Improvement of Pozzolanic Properties of Oil Palm Boiler Ash Through Heat Treatment

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Abstract. This paper presents the improvement of pozzolanic properties of oil palm boiler ash (OPBA) through heat treatment. The OPBA was obtained from oil palm mill in Pahang, Malaysia. The composition of OPBA was measured using X-ray fluorescence spectrometer which was used for its initial classification. It was found that freshly obtained OPBA had high carbon content (33.9%) and cannot be classified as pozzolan with only 15.73% of Al_2O_3, SiO_2 and Fe_2O_3. Upon heating up to 600 ºC for 2 h, the carbon content was eliminated and heated OPBA can be classified as pozzolan class F. When used as partial cement replacement, the 60-day compressive strength of OPBA-cement mixture peaked at 47.8 MPa for the pozzolan content of 15%. The compressive strength of OPBA-cement mixture decreases as the pozzolan content increases.

1 Introduction

Cement is one of the important building materials nowadays and there are various types of cement's hydration characteristics due to the different ratios of the chemical compound [1]. These major chemical compounds such as tricalcium silicate, C_3S, dicalcium silicate, C_2S, tricalcium aluminate, C_3A and tetracalcium aluminoferrite, C_4AF were formed from the main chemical compositions of cement through the chemical reactions during mixing with water while these compositions were also known as Bogue compound since these chemical compounds were quantified through the Bogue model [2]. The C_3S had formed at the early age and contributed to the early strength of cement, however, the C_2S formed at a later age and provided the later strength. While the C_3A not only provided early strength within 24 hours but also released a large amount of heat of hydration. Last but least, the C_4AF assisted the cement manufacturing process as well as acting as a filler cement [3]. The content of Bogue compounds of different types of cement were listed in the ASTM C150-07 standards.

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The supplementary cementitious material (SCM) that is rich in alumina or silica could produce the cementitious product only if under suitable conditions or else it showed no or little cementitious behavior, while this process was known as pozzolanic reactivity [4]. There were several sources of SCM which been widely used as cement replacement, however, recently the utilization of waste products such as industrial waste or agricultural waste as SCM is gradually gaining researchers' attention. Due to the threatening production rate and the negative environmental impact of disposing of these wastes, turning those potential waste into a cement replacement not only reduced the disposal of the waste but also reduced the demand for the cement at the same time [5]. Oil palm boiler ash (OPBA) can be considered as agricultural waste which is a burning residue from the incineration process of the oil palm waste during the production of crude palm oil [6]. Due to a high content of silica and thus, it could be further investigated to become a potential SCM [7].

The received OPBA was reported to have inconsistent physical properties, chemical content as well as morphology. The large particle size of OPBA had a smaller specific surface area than those OPBA with smaller particle size which led to the reduction in the contact area between the OPBA and calcium hydroxide as well as water. Besides that, the smaller particle size of SCM could provide the nucleation site and promoted the hydration process as well as improving the workability of concrete [8]. In terms of the chemical composition, the OPBA was reported to have a variety of silica content in the range of 41.8% to 69.02% and the loss of ignition (LOI) value which can be indicated the content of unburnt carbon is more than 5.46% [9-15]. Low silica content may lead to low pozzolanic reactivity while the high content of unburnt carbon led to the increase the water demand of concrete and thus reduced its workability. Unfortunately, the silica content of OPBA is influenced by the type of palm oil waste that had been incinerated where the kernal-based OPBA has higher silica content than other parts of palm oil waste [16].

Conducting treatment on the OPBA either through chemical treatment, thermal treatment, mechanical treatment, or a combination of both treatments was utmost importance for improving the raw OPBA particle's characteristic until satisfying the ASTM C168-19 or BS 8615-1 standards and later increased the OPBA's pozzolanic properties. The combination treatment which included the mechanical and thermal treatment has frequently been carried out on the OPBA to reduce its particle size, increase its specific surface area, improve the sum of silica, alumina as well as ferrite content and reduce the LOI value [9,17]. The effect of the thermal treatment on the OPBA was presented in [18-19] research where the treated OPBA concrete had a higher replacement rate of OPBA and the early age compressive strength than the untreated OPBA concrete. In addition, the workability of the concrete that contains raw OPBA was reported reduced as the slump value decreased when the addition of OPBA in concrete. In contrast, the workability of concrete that contained treated ultrafine OPBA increased in the slump value as the replacement rate increased up to 60% while the untreated ground OPBA-based concrete only had an increment in slump value only when the replacement rate of 20% and further increasing replacement rate led to a reduction in slump value.

The effect of those treatments on the OPBA could be observed through the compressive strength of the pozzolana-based concrete [20]. However, this process took longer a period for obtaining the results that revealed the impact of the treatment process. Hence, predicting the compressive strength of the pozzolanic concrete through the mathematical equation that considered the impact of curing age, water to binder ratio, pozzolan replacement rate, fineness of pozzolan and content of the specific bogue compound could be carried out for evaluating the improvement of OPBA. A simplified mathematical model was used for predicting the compressive strength of fly ash-based concrete within different curing periods [21]. The model showed acceptable accuracy with the deviation of the actual compressive strength and predicted value from the model was within the limits of ±15%.

In short, those factors such as chemical properties, unburnt carbon content and the particle size of OPBA affected the pozzolanic property of OPBA significantly. Thus, the combination treatment processes were carried out on the OPBA and later analyzed for the particle size distribution, chemical properties, morphology and mineralogy. Later, the compressive strength of the pozzolanic concrete that contained the treated OPBA was predicted through the mathematical model that considered the impact of OPBA particle characteristics as well as the content of the Bogue compound.

2 Methodology

2.1 Oil palm boiler ash

The oil palm boiler ash (OPBA) in this work was obtained from Palm Oil Mill belonging to LKPP Corporation located in Lepar, Pahang, Malaysia. The OPBA was collected at the exit residue collector of the palm oil boiler. The specimen was dried in the oven and sieved through a 300 μm sieve before being further used. The sieved specimen is denoted as raw OPBA. The raw OPBA was subjected to be ground in Los Angeles Abrasion machine for 15000 cycles until passing the 45 μm sieve with a passing rate of 90% and these OPBA were addressed as ground OPBA. Next, the ground OPBA was heated in a furnace at temperatures up to 600 ºC within two hours to reduce its carbon content. In this stage, the OPBA was named treated OPBA. After that, the treated OPBA was subjected to the second grinding stage in different cycles which either was 50,000 cycles or 110,000 cycles while this OPBA was noted as nano OPBA. The weight ratio of the OPBA to the iron ball was 1:10 and there were two types of diameters of iron ball which were either 50 mm or 20 mm.

2.2 Surface morphology and surface composition analysis

A scanning electron microscope (SEM) was used to assess the surface morphology of OPBA (Hitachi TM3030, Japan). Carbon tapes with double-sided adhesive were used to mount the specimen on stubs. Additionally, the device has an energy dispersive X-ray detector based on silicon drift detectors (Oxford Instruments), to measure the particle surface composition.

2.3 Measurement of particle size distribution

The particle size distribution as well as the particle size of various type of OPBA was studied through the particle size analyzer by using the Zetasizer Nano S90 machine at Fluid Centre Universiti Malaysia Pahang which was adopted to the method in [22]. The types of OPBA which was tested were ground OPBA, treated OPBA, 50,000 cycles nano OPBA, 80,000 cycles nano OPBA and 110,000 cycles nano OPBA.

2.4 Measurement of oxides composition

About 6 g of OPBA was mixed with boric acid, then heated at 100 ºC for an hour to remove the moisture content. The pressed powder pellet was prepared using a stainless-steel dye-cast with a diameter of 30 mm. The composition of OPBA was measured using a wavelength dispersive X-ray fluorescence spectrometer (WDXRF, ZSX Primus II, Rigaku Co., Tokyo, Japan). The equipment generates X-rays using a Rh cathode plate and a 4 kW end-type X-ray generator. Each test was conducted in a vacuum at 50 kV and 60 mA.

2.5 Estimation of compressive strength

The Bogue compound consists of the components of concrete that combine in the presence of water to generate more complex compounds. Bogue compound of OPBA-cement mixture can be estimated as follows:

$$C_3S = 4.071CaO - 7.6SiO_2 - 6.718Al_2O_3 - 1.43Fe_2O_3 - 2.852SO_3 \quad (1)$$

Originally, the clinker properties were estimated using equation (1). Over the course of a year, however, the correlation was refined to permit the measurement of Bogue compound in cement and cement-pozzolan mixtures. The compressive strength (F_x) of concrete at different days can be estimated using the Bogue compound as follows [23]:

3 days, $F_3 = 13.668C_3S^{0.0964}$ (2)

7 days, $F_7 = 15.829C_3S^{0.153}$ (3)

28 days, $F_{28} = 25.349C_3S^{0.12}$ (4)

60 days, $F_{60} = 35.749C_3S^{0.0721}$ (5)

3 Results and discussion

3.1 OPBA surface morphology and composition

Table 1 shows the composition of selected oxides in various OPBA samples. Initially, the OPBA collected from the oil palm mill had a high carbon content (33.9%). The OPBA, as it is, is not a pozzolan with only 15.73% of Al_2O_3, SiO_2 and Fe_2O_3 content. It was found that after being subjected to heating at 550 ºC, the carbon content reduced to 7.84%, which resulted in the pozzolan content increasing to 57.45%, thus making it a pozzolan class C. Upon heating at 600 ºC, the pozzolan content increased further to 70.96%, which makes it a class F pozzolan. Thus, it is important to pre-treat the OPBA before using it as a pozzolan.

Table 1. Variation of level for variables.

Oxides	*OPBA*	*OPBA 550 ºC*	*OPBA 600 ºC*
Al_2O_3	0.69	3.89	6.36
SiO_2	13.70	48.50	58.00
SO3	2.19	1.34	1.58
CaO	3.29	7.29	9.03
Fe_2O_3	1.34	5.06	6.60
ZnO	0.01	0.02	0.02
Pozzolan (%)	15.73	57.45	70.96
Classification	Non pozzolan	Pozzolan Class C	Pozzolan Class F

Figure 1 shows the surface morphology of fresh OPBA obtained from an oil palm mill. It was evident that it contained a lot of burned carbonised fibre, which comprised 33.9% of the total compound in OPBA. The particulate matter consists of a mixture of large (~100 µm) and small particles (<10 μm). The OPBA was subjected to further heating up to 600 ºC to remove the carbon content, as well as grinding to obtain a smaller particle size.

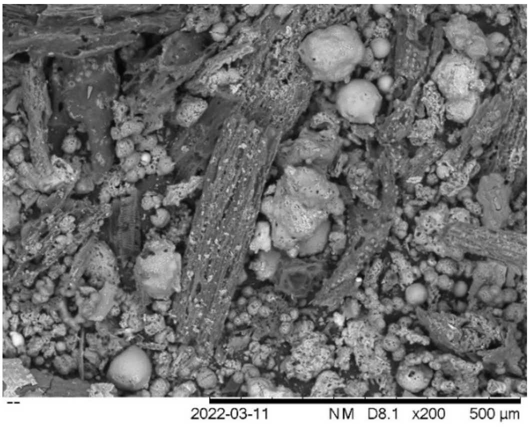

Fig. 1. Surface morphology of OPBA

3.2 Compressive strength of OPBA-cement mixture

The OPBA pozzolan may be used as a partial cement replacement. Figure 2 shows the predicted compressive strength at different day of OPBA-cement mixture with a cement replacement ranging from 15 to 24%. Only the OPBA 600 ºC pozzolan class F was used in this calculation. The compressive strength was calculated using eq. (3) to (6). It was found that cementitious material with a larger pozzolan composition (24%) has a lower compressive strength compared to those with less pozzolan content (15%). However, even at 24% cement replacement, the predicted concrete compressive strength after 60 days is greater than 30 MPa, i.e., 36.1 MPa.

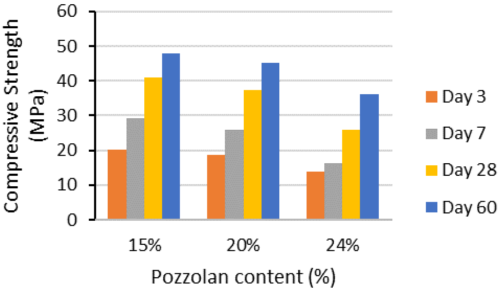

Fig. 2. Predicted compressive strength of OPBA-cement mixture

3.3 Particle size distribution

Table 2 presents the average particle size of OPBA. Using the Los Angeles Abrasion (LA) machine, the OPBA particle size was successfully decreased to nanometers. As grinding time increased, the OPBA particle size decreased. After 110,000 cycles of grinding in the LA machine, the OPBA particle size was reduced from 1.147 μm to 103.1 nm, which was smaller than the OPBA particle size reported in [22]. This 100K nano OPBA had a particle size comparable to other studies that focused on nOPBA in the range of 20 to 150 nm [17, 24-26]; nevertheless, the required grinding time was longer than in other studies. For the 50K nOPBA particle distribution, the intensity ranged from 141.8 nm to 220.2 nm, with a peak intensity percent at 190.1 nm. In contrast, for the 110K nOPBA, the particles exhibited a higher intensity between 91.28 nm and 141.8 nm, with the majority having a size of 122.4 nm. Figure 3 illustrates the particle size distribution for 50K cycles nOPBA, whereas Figure 4 illustrates the particle size distribution for 110K cycles nOPBA. The finer particle size of OPBA had a superior filler effect, which can provide a nucleation site for the subsequent hydration of cement, and enhanced the slump value of the mortar or concrete mix by providing lubricating effects [24-25].

Table 2. Average particle size of various OPBA.

Sample	***Average Particle Size***
OPBA	1.147 µm
50k cycles nano OPBA	307.2 nm
110K cycles nano OPBA	103.1 nm

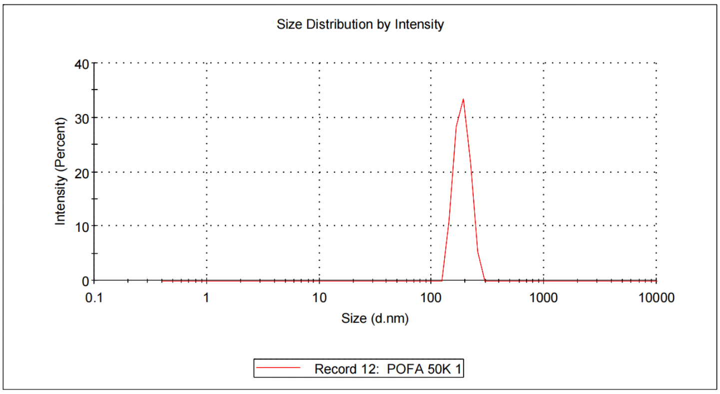

Fig. 3. Particle size distribution of 50K cycles nOPBA

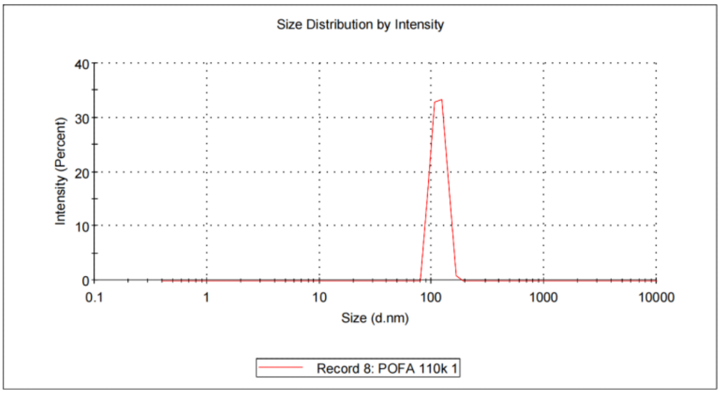

Fig. 4. Particle size distribution of 110K cycles nOPBA

4 Conclusion

Oil palm boiler ash may be used as pozzolan upon heating to eliminate its carbon content, and thereby increasing its pozzolan content to 70.96% which fit the specification of pozzolan class F. When used as partial cement replacement, the 60-day compressive strength of OPBA-cement mixture peaked at 47.8 MPa for the pozzolan content of 15%. The compressive strength of OPBA-cement mixture decreases as the pozzolan content increases. Upon grinding with the LA machine, the OPBA particle size was reduced from 1.147 μm to 103.1 nm, which may improve its cementitious properties.

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