

Review

The Utilization of Agricultural Waste as Agro-Cement in Concrete: A Review

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Abstract: Concrete, as the world's most implemented construction material, is increasingly being used because of the rapid development of industrialization and urbanization. Limited resources and progressive depravation of the environment are forcing scientific efforts to seek alternative and effective materials from large amounts of natural resources as additives in the partial replacement of cement. Cement is a main constituent of concrete. To solve and minimize environmental issues, research works attempting to employ the wide availability of agricultural wastes, such as sugar cane bagasse, rice husk, sugar cane straw, and palm oil fuel, among others, into cement, and to finally bring sustainable and environmentally friendly properties to concrete are being examined. Agro-waste materials are crushed into fine and coarse aggregates or are burnt into ash, and are then mixed with cement, which is known as agro-cement. The replacement of aggregates, either partially or fully, is also deemed as a sustainable material in construction. This paper mainly reviews the current research on agro-cement that has been researched and applied for the enhancement of the strength and durability of concrete. It further summarizes the relevant knowledge and techniques, while providing optimal parameters for applying agricultural wastes in concrete.

Keywords: agro-cement; concrete; agricultural waste; construction; durability

1. Introduction

As a binding medium, concrete is one of the most popular and widely used civil engineering materials for sustaining the fast-growing global population and for rapid urban development, especially in developing countries [1]. The emergence of concrete mixed with cement, aggregates, water, and reinforced steel bars also has uses in the areas of the military, transport, hydraulics, and construction [2]. However, it is inevitable that a series of issues will arise when it comes to traditional concrete. On the one hand, the construction of concrete materials is an extravagant process and depletes high amounts of energy. On the other hand, because of the massive use of concrete, quite a few concrete product wastes are either discarded or are difficult to dispose of, as most of these are not of a recyclable nature, and have the inherent drawback of creating environmental pollution [3–5]. The increased demand of infrastructures also leads to large amounts of cement usage being disposed of in limited landfill space, resulting in the emission of huge amounts of greenhouse gases [6,7]. It is estimated that 800 kg of the greenhouse gas, carbon dioxide (CO₂), is emitted into the ecosystem when manufacturing one ton of cement [8]. Therefore, the state of the art for sustainable, unconventional, natural, and recycled building materials should be taken into account [9].

As sustainable and feasible materials, ubiquitous and inexpensive agro-wastes were the inspiration for this study. According to the statistics, biomass accounts for only about 9% to 14% of energy sources in industrialized and developing countries [10]. Most residues are generally left behind or burned in fields, which can lead to serious environmental issues. On the other hand, biomass energy production can be regarded as a renewable energy process that does not emit additional carbon dioxide into the ecosystem [11]. These agro-waste materials do not just play the role of supplementary cementitious materials, but also serve as alternative aggregates in construction [7]. Developed countries are typically ahead of developing countries in terms of handling and utilizing agricultural waste [6]. At the same time, developing countries are paying a lot of attention to the proper utilization of agricultural waste. In Thailand, the resource utilization of palm oil ash is of great concern, as the palm oil industry plays an important role in local agro-industries [12]. Nevertheless, an enormous amount of solid wastes, including the residues of palm fiber, shells, and empty fruit bunches, are produced annually. The annual increase in palm oil ash disposal creates big problems, such as air pollution and potential health and safety threats after incineration, in addition to occupying considerable space. However, many investigators have focussed on using agro-waste ash as constituents in cement. Studies have revealed that agro-waste ash contains a high amount of silica in amorphous form, and could be used as a pozzolanic material [13–15]. Researchers have shown the importance of agro-waste ash, by partially replacing 10–30% of cement with agro-wastes in order to achieve high-strength concrete [16]. Furthermore, despite such replacements, cement incorporating agro-waste ash has exhibited a great performance in mortar and concrete, even under exposure to a hydrochloric acid solution [17]. Various studies from all around the world have confirmed the significance of agro-wastes; considering future applications and the introduction of new types of such wastes, it is important to gather all related information in one place.

2. Methodology

The purpose of this article is aimed at summarizing the properties of agricultural wastes according to their physico-chemical levels and by morphological analysis, as well as considering their current applications in concrete and the improved mechanical properties of mixed agro-cement. We discuss the properties of agro-wastes as the basis for agro-cement, in addition to the morphological and mineralogical characterizations of agro-waste. The application of agro-cement for improving the mechanical properties of mixed agro-wastes in concrete is highlighted. It is very important to know the cost of any new technology in sustainable construction; thus, a cost analysis of agro-cement in concrete production is performed. Furthermore, in terms of previous findings, the paper also provides relatively optimal schedules (such as the preference of supplemented agro-wastes and the optimum proportions) for adding agro-waste into concrete. Research into the addition of a single agricultural waste to concrete has matured; however, mixed agricultural wastes in concrete are understudied. Thus, research on combining the advantages of different agricultural wastes as part of sustainable materials applied to concrete is worth considering.

In order to carry out the systematic review for this article, the authors conducted a study of the literature by going through articles published in international scientific journals up until July 2020 in the area of agro-cement. To that effect, and considering their relevance in related research, the following databases were analyzed: ScienceDirect and Scopus. A standard assumption was made with regard to searching for the titles of publications, because the keywords that are the main focus of the study are usually used in the title [18].

An analysis of the contents of all of the publications (articles, book chapters, and proceedings papers) that came up as a result of the search using the queries “agro-waste” and “agro-cement” was conducted. The ScienceDirect search engine showed 1823 publications with those keywords. On the other hand, Scopus showed 1294 in total with “agro-waste” OR “agro-cement”, which was further refined to 149 documents within the results with the keyword “cement” and 177 with the keyword “construction”. All of these publications were studied and, after being confined to the topic, the most relevant were referred to while preparing this article.

3. The Properties of Agro-Waste

The utilization of agro-residues in concrete has attracted interest from both science and construction industries, because of the sustainable benefits offered by such residues, in addition to their cost effective and environment friendly nature compared with Portland cement. Crop residue represents more than 50% of the global agricultural biomass [19]. The top ten CO₂ emitting countries according to crop residues are shown in Figure 1. However, only small percentages of such residues are being used for papermaking or panel processing; most of them are either left behind or burned by farmers on the spot, which not only occupies precious land, but also destroys the local ecological environment. Hence, transforming agricultural residues into sustainable and low-energy construction materials could be a practical solution for nature, the environment, and future generations [20]. Recently, with the development of socio-economic aspects and the progress of science and technology, resource utilization in agro-wastes is booming because of their availability and low-cost nature. Moreover, agro-wastes contain fiber that shows a good stiffness–toughness balance, high efficiency with thermal insulation properties, tensile property, and the has the characteristics of biomass ash [21]. In agriculture, it is a waste, but for the construction industry and scientific research, it presents great potential as an additive, which enables it to reduce energy demand during both construction and service life. Furthermore, agro-cement has a good thermal insulation function, which properly handles both the problem of agricultural waste disposal and the thermal effect of urban construction [20].

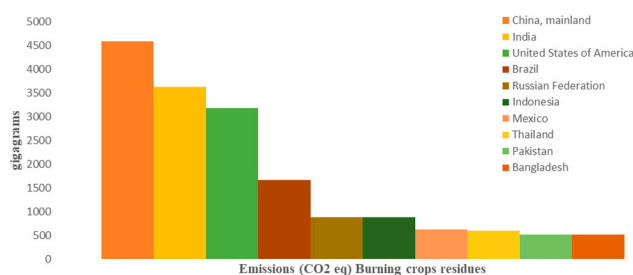


Figure 1. Top ten CO₂ equivalent emitting countries by crop residues with average values during 2010–2017 (Source: Food and Agriculture Organization of the United Nations).

The excessive use of concrete in construction in urban areas causes problems related to thermal comfort and energy expenditure [22]. In order to mitigate such problems, green materials could be a better alternative. Agro-waste materials, including hemp, husk, straw, coconut, and flax, have been deployed in construction to allow for better thermal insulation in buildings [23–26].

Generally, agricultural waste materials refer to sugarcane bagasse ash, rice husk, wild giant reed, sawdust, groundnut shell, oyster shell, tobacco waste, palm oil fuel ash, coconut shell, and so on [27]. They all have a common property of being treated as fine aggregates that provide an additional pozzolanic property in construction materials [28]. It is noteworthy that during combustion, up to 95% of the substances in agro-residues gets turned into amorphous silica [29]. The additional benefits of agricultural waste materials are associated with an improved durability of the resultant structure and a reduction in the permeability of the cement matrix after exposure of mortars to acid attack [30]. In particular, in Asia and Latin American countries, investigation in the agro-industrial division entered a new range of wastes, namely pozzolans, which are regarded as an inexhaustible source of alternatives [27,31–36]. These agro-wastes are not accumulated in landfills and can bring a series of environmental, technological and social issues because of their uncontrolled disposition. However, once activated under the range of 600–800 °C, according to their chemical and physical composition, these agro-wastes can achieve an excellent performance as supplementary cementitious materials in order to improve the performance of mortars and concretes [37]. The compositions of agro-wastes ash primarily include SiO₂, CaO, Al₂O₃, and Fe₂O₃, which have a close correlation with Portland cement [12,38–46]. Table 1 summarizes the physico-chemical properties of the agro-wastes of local areas of various countries. The components of agro-wastes ash and their correlation with cement makes them a perfect alternative to cement materials [46].

Table 1. Physical and chemical properties of agro-wastes, including rice husk ash (RHA), palm oil fuel ash (POFA), and sugarcane bagasse ash (SCBA).

Physical and Chemical Properties	RHA of Local Areas					POFA of Local Areas		SCBA of Local Areas	
	China [38]	Iraq [39]	Iran [40]	Brazil [41]	Pakistan [42]	Malaysia [43,44]	Thailand [12]	Brazil [45]	India [46]
Average size (μm)	2.18	-	-	4.3	-	14.53	10.1	-	-
Specific surface area (m^2/g)	-	-	-	33.672	-	0.915	-	-	-
Loose bulk density (g/cm^3)	2.5	-	-	-	1.2	1.8	-	-	-
Silicon dioxide (SiO_2) (%)	85.93	88.23	91.42	82.6	77.19	47.37	20.9	43.34	69.64
Calcium oxide (CaO) (%)	2.87	1.58	1.03	0.9	2.88	11.83	65.4	22.16	6.26
Aluminum oxide (Al_2O_3) (%)	2.20	10.8	0.114	0.4	6.19	3.53	4.7	10.45	1.94
Ferric oxide (Fe_2O_3) (%)	1.12	-	0.197	0.5	3.65	6.19	3.4	8.31	2.05
Magnesium oxide (MgO) (%)	0.73	0.58	0.821	-	1.455	4.19	1.2	1.48	3.29
Potassium oxide (K_2O) (%)	3.76	4.23	2.596	1.8	1.815	-	0.3	2.18	8.72
Sodium oxide (Na_2O) (%)	-	-	1.12	0.1	-	-	0.2	0.19	0.91
Loss on ignition (LOI)	1.55	-	2.109	11.9	5.429	1.84	0.9	7.61	-

-: stands for unsure or undeclared data.

4. Microstructures Analysis and Mineralogical Characterization

4.1. Morphological Characteristics

The overall morphological composition when adding agro-wastes into concrete reflects the process of forming a crystalline compound; however, there could be differences in the crystal morphologies based on the combustion temperature. Scanning electron microscopy (SEM) images revealed that off-white rice husk ash (OWRHA) consisted of very irregular shaped particles with a high specific and porous cellular surface area [47], while sugarcane bagasse ash (SCBA) had a variety of particle shapes with sizes up to 150 μm [48]. SCBA has large tubular-shaped particles with highly irregular shapes (Figure 2), as has been confirmed in many studies [49,50].

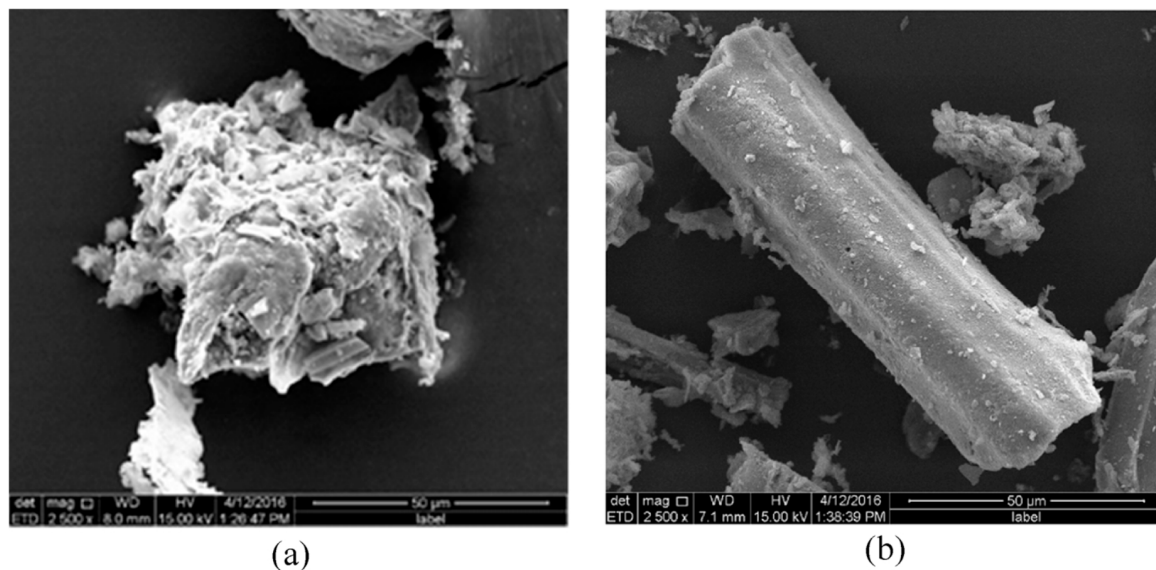


Figure 2. SEM images of two different types of sugar cane bagasse ash. Reprinted with permission from the authors of [50]. (a) SCBA-B (b) SCBA-A.

The fibers from agro-wastes can be encapsulated within calcium silicate hydrates (C-S-H) in order to provide an additional cementing property to concrete. In a recent SEM analysis of concrete containing different concentrations of bottom wood ash (WBA) with 1.5% banana fiber, the interaction of the C-S-H from banana fiber with a cement matrix was shown [51]. Off-white rice husk ash was also found to have irregular shaped particles with a porous cellular surface (Figure 3) [52].

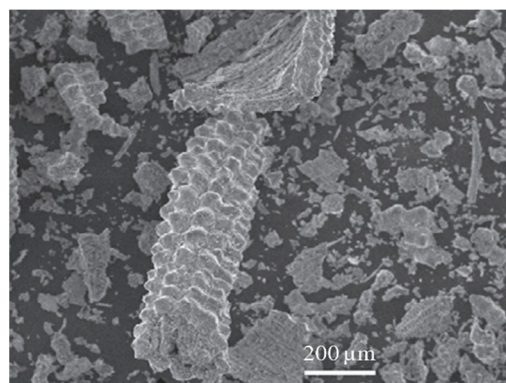


Figure 3. SEM micrograph of off-white rice husk ash. Reprinted with permission from the authors of [52].

Considering the effect of the surface area, smaller particles make a slight difference in the total surface area of concrete. On the other hand, larger particles emerge as residues remaining in hardened concrete, which play a role in combating excess porosity [52].

4.2. Mineralogical Characterization

Generally, the mineralogical characterization of agro-wastes are analyzed by X-ray diffraction (XRD), Fourier Transformation Infrared Spectroscopy (FTIR), and a thermogravimetric analyzer (TGA). XRD is also adopted to determine the crystallinity behaviors of the microcrystalline crystals from agro-wastes [53]. The majority of crystalline components in agro-wastes ash were identified as quartz using XRD. The characteristic diffraction angles (2θ) of some substances were identified as cristobalite, kaolinite, and gibbsite under XRD in various agro-wastes. It was further confirmed that many agro-wastes are also composed mainly of amorphous silica [54,55]. Thermal analysis, in which thermal changes and weight loss are analyzed, identified minerals, including carbonates, in agro-wastes ash [47,52,56,57]. The data obtained by various researchers using TGA are summarized in Table 2. The results of the FTIR obtained from many related studies entail the necessary functional groups in the formation of minerals while using agro-wastes in cement or concrete (Table 3). The mineralogical properties of agro-wastes make it suitable to be used or for application in concrete.

Table 2. Thermogravimetric analysis of ash.

Types of Ashes	Temperature	Peak	Indication	Reference
Brazilian sugar cane bagasse ash	50 °C	Endothermic reaction	Absorbed water loss	[47]
	251 °C	Endothermic reaction	Dehydroxylation process of gibbsite	
	451 °C	Endothermic reaction	Kaolinite dehydroxylation process	
	572 °C	Endothermic reaction	Carbonates decomposition	
Heat-treated palm oil fuel ash cement hydration products	30–250 °C	Endothermic zones	Evaporation of moisture and calcium silicate hydrate (C-S-H)	[56]
	300–550 °C	Endothermic zones	Dehydration of calcium hydroxide	
	Beyond 600 °C	Endothermic zones	Complete decomposition of C-S-H and CaCO_3	
Sugarcane bagasse ashes from a sugar industry in Brazil	350–550 °C	Mass loss	Owe to organic matter	[57]
	417 and 497 °C	Endothermic	Oxidation/volatilization processes	
	671 °C	Endothermic	Decomposition of some carbonates	
	438 and 502 °C	Exothermic process	Oxidation/volatilization of organic matter	

Table 3. FTIR of the characteristic bands.

Agro-Wastes	Frequency	Corresponding Bands	Reference
Barley straws or/and wood shavings	1005 cm^{-1}	Si-O: Silicate, C-S-H	[39]
	3660 cm^{-1}	O-H: Portlandite, Ca(OH)_2	
	870 cm^{-1}	C=O: Calcite, CaCO_3	
Brazilian sugar cane bagasse ash	3451–3463 cm^{-1}	O-H	[47]
	1641 cm^{-1}	H-O-H	
	1446 and 898 cm^{-1}	CO_3^{2-}	
	2490, 2883, and 1405 cm^{-1}	Coke particles traces	
	1093, 1106, 1176, 798, 696, and 472 cm^{-1}	Si-O of the quartz	
Off-white rice husk ash	1220 and 1080 cm^{-1}	-O-Si-O- (asymmetrical stretching band)	[52]
	773 cm^{-1}	-O-Si-O- (symmetrical stretching band)	
	466 cm^{-1}	Si-O bending	
	3436 cm^{-1}	Free water bands	

5. Applications of Agro-Waste Materials in Concrete

The form of application of agro-wastes in concrete is roughly divided into two parts: (1) Without chemical process, usually after physical treatment, such as chopping, cutting, and levigation. These materials are added into concrete in order to partially replace the cement, without variation or decreasing the performance of concrete, through applying agro-wastes. (2) Through chemical combustion, where the burned agro-wastes constitute some of the conglomerant substances that could be exploited and partially displace the function of cement. So far, agro-waste admixtures have successfully been applied in Portland cement either with concretes, mortars, or pastes as the supplementary cementitious materials.

5.1. Agro-Wastes Ash as an Active Pozzolans for Cement

Alkaline activated material (AAM), as a kind of binder, is one of latest directions in constructing building materials and structures. From sugar cane straw ash (SCSA) as a solid precursor and alkali-activated binder bases on blast furnace slag (BES), studies have revealed SCSA as an efficient alkaline activated material (AAM) that also served as a silicon source in AAM [58].

Bamboo leaf ash (BLA), RHA, and SCBA, obtained by burning the biomass, are known to have an amorphous nature with high silica, and show a high pozzolanic reaction when used as binder to produce concrete [59,60]. In a thorough study, it was found that the pozzolanic nature of SCBA and RHA refines the pore structure in mortar and concrete, which significantly reduces permeability against water, sulfate, and chloride penetration [61]. Bagasse ash has also been recommended widely as a pozzolanic material in many studies [62–64].

5.2. Asphalt Concrete Mixture with Agro-Wastes as a Filler

Environmentally friendly policies encourage increasing the utilization of agro-wastes materials based on their unique performance. Using waste powder, such as bag house fines, municipal solid waste incineration ash, or waste ceramic materials, as a mineral filler in mixed asphalt concrete has been studied by several researchers. The development and consumption of waste as supplementary cementitious materials were studied at-large, as the generation of agro-wastes is extremely prevalent in many parts of world. Biomass ashes are suggested as a sustainable replacement to low-cost construction materials, which can also be used as a mineral filler in asphalt mixtures [65].

Rice husk ash (RHA) has been evaluated as a filler in hot mix asphalt (HMA) concrete [66]. The results showed that RHA can replace conventional mineral filler, in turn minimizing the numerous wastes from agriculture. Furthermore, two types of biomass ashes, date seed ash (DSA) and RHA, were mixed to replace conventional filler with DSA and RHA fillers. The results suggest that 100% DSA could be regarded as the optimal percentage, and hot mix asphalt (HMA) mixtures with a 75% RHA substitution demonstrated a suitable performance. Overall, the Marshall stability, stiffness, and rutting performance of asphalt mixtures were enhanced under the application of RHA and DSA. Furthermore, compared with the control mixture, HMA incorporated with RHA and DSA exhibited a particularly improved fatigue resistance, which means that the fatigue life of the resulting concrete will be longer with agro-wastes [67]. While comparing 2% cement as a conventional filler when preparing asphalt, the different proportions of RHA (2% to 4%) as an alternative filler were found to be better than a mineral filler by lowering the optimum bitumen amount in an asphalt concrete mix [68].

5.3. Application of Agricultural Residues on Building Insulation

The process of agricultural production leaves behind plenty of residues, which cause disposal problems. However, such bio-based wastes have the natural advantage of having hygrothermal properties, namely thermal and hygric properties, in order to maintain the performance of buildings as insulation materials. They create a breathable wall in construction and also reduce the risk of moisture build-up and the resulting microbial growth. Some research has demonstrated that hemp,

straw, and olive residues mixed with concrete have shown excellent thermal insulation properties. The excellent thermal insulation properties of hemp have been reported in many studies [69–71].

Concrete with a bio-composite of hemp and lime has not only shown good thermal insulation properties and an acceptable mechanical resistance performance, but has also been found to be lighter than common concrete [69]. Straw–concrete has also been studied in a mixture of binders of lime with gypsum plaster. The use of olive stone as an additive in cement lime mortar has also widely been investigated for improving thermal insulation. It was observed that amending 70% olive stone resulted in a decrease in the mortar thermal conductance by 76% [72]. Concrete containing 10% and 20% of cork was found to lower the thermal conductivity of concrete by approximately 16% and 30%, respectively [54]. With increasing the cork dosage (10–80%) in mortars, a decrease in thermal conductivity was presented by other researchers [73]. The addition of barley straw was shown to improve the thermophysical properties of sand concrete by reducing the thermal conductivity and diffusivity by 5.71% and 21.97%, respectively [74].

6. The Improved Mechanical Properties of Mixed Agro-Wastes in Concrete

6.1. The Effect of Agro-Wastes on Strength

Abundant agriculture wastes create advantages for their potential as replacement materials in the construction industry, especially in countries producing a large quantity of agricultural raw materials. For example, coconut shell (CS) has promising application as a coarse aggregate in concrete production, especially in areas where crushed stones are expensive. Coconut shell has widely been used in concrete to study plastic shrinkage and deflection characteristics, using five mixtures with different coconut shell aggregates (CSA), namely, S1 (100% CS), S2 (75% CS and 25% CSA), S3 (50% CS, 50% CSA), S4 (25% CS and 75% CSA), and S5 (100% CSA) [27]. As it turns out, from the summary of cracks and the deflection test, coconut shell played a vital role in reducing plastic shrinkage cracks in the concrete. The mixture with S5m where aggregate was totally replaced by coconut shell aggregate (CSA) in the mortars, achieved the highest compressive strength. Researchers found out that a 20% replacement of industrial ash (sugar cane ashes) and laboratory ash blended with ordinary Portland cement (OPC) could meet the standard of common cement [8]. For 20% bio-ash blended cement mortars, the compressive strength was reduced by up to 5.1% with regard to the OPC mortar; however, it complied with the standardized mechanical requirements.

In another study, although compared with OPC, the compressive strength decreased slightly; 25% substituted palm oil clinker (POC) as a coarse aggregate incorporated into the concrete resulted in the best result in terms of compressive strength (6.72 MPa versus control 10 MPa) compared with the other replacements. Meanwhile, the results indicated that POC as a coarse aggregate was not fit for application in construction [75]. Similar results were also found by another group of researchers [76]. Rice husk ash (RHA) as a mineral filler mixed into asphalt concrete revealed an almost 10% higher tensile strength compared with that of OPC [66].

In one recent study, the replacement of cement by 7.5% RHA and other Earth materials increased the compressive strength of concrete [77]. With this replacement, at 28 days, the compressive strength was 4.1% higher than the concrete containing 100% cement (control). Agro-waste can accelerate C-S-H formation through an effective pozzolanic reaction. Furthermore, the extracted micro-silica (EMS) from RHA as a substituent of cement, by 5% and 15%, was shown to improve the high-density C-S-H phases, resulting in incremental improvements in compressive strength and ultimately a high-performance sustainable cement mortar [78]. The EMS with a replacement percentage of 5% and 15% improved the compressive strength of the mortars by 64.2% and 51.6%, respectively, and further increased the flexural strength by 46.8%, and 24%, respectively.

The studies suggest that the majority of agro-wastes with incineration processing could serve as fillers in concrete, resulting in sufficient engineering properties in the resulting concrete. Although the increasing content of agro-residues decreased the compressive strength, by contrast, the flexural

strength had significant improvements [21]. Palm oil fuel ash, one of pozzolanic by-products in the development of oil palm shell geopolymer concrete (OPSGC) was investigated, and resulted in higher values of flexural and splitting tensile strength concrete compared with normal weight geopolymer concrete [79]. Indeed, ternary blended-cement-RHA-SCBA was presented as a high-performance concrete, where RHA played a major role in improving compressive strength, owing to its higher pozzolanic activity [41]. The concrete obtained using coconut shell aggregates showed a better response in the pulse velocity with a high strength, and was concluded to be a concrete with a long-term performance [34]. All of these studies implied the potential structural application of agro-residues, and simultaneously reduced agricultural waste disposal in the environment.

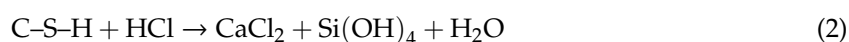
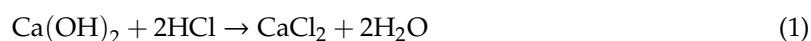
6.2. Permeability and Other Durable Parameters

Chloride-ion penetration resistance reflects the resistance of the permeable capability, often used in the evaluation of the electrical conductance of partially replaced cementitious materials. The performance of various agro-waste ashes, including rice husk ash and palm oil fuel ash, among others, was evaluated in concrete, and most of the results showed a profound effect from these pozzolanic materials for improving the durability of the resulting concrete by lowering the chloride ion permeability [56]. Based on the water absorption and permeability tests, it was found that rice husk ash in concrete resulted into a reduction in water absorption and permeability by as much as 26% and 78%, respectively, compared with the control sample [80].

Other durability parameters involving some agricultural wastes in cement, such as freezing and thawing resistance, chemical attack, setting time (including initial and final), carbonation, water absorption, and expansion tests, were also researched. The expansion percentage also reflects that cement or cement with mixtures under the condition of a sulfate solution or acid solution show a matrix volume shift. Because of the intrinsic characteristics of agro-wastes, research states that a higher replacement of agricultural wastes could increase the ratio of water/binder, thus the blended cement has a lower resistance when attacking sulfate or chloride [12,81]. However, adding fine agro-wastes through grinding into cement has been confirmed to have a better ability to resist CO₂ ingress [82]. The presence of additional silica particles provided by agro-cement can accelerate the pozzolanic reaction and create a consolidated cement matrix that can resist the attack of supercritical CO₂. The capability of freeze-thaw resistance indicates part of the concrete durability. Investigations have indicated that more fine particles of agro-residues add more improvement to the freezing and thawing counteractive ability [28]. Some of the significant parameters are listed below.

6.2.1. Chemical Attack

The ability of concrete to resist diverse aggressive environments is a key durability issue that influences the performance of concrete structures, especially attacking from ambient sulfate and acid, which form a chemical attack. The porous structure of concrete allows for the acid substance to enter, in conjunction with the hydrated product, e.g., Ca (OH)₂ and C–S–H, and form gypsum and ettringite, which expand in their natural state and eventually lead to the deterioration of the concrete surface. Generally, once the cement matrix with an alkaline nature encounters an HCl acid attack, the progressive neutralization develops soluble CaCl₂ salt and water. Accordingly, the mechanism is exhibited as follows in Equations (1) and (2) [17]:



Hence, it is necessary to study the acid and sulfuric acid resistance of concrete. One study exploited an impressed voltage for off-white rice husk ash-cement in an accelerated corrosion test that provided the value information of the permeation characteristics of the concrete [52]. The tests indicated that 15% replacement with cement had the optimum resistivity for preventing erosion. An investigation on

a recycled concrete aggregate found that it is more susceptible to get damaged with acid and sulfate attack compared with a normal aggregate, because of its higher porosity. However, after being modified and replaced with rice husk ash (RHA), palm oil fuel ash (POFA), and palm oil clinker powder (POCP), there was nearly 30% minimal concrete deterioration under a hydrochloric acid (HCl) and magnesium sulfate (MgSO_4) solution [17]. It has been confirmed by research that cement mortars containing black rice husk ash (BRHA) can improve resistance to sodium sulfate attack, and can also impair resistance to magnesium sulfate attack [83]. In general, replacing 20% cement by BRHA leads to the successive reduction in the corrosion of concrete under both HCl and H_2SO_4 attack. In addition, sulfate ions can react with other calcium compounds in a cement matrix, which leads to more permeation and easy corrosion in concrete [30]. In a rapid chloride permeability test (RCPT), because of the fineness and rate of reactivity of sugarcane bagasse ash (SCRHA) in concrete, agro-cement enhanced the resistance of chloride penetration in concrete at concentration up to 25% SCRHA [84]. It was also found that the reaction of SCRHA with free lime in Portland cement produced an additional C–S–H gel [85]. Apart from simply using biomass wastes from agriculture, mixing this with waste polypropylene carpet fibers has the advantage of being very lightweight, having superior resistance to sulfate and acid attacks, and possessing a hydrophobic nature from the carpet fibers, in addition to facilitating in disposal of textile and carpet industrial waste.

6.2.2. Water Absorption

The susceptibility of concrete to the penetration of water depends on capillary suction, which affects the performance of structures. The partial replacement of cement with various percentages and types of agro-waste ash has shown their effectiveness in reducing water absorption of concrete [86]. Off-white rice husk ash (OWRHA), with 15% replacement by weight, showed a reduction in the coefficient of water absorption for the OWRHA blended concrete compared with the 0% benchmark concrete [52]. When basic oxygen furnace slag (BOFs) and RHA were utilized in the partial replacement of cement, water absorption increased considerably. However, high substitution-rate composite cement mortar with RHA and BOFs showed an adverse performance in terms of water absorption with a replacement of more than 60% by the weight of the binder [38]. The mortars containing extracted micro-silica (EMS) from RHA at a replacement percentage with cement of 5% and 15% were found to have a lower porosity by 6.3% and 5.1%, respectively, at 14 days, while they were 5.4% and 3.1% lower than that of the control mortars, respectively, at 28 days [78].

The effects of polypropylene fibers and rubber particles on the mechanical properties of a cement composite with rice husk ash resulted in lower water absorption values due to the rice husk ash being finer than the cement [87]. In another study, concrete made with 10% RHA achieved the minimum water absorption in a chemical process supplemented with microbial calcite precipitation [88]. Furthermore, RHA blended with metakaolin was also used in concrete, which showed a slightly reduced water absorption compared with only OPC or RHA, because of the production of an additional calcium silicate hydrate (C–S–H) gel [83]. With the addition of an extra superplasticizer, RHA was effective in reducing the water absorption of concrete, even at a high amount. The micro filler effect and additional C–S–H products filling the pores lead to a reduced volume of large pores, and the water binder ratio caused decreasing water absorption in such cases [42].

6.3. Setting Time (Initial and Final Setting Time)

The curing time of the concrete in the partial replacement of Portland cement Type I with palm oil fuel ash (POFA) was investigated [12]. The results revealed that both the initial and final setting time increased with the addition of POFA (Table 4); in addition, the results also depended on the fineness and degree of replacement of POFA [12]. Furthermore, large particles with a high porosity of non-combusted palm fiber increased the water-to-binder ratio of concrete, thus leading to high setting times. Other researches obtained a similar behavior with longer setting times of POFA concrete

through using other pozzolans, like fly ash and sawdust ash. The hydration of the cement setting time is usually slower than the pozzolanic reaction between pozzolan and calcium hydroxide.

Table 4. Research on the setting time based on the variety of replacement agro-waste.

Substituent	Optimal Proportion of Replacement	Setting Time	Reference
Arhar stalk	0% to 25% replacement by weight	Increase	[1]
POFA	10% replacement by weight	Slight increase	[12]
SDA	0% to 30% replacement by weight	Increase	[15]
SCBA	20% replacement by weight	Increase	[85]

The setting time also increased when the cement was partially replaced with other agro-wastes, including sawdust ash (SDA) and sugarcane baggase ash (SCBA). The initial setting time of the cement with SDA (10–30%) increased and ranged from 1 h 30 min to 2 h 05 min compared with 1 h 26 min for the only cement paste, while the final setting times were 3 h 56 min to 4 h 20 min, and 3 h 35 min, respectively [15]. By replacing the cement with 20% SCBA, the initial and final setting times of the cement increased by 7 and 24 min, respectively, compared with the cement paste [85].

7. Interaction between Agro-Cement and Cement Matrix

Agricultural wastes as agro-cement have a pozzolanic property that helps improve the mechanical properties of concrete. The lignin and cellulose present in agro-cement can be converted to silica and can provide pozzolanic reactions. When agro-cement is mixed with Portland cement, it reacts with lime and decreases the amount of lime required; however, it increases the amount of C-S-H gel, thereby improving the cement quality [89]. The fine agro-cement particles have been shown to reduce the porosity and density of the cement matrix during chemical reactions between, which increased the compressive strength of the resulting structure. Agro-cement could give rise to an increasing number of nucleation sites in the cement matrix and cause additional C-S-H gel formation. It helps produce strong bonds inside the matrix that increases the compressive strength of concrete. In brief, the increased C-S-H formation during the reaction between agro-cement and Portland cement continuously fills more pores (microfilling) with hydration, and forms a denser structure in the cement matrix [89].

The partial replacement of cement with agro-cement, allows for a slow but long-term increment in the durability of concrete, due to the pozzolanic reaction. Further, the mesoporous nature of agro-cement particles results in a reduction of the effective water–binder ratio in the cementitious matrix, which ultimately improves the compressive strength of concrete [90]. As agro-cement contains a high amount of silica, it enhances the potential in the cement matrix to react with water molecules to form $\text{Ca}(\text{OH})_2$, which can improve the concrete strength. Additionally, another reaction product of same reaction, calcium silicate hydrate ($3\text{CaO} \cdot 2\text{SiO}_2 \cdot 3\text{H}_2\text{O}$), formed around sand particles, influences the pore size distribution of the matrix [89]. The agro-cement containing fine particles of SiO_2 improves the porous structure of concrete, because these particles become uniformly distributed in the cement–aggregate matrix [91].

8. Cost Analysis

Despite the advantages of using agro-waste as pozzolanic or secondary cementitious materials in mortar or concrete, the cost of the resulting product is always a key factor. A cost analysis of the concrete used in already-mixed concrete was performed in one of the studies [92]. The results concluded that concrete containing 5% RHA as a partial replacement for OPC had a lower or comparable cost per m^3 than concrete with 100% OPC, for achieving compressive strengths between 35 MPa and 55 MPa. In general, at a water–binder ratio of 0.35 and 0.50, the cost was USD159.68 and USD122.13, which ultimately produced 56 and 43 MPa, respectively, of 28 d compressive strength. On the other hand, at a similar water–binder ratio, the costs of concrete were a little lower (USD156.22 and USD120.17); however, the obtained 28 d compressive strengths were only 54 MPa and 37 MPa,

respectively. The cost per m³ of the higher replacement levels, such as 10%, 20%, and 30%, was more than that of the reference cement. It is noteworthy that the cost calculation is feasible or economic only when agro-wastes are available locally. For example, if RHA produced in India is used in other country, it will add an additional cost for the RHA, which could be 50 USD/m³ (including grinding, incineration, and transportation costs) [93]. Further study of more agro-wastes mixed with cement in a cost analysis should be taken into account for practical applications on construction.

9. Conclusions

Agro-wastes can serve as alternative eco-efficient and sustainable pozzolans for future concrete industries. The incorporation of these residues into cementitious materials has proven that the addition of wastes is not only advantageous to the environment, but also brings about a great performance of concrete properties. At present, rice husk ash is recognized as the most appropriate alternative material for volcanic ash, while other agricultural wastes are also being studied at a large scale. Generally, they have similar characteristics to ordinary Portland cement and can be effectively used in construction. Up until now, only a few studies have conducted cost analyses on the application of agro-waste, mainly RHA in cement, and a complete economic analysis with most agro-wastes is not reported, which is necessary for their future application in construction. To some extent, although the application of agro-wastes with a partial replacement of cement was recognized by the public, the existence of their limitations, such as the addition of a high level of agro-wastes ash becoming more susceptible to scaling, is still not completed. Future study should pay more focus on aspects including the modification of agro-cement with a superplasticizer, large-scale actual application and life cycle assessment of agro-cement, and appropriate schemes for various agricultural residues with cement. This is expected to greatly amplify the scope of recycled agriculture, while rational disposal and optimal applications of agricultural waste can be achieved.

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