Influence of groundnut shell ash on the properties of cement pastes

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Abstract. This paper presents the effect of groundnut shell ash (GHA) on the properties of cement paste. Cement pastes containing GHA as cement replacement in different proportions up to 50% by weight were prepared. At fresh state, the consistency and setting times of the pastes were checked, while at hardened state, soundness and compressive strength of the pastes were determined. In addition, the microstructure of the hardened paste was investigated using the Fourier Transformed Infrared (FTIR) technique. The results show that GHA increased water demand and delayed setting times, but improved soundness of cement paste. Moreover, compressive strength enhancement of hardened cement paste due pozzolanic reaction as evidenced by the microstructure analysis (FTIR) was observed with up to 10% GHA replacing cement. Thus, GHA is a good potential material for cement replacement in cement paste.

1. Introduction

Currently and for the foreseeable future, Portland cement remains the binder of choice for concrete to develop infrastructures for our socio-economic needs [1]. However, cement production is characterized with both high energy consumption and the emission of enormous greenhouse gases to the atmosphere, which contribute to economic and environmental sustainability pressures in the construction industry. This calls for the utilization of supplementary cementitious materials (SCMs), such as; fly-ash, slag, and metakaolin, as partial replacement of Portland cement for the production of cement-based materials. Since, most of the SCMs are predominantly industrial by-products; their successful inclusion into cement-based material would equally guarantee an effective means of waste management for the industries from which the wastes are generated. Similar to other industries, agricultural industry also generates wastes, commonly known as agro-wastes. The typical agro-wastes among others are; palm kernel shell, bagasse, rice husk, and groundnut shell. Interestingly, because of the high calorific values of these wastes, they are often utilized as biofuels in boilers for energy production [2-4]. In addition, most of the ashes (residues) generated from burning the biofuels which are mostly disposed of in landfills can be used as cement replacement materials in concrete, owing to their pozzolanic characteristics [3].

Groundnut shell is an agro-waste generated from milling of groundnut. Groundnut production worldwide had reached about 42.31 million tons in 2014, and it was projected to continuously increase annually (FAO, 2014) [5]. China, India and Nigeria are the first three leading countries that contributed about 37.3%, 15.5% and 8.1% of the total global groundnut production, respectively. These countries are still leading in the production of groundnut. Approximately, groundnut constitutes
about 25-40% shells. And in every one ton of the shells, 2.5% ash is produced [6, 7]. Therefore, the
total global groundnut ash produce could be up to 0.42 million tons. So far, the ash has less economic
value; instead, it becomes an environmental nuisance when disposed of in landfills, causing soil,
groundwater and air pollutions.

Groundnut shell was used as fine aggregate replacement to produce lightweight concrete [4, 8]. The
shell was equally utilized to produce insulation board and wardrobe [9, 10]. However, there are limited
studies on the use of groundnut shell ash as cement replacement in cement based material. Therefore,
the aim of this study is to investigate the effect of groundnut shell ash on the properties of cement
paste. The properties examined include; consistency, setting times, soundness and compressive
strength. Equally, the microstructure of the pastes was checked using the Fourier Transformed Infrared
(FTIR).

2. Materials and Methods

2.1 Materials
Limestone Portland cement and groundnut shell ash (GSA) were used as binders in this study. The ash
was obtained by burning groundnut shell to 700°C in an incinerator. The shell was sourced from a
groundnut milling factory located in northern Nigeria. To improve its reactivity, the ash was ground to
finer particles after heating. The grinding was conducted using a les Angeles grinding machine. After
grinding, the medium particle size of the ash was found to be 11.42µm which is less than that of
cement 15.90µm as shown in Table 1. The chemical compositions of the binders are shown in Table 1. Based on its chemical composition, GSA constitutes silica, calcium oxide and alumina as the major
oxides. The summation of silica, iron oxide and alumina is 46.94%, which is less than the minimum of
50% stipulated by the ASTM 618 [11] for Class C pozzolan. However, due to its high calcium oxide
content (21%), but low SO3 (≤ 5%) and LOI (≤6%), GSA may loosely be classified as Class C
pozzolan.

| Chemical composition (%) | OPC | GSA |
|--------------------------|-----|-----|
| Silicon dioxide (SiO2)   | 19.78 | 31.80 |
| Aluminum oxide (Al2O3)   | 3.90 | 10.12 |
| Iron oxide (Fe2O3)       | 3.00 | 5.03 |
| Calcium oxide (CaO)      | 63.38 | 20.79 |
| Magnesium oxide (MgO)    | 2.00 | 8.77 |
| Sulfur trioxide (SO3)    | 2.85 | 2.46 |
| Sodium oxide (Na2O)      | 0.75 | 0.09 |
| Phosphorus pentoxide (P2O5) | 0.12 | 4.82 |
| Chloride (Cl)            | 0.01 | 0.35 |
| Potassium oxide (K2O)    | 0.18 | 12.51 |
| Titanium oxide (TiO2)    | -   | 2.07 |
| Zinc oxide (ZnO)         | -   | 0.19 |
| Mn2O3                    | -   | 0.81 |
| SrO                      | -   | 0.16 |
| Loss on Ignition (LOI)   | 1.90 | 7.95 |
| SiO2 + Fe2O3 + Al2O3     | -   | 46.94 |
| Physical properties      |     |     |
| Specific gravity         | 3.15 | 2.22 |
| Strength activity index (%) | - | 82  |
| Median particle size, D50 (µm) | 15.90 | 11.42 |
2.2 Preparation of Samples
Six different paste mixes constituting GHA in different proportions were produced. Constant water to binder ratio of 0.36 was used for all the mixes. The mix proportions are shown in Table 2. The mix without GHA (100% cement) represents the control sample upon which the other mixes were compared to. 50mm cube moulds were used to cast the samples for compressive strength test. After 24 hours of casting, the samples were demoulded and then cured in water for 7 and 28 days before testing. The result reported is the average of three samples.

| Paste type | Cement (%) | GHA (%) |
|------------|------------|---------|
| Control    | 100        | 0       |
| 10GHA      | 90         | 10      |
| 20GHA      | 80         | 20      |
| 30GHA      | 70         | 30      |
| 40GHA      | 60         | 40      |
| 50GHA      | 50         | 50      |

2.3 Methods
The consistency and setting times by Vicat needle of the mixes were determined in accordance with the ASTM C 187[12] and ASTM C191 standards respectively. Soundness of binders by Le-Chateliers method (IS: 4031- Part 3- 1988)[13] and compressive strength based on ASTM C 109 [14] were also determined. The compressive strength test was done after 7 and 28 days of curing.

3. Results and Discussion
3.1 Consistency
The consistencies (water demands) of the different mixes are shown in Figure 1. It can be observed that the specimens with GHA required more water than the control to achieve the desired consistency recommended by ASTM C 618 [11]. And the rate of water demand increased with the increasing GHA content. In fact, the water demand for the blended specimens with 10%GHA, 30%GHA and 50%GHA was higher than that of the control by 46%, 100% and 146% respectively. The spongy nature of GHA particles which is typical to most agro-waste ashes, leading to their high surface area may be responsible for the high water requirement [15].
3.2. Setting Times
Figure 2 presents the initial and final setting times of the control and blended pastes. It can be seen that GHA retarded both the initial and final setting times of cement paste, and the retarding effect increased with the increasing ash content. However, it is noteworthy that at all the replacement levels, the minimum initial setting time (60mins.) and the maximum final setting times (600mins.) recommended by the ASTM standard [16] were not exceeded. This implied that, GHA may be a suitable material for use where retardation of setting time is significant. The retarding effect exhibited by GHA is similar to those of the other ashes such as, rice husk ash, fly ash and palm oil fuel ash which are characterized with a low reactivity [3, 17].

![Figure 2. Setting Times](image)

3.3. Soundness
Soundness indicates the ability of hardened binder paste to resist expansion due to excessive content of magnesia or free lime content in the binder [18]. The expansion of the control and blended specimens are depicted in Figure 3. Remarkably, none of the specimens exceeded the maximum allowable expansion of 10mm stipulated by the Indian Standard (IS: 1489-1991: Part 1) for sound Portland cement. Apparently, despite its high magnesia content as shown in Table 1(chemical composition), GHA improved the soundness of paste and the extent of the improvement increased with the ash content. Compared to the control, the expansion of blended specimens with 10%, 30% and 50% GHA were less by 8%, 28% and 56% respectively. The pattern of soundness improvement exhibited by GHA is similar to that shown by fly ash reported in [3].

![Figure 3. Expansion](image)

3.4. Compressive strength
The influence of GHA on the compressive strengths of the cement paste specimens at 7 and 28 days are shown in Figure 4. At early age, 7 days, all the specimens with GHA showed compressive strength
lower than that of the control. The strength reduction effect of the blended specimens increased with the ash content. However, at 28 days, strength comparable to that of the control was achieved when 10% GHA was used. Therefore, the optimum replacement level of GHA to improve compressive strength of cement is 10%. The strength reduction effect of GHA on the paste at early age may be unconnected with the low pozzolanic characteristic of agro waste ashes. However, dilution effect may be attributed to the reduction of strength for the specimens containing GHA above 10% levels at 28 days. The trend of strength development of GHA observed in this study is similar to that when fly ash was used to replace cement in concrete [3].

![Figure 4. Compressive strength](image)

3.5. **FTIR**

The IR-spectra of the control and blended samples (with 10% GHA) are shown in Figure 5. It can be observed that Ca(OH)$_2$ is present in both the samples as evidenced by the appearance of the OH-stretching band at 3642 cm$^{-1}$. Similarly, the detection of the asymmetric Si-O stretching band ($v_3$) at 954 cm$^{-1}$ confirmed the formation of calcium silicate hydrate (C-S-H) in the samples. The C-O stretching ($v_3$) at 875cm$^{-1}$ and bending at 1424 cm$^{-1}$ indicated the existence of calcite. However, compared to the control, the blended sample has less Ca(OH)$_2$ but more CSH content as reflected by their respective intensities. This highlighted the evidence of pozzolanic reaction between GHA and cement hydrate. Thus, the improvement of compressive strength shown by the blended sample can be attributed to the pozzolanic reaction.
4. Conclusion
Based on the results obtained in this study, the following conclusions were drawn:

a) Groundnut shell ash (GHA) increased water requirement, delayed both initial and final setting times, but improved soundness of cement paste.

b) Compressive strength of hardened cement paste improved with 10% GHA replacing cement. Therefore, 10% is the optimum replacement level of GHA in cement paste.

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