Applications of Nano palm oil fuel ash and Nano fly ash in concrete

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Abstract: This paper discusses the applications of Nano waste materials including palm oil fuel ash and fly ash in the concrete production. The implementation of nanotechnology has been instrumental in the development of significant interest among the stakeholders to improve the mechanical and chemical properties of materials involved in the production of concrete. Although many researchers have shown the potential of nanomaterials to increase strength and durability of concrete and improve its physical and chemical properties, there is still a knowledge gap regarding the preparation of Nano waste materials from agricultural waste to use as cement replacement instead of non-renewable materials. Therefore, it should be focused on to study Nano- waste materials to benefit from these characteristics during preparation of concrete mixtures. Therefore, this paper highlights the potential of waste materials in the Nano size to partially replace cement in concrete and achieve the same or better result than the traditional concrete. This paper recommends to conduct further experimental works to improve the concrete material properties by investigating the properties of waste materials in Nano size.

1. Introduction and background

Nanotechnology is the re-engineering of materials by manipulation at the atomic level to get specific properties of nanomaterials [1]. It is concerned with the adjustment and understanding of materials on the nanoscale (<100 nm) which have chemical properties that are to be determined by quality technicians. In case of nanomaterials, the effects of the surface are dominate instead of bulk properties [2]. Many researchers have examined the nanomaterials in biology, chemistry, and physics; and have investigated Feynman’s ideas regarding manipulation and adjustment of the small-size materials similar with nanoscale and atomic scale [3]. The word ‘nanotechnology’ is related to the small size materials with the specific definition differing from field to field. In general, it can be said that these materials are not more than 100 nm in size, which can be manipulated and their characteristics changed to produce new features and specifications that can be benefitted from [4]. Nanotechnology has been explored to a considerable degree to target the problems in the design and construction of practical structures with one or more dimensions;
to benefit from the characteristic of nanomaterials [5]. Nano particles or ultrafine particles can increase the density due to filler effect and thus enhance the durability and compressive strength of concrete produced. Besides that, these also decrease the absorption of water and improve the microstructure properties to protect against sulphate and acid attacks. Due to the damaging effects of cement on the environment and its high financial cost, Nano particle additives have been used in wide variety in a range of proportions to reduce the quantity of cement in concrete. However, the high cost of Nano particles additives such as Nano silica made the researchers consider alternative methods through manipulation of the materials that have same chemical compositions as cement such as palm oil fuel ash POFA and fly ash FA to replace cement by different percentages. Therefore, this paper reviews the effects of cement replacement by Nano POFA (NPOFA) and Nano FA (NFA) on the concrete properties.

2. Production of Nano Materials

Nano materials can be obtained from various sources by different methods to give unique properties not available in the original particles [6]. There are two approaches to prepare Nano particle size from the original materials, the first approach is top-down [7], while bottom-up is the second approach [8]. Selection of a suitable approach depends on many factors such as cost, suitability, and behaviour of Nano particles [3, 9]. Milling by the grinding machine is one of the applications of the top-down approach [10]. Due to the ease of this approach and availability of the machine, many researchers select this method to prepare Nano particles from the waste materials without any chemical additions [10], which would be bottom-up approach. Despite a few disadvantages of the top-down approach due to many factors such as limitations on types and number of milling balls and the speed of milling, the quality of Nano particles can be improved [7, 11, 12]. High energy ball milling is one of the machines developed to grind micro particles to the Nano size.

3. Nano waste materials

Many researchers have investigated the waste materials in Nano size, which are prepared by grinding in Laos Angeles machine and/or high energy ball mill [13, 14]. The presence of significant amount of silica oxide content and other materials in some of waste materials in fine particle size has encouraged academics and researchers to grind the particles into micro and Nano particle size. In the following subsections, the agro-waste materials (POFA and FA) in Nano size used as replacement cement in ultrafine and Nano particle size have been discussed.

3.1 Palm Oil Fuel Ash (POFA)

Palm oil fuel ash is a by-product obtained from the burning of palm oil shell and husk in palm oil mills to generate electricity. Many researchers have studied the effects of Nano POFA on the concrete properties as shown in Table 1.

| Ref.   | Particle size | Field of study                                      | Results                                                                 |
|--------|---------------|-----------------------------------------------------|------------------------------------------------------------------------|
| [13]   | less than 1 µm| heat of hydration and compressive strength of cement mortar | higher strength than cement mortar and reduces hydration heat          |
| [14]   | 20 – 90 nm    | study morphological analysis of hardened cement paste | NPOFA particles have high density due to the filling effect.           |
| [17]   | 50 nm         | study the shape and texture of raw and Nano-structured POFA | The raw POFA had an irregular spongy shape, while Nano POFA had irregular and crushed shape |
POFA has a high content of silica ranging from 43 to 66%, as can be seen in Table 2. The grinding of POFA by the grinding machine increases the amount of silica oxide SiO$_2$. The loss of ignition LOI is achieved due to burning of the carbon in the heating process by gas or electric furnaces, as given in Table 2 [15, 16].

Lim et al. [13] studied the effects of cement replacement by high volume Nano palm oil fuel ash NPOFA (up to 80%) to produce concrete with high performance quality. The study investigated the composite morphology, strength activity index, the hydration temperature, microstructure properties, and thermal conductivity. The POFA was ground many times to obtain particle size less than 1 µm. The colour of POFA collected was dark in the first round, which was then dried in electrical oven for 24 hours at 110°C. The dried POFA was sieved by 300 mm, and the passing quantity was again ground by Los Angeles machine. The POFA thus produced in micro particle size was heated in a gas or electric furnace at 500°C to burn the carbon particles and enhance the microstructure properties and pozzolanic reaction. The treated POFA by furnace was ground once again by high energy ball milling for 30 hours to get particles size less than 1 µm. In this case ultrafine POFA [13] or Nano POFA [17] was produced. The main composite in the Nano POFA is SiO$_2$ which ranges from 55 to 72% of total. The results of the study indicated that Nano POFA can be used as cement replacement up to 80% to achieve higher strength than normal concrete at a later age. In addition, it also reduces the hydration heat of concrete.

Table 2. Chemical composition of ground POFA and ultrafine/Nano POFA.

| Chemical composition | Lim et al. [13] | Ultrafine POFA | Johari et al. [16] | Ultrafine POFA |
|----------------------|----------------|----------------|-------------------|----------------|
| SiO$_2$              | 35.5           | 69.3           | 51.18             | 65.01          |
| Al$_2$O$_3$          | 1.9            | 5.3            | 4.61              | 5.72           |
| Fe$_2$O$_3$          | 1.1            | 5.10           | 3.42              | 4.41           |
| CaO                  | 8.3            | 9.15           | 6.93              | 8.19           |
| K$_2$O               | 6.5            | 11.10          | 5.52              | 6.48           |
| MgO                  | 4.1            | 4.10           | 4.02              | 4.58           |
| SO$_3$               | 2.36           | 1.59           | 0.36              | 0.33           |
| LOI                  | 20.9           | 1.3            | 21.6              | 2.53           |

Figure 1. Colour of POFA before and after treatment [13].
Rajak et al. [14] studied the effects of Nano POFA and micro POFA on cement mortar and the comparison between the two. The NPOFA was prepared with average particle size ranging between 20 nm to 90 nm. The range of replacement of 10 – 50% of cement by NPOFA was used to prepare NPOFA mortar. The authors performed the morphological analysis of hardened cement paste (HCP) containing Nano POFA (NPOFA) and Micro POFA (MPOFA) at curing ages of 7, 28, and 90 days. The authors prepared the Nano POFA with high specific surface area of 145.35 m²/g by milling the micro POFA through high energy ball milling machine for 30 hours. The average particle size of Nano POFA obtained from grinding MPOFA ranged between 20 to 90 nm as shown in Figure 2. The authors concluded that NPOFA has filler actions and pozzolanic behaviours more than MPOFA particles due to the production of further C-S-H gels. This behaviour leads to improve the durability and mechanic properties of hardened cement.

Figure 2. Particle sizes of NPOFA by TEM test analysis [14].

3.2 Fly Ash (FA)
Prince et al. [18] studied the effects of Nano FA on the compressive strength and workability of concrete grades 20, 30, 40, and 50. The results of the study indicate increase in the workability value when the Nano FA amount is increased, which ranged between 90 to 140% of that of the normal concrete. The compressive strength also increases due to addition of 10% of Nano FA to the concrete mix, which was recorded between 17 to 46% more than normal concrete at 28 days. A study was conducted by Raghavendra et al. [19] to prepare the Nano FA by utilization a planetary ball mill in a stainless steel chamber with zirconia balls with diameter of 5 and 10 mm. 6 hours was the duration of milling and the rotation speed of the planet carrier was 400 rpm. The results show increase in the surface area of Nano fly ash from 0.31 to 24.65m²/g and improvement in the chemical composition of Nano FA. Tudjono et al. [20] studied the effects of Nano FA and Nano lime on the compressive strength of concrete through replacement of cement by different dosages (of Nano FA and Nano lime) from 0% to 15% at intervals of 2.5%. To prepare Nano FA and Nano lime into Nano particles, the researchers used a Planetary Ball Mill (PBM). XRD test was used to analyse Nano FA and Nano lime size required to ensure the particles were within Nano size after grinding process. The
researchers found a relation between 2 theta and intensity as illustrated in Figure 3. Scherer’s formula has been used to analyse the numbers to get the particle size of FA and lime, before and after grinding process, whereas the particle size was 44.39 nm, 21.03 nm for Nano FA and Nano lime, respectively. The compressive strength of mortar at 7 days was obtained as in Table 2. The compressive strength of control sample was 26.47 MPa.

![Figure 3. Test of XRD for (a) Fly Ash (b) Nano Fly Ash (c) Lime (d) Nano Lime [20].](image)

Murthy et al. [21] conducted their study by grinding micro fly ash MFA with Al into Nano particle fly ash NFA by high energy ball milling machine for 30 hours. The Nano FA particles of 23 nm size were obtained. Figure 4 shows the Nano FA mix before and after grinding process.

![Figure 4. Al/Nano fly ash (a) before ball milling, (b) after ball milling for 20 min [21].](image)
Jemimah et al. [22] studied the effects of replacement of cement by Nano FA on the compressive strength at different ages of 3, 7, and 21 days. The researchers showed that the compressive strength increases with the addition of more quantity of Nano FA as cement replacement. It was found that 30% of Nano FA as cement replacement gave the optimum value of compressive strength and 20% was the next optimum value. Besides that, the authors also studied the effects of the Nano FA on the initial and final setting times of cement mortars due to replacement of cement weight by 0%, 10%, 20%, 30%, 40%, and 50%. The results illustrated that increasing dosage of Nano FA lead to delay of initial and final setting time, whereas the final setting time was 7.84%, 21.57%, 30%, 53.92%, and 80.39% due to the replacement of cement by POFA with 10%, 20%, 30%, 40% and 50%, respectively. Roychand et al. [23] studied the effects of Nano silica and silica fume individually and in combination with the accelerator and hydrated lime, on the ultra-fine fly ash to replacement cement by 80% of total weight. The authors concluded that Nano fly ash when combined with Nano silica can replace cement by 80% of while maintaining the same properties obtained when the ordinary cement was used.

4. Conclusion
The NPOFA and NFA particles from waste materials show good pozzolanic behaviour due to high silica content and high specific surface area in addition to being lower in the Los of Ignition (LOI). The pozzolanic behaviour of NPOFA particles leads to the production of secondary C-S-H gels via pozzolanic reactions with free lime. Using these wastes in Nano particle size can reduce the cement quantity in concrete production up to 80% and thus reduce the environmental impact due to generation of CO₂ resulting from cement production as well as lower the cost. This study recommends conducting further experimental works to prepare Nano particles from other waste materials to improve the characteristics of concrete to make it more environmentally friendly and economic material.

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