Utilization of fly ash: basic oxygen furnace slag as a raw material in geopolymerization

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Abstract. The aim of this project was to develop a basic oxygen furnace slag (BOFS) and fly ash (FA) based geopolymer. The developed geopolymer were required to have strength to withstand hydraulic load. In respect to BOFS and FA, there are two main ways in which they can be handled following the best practices of conserving the environment. The two are disposal and utilisation, the disposal thereof is a problem because it increases the amount of FA annually since they are not consumed completely yearly. Results also showed that wastes beneficiate FA and BOFS can be utilised for other applications and this will reduce these wastes in the landfills. The development of the geopolymer to investigate the optimum conditions to enhance strength has resulted in a 20% FA mass blend ratio, 9 M concentration of sodium hydroxide, 20% liquids solid-liquid ratio and 80 °C curing temperature. The addition of hydrogen peroxide to the geopolymer increased the porosity of the geopolymer.

1. Introduction

In South Africa alone, 35 million tons of coal ash is generated annually, 29 million being fly ash and 6 million is bottom ash [1]. Kruger (2015) has stated that the main sources of fly ash (FA) are coal fired power stations and cement producers are the main consumers of FA. Kruger (2015) did a study of what FA is currently used for and has found that the cement making industry uses about 72% of the total FA volume (2.5 million tons) consumed yearly in South Africa. Out of the 29 million tons produces, only 2.5 million tons is consumed and the remaining annually piles up in our landfills. It is estimated that by 2020 42 million tons of coal ash will be generated yearly on average. Kruger (2015) has outlined the FA grades as unclassified, air-classified and twice-classified where they are can be characterised as sourced directly from power plant, sub 45µ and sub 8µ respectively. Generally the grades are based on the size of the FA particle. The finer FA is less likely to contain impurities, as opposed to bottom ash which is most likely to be mixed with other solids (e.g. any solid particle that could fall to the ash collection system). However, because it is too fine, it is the most problematic because there are limited ways in which one can handle it [2]. In South Africa, the process of steel making mainly takes place in a basic oxygen furnace. This process involves the mixing of iron ore, oxygen, limestone and coke as the feed materials [3]. While the goal is to produce steel, one of the waste by-product in this regard is basic oxygen furnace slag (BOFS). The BOFS results when the limestone is reduced to lime which reacts with the impurities like silica resulting in a slag which forms and floats on top of the molten iron [4]. BOFS is therefore a heterogeneous mixture of calcium, silica, manganese, sulphur and other impurities. Mahieux et. al (2009) has stated that the production of steel
results in 100 – 200kg of BOFS generation for every ton of crude steel produced [5]. This steel has a low market demand and mostly thrown into the landfills upon generation. According to [6], geopolymers are a new form of binder which means they can be considered as new materials for coatings and adhesives, new binders for composites and new cement for concrete. Yuanyuan (2015) has studied the removal of Cu2+ from aqueous solution using porous geopolymeric spheres [7]. His research has revealed that metakaolin-based geopolymeric spheres have been synthesised successfully. Other less frequent uses of FA include: water stabilisation and solidification, mine reclamation, road sub base and geopolymisation being the emerging use of FA [8]. Geopolymerisation involves chemically condensing the tetrahedral aluminosilicate units using alkali activators (metal ions), usually a soluble silicate, by virtue of balancing the charge associated with the tetrahedral aluminium molecule [9]. A pozzolanic reaction of the FA with moisture and an alkaline activator results in a FA slag, which could be relatively hard enough to be used as a membrane to treat mineral effluents was developed [10]. Novais, et al. (2016) have developed a FA based geopolymer for the adsorption of lead from waste water [11]. The experimental set up exhibited good results, with a removal capacity range of between 0.95 -6.34 mg lead per unit gram of geopolymer. The synthesis of geopolymers follows one of two routes, acidic and as well as alkaline medium. The most commonly used route is the alkaline route [12] and this project will use sodium hydroxide. The process involves the dissolution of the aluminosilicate and then the condensation of the free aluminate and silicate units to form a structure of silico-aluminate which is three-dimensional [13]. This chemical reaction applies to both class F and class C FA with class C being the more spontaneous of the two [10]. Class C has some self-cementing properties, however, unlike class F, it contains reasonably higher alkali and sulphate contents and in the presence of water it hardens and gets stronger with time [10]. The application of geopolymers is categorized into three, namely, geopolymer resins and binder, geopolymer cements and concrete as well as arts and archaeology [6]. Owing to the pozzolanic nature of FA, the application explored in this project falls under the cement and concrete category because a slag will be casted using the procedure of brick making. According to Davidovits (2015), geopolymers are a new form of binder which means they can be considered as new materials for coatings and adhesives, new binders for composites and new cement for concrete [6].

The production of FA and BOFS are also something that cannot be avoided, correct disposal measures or utilization needs to be studied in order to protect the environment. Rycroft (2017) has argued that the uses of FA are perceived as limited because of the lack of knowledge thereof. There are 150 known uses of FA (existing and emerging potential uses) [14]. These include, cement, concrete and brick making, geopolymers, zeolites, AME treatment and mine backfilling, rubber and plastic fillers, etc. [14]. Mahieux et.al. (2009) also argued the same for BOFS saying that it too has a low market demand [5]. The aim of this project is to develop a porous geopolymer which can withstand hydraulic load and also remove metals from acidic industrial effluents.

2. Experimental details

2.1. Material

There materials were used to synthesis the FA/BOFS based geopolymer. The FA was obtained from Camden Power Station and the BOF-slag from Arcelormittal South Africa. Deionised water was used and reacted with a strong alkaline (NaOH) and Sodium Silicate which (Na2SiO3) was supplied by Sigma Aldrich.

2.2. Sample Preparation

The two wastes fly ash and BOF slag were crushed then pulverised to ensure that the particle size is kept below 500µm. A solution of the NaOH and H2O2 was prepared using deionised water.

2.3. Geopolymer Synthesis
2.3.1. **Effect of the blend ratio (FA: BOF-slag).** This is the first and foremost step in the geopolymer synthesis. A total mass of 250g was weighed and the ratio varied from: 0 %, 20 %, 40 %, 60 %, 80 % and 100 % by mass of FA. 3 M solution of NaOH was prepared and mixed with the solids at a ratio of 25 % liquid to make a paste cast in the 50mm cube moulds. The paste was cast at room temperature for 24 hours and cured at the temperature of 80°C, over 6 days. The unconfined compressive strength (UCS) of the geopolymers was determined in order to find out the mix design that yielded the highest strength.

2.3.2. **The effect of the sodium hydroxide (NaOH) concentration.** After obtaining the optimum FA: BOF-slag ratio, this parameter was controlled throughout the experiment. The next step was to find the best sodium hydroxide concentration. The concentrations was varied from 3 M, 6 M and 9 M. These prepared solutions were mixed with the solids at a ratio of 25% to make a paste. The paste was also cast at room temperature for 24 hours and cured at 80°C for 6 days. The UCS of the geopolymers was determined to find out the NaOH concentration that yielded the highest strength.

2.3.3. **The effect of solid liquid ratio.** After finding obtaining the optimum NaOH concentration, this parameter was also controlled throughout the experiment. The FA and BOF-slag in their powder form was weighed and a solution of NaOH mixed at different solid liquid ratios. The ratios were selected based on workability of the paste. 15 %, 20 %, 25 % and 30 % by weight of NaOH solution was added to the solids to make the paste. This was conducted in order to vary the consistencies of the paste to test for the optimum solid-liquid ratio and this paste which will be poured inside the 50mm cube moulds.

2.3.4. **The effect of curing temperature on strength.** After determining the optimum solid-liquid ratio in respect to the obtained UCS, this parameter was controlled throughout the experiment. The curing temperature was investigated and the temperature varied to investigate the effect of temperature. The curing temperature was varied between 25 °C, 40 °C, 80 °C and 100 °C for a period of 6 days, thereafter the UCS the geopolymers was determined.

2.3.5. **The effect of porosity on strength.** The solid-liquid ratio that yielded the highest strength was cast again and varying volume of a blowing agent (hydrogen peroxide) was added to increase the porosity of the geopolymers. The volume of hydrogen peroxide was varied between 1 ml, 1.5 ml and 3 ml. The effect of open porosity was then analysed. The analysis was conducted by casting and curing the brick for a duration of seven days, weighing the brick and recording the mass as Mdg, soaking the geopolymer in deionised water for 24 hours, removing any access water on the surface of the geopolymer and weighing the geopolymer again to find Mwg. Then the open porosity was calculated using the following equation:

\[
\text{Open Porosity} = \frac{M_{\text{dg}} - M_{\text{wg}}}{\rho_{\text{water}} \times \text{Volume of geopolymer}}
\]  

The UCS tests were conducted again in order to determine the best strength when the geopolymer is porous.

2.3.6. **Characterisation of fly ash and basic oxygen furnace slag.** A uniaxial compressive strength (UCS) testing apparatus (Matest, spa treviolo) was used for testing the strength of the geopolymer. X-Ray fluoroescence (XRF: Rigaku ultima IV) was used to study the elemental composition of the geopolymer. The morphology of the geopolymer was studied by using a Scanning Electron Microscopy (SEM: Tescan Veg 3 XMU).
3. Results and discussion

3.1. **Micrograph of FA and BOF slag (SEM analysis)**
The samples were characterised individually, the SEM in figure 1 has shown that FA (A) exhibited a spherical shape while BOFS (B) had shapes ranging from subangular to sub-rounded. This agrees with literature as stated by [15-16].

3.2. **Elemental composition of FA and BOF slag (XRF analysis)**
Table 1 shows the elemental compositions of the two raw materials. According to Charles & Carraher (2016), the XRF results shows that the FA used is a Class C FA because it has a calcium oxide content greater than 10 wt % [10]. Li et.al. (2013) added that Class C FA results when a stronger coal is combusted [17]. This shows that the CaO content is important in enhancing the strength of the geopolymer. BOFS on the other hand has a greater CaO content, which plays a significant role in strength development of the material; resulting into a stronger geopolymer.

| Component | Al₂O₃ | SiO₂ | CaO | Fe₂O₃ | CuO | MgO | Other |
|------------|-------|------|-----|-------|-----|-----|-------|
| Amount in FA (mass %) | 20.34 | 45.00 | 12.55 | 14.60 | 0.01 | 1.60 | 5.90 |
| Amount in BOFS (mass %) | 4.21 | 10.15 | 47.50 | 27.73 | 0.00 | 3.63 | 6.78 |

3.3. **Particle size distribution**
The particle size distribution of the FA and the BOFS were analysed using a 1500g sample of each material. Figure 2(a) and figure 2 (b) shows the results of both the raw materials. FA was finer than
the than the BOFS, with nearly half of the sample being less than 0.5µm. BOFS had approximately 100g of the 1500g sample being less than 0.5µm. This shows that there was a need to homogenise the samples in order to eliminate any error which could arise from the size distribution factor. The size reduction was achieved using a rod mill. The rod mill was loaded with 12 rods and to achieve size homogenising below 0.5µm the crushing was set for a duration of 30 minutes per 1000g sample. After the size reduction, all the sample managed to pass through a 0.5µm screen (i.e. 100 % recovery of desired product). In addition, crushing the BOFS results in more CaO being exposed and thus contributes to overall strength development of the geopolymer [16].

3.4. Effect of the BOFS: FA ratio, sodium hydroxide (NaOH) concentration and solid-liquid ratio on the UCS of the geopolymer

The results for the unconfined compressive strength (UCS) at different FA:BOFS, the effect of sodium hydroxide concentration and effect of solid-liquid ratio is shown in Figure 3, Figure 4 and Figure 5, respectively. The geopolymer developed with a 0 % FA (100 % BOFS) had a higher strength as opposed to the one with 100 % FA. The XRF results of these geopolymers have shown that 100 % FA has a high CaO content which is believed to enhance the strength of geopolymers [10]. The different ratios have resulted in 20 % FA yielding the highest strength and has a reasonably high amount of CaO as well. The increase in the concentration of sodium hydroxide has resulted in the increase of the UCS.

![Figure 3. UCS at varying FA:BOFS.](image)

![Figure 4. UCS at varying NaOH concentration.](image)

![Figure 5. UCS at varying solid-liquid ratio.](image)

This supports the conclusion reached by [10] who stated that the pozzolanic reaction of the FA with moisture and an alkaline activator results in a FA slag which could be relatively hard enough to be
used as a backfill paste. The use of the alkaline medium (NaOH) promoted polymerisation of the aluminosilicates resulting in stronger bonds. In this experiment, the concentration was limited at 9M and greater concentrations were not investigated in order to make the project feasible when commercialised.

The solid-liquid of 20% resulted in the highest UCS. The SEM of the geopolymer resulting from the different solid-liquid ratios is presented in Figure 6.

The study of the optimum solid-liquid ratio is highly influenced by the workability of the paste created. When making the paste in the nominal solid-liquid ratios, 15% liquid was too dry, and the liquid medium was not enough to allow interactions with the FA and BOFS and the alkaline solution. 20% and 30% solid-liquid ratios were reasonably workable and had a texture of plastering cement (construction industry).

The 30% solid-liquid ratio was too wet and not workable, hence there was no need to investigate it any further. The 20% solid-ratio was the optimum amongst the two workable solid-liquid ratios (20% and 30%), having the highest strength. The SEM results show increasing ‘white particles’ moving from A to D. These ‘white particles’ can be considered as the moisture and thus an increase in moisture is inversely proportional to the strength as supported by the workability and the UCS results in figure 5.

3.5. The effect of curing temperature on UCS and hydrogen peroxide on the open porosity and UCS

The UCS test was conducted on the geopolymers to find out which curing temperature gives the highest strength and to determine the effect of hydrogen peroxide on the open porosity and UCS. The obtained results are presented in Figure 7 (a) and Figure 7(b). The strength of the geopolymer tends to increase as the temperature increases. However, increasing the temperature beyond 80 °C decreases the strength again.
This means that 80 °C is the optimum curing temperature for the geopolymerisation of FA: BOFS. The open porosity of the geopolymers generally increases with an increased hydrogen peroxide dosage. This is because hydrogen peroxide is considered a blowing agent in the process of geopolymerisation, therefore, increasing the dosage of hydrogen peroxide makes the geopolymer more porous. The SEM of the developed geopolymers in Figure 8 shows the effect of temperature as it was increased. The moisture particles decrease from A to D due to the temperature. There were cracks observed on the geopolymer, the weaker geopolymers was seen to have cracks. No cracks were found on C which justifies why it had the highest strength.

4. Conclusion
The characterisation of the geopolymer has proven to align with literature. The SEM results has confirmed that FA is spherical and BOFS ranges from sub-rounded to sub-angular. The XRF results have shown that FA is an aluminosilicate material. BOFS had a high relative proportion of CaO, a constituent that contributes to material strength. The particle size distribution and the moisture content of the FA and BOFS have resulted in a need for further homogenising and to be cured at elevated temperatures respectively.

The geopolymer synthesis process has resulted in reliable optimum conditions and was supported by UCS, SEM and XRD analysis. The blend ratio proved to be influenced by the CaO content and the optimum was found to be 20 % FA, with a relatively high amount of CaO. Increasing the concentration of sodium hydroxide resulted into the increase in UCS, however, the maximum concentration was limited at 9 M for this project. The solid liquid ratio was influenced by the workability of the paste and out of the two most workable pastes (20 % and 25 %), 20 % had the highest strength. The optimum curing temperature that yielded the highest geopolymer UCS was at was 80 °C. It was observed that 25 °C, 40 °C and 100 °C had cracks on their surfaces which explains why the strength was lower.

The effect of porosity was negative on the development of the geopolymer as it decreased the strength when hydrogen peroxide was increased. The porosity increased with an increased dosage of hydrogen peroxide. South African waste fly ash and basic oxygen fly ash can be used to make a geopolymer.

This results presented provide an opportunity for utilisation of wastes as surface capping material or as paste backfill. Curing over longer period at room temperatures should be investigated. This will allow for reduction in energy consumption.

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