building material, for producing greener concrete composites towards industrializing ecofriendly buildings.

In conclusion, this review of the state-of the-art has exhibited the positive impacts of RHA in making sustainable, ecofriendly concrete, to help the industry participate in setting a safe, sustainable, clean and healthy environment. However, as RHA is deemed as one of the alternative supplemental cementing materials in concrete, several further research investigations are recommended for production of renewable and green concrete composites:

-　　Further investigations are recommended to ensure that the correlation of production–structure–performance is clear;

- Most of the RHA-based concretes are brittle and sensitive to cracking, and such behavior not only imposes constraints in applications, but also affects the long-term durability of the RHA concretes;
- The use of RHA-based concretes for toxic metals adsorption and immobilization and for sealing CO_2 is still unsatisfactory;
- New applications of RHA concretes are worth exploring and can be found, such as RHA-based concretes with biomass can be developed as a class of novel lightweight fire-proofing;
- To further study the potential use of RHA materials to develop self-consolidating and high-strength performance concretes;
- To increase the strength and durability of RHA in a hardened state using fibers; and
- To further extend the possible utilization of RHA in the construction of green buildings and future sustainable cities with a reduced carbon footprint.

Abbreviations

ASR	Alkali–silica reaction
BET	Brunauer–Emmett–Teller
CO_2	Carbon dioxide
CPR	Chloride penetration rate ratio
FA	Fly ash
GGBFS	Ground granulated blast furnace slag
HRWR	High-range water reducers
C-S-H	Hydrates of calcium silicate
HCL	Hydrochloric acid
ITZ	Interfacial transition zone
MIP	Mercury intrusion porosimetry
MK	Metakaolin
MoE	Modulus of elasticity
NT	Nano-TiO_2
OPC	Ordinary Portland cement/concrete
PF	Polypropylene fiber
RCPT	Rapid chloride permeability testing
RiH	Rice husk
RHA	Rice husk ash

SCC   Self-compacting concrete
SF   Silica fume
SSA   Specific surface area
SP   Super-plasticizer
SCM   Supplementary cementitious material
UHPC   Ultrahigh-performance concrete
W/C   water to cement ratio
XRD   X-ray diffractograms

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