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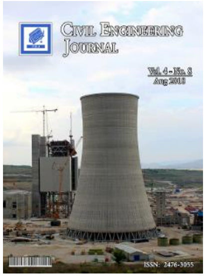

Utilization of Palm Oil Fuel Ash and Eggshell Powder as Partial Cement Replacement - A Review

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Abstract

The increase in population leads to increase in construction of houses and other buildings to accommodate these people. The extensive use of concrete for constructional purposes leads to release of Carbon Dioxide (CO2) gas into the atmosphere which adds to the already increased global warming. The increase in urbanization has also lead to increased generation of waste materials. These waste materials are by-products, which are disposed in landfills causing environmental and health issues. The utilization of agricultural wastes as cement substitute is a great alternative for reducing the use and production of cement, which contributes to 5% to 7% of global CO2 emissions alone. Palm Oil Fuel Ash (POFA) Eggshells are two major agricultural wastes, which are generated in abundance in Malaysia. This paper reviews the combined utilization of Eggshells Powder (ESP) and POFA as potential partial cement replacement material and development of bio-concrete, which may help in reducing the environmental issues that are caused by the agricultural by-products. They have been used successfully but individually in concrete. The pozzolanic activity triggered by POFA requires Calcium Hydroxide which cement provides to a limit. Eggshells when grinded into Eggshells Powder (ESP) are rich in calcium oxide and can provide the required calcium hydride and enhance the pozzolanic reaction.

Keywords: Pozzolanic Activity; Solid Waste Management; Partial Cement Replacement; Sustainable Concrete; Supplementary Cementitious Material (SCMs).

1. Introduction

Since its invention in early 1824, cement has been used in almost all the structures of the world as a major component of concrete. Cement, due to its cohesive properties is a well-known binding material. It is one of the ingredients which make concrete, others being fine aggregates, coarse aggregates and water. While each and every ingredient has its significant role in the mix, cement plays the most important role and it will remain the key material which satisfies the global housing demand [1]. When water is mixed with cement, a cement paste is created which glues together fine and coarse aggregates and hardens to become a solid component known as concrete. Though cement gives concrete its strength, its production however causes harm to the environment. The production of cement requires materials such as calcium, silica, alumina and iron which are extracted from limestones, rocks, chalks, shales and clay, thus reducing the natural resources. Furthermore, carbon dioxide (CO_2) gas is released during the manufacturing process in which the raw

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materials are heated up to 1400ºC in the kiln. The production of cement is one of the main contributors to global CO_2 gas emissions and is reported that it amounts to 5% to 7% of global CO_2 emissions [2].

Due to depleting natural resources and increase in CO_2 gas emissions, the construction industry has focused to achieve sustainability in construction. Sustainability is a process in which exhaustion of natural resources is avoided to maintain an ecological balance for future generations. The sustainability can be achieved in concrete by utilizing waste materials which are processed from agro-industrial processes. The utilization of waste products as supplementary cementitious material (SCMs) can reduce the negative impact on the environment which is caused by the production of cement. SCMs do not possess any cementitious properties, themselves, but react to form cementitious compound when used with cement. Waste products are those products which are produced during the industrial and chemical processes and have little to no potential usage upon production, thus, are thrown or disposed. The disposal of these waste products has negative impact on the environment and on the human health. Due to scarcity of land, the solid waste management has become need of the hour in a world which has seen population grow from 2 billion in early 1900's to 7.3 billion in 2017 [3]. This paper aims to review the potential of combined utilization of Egg shells and Palm Oil Fuel Ash (POFA), both agricultural wastes which are generated in abundance in Malaysia.

2. Egg Shells

The purpose of foods is not just to satisfy the hunger and provide nutrients but also prevent nutrient-related diseases and improve the physical and mental well-beings of consumers [4, 5]. Eggs are a cheap source of nutrient and due to this it is being consumed in large quantities on a daily basis all over the world. It has been reported that approximately 2.8 million eggs are consumed daily in Malaysia alone [6]. The weight of egg varies depending upon its size and type, but on average the weight of medium size chicken egg is approximately 52.23 grams [7], the shell of egg, commonly known as eggshell, is a waste material, it makes up of 11% of total weight of egg [7-9].

Most of the egg shells are disposed in the landfills without proper treatment as traditionally it is considered to be of no use. The disposal of egg shell has the potential to cause significant environmental pollution, due to its availability and chemical composition, hence proper management and treatment is required [10]. Chicken egg shells has been listed worldwide as one of the worst environmental problems, causing undesirable odours, which can cause irritation and affect the well-being of humans. Due to the continuous disposal of wastes, landfilling has become a serious environmental issue in Malaysia, such that the number of the landfill has increased significantly from 49 landfills in 1998 to 161 in 2002 [11].

2.1. Egg Shells Powder (ESP)

According to Thapon and Bourgeois [12, 13] shell is approximately 11% of the total weight of the egg and it presents contents of calcium carbonate (94%), calcium phosphate (1%), magnesium carbonate (1%) and organic substances (4%). So, egg shell is a rich source of mineral salts, mainly calcium carbonate. Unfortunately, egg shell is an egg product industry residue. Due to egg shells containing high amount of calcium and its effect on environment, researchers have attempted to achieve sustainability by reusing or recycling eggshell waste in concrete as supplementary cementitious material (SCM). Since egg shells is to be used as SCM or partial cement replacement, eggshells requires to be in powder form or be fine as cement. Therefore, once the raw egg shells which are collected from different sources are first washed to remove the yellowish fluid which may be attached on the shells with potable water and then put in oven for 24 hours to remove the moisture content [11]. Once the moisture is removed, it undergoes grinding process using the ball grinder. The length of duration of grinding of egg shells in powder depends upon the target fineness required. The Table 1 shows the chemical composition of cement and ESP, while the ESP after grinding is shown in Figure 1.

Table 1. Chemical composition of OPC and ESP

Chemical Element	OPC	ESP		
	Yerramala [14]	Parthasarathi et al. [15]	Khalid et al. [16]	Yerramala [14]
CaO	60.1 %	50.7 %	47.9 %	52.1 %
SiO_2	21.8 %	0.09 %	0.11 %	0.08 %
Al_2O_3	6.6 %	0.03 %	-	0.03 %
MgO	2.1 %	0.01 %	-	0.01 %
Na_2O	0.4 %	0.19 %	0.14 %	0.15 %
SO_3	2.2 %	0.57 %	0.38 %	0.62 %
P_2O_5	---	0.24 %	-	---
Fe_2O_3	2.6 %	0.02 %	Traces	0.02 %

Figure 1. Finely grinded ESP

2.2. ESP as Supplementary Cementitious Material (SCM)

From Table 1, it is evident that, eggshells contain almost identical amount of Calcium Oxide (CaO) commonly known as lime. CaO when present in sufficient amount forms silicates and aluminates of calcium in cement. Cement requires precise quantity of CaO as upon deficiency of CaO strength will decrease while delaying the setting time. Excessive amount of CaO causes cement to be unsound and enables it to expand and disintegrate.

Ujin [17] used 1% and 2.5% of eggshells ash by weight as cement replacement utilizing different water-cement ratios. It was concluded that eggshells can be used as cement replacement since the addition of eggshells increased the compressive strength. A study conducted by Dhanalakshmi [18] found that 7.5% of ESP to be optimum dosage when cement was replaced by 0% to 12.5% with an increment of 2.5%. No change was noticed when the determined optimum dosage of ESP was added with fly ash ranging from 0% to 30%. It was concluded that increase in ESP dosage above the determined optimum level reduces the compressive strength, density and workability. Upon the cement replacement of 2.5%, the tensile strength showed a decrease of 23.36%, but it started to gain strength with the increase in dosage such that when the cement was replaced 7.5% of ESP it showed an increase of 1.76% compared to control sample. This is not significant increase but considering that 7.5% of cement is reduced and strength is not decreased it is sufficient. Furthermore, Fly Ash was added to the optimum dosage of ESP, which did not increase the compressive and tensile strength.

However, Yerramala [14] found that when fly ash was added along with ESP, the concrete's performance was enhanced. It was found that 5% cement replacement with ESP to the optimum dosage, at which the highest strength was achieved. It was also noticed that even at 10% replacement of cement with ESP, the strength though was lower than what was achieved at optimum dosage, but still it was higher than the controlled sample. Ansari [19] studied the effect on concrete in which cement was replaced by 4 different dosages of ESP, 0%, 10%, 15% and 20%. The results showed that 15% replacement by ESP at the maximum increase in compressive strength suggesting this to be the optimum value. Although interestingly the compressive strength at 20% replacement was still significantly higher than the controlled 0% replacement, thus suggesting that it is still possible to use up to 20% ESP.

Gowsika et al., [20] underwent the experimental investigation of ESP as a partial cement replacement. Concrete of M20 grade was designed and 5% ESP was used along with fly ash, micro-silica and saw dust ash. It was found that 20% of micro-silica could be used along with 5% ESP without reduction in compressive strength, while 10% microsilica with 5% ESP yielded higher tensile strength compared to other compositions.

3. Palm Oil Fuel Ash (POFA)

3.1. Origin of POFA

Tropical countries cultivate Oil Palm trees as they are cash-crop. Palm oil is extracted from the fruits produced from the Oil Palm trees which is exported throughout the world. Malaysia, Thailand and Indonesia, the three South East Asian countries account to 90% of the total export of Palm oil in the world [21]. Due to being cash-crop in these countries, the plantation and cultivation of Oil Palm trees has increased over the years. With the increase cultivation, however, increases the generation of solid wastes. Palm oil fuel ash is one solid waste generated from the palm industry.

When the oil is extracted from the fresh palm fruit, both husk and shell are burnt at temperature ranging from 800°C to 1000°C as boiler fuel in palm oil mill to produce steam. This steam is then used in turbine to produce electrical energy, which is supplied to the mill for milling operations as well as domestic or estate use [22]. A waste ash is produced because of the burning process and this ash is known as Palm Oil Fuel Ash (POFA). Its color varies sometimes from whitish grey to darker shade depending upon the content of carbon contained in it. 5% POFA is produced after the combustion in the steam boiler [23]. This POFA causes a nuisance to the environment. Since the tropical countries continuously increase the production of palm oil each year, the quantity of POFA keeps on increasing, thus creating a large environmental load [22]. With environmental awareness growing, shortage of landfill and its ever-increasing cost, utilization of these agro-industrial waste materials and byproducts has become ever-so exigent that attractive alternative to landfill disposal be developed. Using waste by-products not just gets them utilized in concrete, reduces the cost of cement and concrete manufacturing, but also has several ancillary advantages such as land-fill cost reduction, energy saving, and protecting the environment form possible pollution effects [24].

3.2. Pozzolanic Nature of POFA

Though the chemical composition and colour may vary from source to source as shown in Table 2, POFA is well-known pozzolanic material. Pozzolanic materials, or pozzolans, are those siliceous or siliceous and aluminous materials which, like SCMs do not possess cementitious value themselves but when produced finely and in the presence of water, will chemically react with calcium hydroxide to form compounds possessing cementitious properties [25]. In other words, pozzolans are silicate-based which consume the lime that is produced by hydrating cement to create secondary cementitious materials.

Table 3 is the criteria and classification of pozzolanic materials according to ASTM C618-17a. Based upon ASTM-C618-17a, pozzolanic materials can be classified into three classes (Class N, Class F and Class C) basically depending upon their sum of silica, aluminum and iron content. Table 2 shows that POFA is rich in Silica Dioxide (SiO_2). It has been proven that POFA is a pozzolanic material, which can be used as partial cement replacement. Pozzolans are silicate-based that consume the (CaO) lime which is generated by hydrating cement to create additional cementitious materials.

The original size of POFA is approximately 2.3 mm [26]. Generally, the finer the pozzolanic material, the more reactive it will be. Coarseness in materials lowers the pozzolanic activity. Therefore, to improve the pozzolanic activity, the POFA is required to be grinded. The raw POFA once processed in the palm mills is kept in open air as shown in Figure 2, where it can absorb moisture content and other organic materials. Therefore, once the raw material is collected, it is then sieved through 300 um, to remove the large particles and any impurities it may contain and then put in oven to dry for 24 hours [27]. Once the POFA is oven-dried it can now be put into Los Angles Abrasion Machine for grinding. The length of grinding will depend upon the fineness required. It is also worth mentioning that grinding also has impact on the surface area of particles as well as the chemical composition although it is minimal. The grinded POFA is shown in Figure 3.

Table 2. Chemical Composition of POFA

Chemical Element	OPC	POFA		
	Yerramala [14]	Ranjbar et al. [27]	Awal and Abubakar [28]	Hassan and Abdu [29]
SiO_2	21.8 %	53.5 %	59.62 %	66.91
Al_2O_3	6.6 %	1.9 %	2.54 %	6.44 %
Fe_2O_3	4.1 %	1.9 %	5.02 %	5.73 %
CaO	60.1 %	9.2 %	4.92 %	5.56 %
MgO	2.1 %	4.1 %	4.52 %	3.13 %
Na_2O	0.4 %	1.3 %	0.76 %	0.19 %
K_2O	0.4 %	6.1 %	7.52 %	5.20 %
SO_3	2.2 %	---	1.28 %	0.33 %

Table 3. Chemical Composition of POFA

	Class		
	N	F	C
$SiO_2 + Al_2O_3 + Fe_2O_3$ (min %)	70	70	50
SO_3 (max %)	4.0	5.0	5.0
Moisture Content (max %)	3.0	3.0	3.0
Loss on Ignition (max %)	10.0	6.0 *	6.0

* The use of Class F pozzolan containing up to 12.0% loss on ignition may be approved by the user if either acceptable performance records or laboratory tests results are made available.

Figure 2. POFA in open air

Figure 3. Grinded POFA

3.3. POFA as Supplementary Cementitious Material

Tay et al., [31] investigated the use of ungrounded POFA as a cement replacement material for concrete. It was determined that POFA had a low pozzolanic property and it was suggested that no more than 10% of ungrounded POFA be used. It was also reported that up to 50% of cement replaced with POFA had no significant impact on the properties of concrete. Though Awal and Hussin [32] reported that due to being ungrounded, POFA had low pozzolanic reaction. Many researchers developed methods and procedures to produce fine grinded POFA. Recent studies have shown that due to being grounded, POFA has good pozzolanic property could successfully be used as cement replacement of more than 10%.

Tonnayopas [33] used 5–30% ground POFA and based upon the results, it was concluded that its addition in concrete, the strength initially decreased at early ages but at 28 days the concrete containing 5–15% POFA achieved the ASTM C618 prerequisite, similarly Sata et al., [34] also investigated the strength development of incorporation of POFA in concrete using 10%, 20% and 30% content of POFA by weight of cement, and found that specimens comprising of 10-20% POFA resulted in decreased at 3 days, 29.3 and 28.6 MPa, while comparing them with controlled OPC specimen, 30.8 MPa but the strength increased significantly after 28 days of curing for specimens containing 10% POFA (40 MPa) and 20% POFA (39.6 MPa) at the same time the controlled specimen resulted in strength of 39.6 MPa. It was also reported that the specimen with 30% POFA showed decreased strengths at all ages (26.5, 30.6 and 36.8 MPa at 3, 7 and 28 days of concrete age respectively).

Ranjbar et al. [27], used 10%, 15% and 20% of POFA as a cement replacement to study the durability and mechanical properties of self-compacting concrete (SCC). It was found that by incorporating POFA in the SCC not only enhanced the acid and sulfate resistance but lead to reduction in workability. With the increase in the POFA content in the SCC, it was noticed that early strength was less than to the normal specimen, while the final strength was comparable to the normal concrete, this is attributed to the pozzolanic nature of POFA. POFA was used studied by Chindaprasirt [35] and found that it is a good potential for concrete production and observed that ground POFA replacing OPC partially resulted in a higher water demand for a given workability, concrete with 20% ground POFA gained slightly higher compressive strength (29.4 MPa) as compared to conventional concrete whose compressive strength was (28.2 MPa), but the strength gradually decreased when the POFA content began to increase and as such also increased the permeability of concrete.

Similarly, POFA has also been used in foamed concrete as a cement replacement. Abdul Munir et al [36] utilized the POFA as a cement replacement in producing lightweight foamed concrete for non-structural building material. In this study experiments were conducted by replacing 10%, 20%, 30%, 40% and 50% of POFA by weight of cement in the foamed concrete of densities 800 kg/m^3 and 1000 kg/m^3. The results showed that by adding 50% POFA the compressive strength decreased to about 30-40% compared to the controlled specimen. While 20% cement replacement by POFA in the foamed concrete was found to be still acceptable compressive strength for non-structural building element such as concrete blocks.

4. Combined Utilization of ESP and POFA

Though the ESP and POFA have been used individually in concrete as partial cement replacement, both have faced restriction on how much they can replace cement in concrete. From the literature review it is evident that ESP can be used to replace cement up to 10%, while POFA can be used up to 20% by weight of cement, without losing strength. The POFA triggers pozzolanic reaction when it comes in contact with water. This pozzolanic reaction then consumes the calcium hydroxide, Ca $(OH)_2$, available in cement and develop calcium silicate hydride (C-S-H) gels, as shown in Equation 1, which are responsible for gaining strength in concrete. It has been reported that the freely available Ca $(OH)_2$ from cement is limited, approximately 22%. To enhance the pozzolanic reaction and utilize more content of POFA, it is hypothesized that additional Ca $(OH)_2$ be provided in concrete. Since ESP has high content of calcium oxide, CaO, which when in contact with water, turns into Ca $(OH)_2$ as shown in Equation 2. Since eggshells are also waste materials which are thrown away into landfills and cause environmental and health issues, therefore, its combined utilization in concrete along with POFA is potentially beneficial alternative for reducing cement content while reducing, reusing and recycling waste materials to achieve sustainability.

$$\mathrm{Ca(OH)_2 + SiO_4 + H_2O \rightarrow CaH_2SiO_4.2H_2O} \quad (1)$$

$$\mathrm{CaO + H_2O \rightarrow Ca(OH)_2} \quad (2)$$

5. Conclusion

Tropical countries such as Malaysia consider Palm Oil as their cash crop and due to this the plantation of Palm tree has increased over the years. Though exporting Palm Oil is beneficial for the economy of Malaysia, it also has negative environmental impacts. POFA, a solid waste by-product of palm oil industry, is typically disposed into landfills without any profit and in some cases palm oil mills, have to pay for disposal. The number of landfills has increased significantly over the years due to generation of waste by-products. Due to scarcity of land and health issues, the solid waste management has become a serious topic. The waste materials from agro-industrial and food processes have been utilized in concrete, mostly as cement replacement, in an aim to reduce the cement, whose production causes global warming and climate change, as well as solving the environmental problems that such waste materials develop. With the help of X-Ray Fluorescence (XRF), it is possible to understand the chemical compositions of waste materials, thus helping in better utilization of such materials. POFA has high content of silica making it a potential pozzolan material which many researchers have proved to be. Recent studies have shown that POFA can be used as cement substituting material and is successful in enhancing the properties of concrete which is beneficial. But the utilization of POFA is limited as pozzolans require calcium hydroxide with water to react and produce calcium silicate hydrate (C-S-H) which is responsible for strength gain in concrete. Though, portlandite, a term cement chemist used to refer calcium hydroxide, is produced during the hydration of cement.

Recent studies have shown that, individually, POFA and Eggshells (in grinded powder form ESP) can be used as partial cement replacement, but to a certain limit. Based upon the chemical composition, Silica rich POFA can become reactive if it comes in contact with CaO (lime), consuming it to give more strength. Cement has limited excessive CaO but still when POFA was added it gave increased the strength significantly. It is therefore hypothesized that ESP be added alongside with POFA as hybrid partial cement replacement. ESP, which has significant amount of CaO, can allow the reactive silica of POFA to consume the excessive lime from it, resulting in enhancement in the strength of concrete. A reduction in the dependency on cement can lead to reduction manufacturing of cement and thus also resulting in reduction of CO2 emissions. While, the utilization of waste products can also reduce the environmental issues and impacts that are brought by with disposal of waste products in landfills.

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