ALKALI ACTIVATION OF FAYALITE SLAG

Adediran Adeolu Idowu

MASTER DEGREE PROGRAMME (BCBU) IN ENVIRONMENTAL ENGINEERING

Master’s thesis
August 2017
ALKALI ACTIVATION OF FAYALITE SLAG

Adediran Adeolu Idowu

Supervisor(s): Yliniemi, Juho
Adesanya Elijah Damilola
MASTER DEGREE PROGRAMME (BCBU) IN ENVIRONMENTAL ENGINEERING
Master’s thesis
August 2017
ABSTRACT
FOR THESIS
University of Oulu Faculty of Technology

Degree Programme (Bachelor’s Thesis, Master’s Thesis)  Major Subject (Licentiate Thesis)
Master’s Degree Programme (ECE) in Environmental Engineering  Environmental Engineering (Fibre and Particle Engineering)

Author  Thesis Supervisor
Adediran Adeolu Idowu  Juho Yliniemi, Adesanya Elijah Damilola

Title of Thesis
Alkali Activation of Fayalite Slag

Abstract

In this thesis, alkali activation of fayalite slag was investigated. The slag utilized is a waste by product from nickel production, the activation of which resulted in the formation of a geopolymer binder of acceptable properties. The need for a reduction in overall waste output as well as the cementitious properties exhibited by this slag motivated this study.

The literature section of this research provides an insight on the previous work in the area of geopolymerization, the source materials used, the activators employed as well as the properties exhibited by various geopolymer products. The experimental section reports the particle size distribution and particle size optimization as well as geopolymer synthesis. The size reduction was carried out by milling for a required time while the particle size optimization and mix design was done with “Elkem Material Mixture Analyser (EMMA).

The milling reduced the particle size of fayalite slag to 10.08µm after 3 hours which is sufficient fineness for most geopolymer precursors. Different mix compositions were activated with potassium silicate and sodium hydroxide at varying mass ratio with the one activated with 50:50 mass ratio of NaOH /K₂SiO₃ had the highest mechanical strength. The workability and setting time were good for the mixtures with liquid to solid ratio from 0.1-0.2. Compressive strength test were carried out on various mix compositions and the result shows the maximum compressive strength of 16.5 MPa was achieved at room temperature after 28 days. The water absorption was very low (5%). It was also noticed that the strength after water absorption was higher than the unconfined compressive strength due to subjection of slag geopolymer to elevated temperature before water absorption.

The alkali activation of fayalite slag has shown promising properties which could further be improved for better mechanical performance.
The purpose of these research is to convert metallurgical waste (fayalite slag) into inorganic polymer product as well as examine their properties as a potential alternative to portland cement. The research work was carried out at Fibre and Particle Engineering Laboratory, University of Oulu. I want to bless the almighty God for his power, guidance and wisdom over my life.

However, it is my conviction that this thesis wouldn’t have been possible without the support of my supervisors. It is in the spirit of this that I am acknowledging the effort of my lead supervisor Juho Yliniemi, his constructive criticism and meaningful suggestions coupled with reasonable understanding and mentoring has made this thesis a reality. Also to my co-supervisor and brother, Adesanya Elijah Damilola, I really appreciate your patience, direction as well as support throughout the course of the thesis.

Furthermore I will like to appreciate the head of the research unit in person of Prof. Mirja Illikainen for the opportunity to learn from this great team. I also appreciate the contribution of the laboratory staffs who were always willing and ready to provide the necessary support needed during my experimental work. I would like to specifically thank Jarno, Jani and Elisa for their unflinching support during my time in the laboratory I want to say a big thank you.

Finally, my acknowledgement won’t be complete without remembering my parents (Mr and Mrs Adediran) and my siblings (Taiwo, Kehinde and Adeleye) who has been the pillar of support through thick and thin and also to my friends. May God bless you all.

Oulu, 15.8.2017 Mr Adediran Adeolu
TABLE OF CONTENTS

ABSTRACT ................................................................................................................. 3
PREFACE .................................................................................................................. 4
TABLE OF CONTENTS .......................................................................................... 5
ABBREVIATIONS AND DEFINITIONS ................................................................. 7
1 INTRODUCTION ...................................................................................................... 8
   1.1 Background ...................................................................................................... 8
   1.2 Aims ............................................................................................................... 9
   1.3 Objectives ...................................................................................................... 9
2 LITERATURE REVIEW .......................................................................................... 10
   2.1 GEOPOLYMER ............................................................................................. 10
   2.2 Source Materials .......................................................................................... 12
       2.2.1 Nickel Slag ............................................................................................ 12
       2.2.2 Ground Granulated Blast Furnace Slag (GGBFS) .................................. 13
       2.2.3 Metakaolin ............................................................................................ 14
       2.2.4 Fly Ash .................................................................................................. 15
   2.3 Alkali Activators ........................................................................................... 17
       2.3.1 Sodium Hydroxide NaOH .................................................................... 18
       2.3.2 Potassium Hydroxide KOH .................................................................. 19
       2.3.3 Sodium Silicate Na_2SiO_3 ..................................................................... 19
       2.3.4 Potassium Silicate K_2SiO_3 .................................................................. 20
   2.4 Milling ............................................................................................................ 21
   2.5 Particle size Distribution ............................................................................... 22
       2.5.1 Sieve Analysis ......................................................................................... 23
       2.5.2 Laser Diffraction Particle Analysis ......................................................... 24
   2.6 Elkem Material Mixture Analyzer (EMMA) .................................................. 25
   2.7 Other Parameters .......................................................................................... 26
       2.7.1 Liquid to Solid Ratio .............................................................................. 26
       2.7.2 Curing Conditions .................................................................................. 27
       2.7.3 Setting Time ............................................................................................ 28
3 EXPERIMENTAL AND RESEARCH METHODOLOGY ...................................... 30
   3.1 Geopolymer Constituents .............................................................................. 30
3.2 Sieving Test

3.3 Milling experiments

3.4 Density Measurement

3.5 Laser Diffraction Particle Size Distribution Analysis
   3.5.1 Dry Method (Dry Powder Module)
   3.5.2 Wet Method (Universal Liquid Module)
   3.5.3 Rate/Speed of Stirring

3.6 Geopolymer Synthesis
   3.6.1 Curing
   3.6.2 Compressive Strength
   3.6.3 Water Absorption

4 RESULTS AND DISCUSSION
   4.1 Material Milling and Characterization
      4.1.1 Sieving test results
      4.1.2 Particle size distribution (PSD) analysis
      4.1.3 Density
   4.2 Physical appearance of geopolymer samples
   4.3 Compressive Strength
   4.4 Setting time
   4.5 Microstructural Characterization
      4.5.1 Optical Microscopy
      4.5.2 Scanning Electron Microscopy
   4.6 Water Absorption

5 SUMMARY

6 BIBLIOGRAPHY

APPENDICES:

APPENDIX 1.
## ABBREVIATIONS AND DEFINITIONS

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al₂O₃</td>
<td>Aluminium oxide</td>
</tr>
<tr>
<td>ASTM</td>
<td>American Society for Testing and Materials</td>
</tr>
<tr>
<td>CaO</td>
<td>Calcium oxide</td>
</tr>
<tr>
<td>CO₂</td>
<td>Carbon dioxide</td>
</tr>
<tr>
<td>Cu</td>
<td>Copper</td>
</tr>
<tr>
<td>EMMA</td>
<td>Elkem Material Mixture Analyzer</td>
</tr>
<tr>
<td>Fe</td>
<td>Iron</td>
</tr>
<tr>
<td>FeO</td>
<td>Iron (II) oxide</td>
</tr>
<tr>
<td>FS</td>
<td>Fayalite slag</td>
</tr>
<tr>
<td>FS 30</td>
<td>Fayalite slag (30 minutes milled slag)</td>
</tr>
<tr>
<td>FS 180</td>
<td>Fayalite slag (3 hours milled slag)</td>
</tr>
<tr>
<td>K⁺</td>
<td>Potassium alkali ion</td>
</tr>
<tr>
<td>K₂SiO₃</td>
<td>Potassium silicate</td>
</tr>
<tr>
<td>MgO</td>
<td>Magnesium oxide</td>
</tr>
<tr>
<td>Na⁺</td>
<td>Sodium alkali ion</td>
</tr>
<tr>
<td>NaOH</td>
<td>Sodium hydroxide</td>
</tr>
<tr>
<td>Ni</td>
<td>Nickel</td>
</tr>
<tr>
<td>SiO₂</td>
<td>Silicon dioxide</td>
</tr>
<tr>
<td>USCS</td>
<td>United States soil classification system</td>
</tr>
</tbody>
</table>
1 INTRODUCTION

1.1 Background

Slags over the years have emerged as a suitable alternative to Portland cement (Maragkos et al., 2009). It is an industrial by-product or in some countries a waste product which are readily available and can be used as an important aggregate in a concrete (Kuo and Shu, 2015). It has shown considerable mechanical and structural properties as well as having a low carbon footprint in their utilization in alkali activated materials (AAM) which has boosted their acceptability (Sajedi, 2012). Various types of slags are produced depending on the industrial process and mineral ores refined.

Slags are synonymous with metal production (Mills, 2011). It is a principal by-product obtained in the separation of metal from the ore (Jia et al., 1999). Considerable amount of slags are generated during the smelting process, thereby increasing the volume of waste products discarded on a yearly basis (Mihailova & Mehandjiev, 2010). The need for proper and sustainable waste management as well as reduction in the environmental load of this industries has mandated researches on the possible replacement of the cement with slag products which until now has found little or no useful applications especially non-blast furnace slag (BFS). Coupled with this is the need to comply with EU waste framework directive in promoting reuse and recycle as well as reduction of CO₂ emissions (WFD, 2008).

In nickel production, a non-ferrous slag called fayalite slag is produced from the reaction between already oxidized iron sulphide and silica (Perederiy, 2011). Fayalite has been discovered to belong to mineral group called olivine together with forsterite which are predominantly silicate minerals and are present in some rocks on the earth surface (Machiels et al., 2014). Also, slags are known to have a varying chemical composition and mineralogy depending on the ore processed and the temperature at which it is melted, this oxides includes CaO, MgO, SiO₂, Al₂O₃ and FeO (Fernandez-Jimenez et al., 2014).
The fayalite slag produced from copper or nickel ore subjection to furnaces has shown a good prospect in being utilized as a precursor in AAM (Katsiki et al., 2017). It is rich in iron and silica which at lower pH dissolves in acid under anoxic conditions (Perederiy, 2011). It is an important inorganic polymer precursor because of its glassy composition. Inorganic polymers belong to a wide range of binders that are alkali activated. Though most binders are produced from calcio-aluminosilicate precursor activated in alkali solution, an inorganic polymer from Fe-Si precursors i.e. fayalite slag activated in alkali solution has also been developed.

Though iron silicate glasses have similar properties as aluminum silicate such as vitrifying, non-ferrous nature and bivalency, the structure, composition and characteristics are different (Machiels et al., 2014). Hence the need to study them. These research is concerned with alkali activation of fayalite slag glasses that are rich in iron and silica with little amounts of Ca-Al-Na-K-P-Ti-S-Cl.

1.2 Aims

- To develop a geopolymerization matrix for fayalite slag.

1.3 Objectives

This research intends to achieve this stated objectives

- To optimize the particle size distribution of fayalite slag in order to achieve maximum particle packing.
- To determine the optimal alkali activator and optimum amount of alkali activator required for slag geopolymer synthesis.
- To characterize the geopolymer product for physical, mechanical and microstructural parameters.
2 LITERATURE REVIEW

2.1 GEOPOLYMER

Geopolymer can be defined as ceramic- or concrete type material which are produced from aluminosilicate materials that have been activated by an alkali (Zhang et al., 2017). This process is termed geopolymerization. Geopolymers are also sometimes referred to as “geocements”, hydro ceramics and “alkali-bonded ceramics”. Geopolymerization has emerged as a new technology for the utilization of natural and waste by products that are rich in aluminosilicate contents (Palomo et al., 1999). Any material with high aluminosilicate content can be potentially utilized as geopolymer precursor as they react in strongly alkaline environment.

The role of alkali activators in the polymerization process cannot be overemphasized (Joshi and Kadu, 2012). The alkaline base provides the metal which serves as a balance for chemical bond (Santa et al., 2016). The characteristics exhibited by various activators greatly influence the properties of the material synthesized by them. Ryu et al., (2013) observed that the concentration of alkaline activator determines the strength of fly ash based geopolymer. The stability of geopolymer is a function of the properties of the source material, proper mix and effective design to comply with a specific purpose (Singh et al., 2015). The mechanical and microstructural properties of geopolymer material is influenced by the chemical composition of the source material.

The concept presented in Figure 1 has been documented by various authors and it was broadly classified into distinct process namely; the use of alkali metal hydroxide to dissolve the source material, diffusion of the already dissolved aluminum and silica, the addition of a silicate solution thereby undergoing a polymerization reaction with the dissolved Al and Si resulting in the production of a gel stage and finally the consequent hardening of the gel material (Duxson et al., 2007).
The creation of polymer-type structure after the alumino silicate materials has been dissolved, results in the rearrangement of their structure which relies on kinetic and thermodynamic properties of the material. This rearrangement determines the properties displayed by the geopolymer (Sarmin et al., 2014).

The alkali hydroxide plays a critical role in dissolving the source materials while sodium and potassium helps in binding, activating, dispersing or acts as plasticizing agent. This is followed by the polycondensation of the dissolved material which is a function of particle size, reaction concentration and the rate at which the aluminosilicate materials dissolve. The polycondensation of dissolved mixture yields output of desired qualities (Komnitsas and Zaharaki, 2007).

Geopolymers exhibits different properties depending on the source materials and the formation process. Some of the important physical properties include but not limited to the following; reduced shrinkage, increase surface smoothness. Some chemical properties demonstrated by geopolymer is their high resistance to acid attack. This properties are reflected in the output material (Comrie et al., 1989).

Figure 1: The concept of geopolymerization (Source: Sarmin et al., 2014).
2.2 Source Materials

Source materials for alkali activation are usually calcium-aluminosilicates whose dissolution in the alkali medium is critical to the formation of the inorganic binders. Some of these source materials includes various slags, fly ash, volcanic ashes, metakaolin and calcined clay.

2.2.1 Nickel Slag

Nickel slag belongs to the class of metallurgical industrial wastes that are non-ferrous in nature. They are produced in large quantity during the extraction and refining of nickel. They are majorly round in shape and the granules are black in colour (Jian et al., 2013). Most metallurgical slags has varying amount of silica (SiO$_2$), alumina (Al$_2$O$_3$) and lime (CaO) embedded in them depending on the metal produced (Barati et al., 2011). In terms of chemical composition and mineralogy, nickel slag predominantly consist of SiO$_2$, MgO, and FeO together with some crystalline minerals and non-crystalline minerals. The characteristics exhibited by both crystalline and non-crystalline minerals is a function of the cooling temperature employed in the process.

Apart from the fact that nickel slags are waste by-products from nickel ore melting at high temperatures, they are discovered to have some properties such as minimal absorption rate and hardness. During nickel smelting, four crystalline slags were observed which are fayalite (Fe$_2$SiO$_4$), magnetite (Fe$_3$O$_4$), silica (SiO$_2$) and matte (Fe, Ni, Cu) (Perederiy and Papangelakis, 2017).

Fayalite is an important non-ferrous slags produced from the oxidation of iron sulfide to iron oxide and consequent reaction with silica. It has a molecular formula of Fe$_2$SiO$_4$ or 2FeO-SiO$_2$. Non-ferrous slags produced from smelting and other refining processes is made up of 32-52 percent iron separated into major component (fayalite) and minor component (magnetite) together with small quantities of nickel, cobalt, copper and zinc (Li et al., 2009).

In this work, this slag is referred to as “fayalite slag” from now on. This is the type of slag used in this work.
Nickel slags has found potential applications as aggregate in concrete, as a result of the standardization of a wide range of non-ferrous metal slag by the Japanese industrial standard, most especially the application of ferronickel slag to concrete and pile structures (SAKOI et al., 2013).

Iron silicate glasses are very rich in iron but possesses small quantity of aluminum. They can be found in natural sources such as rocks or it can be synthesized in the laboratory. Iron plays a crucial role in determining the properties of the glass and therefore needs to be studied for effective geopolymerization (Malki et al., 2015). Even though, aluminum and iron cation are part of the glass, they seem to have different molecular behavior (Antoni et al., 2004).

The presence of iron oxide helps in stabilizing silicate glasses (Ottonello et al., 2011). Burkhard (2000) concluded that the chemistry of iron coupled with that of the added alkali influences the glass elasticity. An alteration in chemical composition of the glass can have a resultant effect on its physical properties (Mysen and Richet, 2005).

Onisei et al (2015) observed a transformation in the microstructure of iron silicates as a result of change in activating solution due to their highly reactive nature. Their occurrence in metallurgical slags as well as their ability to undergo polymerization has made them a potential inorganic polymer precursors (Machiels et al., 2014).

2.2.2 Ground Granulated Blast Furnace Slag (GGBFS)

GGBFS is a by-product obtained from iron and steelmaking processes (Sajedi, 2012). Due to the cooling process, they are glassy in nature and can be milled into powdery form (Snellings et al., 2012). The raw materials used in the production process determines the chemical composition of the slag material. Most blast furnace slags are rich in CaO, SiO₂, Al₂O₃ and MgO with a high percentage of calcium silicate and this are important constituents of silicate glasses (Li et al., 2010).

GGBFS is one of the most important materials used as precursors in the geopolymers synthesis because of its pozzolanic properties (Gong and White, 2016).
The reactivity of blast furnace slag is very high when activated by an alkali in relation to fly ash and metakaolin that have low calcium contents. The high reactivity is due to the presence of calcium in the material which causes a sudden rearrangement and depolymerization in the Ca-Mg aluminosilicate glassy phase (Haha et al., 2011).

Blast furnace slag is highly amorphous with minor traces of crystalline phase such as merwinitie and akermanite. The crystalline phase is quite inert in nature while the vitreous phase are active (Pacheco-Torgal et al., 2014). The slag composition, activator type together with the pH of the environment has a significant impact on the hydration products of activated blast furnace slag (Lothenbach et al., 2011).

Finer particles of blast furnace slag undergoes a quick chemical reaction when activated by an alkali or used in blended cements. In other words, the smaller the particles, the faster the activation reaction (Wan et al., 2004).

### 2.2.3 Metakaolin

Metakaolin otherwise called calcined kaolin is a product of calcination of kaolinite. It is another form of pozzolan product produced from dehydroxylation of kaolinite clay that are amorphous in nature (Dinakar et al., 2013). It has a chemical formula $\text{Al}_2\text{Si}_2\text{O}_7$ formed from the bonding of hydroxyl ion with aluminosilicate network. The calcination processing temperature ranges from 650°C - 800°C (Palomo et al., 1999).

According to Dinakar et al., (2013), the chemical composition of metakaolin are silica (54.3%), alumina (38.3%) and ferric oxide (4.28%) together with other components that are of limited quantity.

The temperature required to break down the bonding structure is not enough to produce a liquid phase required thereby resulting in an amorphous phase. At higher temperature, a crystalline low activity substance known as mullite is produced. It has an irregular structure made up of aluminum and silicon together with some impurities such as muscovite (Li et al., 2010).
The binding phase of metakaolin-based geopolymer is a sodium-aluminate-silicate-hydrate gel which depends on factors such as type of activator as well as the curing temperature to determine its mechanical properties (Criado et al., 2010). In relation to particle size, metakaolin is bigger than silica fume but it has been viewed as perfect replacement for silica fume in terms of increased durability, availability and mechanical performance of concrete.

Owing to this chemical composition, it has been established that metakaolin is one of the reliable sources of alumino-silicate oxides for geopolymerization (El-Diadamony et al., 2016). Kaolinite and metakaolin has been widely used in geopolymers synthesis because of good mechanical properties exhibited by their products when activated by sodium hydroxide solution (Xu and Deventer, 2000).

Metakaolin are also known to disintegrate very fast and quickly in activating solution and their products minimizes salt and water movement (Sarmin et al., 2014). Dinakar et al., (2013) concluded that the filler effect present in metakaolin particles has a significant impact in reducing water and chloride permeability as well as rate of absorption and porosity of the concrete.

### 2.2.4 Fly Ash

Fly ash is a waste by product obtained from the combustion of coal (Taylor, 1997). The residue laden fine particles are heterogeneous in nature with the major constituents being SiO₂, Al₂O₃ and Fe₂O₃ together with CaO as minor constituents (Zhuang et al., 2016). The chemical composition of fly ashes vary with the origin and constituents of the coal even though it has been established that all fly ashes be it crystalline or amorphous contain considerable amount of silicon dioxide and calcium oxide.

Unlikely granulated blast furnace slag with porous texture and angular particle shape, fly ash are spherical in nature with phases that are vitreous and crystalline (Pacheco-Torgal et al., 2014). The variability in the composition depends not only on the impurities found in the coal but also on the nature and procedure used in the combustion and quenching (Provis et al., 2009). Fly ash has typically particle size lower than 0.075mm
and a specific gravity of 2.1-3.0 (Ahmaruzzaman, 2010). Other substances that may be present in small amount include arsenic, boron, beryllium and chromium.

Coal fly ash is regarded as a pozzolan because of its ability to produce cementitious products from the reaction between aluminosilicate, CaO and alkaline solution. Based on the variation in the quantities of calcium oxide the ASTM classified it as class F and class C. The fly ashes produced from sub bituminous coal has a high amount of CaO and reduced Si and Al in their structure.

Aluminosilicate glasses and calcium compounds in crystalline form are present in fly ashes that has above 15% of CaO while fly ashes with only 10% of CaO has only aluminosilicate glasses (Van Jaarsveld and Van Deventer, 1999). In geopolymerization synthesis, fly ash containing low calcium (class F) is most widely used so that high calcium (as in class C) will not disrupt the synthesis thereby changing the microstructure of the geopolymers. The formation of geopolymers by activating aluminum and silica in fly ash also involves trapping and incorporating the trace metal into the structure (Zhuang et al., 2016).

The result of activating low-calcium coal fly ash with an alkali solution produces an N-A-S-H gel which is quite different from the gel produced during the alkaline activation of a slag (Duxson et al., 2005a). The use of fly ash in concrete applications may be due to its particle size and shape as well as the pozzolanic and glassy properties (Ahmaruzzaman, 2010).

Fly ash has found applications in geopolymerization because of its aluminosilicate contents, increased durability and workability as well as reduced water demand (Granizo et al., 2002). Even though it is widely used, the low reactivity of fly ash geopolymers has been a subject of concern. The dissolution rate of the fractions (amorphous and crystalline) in fly ash varies when activated by an alkali solution (Rangan et al., 2005). Van Jaarsveld (2002) concluded that the slow setting experienced by fly ash geopolymer product may be due to incomplete dissolution of fly ash prior to hardening.
2.3 Alkali Activators

Alkali activation of these source materials cannot take place without a strong alkaline solution as one of the feed material. The substance used are called alkaline activators while the process is called alkali activation. A wide range of alkaline liquid are utilized in geopolymerization some of which include a mixture of sodium hydroxide (NaOH) and sodium silicate (Na$_2$SiO$_3$). Also included is potassium hydroxide (KOH) and potassium silicate (K$_2$SiO$_3$), Rubidium hydroxide (RbOH) and caesium hydroxide (CsOH).

An activation process is basically a reuse process that helps in the conversion of vitreous elements into cementitious structures (Lin et al., 2014). It is to be noted that dissolution rate of the raw materials/precursors depends on the type and concentration of the activation solution employed and also the composition of the precursor material. The dissolution rate changes with the change in pH of the activator. There is variation in the alkali cations produced by different activating solutions in terms of sizes, charge density and hydration potential. This controls the aluminosilicate network and determines the degree of polymerization (Duxson et al., 2005a).

Most aluminosilicate materials are highly soluble in acidic solution but the materials formed produces unstable hydrates with no binding capacity while at a higher pH, a hydrates is formed from the dissolution of the material thereby yielding a material with high binding capacity. The anions (such as silicate anion ) in the activating solution plays a prominent role in structural build-up of the geopolymers since the geopolymer hydration characteristics is influenced by the type of activating solution used (Zivica et al., 2014).

Cheng and Chiu (2003) concluded that the rate of activation is a function of particle size distribution, characteristics of the source material as well as activating solution concentration. The choice of activator to be used does not depend only on the concentration of the alkaline solution but rather it should take into cognizance the durability, acid resistance and shrinkage. The use of soluble silicates together with alkali hydroxides increases the rate of polymerization (Xu and Deventer, 2000).
2.3.1 Sodium Hydroxide NaOH

The alkaline activator most widely used in geopolymerization is sodium hydroxide. This is due to its relatively cheap cost, easily available and has a low viscosity (Vickers et al., 2015). The concentration of the OH⁻ species in the alkaline solution of sodium hydroxide should be taking into perspective during the synthesis as this determines the pH of the solution (Sarmin et al., 2014).

Sodium hydroxide deployed as an activating solution in geopolymerization has resulted in notable geopolymers structures (Provis et al., 2005b). This is because the aqueous concentration of NaOH in the synthesis has a dual role of participating in the destabilization and bonding of the structure formed. Gao et al., (2014) noticed an improvement in the geopolymerization reaction of nano-sized metakaolin based geopolymer as a result of increased dissolution of Si and Al when concentration of sodium hydroxide was increased.

The negatively charged aluminates uses the alkaline metal cation to stabilize under the influence of OH⁻ as a catalyst. If there is too much concentration of OH⁻ in the reaction, it can cause the precipitation to occur quicker thereby yielding a product with a reduced compressive strength. Sodium cations has been proved to release silicate and aluminate monomers (Duxson et al., 2005).

The smaller size of sodium cations compared to potassium cations also makes it a preferable choice in the formation of zeolite structure during geopolymerization. The size together with an increased charge density of sodium cations enable easy movement through the gel structure (Xu and Deventer, 2003). It is known that the aluminosilicate dissolution rate is a function of alkali metal ion.

Sodium cation is more visible in reactions because of its ability to react with small monomers coupled with the crucial role played by particle size in the reactivity of a solution. Therefore minerals tend to dissolve easily because of the high solubility rate of Al³⁺ and Si⁴⁺ in NaOH solution (Xu and Deventer, 2000). However, if there is too much sodium in the geopolymers it may lead to efflorescence.
2.3.2 Potassium Hydroxide KOH

Aluminosilicate minerals can also be activated by potassium hydroxide typically resulting in the formation of zeolitic structures (Duxson et al., 2007). Metakaolin activated with potassium hydroxide lowers crystallization and carbonation is also most likely. The bigger size of alkali metal ion present in potassium hydroxide compared to sodium hydroxide which is $K^+$ means that it will react with bigger silicate monomers (Provis and Deventer, 2009).

This invariably means that minerals synthesized with potassium hydroxide solution is likely to produce a geopolymers of acceptable compressive and tensile strength because of lower surface charge density of $K^+$ cation which increases geopolymerization. The high basicity of $K^+$ compared to $Na^+$ makes it possible for silicates to dissolve quickly. Too much potassium hydroxide in a geopolymer mixture can cause a reduction in compressive strength due to the same explanation with sodium hydroxide.

Cheng and Chiu (2003) found an optimum molar concentration for granulated blast furnace slag to be 10M and noticed that an increment in the molar concentration of potassium hydroxide of more than 10M during activation resulted in an increase in $K^+$ thereby reducing the compressive strength. The rate of polycondensation in the synthesis increases when activated with potassium hydroxide solution thereby boosting the strength of the geopolymer product (Phair and Deventer, 2002).

2.3.3 Sodium Silicate $Na_2SiO_3$

Sodium silicate also called “water glass” or “liquid glass” can also be used as an alkaline solution for activating aluminosilicate minerals. They can exist in both aqueous and solid form and has found so many applications in its usage as cement, concrete sealant, admixtures and fire resistant (Phoo-ngernkham et al., 2015). Their binding ability, adhesive properties and their availability has made it a very useful material in geopolymerization (Dimas et al., 2009).

Sodium silicate reactions vary in both alkaline and acidic media. The reaction in the acidic medium produces silicic acid which when further heated produces a glassy silica
gel while their reaction in alkaline solution is stable. They can also react with alkali metal cations forming insoluble silicates. Criado et al., (2007) noted an increase in ionic species polymerization which in turn increases the mechanical resistance of a geopolymer product when activated by a water glass.

Sodium silicate solutions can be used solely as an alkaline activating solution or in combination with sodium hydroxide or potassium hydroxide. The combination of sodium silicate and sodium hydroxide as an activator can significantly increase the compressive strength of a concrete (Hardjito et al., 2004). The formation of geopolymer synthesis in fly ash based geopolymers is influenced by increased viscosity of sodium silicate solutions (Zhuang et al., 2016). The viscous nature of sodium silicate solution depends on its concentration, temperature and modulus.

2.3.4 Potassium Silicate $\text{K}_2\text{SiO}_3$

The use of potassium silicate in geopolymer synthesis has been widely reported. They can undergo synthesis in the laboratory and are also widely available. The physical properties of potassium silicate solutions is similar to that of sodium silicate but the viscous nature of potassium silicate can be a bit higher than that of sodium silicate when they are of equal concentration (Vickers et al., 2015).

Potassium silicate solutions is composed of silicate anions that are tetrahedral in nature. Xu and Van Deventer (2002) concluded that geopolymer synthesized with potassium silicate produces a fly ash of high compressive strength with no cracks. This may be due to the presence of $\text{K}^+$ in the solution which has large cation that speed up the production of geopolymer structures (Van Jaarsveld and Van Deventer, 1999).

Their inclusion in geopolymerization as an activator produces a strong and durable geopolymer (Nugteren et al., 2009; Yliniemi et al., 2016). It reacts with other materials easily due to its increased solubility and even at higher temperatures does not cause efflorescence (Vickers et al., 2015). However, potassium silicate is more expensive than sodium silicate.
2.4 Milling

Milling helps in releasing essential materials from large compact materials by breaking them down into smaller particle sizes (Sibanda et al., 2016). The widely used method of reducing materials to comparatively fine sizes is by ball mill because of its efficiency at increased energy inputs (Fuerstenau et al., 1999). A ball mill is used to convert a slag material into powdery substances. The ball mill container is cylindrical in shape which can be rotated by a mechanical device as illustrated in Figure 2. The powdery substances desired can be obtained by modifying the steel balls specifications. The cylinder is being rotated by the action of centrifugal force that raises the balls and allows it to fall on the material thereby grinding the material.

Figure 2: A schematic illustration of ball milling (Fuerstenau et al., 1999)

The milled substances produced can be utilized in concrete and can have a significant impact on the shear strength, compressive strength and tensile strength of the concrete. Komnitsas et al., (2007), explained that the reactivity of non-ferrous slags when used in the synthesis of geopolymers is very low when compared to the blast furnace slag. The subjection of the slag to milling can improve the reactivity of the slag.

Kumar (2010) concluded that milling decreases the particle size as well as increase the flow of heat during alkali activation. An increase in time of milling can also increase compressive strength of the geopolymers. An important factor in milling is the mill speed which determines the milling efficiency and how fine the material will be. Also of
importance is the diameter of the milling container, the diameter of the ball to mill as well as the ball size (Deniz, 2004).

In other words, the particle size obtained is a function of the size of the ball and the milling method which in turn determines the efficiency of the ball mill (Fuerstenau et al., 1999). The ball filling in the mill determines the impact of breakage. An increment in ball filling increases the breakage and continue to reduce as an optimum level is attained (Fortsch, 2006). The milling process has little or no effect on the slag composition as the significant oxides present in them does not witness any visible change (Bouaziz et al., 2016).

2.5 Particle size Distribution

Particle size distribution is an important property of a material that provide an insight into the size and distribution of material within a given fraction (Pieri et al., 2006). Criado et al., (2007) emphasized the influence the particle size have on the activation rate as well as the chemical composition of the geopolymer product. It was originally used in determining various soil properties as well as grain size analysis.

Based on the above stated reasons, the reactive ability of the slag and its retaining capacity as a function of particle size distribution has been understood (Tan et al., 2014). The analysis can be done by calculating the different fractions inherent in the material and characterizing them based on the material (Beuselinck et al., 1998). Various particle size distribution methods are employed in analyzing the physical and chemical properties of a material each having its own advantages and disadvantages.

The coarse fractions are usually analyzed using sieving method while the fine fraction are analyzed with the help of hydrometer. Other ones include powder and gel homogeneity determination as well as laser diffraction method (Eshel et al., 2004). Most recently is the use of mathematical models and methods in characterizing particle size distribution (Marti, 2002). Celik (2009) noted that particle size distribution plays a crucial role in controlling the activator demand, setting and hydration reactions.
It has been established that GGBFS slag containing large number of small particles has higher cementitious phases since aluminate and silicate occurs in smaller particles (Wang et al., 2011). The whole idea of particle size distribution is to give an insight on the hydration of slag particles as well as reactivity rate of each fractions.

Tan et al., (2014) observed that slag containing large number of fine particles has higher reactivity rate than the one with coarser particles due to large surface area inherent in fine particles. Zhang et al., (1999) noticed the influence of a smaller particle size on the alkali silica reaction and concluded that there exist a larger surface area in material with smaller particle size and this increases both expansion and reaction rate as compared to coarser materials.

2.5.1 Sieve Analysis

Sieving test is carried out to determine the particle size distribution of a granular material. In other words, it is used in fractionating mixed granulated material of identical dimensions (Obradovic et al., 2009). The procedure is performed when each particle fractionating component is to be measured for further analysis such as flowability and rate of solubility. It entails pouring a known sample of slag material into a sieve under constant agitation to allow the passage of materials through the sieve openings.

The modification of the sieve vibration and amplitude helps in breaking down the agglomerates formed in the material (Obradovic et al., 2009). For an accurate result, a reduction in the percentage passing is expected with an increase in sieving time (Syvitski, 2007).

Sieving is made possible through the arrangement of sieves such that the sieves containing the coarsest material is on top and pan containing the residue is at the bottom. Depending on the sieve sizes, vibration produced by the equipment allows the passage of smaller particles while larger particles are retained in the sieve (Gee and Or, 2002). In fly ash material activation, screening has been found to increase the surface area thereby increasing the amount of material that can be activated with an alkali (Silverstrim et al., 1997). Sieving is one the most widely used technique to determine
the particle size distribution of any material because it is easy to use as well as quick analysis. The sieve analysis is assumed to be complete when the amount of material passing through in a two minutes operation is not more than two percent of the overall sample weight.

2.5.2 Laser Diffraction Particle Analysis

The need for accurate and concise method to measure particle size distribution of materials has led to the emergence of laser diffraction particle analyzer. The diffraction method is a standardized one and can either be dry or wet method depending on the material to be analyzed and the dispersant to be used (Arvaniti et al., 2015).

Laser diffraction particle analyzer has found applications in size distribution of emulsions and slags. The reason for its wide usage is due to its detailed and comprehensive examination of various fractions that makes up the material which other methods might not be able to analyze (Beuselinck et al., 1998). The possibility of standardizing them for some specific systems has enhanced the reliability of their data (Stojanovic et al., 2012). The data obtained is a function of the material type, the apparatus, measurement procedures and interpretation of results.

The Fraunhofer diffraction mechanism is the basis for laser diffraction analysis which stipulates that the scattering intensity of a particle is related to the particle size of the sample. The size of the particle decreases with an increasing angle during analysis (Loizeau et al., 1994). The wide acceptability of this method over other conventional methods for particle size distribution analysis is partly due to some the advantages it possess. It has the ability of utilizing small amount of samples (0.5-1g) for analysis. It also has increased repeatability, quick analysis and can fractionate particle sizes (Brah and Verma, 2011).

Even though the method is based on spherical assumption of particles, the high repeatability of this method gives a comprehensive and clearer insight into the various particle sizes (Xu, 2015). However, there is probability of unequal representation of all the particles sizes in a batch sample during analysis.
2.6 Elkem Material Mixture Analyzer (EMMA)

Elkem material mixture analyzer software is typically used for concrete, its application has been previously reported in cement applications (Fennis and Walraven, 2012). The software has also been used to determine the particle size distribution of a wide range of products such as paste, mortar and other cementitious materials. It helps to calculate the optimum particle packing required for a particular mixture that can enhance mechanical strength as well as minimize liquid addition (Funk and Dinger, 2013). The filling of the void spaces in larger particles by fine particles gives an optimum particle packing as illustrated in Figure 3.

An accurate analysis of particle sizes offers the possibility of getting a mixture with better workability and mechanical properties. The flowability of the mixture can be adjusted by addition and subtraction of materials. Any slight alterations in the composition of the materials can affect the particle size distribution curve as well as their properties. This gives an idea of the optimum mixture combinations needed for a particular mix design.

The value of the distribution modulus (q) influences the workability of the mixture. While a higher q value provides a steeper slope and poor workability, a lower q value raises the fine content thereby providing a better workability (Silva et al., 2010). A distribution modulus that is close to or equal to 0.37 improves the material packing density thereby reducing the amount of water needed.

Silva et al., (2010) also discovered that an Andreasen distribution modulus (q) close to 0.22 results in an optimum thickness for the paste. The knowledge of material been used for the mixture is crucial in the calibration of the q value chosen for the mix. The optimum particle packing of the mix design obtained from the mixture is therefore compared with the Andreassen model (standard particle packing). Other parameters needed for the mixture will be calculated and added during laboratory experiment.
Other parameters that are considered in geopolymerisation that could influence its synthesis and properties are discussed below in the subsection namely: liquid-to-solid ratio, curing conditions and setting time

2.7.1 Liquid to Solid Ratio

In this thesis however, we use the term “liquid to solid ratio” meaning the mass of the potassium silicate + NaOH (=water + liquid Na₂O + liquid K₂O + liquid SiO₂) as against the mass of fayalite slag

The mechanical properties of most geopolymer is generally influenced by liquid to solid ratio. Xu and Deventer (2000) confirmed that geopolymer synthesis requires a source material- alkaline solution ratio of 3 resulting in gel formation. Cheng et al., (2015) concluded that there exist a relationship between porosity and liquid to solid ratio. He observed that an increment in liquid to solid ratio causes a decrease in values of porosity but causes an increase in the mechanical and compressive strength of waste catalyst metakaolin geopolymers.

Kumar (2016) in contrast opined that the compressive strength of fly ash increases with a decrease in liquid binder ratio which is partly due to hydroxide ions which helps in quick dissolution. The use of highly alkaline NaOH in this work helps in dissolving the
source material quickly. Also the importance of water in geopolymerization cannot be overemphasized as it hydrolyses $\text{Al}^{3+}$ and $\text{Si}^{4+}$ ion (Zuhua et al., 2009).

Provis et al., (2009) discovered that the activating solution with low silica content such as NaOH can provide an increased binder strength even at higher liquid to solid ratio. Gao et al., (2014) while working with nano silicate metakaolin based geopolymers concluded that there exist a variation in compressive strength of the product as a result of increment in the liquid to solid ratio. Yao et al., (2009) stressed the importance of solid liquid ratio to geopolymerization synthesis and concluded that the synthesis of geopolymer could be extended if the liquid to solid ratio is high.

2.7.2 Curing Conditions

The temperature at which geopolymers are cured has a significant influence on the geopolymerization (Helmy, 2016). Another parameter which can be involved in this reaction is humidity and the ambient air. An increase or decrease in temperature impact on the strength of the mixture (Jansen and Christiansen, 2015). Various studies carried out by researcher’s shows that curing at higher temperatures increases mechanical strength. There is a limit to which the heat temperature should reach above which the strength of the geopolymer tends to decrease (Lemounga et al., 2016).

A temperature of 60°C is suitable for curing with a maximum being 100°C irrespective of the material. Curing could either be an elevated or intermittent one. The type of curing to be employed must take into cognizance some factors such as liquid solid ratio, molar ratio as well as the resting period (Al Bakria et al., 2011).

Mo et al., (2014) explained that curing at elevated temperature enhances quick dissolution of metakaolin thereby minimizing the time required for setting. It is also to be noted that an increase in temperature invariably means that there will be reduction in polymerization rate of the materials and this will be reflected in geopolymer mixture properties.

Chindaprasirt et al., (2007) concluded that a large part of moisture that is needed for geopolymerization will be lost when curing fly ash geopolymer at high temperature.
thereby reducing their strength. This was further buttressed by Hardjito et al., (2004) which states that an increment in curing temperature above 60°C does not correspond to an increment in compressive strength for fly ash based geopolymer. The strength of a geopolymer is also related to the curing time.

Rovnanik (2010) studied the effects of curing on metakaolin at various temperatures and concluded that metakaolin display a good mechanical strength for the first few days when cured at elevated temperature but a shows a rapid decline in properties as it approaches the 28 day as compared to the ones cured at room temperature.

Khale and Chaudhary (2007) emphasized that continuous curing at higher temperature dries up the water in the mixture which leads to a structural failure. Vu et al., (2012) noted that the curing temperature causes an alteration in the hydration reaction thereby affecting the microstructure of the cement paste. Taylor (1997) discovered the rapid rate of cement paste hydration when the temperature was increased.

Escala- Gacaria and Sharp (1998) confirmed that the pore size and density of the cement paste increased with increase in temperature. The rapid change in the microstructure affects the mechanical properties of the paste thereby making them weaker. The sudden absence of water causes the mixture to squeeze and shrink and might sometimes crack as a result of incomplete geopolymerization process (Cervera et al., 2002).

2.7.3 Setting Time

The initial setting of geopolymer occurs when aluminosilicate materials condensation and precipitation rate is higher than its dissolution rate (Duxson et al., 2005). The setting time provides a detailed information on the setting process as well as changes in microstructure prior to hardening (Puligilla and Mondal, 2013). A lot of factors can influence the setting of hardened products.

Chemical addition in cement and concrete research has been found to influence the hydration of the cement and can either fasten or reduce setting time (Lee and Van Deventer, 2002). Chang (2003) discovered that there exists a relationship between
activator concentration and setting (initial and final setting). According to IS 4031 (1988), the initial setting time is calculated from the time the activator is added to the source material up to the time the Vicat needle cannot penetrate a distance of less than 3mm from the bottom of the mould. The final setting time occurs when the mixture has attained some firmness up to 37mm.

Perna and Hanzlicek (2016) also confirmed that even though the use of blast furnace slag was found to increase the setting time, a slight modification in the binder ratio as well as mixing ratio results in the alteration of setting times.

Gao et al., (2015) when blending nano-silica with fly ash and slag noticed an alteration in setting time as a result of faster dissolution rate which quickens the reaction process thereby resulting in short setting time. Lee and Van Deventer (2002) concluded that the presence of aqueous salts has an effect on the setting times. While the introduction of calcium salts reduces the setting time, the magnesium salt does not reflect a significant influence on the setting time.
3 EXPERIMENTAL AND RESEARCH METHODOLOGY

3.1 Geopolymer Constituents

This chapter discusses the various methods and techniques that were employed in executing the research work in order to accomplish the stated aims and objectives. This is to explain in a detailed manner how the research was carried out. It also discusses the materials and methods, sampling, analytical procedures, sample size of research work, research instrument and sampling.

The material used for the research is fayalite slag (Figure 4). It is an important waste/by-product obtained from nickel production. Similarly to the fayalite slags described in the literature review, this slag composes mainly of iron and silicon as shown in Table 1. Owing to its chemical properties or composition, it is an important source material in this synthesis.

Figure 4: As-received fayalite slag.
Table 1: Chemical properties of fayalite slag

<table>
<thead>
<tr>
<th>Oxides</th>
<th>XRF (% Content)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CaO</td>
<td>1.5</td>
</tr>
<tr>
<td>SiO$_2$</td>
<td>34.8</td>
</tr>
<tr>
<td>Al$_2$O$_3$</td>
<td>2.5</td>
</tr>
<tr>
<td>Fe$_2$O$_3$</td>
<td>52.5</td>
</tr>
<tr>
<td>Na$_2$O</td>
<td>0.5</td>
</tr>
<tr>
<td>K$_2$O</td>
<td>0.5</td>
</tr>
<tr>
<td>MgO</td>
<td>5.1</td>
</tr>
<tr>
<td>P$_2$O$_5$</td>
<td>0.1</td>
</tr>
<tr>
<td>TiO$_2$</td>
<td>0.2</td>
</tr>
<tr>
<td>SO$_3$</td>
<td>0.6</td>
</tr>
<tr>
<td>Cl</td>
<td>0.3</td>
</tr>
</tbody>
</table>

3.2 Sieving Test

The particle size distribution of fayalite slag was determined according to the standard EN 933-1. The materials used for the sieving test are weighing balance, sieve shaker, set of sieves, cleaning brush and slag. For the sieving test, 2000g of a representative fayalite slag was taken and weighed on the weighing balance. A set of sieves with the following sizes (4, 2, 1, 0.5, 0.25, 0.125, and 0.063) mm and pan are utilized for the analysis. Before the analysis, the set of sieves are cleaned from any previous particles or waste by a cleaning brush. The set of sieves were carefully arranged in ascending order from sieve size 4mm at the top to 0.063mm sieve size at the bottom with the pan placed below the sieves to collect the residue.

The selected fayalite slag was poured into the top of the coarsest aperture sieve and covered with a cap to prevent loss of slag powder. The whole sieve arrangement was shaking with the help of vibratory action provided by the sieve shaker as shown in Figure 5. The sieving time and the optimal amplitude is a function of material needed for sieving analysis. The movement of the sample was used to determine the amplitude and this was done by starting with a relatively low sieving time.

An amplitude of 1.5 was chosen while the sieving time was varied from 5, 10 and 20 minutes. The mass of the slag that were retained on each sieve and the bottom pan was weighed. The weight of the empty sieve and sieves with slags were recorded.
3.3 Milling experiments

The milling of the slag was carried out using a ball mill machine (Germatec) as shown in Figure 6. The milling machine was put on and allow to stay for few seconds. A 10 litre ball container was placed in the compartment of the ball mill machine for effective reduction of the slag particles. Before the milling experiment, the 10 litre ball container was first cleaned and dried to remove any previous particles.

Different round diameter steel balls was put in the ball container in different proportions. The variation in sizes and number of balls utilized for the experiment is a function of the material and the output desired. Since the particle size of the slag as depicted in the sieve analysis is less than 4mm, a total of 150 balls was used.

The balls used were of diameter 40mm, 30mm and 25mm. The proportion in which they were arranged are 40mm (45 pieces), 30mm (45 pieces) and 25mm (60 pieces). Batches of 2kg (2000g) as well as 5kg (5000g) of fayalite slag was then put in the ball mill container already filled with the round balls at different intervals. The ball container was then covered with a cap and placed into the compartment of the milling machine.
The milling of the slag was done at the interval of 5mins, 10mins, 15mins, 20mins, 25mins, 30mins, 60mins, 120 mins, 180 mins and 240 mins. The speed of the ball mill used is 5.5 drehzahl. The various fractions of the milled slag was compared and taken for further analysis.

![Germatec ball mill machine](image)

**Figure 6**: Germatec ball mill machine.

### 3.4 Density Measurement

The various size fractions obtained from the milling experiment was taken for density measurement. This is important in calculating the quantity of materials needed for synthesis as well as the determination of the appropriate mix design. The density of the slag material was measured using Accu Pyc II 1340 Gas Pycnometer as illustrated in Figure 7. The mass of each milled fraction used for the density measurement was
determined by putting them into 100cm$^3$ sample cup and weigh using analytical weighing balance. The mass of the sample was recorded.

The pycnometer was carefully cleaned to remove dust that might alter the density measurement. The cap surface is also cleaned with a laboratory wipe and greased. The gas pycnometer uses the idea of gas law and gas displacement technique. The gas pycnometer used utilizes an inert gas called helium for its displacement mechanism. The gas cylinder containing helium was switched on to allow the gas move into the pycnometer.

The pycnometer was switched on and allowed to stay for few seconds and the set up was done. The sample cup filled with slag was transferred from the weighing balance into the sample chamber of the instrument compartment of a known volume and tightly covered with a cap fitting. The slag is then analyzed as a result of the helium being passed into the pycnometer which gives the density by dividing the volume into mass of sample.
3.5 Laser Diffraction Particle Size Distribution Analysis

The particle size distribution of the slag was carried out by laser diffraction particle size analyzer (LS 13320 Beckman Coulter, USA). The preparation of the sample was carefully done to ensure accurate and reliable results. The various milled fractions were analyzed differently to determine their particle size. Both universal liquid module and dry powder module were later utilized to get the actual particle size and prevent agglomeration.

The slag particle was therefore oven dried overnight at a temperature of 60°C before milling. There was a reduction in the water content. The slag was also milled for both 30 minutes and 180 minutes and the laser diffraction analysis was done using the same optimized parameters and under the same conditions.

Different results were obtained from the two batches as there is a variation in the water content and the original material used for the mixture. The oven dried batch still looks wet than the previous batch that was not dried.
3.5.1 Dry Method (Dry Powder Module)

The particle size distribution of the milled slag using dry method was carried out utilizing the dry powder module as shown in Figure 8. The module measures the particle size in the range of 0.375 to 2000µm. Unlike the universal liquid module that produces three runs with a single sample, the dry powder module produces just a single run for one sample. A thirty minutes milled slag was used for the particle size distribution analysis. The slag sample was moist and contain 1.4% of moisture. To ensure that the slag sample was completely dry, it was placed in the oven at a temperature of 60°C overnight before milling.

To ascertain the level of reproducibility of results, three samples of equal weight (19g) was measured and used for analysis. It is important to note that the elapsed time for analysis must not be less than 60 seconds in order to obtain an accurate result. Each measured sample was then put one by one into the laser diffraction particle analyzer and analyzed. The result of the three analysis was compared and then averaged.

Figure 8: LS 13320 Beckman coulter (Dry powder module).
3.5.2 Wet Method (Universal Liquid Module)

A three hours milled fayalite slag was analyzed for particle size distribution using the wet method. The wet method utilizes the universal liquid module. A slag sample (range of 0.5g-1g) was put in a glass crucible and measured. A small volume of water is added to the measured slag in the crucible to dissolve and disperse the particles present in slag. The dispersion in water can be done because fayalite slag does not react significantly with water.

The already dispersed slag was further diluted up to 100ml in the glass beaker to enhance further dispersion. This was then placed in the ultrasonic bath for one minute for enhanced dispersion of particles (Okuda, 2013). The mixture is now thoroughly mixed or stirred using a mechanical mixer. The sample injected into the machine was properly dispersed and a representative was taken from the sample and put into the machine.

The instrument measures the particle size in the range of 0.040-2000µm and uses the Fraunhofer diffraction model. During the laser diffraction analysis, some results shows that there is presence of agglomerates in the milled powder. The method of preparation and the instruments used in process operations were modified. Due to the difficulty in achieving some level of reproducibility, a lot of parameters were optimized to obtain a reliable result.

The parameters optimized are rate and mode of stirring, frequency of the ultrasonic, particle dispersion duration, measurement time as well as obscuration levels. This became imperative due to different particle size distribution results obtained from the instrument when analyzing the same material.

To eliminate variation in the PSD results, the analysis was done using the same sample analysed in three replicate sequential runs together with two samples analysed from the same material obtained from the same container. The analysis of same sample in a repeated sequential runs show low level of uncertainty. This were combined together and their results averaged. The milling effect could also have a significant influence on the particle size distribution of the material as the rate of impact of the balls could differ.
even though the number of steel balls are the same. The average was used to arrive at a reliable value for both batches.

3.5.3 Rate/Speed of Stirring

The difference in particle size distribution results is partly attributed to the variation in the stirring rate of the materials so that the representative sample used for each analysis differs from each other. To avoid this variation, an IKA EUROSTAR 20 HIGH SPEED DIGITAL mixer shown in Figure 9 was used for mixing. Since the mixing is turbulent, two plastic barriers were placed in the direction of mixing as shown in Figure 9 to ensure proper mixing and prevent the material from mixing in a spherical manner.

Five analysis performed with different speed yielded different results. It was observed that at low stirring rate, there was little or no force needed to raise or suspend the bigger particles in the material thereby affecting the results. The five analysis has different $d_{50}$ values and the samples with higher $d_{50}$ values was subjected to higher stirring rates. The stirring rate was then regulated and set at a fixed value of 1700 rev/minute to eradicate the fluctuations in the result of the analysis.
Figure 9: High shear speed mixer
3.6 Geopolymer Synthesis

The alkaline activating solution used are sodium hydroxide pellets and potassium silicate solution (Betol K 35T) was used for the experiment. It is composed of $K_2O= 10.92\%$, $SiO_2= 23.9\%$ and $H_2O= 65.18\%$. The mix design is reported in Table 2. A 50:50 mass ratio of both sodium hydroxide and potassium silicate was mixed to produce an alkaline activating solution. The mass ratio was later adjusted to 75:25 as well as 25:75. The reason for the variation is to determine the reactivity rate of the slag material under activating solution of different mass ratio for comparison. The alkaline solution was left to cool for 24 hrs.

The particle packing design for the mortar geopolymers were done with Emma software shown in Figure 10. A wide range of trial mixtures were performed to achieve an optimum mix design for the matrix.

One of the objectives of this research was to optimize the particle size so as to obtain a good mix for the geopolymer matrix. The optimization was done with the help of “Elkem Material Mixture Analyzer”. Various mix design were obtained and value that produces a curve that best fits an Andreassen curve was used. Example of a mix is shown in Figure 10.
Figure 10: An example of a material mixture for mortar matrix. The red line represents the Andreassen curve (ideal mix) while the blue line represents the cumulative particle size distribution curve. In this mix design three different size fractions were used.

The Figure 10 above is the curve generated for the mortar. Since the Emma software generates a curve based on careful selection of the small sized fraction to fill the voids between the bigger particles, getting a curve that best matches the Andreassen curve was time consuming. This is because it is based on trial and error method. An Andreassen curve depicts an ideal mix.

During the optimization, the minimum particle size was placed at 0.1µm while the maximum particle size was placed at 2000µm. The density of each fraction was imputed into the software. The material provide a very good flow and good fit when the Andreassen distribution modulus (q) is 0.27 for mortar. The whole idea of optimizing is to control various size fractions in the mix so as to obtain a suitable mix design that gives highest flowability with minimal liquid addition.

Since a variation in the proportion of different size fractions alters the packing density, it was observed that a change in the proportion or composition of the materials result in a change in the properties of the particle size distribution. The mix design was made by
addition and subtraction of three different size fractions (as received material, FS 30 and FS 180) with the distribution modulus varied from 0.27 to 0.37.

The mix composition generated for the mortar were used in the mix design. Other curve with different q value does not show a matrix with a good fit and are therefore discarded. For mortar, it was discovered that Figure 10 shows a very good fit and flow with the cumulative particle size distribution (blue line) matching the ideal mix q (red line). It therefore shows a mixture that has a very good optimum packing.

According to the Elkem manual, a higher q value produces a mix that is less workable and tends to be coarse. In this research the best particle packing was achieved with a distribution modulus (q) value of 0.27. This is because it was discovered that a mix design with lower q value produces a mix with high level of workability due to the presence of more fine materials in the mixture. The fine materials present occupy the voids in between bigger particles and enhances binding activity.

This is in consonance with the Elkem manual which stipulates that an optimum particle packing can be achieved with a q value of less than 0.36, while a q value of 0.28 is advisable for a self-compacting concrete. Schmidt et al., (2012) concluded that for ultra-high performance concrete, a q value of less than 0.28 provides a mixture with higher percentage of fine material thereby yielding a very good flow. Silva et al., (2010) opined that the maximum paste thickness was achieved with a distribution modulus q of 0.22 due to non-adherence between the bigger particles The Emma was used to combine together different size fractions as a function of the distribution modulus.

The liquid solid ratio of the mix design were also reduced. When using the Emma software, there was a good match between the cumulative particle size distribution curve and the ideal mix curve (Andreassen curve) when a q value of 0.27 was used. This has further confirmed that distribution modulus (q) of 0.27 generates a material mixture that is minimum of void with a very good flow and fit.

During the preparation of the mix design in the laboratory, all mix design were mixed starting with a liquid solid ratio of 0.1. From the Table 2 below, the liquid solid ratio of 0.1 was good for (M8). The liquid solid ratio for the (M9) has to be increased to 0.12 to
increase the fluidity of the mortar. It is evident from the Table 2 below that the mixture composition of (M9) has more percentage of fine materials than M8 and hence the reason for the increase of the activator from 0.1 to 0.12. For M12 and M13 mix design, it can be seen that the three hour milled size fraction is almost equivalent to the addition of both the original material and thirty minutes milled size fraction. This justifies the increment of its activator to 0.15.

Table 2: Mix proportion for GD#1 and GD#1a

<table>
<thead>
<tr>
<th></th>
<th>Notation</th>
<th>Alkaline Activator</th>
<th>Mix Design</th>
<th>Solid total mass (g)</th>
<th>As-received material (g)</th>
<th>FS 30 (g)</th>
<th>FS 180 (g)</th>
<th>Liquid (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>GD#1</td>
<td>M 1</td>
<td>10 M NaOH + K-Sil (50:50)</td>
<td>Mortar, L/S=0.20, q=0.37, RT</td>
<td>100</td>
<td>32.25</td>
<td>46.74</td>
<td>21.01</td>
<td>20</td>
</tr>
<tr>
<td>GD#1</td>
<td>M 2</td>
<td>10 M NaOH + K-Sil (50:50)</td>
<td>Mortar, L/S=0.175, q=0.27, RT</td>
<td>100</td>
<td>28.48</td>
<td>35.59</td>
<td>35.92</td>
<td>17.5</td>
</tr>
<tr>
<td>GD#1</td>
<td>M 3</td>
<td>10 M NaOH + K-Sil (50:50)</td>
<td>Mortar, L/S=0.175, q=0.27, RT</td>
<td>100</td>
<td>32.25</td>
<td>46.74</td>
<td>21.01</td>
<td>17.5</td>
</tr>
<tr>
<td>GD#1</td>
<td>M 4</td>
<td>10 M NaOH + K-Sil (50:50)</td>
<td>Mortar, L/S=0.15, q=0.27, RT</td>
<td>100</td>
<td>24.48</td>
<td>35.59</td>
<td>35.92</td>
<td>15</td>
</tr>
<tr>
<td>GD#1</td>
<td>M 5</td>
<td>10 M NaOH + K-Sil (50:50)</td>
<td>Mortar, L/S=0.15, q=0.37, RT</td>
<td>100</td>
<td>32.25</td>
<td>46.74</td>
<td>21.01</td>
<td>15</td>
</tr>
<tr>
<td>GD#1</td>
<td>M 6</td>
<td>10 M NaOH + K-Sil (100:0)</td>
<td>Mortar, L/S=0.20, q=0.37, RT</td>
<td>100</td>
<td>32.25</td>
<td>46.74</td>
<td>21.01</td>
<td>20</td>
</tr>
<tr>
<td>GD#1</td>
<td>M 7</td>
<td>10 M NaOH + K-Sil (0:100)</td>
<td>Mortar, L/S=0.20, q=0.37, RT</td>
<td>100</td>
<td>32.25</td>
<td>46.74</td>
<td>21.01</td>
<td>20</td>
</tr>
<tr>
<td>GD#1a</td>
<td>M 8</td>
<td>10 M NaOH + K-Sil (50:50)</td>
<td>Mortar, L/S=0.10, q=0.27, RT</td>
<td>100</td>
<td>39.99</td>
<td>40.02</td>
<td>19.98</td>
<td>10</td>
</tr>
<tr>
<td>GD#1a</td>
<td>M 9</td>
<td>10 M NaOH + K-Sil (50:50)</td>
<td>Mortar, L/S=0.12, q=0.27, RT</td>
<td>100</td>
<td>28.48</td>
<td>35.59</td>
<td>35.92</td>
<td>12</td>
</tr>
<tr>
<td>GD#1a</td>
<td>M 10</td>
<td>10 M NaOH + K-Sil (75:25)</td>
<td>Mortar, L/S=0.15, q=0.27, RT</td>
<td>100</td>
<td>28.48</td>
<td>35.59</td>
<td>35.92</td>
<td>15</td>
</tr>
<tr>
<td>GD#1a</td>
<td>M 11</td>
<td>10 M NaOH + K-Sil (25:75)</td>
<td>Mortar, L/S=0.15, q=0.27, RT</td>
<td>100</td>
<td>28.48</td>
<td>35.59</td>
<td>35.92</td>
<td>15</td>
</tr>
<tr>
<td>GD#1a</td>
<td>M 12</td>
<td>10 M NaOH + K-Sil (75:25)</td>
<td>Mortar, L/S=0.15, q=0.27, RT</td>
<td>100</td>
<td>24.99</td>
<td>24.96</td>
<td>50.05</td>
<td>15</td>
</tr>
<tr>
<td>GD#1a</td>
<td>M 13</td>
<td>10 M NaOH + K-Sil (25:75)</td>
<td>Mortar, L/S=0.15, q=0.27, RT</td>
<td>100</td>
<td>24.99</td>
<td>24.96</td>
<td>50.05</td>
<td>15</td>
</tr>
</tbody>
</table>

Using the Kenwood mixer, the various fractions were mixed together for thirty seconds then the walls and bottom of the mixer scraped to ensure uniformity. It was further mixed for another thirty seconds totaling one minute. In reference to Table 2, an already calculated liquid amount for the mixture was then poured into the homogenized powders and mixed for one minute, then the walls and bottom of the mixer was scraped, then the matrix mixed for another one minute totaling two minutes.
3.6.1 Curing

After mixing, the samples were cast into 69mm x 32mm cylindrical plastic moulds, covered and then hit on the table ten times to remove air bubbles before being placed into a small plastic bag. The plastic bags was then tightly sealed to avoid the loss of water due to evaporation. The mortar was cured at room temperature of 23±2°C for 3, 7 and 28 days. Thereafter, they were all placed at room temperature until further analysis.

3.6.2 Compressive Strength

Test specimens were produced using the mix design from Table 2 and were subsequently tested according to standard test method for compressive strength using Zwick/Z100 with maximum loading force of 100 KN. The test was carried out by subjecting the specimen to a compressive load at 2mm/min until it fails.

The test was carried out after 3, 7 and 28 days after casting and curing at room temperature. Before strength test, each end of the specimen were smoothened and polished with the use of a PM 80 and PM 120 sand paper to give a clean, smooth and levelled surface required for testing. For each mix design in Table 2, three samples were tested and the average value reported as compressive strength in megapascal (MPa).

The compressive strength (σ) result was based on the following equation

\[ \sigma = \frac{F}{A} \]

Where

\[ A = \pi r^2 \]

F = Maximum load in N
A = Specimen cross sectional area in mm²

3.6.3 Water Absorption

The water absorption of the fayalite geopolymer samples was determined according to the standard ASTM C642-06. The specimen was first weighed to determine the initial
weight. The geopolymer specimen was later dried in the oven at a temperature of 80°C for a duration of 24 hours. Immediately after removal from the oven, it was weighed again to determine the oven dried weight ($W_1$). The specimen was later taken out of the oven and immersed in distilled water for another 24 hours duration. The specimens are then removed from the water and their surface are cleaned and wiped with an absorbent cloth to remove excess water retained on the mortar. The specimens are then weighed again and this is known as the saturated weight ($W_2$). The percentage water absorption was then determined using the equation:

$$\text{% Water absorption} = \left( \frac{W_2 - W_1}{W_1} \right) \times 100$$

The residual strength was also determined after the water absorption determination.
4 RESULTS AND DISCUSSION

The results of this research is grouped under the following headings for clarity

- Material Milling and Characterization
- Particle size optimization
- Preparation of test series
- Characterization of hardened samples

4.1 Material Milling and Characterization

4.1.1 Sieving test results

The as-received material used for the experiment is a fayalite slag. Before any characterization was done, the sieving analysis of the slag particles was first done. Two batches (GD#1 and GD#1a) of the slag was used and the sieving analysis of both were compared.

![Graph showing sieve analysis comparison between GD#1 and GD#1a](image)

Figure 11: Sieve analysis comparison between GD#1 and GD#1a. Batch GD#1 had slightly smaller particle size.
Figure 11 above shows that the particles have diameter falling in the range of 1-2mm. The comparison shows that there exist some bigger particles in the second batch of the slag (GD#1a). The coefficient of uniformity of GD#1 was found to be 3mm while that of GD#1a was 2.5mm. According to the United States soil classification, if the coefficient of uniformity obtained is less than 6mm, the material is said to belong to the sand range with the bulk in medium to coarse sand. There appears to be a variation in the sieve analysis of different batches of the fayalite slag used for the analysis.

From Figure 11, 23.58% of GD#1 slag passes through a 1 mm sieve size while only 15.65% of GD#1a passes through 1 mm sieve size. The variation in the sieve result is expected to have an influence on the mixture. For this study, both batches were utilized. From the analysis of the two batches, it is obvious that milling of the sample is inevitable before it can be alkali activated as previously highlighted.

### 4.1.2 Particle size distribution (PSD) analysis

The PSD analysis of the different milled fractions was compared with the sieve analysis of the original material as shown in the Figure 12 below. Even though the milling was done from 5 minutes to 240 minutes, it was discovered that after 3 hours of milling the particles are close to the fineness of commercial cement. The reason for milling for an interval of 5 to 240 minutes was to get different fractions distribution that will give the matrix a good filler/packing effect and good mechanical properties.

For this research work, only three fractions were utilized for the geopolymer synthesis out of all the sub groups. This proportion uses both 30 minutes (FS 30) and 180 minutes (FS 180) milled slag together with the as-received material in Figure 4. Particle size of the 30 minutes milled slag was determined using the dry powder module before a reproducible results could be attained while the universal liquid module was utilized in determining the particles size distribution of 180 minutes milled slag as a result of agglomeration of particles after longer hours of milling.
In reference to Figure 12, it can be concluded that the particle size reduces with increasing milling time. The $d_{50}$ of the as-received material reduces from 2mm to 10.08µm after three hours of ball milling. The FS 180 is the finest while the as-received material (GD#1) is the coarsest.

The reason for conducting a new particle size distribution for the second batch (GD#1a) was that it was discovered that the new batch has 0.5% percent moisture more than the previous batch (GD#1) and the presence of larger particles was also noted. Therefore, new particle size distribution analysis to determine the exact particle size and also compare with the first batch was done.

The results of the particle size distribution of both GD#1 and GD#1a are analysed and compared below.
Figure 13: Median size comparison between GD#1 and GD#1a

From Figure 13, it was discovered that median value ($d_{50}$) of the second batch (GD#1a) was higher than that of the first batch (GD#1). For GD#1a, the median value are FS 30: 384.4µm; FS 180: 23.39µm. For GD#1, the median value are FS 30: 245.7µm and FS 180 is equal to 10.08µm. The reason for this may be due to the presence of moisture in the second batch of the slag material which was not fully eliminated even after drying.

It is also to be noted that laser diffraction analysis itself yields varying results even when analyzing the same sample. Hackney et al., (2004) observed that the real causes of non-reproducibility of results during particle size distribution analysis stems from either the dilution process before analysis or the process of sampling itself. Cepuritis et al., (2016) noted that coarsening of the particle size may occur due to insufficient dispersion of the slag particles causing agglomeration of particles to each other as a result of Van der Waals attraction.

Overall both batches shows that after three hours milling, the particles are fine enough as reflected in their median values and are consequently used for the geopolymer matrix.
4.1.3 Density

The density of the each milled fraction was measured by helium pycnometer. From the measurement, an upward trend was discovered with the milling time as there was a steady rise in the density value as the milling is increased. For example, the density of as-received GD#1 material was 3.82 g/cm$^3$, but the density increased to 3.93 g/cm$^3$ after 3 hour milling. In other words, the density increases with the increase in milling time.

![Figure 14: Effect of milling on density of fayalite slag.](image)

From Figure 14, the density values of the first batch of slag (GD#1) is higher than that of the second batch (GD#1a). It is a known fact that various factors can affect the density measurement some of which might be as a result of dust particles interfering with the measurement or inappropriate sampling techniques.

It is important to note that since density is based on mass and volume estimation, the volume estimation by weight of fayalite slag used for milling is expected to influence the density. It was discovered that the density of milled 2kg fayalite slag differs from the density of milled 5kg fayalite slag.
Even though there exist a trend in the density values as the milling progresses just as in the first batch (GD#1), another noticeable observation is the impact a change in sample weight has on the density values. The density values of the 2kg milled slag (3.51g/cm$^3$) are small compared to the densities of the 5kg (3.60g/cm$^3$) milled slag.

There was also a decrease in the error of the second batch as the milling progresses just as in the first batch. The standard deviation of the as-received material is 0.034g/cm$^3$ which gradually reduces with the milling time to 0.025g/cm$^3$ after four hour milling.

4.2 Physical appearance of geopolymer samples.

The geopolymer samples were analysed visually after 3, 7 days and 28 days (Table 3).

Table 3: Effect of curing regime on mortar appearance of GD#1

<table>
<thead>
<tr>
<th></th>
<th>(M1) Mortar, L/S=0.20, q=0.37</th>
<th>(M2) Mortar, L/S=0.175, q=0.27</th>
<th>(M3) Mortar, L/S=0.175, q=0.37</th>
<th>(M4) Mortar, L/S=0.15, q=0.27</th>
<th>(M5) Mortar, L/S=0.15, q=0.37</th>
</tr>
</thead>
<tbody>
<tr>
<td>3 days</td>
<td>Dark, moist with silicate solution on the mortar</td>
<td>Dark, moist with silicate solution on the mortar</td>
<td>Dark, moist with silicate solution on the mortar</td>
<td>Dry, hard with no silicate solution on the mortar</td>
<td>Dark, moist with silicate solution on the mortar</td>
</tr>
<tr>
<td>7 days</td>
<td>Dark, moist with silicate solution on the mortar</td>
<td>Dark, moist with silicate solution on the mortar</td>
<td>Dark, moist with silicate solution on the mortar</td>
<td>Dry, hard with no silicate solution on the mortar</td>
<td>Dark, moist with silicate solution on the mortar</td>
</tr>
<tr>
<td>28 days</td>
<td>Dark, moist with a reduced silicate solution on the mortar</td>
<td>Dark, moist with a reduced silicate solution on the mortar</td>
<td>Dark, moist with a reduced silicate solution on the mortar</td>
<td>Dry, hard with no silicate solution on the mortar</td>
<td>Dark, moist but no silicate solution on the mortar</td>
</tr>
</tbody>
</table>
Table 2: Effect of curing regime on the mortar appearance of GD#1a

<table>
<thead>
<tr>
<th></th>
<th>(M8) Mortar, L/S=0.1, q=0.27, RT</th>
<th>(M9) Mortar, L/S=0.12, q=0.27, RT</th>
<th>(M10) Mortar, L/S=0.15, q=0.27, RT</th>
<th>(M11) Mortar, L/S=0.15, q=0.27, RT</th>
<th>(M12) Mortar, L/S=0.15, q=0.27, RT</th>
<th>(M13) Mortar, L/S=0.15, q=0.27, RT</th>
</tr>
</thead>
<tbody>
<tr>
<td>3 days</td>
<td>Dark, moist with silicate solution on top of the mortar</td>
<td>Dark, moist with no silicate solution on top of the mortar</td>
<td>Dark, moist with no silicate solution on top of the mortar</td>
<td>Dark, moist with silicate solution on top of the mortar</td>
<td>Dark, moist with silicate solution on top of the mortar</td>
<td>Dark, moist with silicate solution on top of the mortar</td>
</tr>
<tr>
<td>7 days</td>
<td>Dark, moist with a reduced silicate solution on top of the mortar</td>
<td>Dry with no silicate solution on top of the mortar</td>
<td>Dark, moist with no silicate solution on it</td>
<td>Dark moist with silicate solution on top of the mortar</td>
<td>No silicate solution</td>
<td>Dark moist with silicate solution on top of the mortar</td>
</tr>
<tr>
<td>28 days</td>
<td>Dark moist with a reduced silicate solution on top of the mortar</td>
<td>Dry with no silicate solution on top of the mortar</td>
<td>Dark, moist with no silicate solution on it</td>
<td>Dark moist with silicate solution on top of the mortar</td>
<td>No silicate solution</td>
<td>Dark moist with silicate solution on top of the mortar</td>
</tr>
</tbody>
</table>

Figure 15: Mortar with floating silicate solution
From the Table 3 above, it is evident that the mortar (M4) with a distribution modulus of 0.27 when activated with a liquid solid ratio of 0.15 provides a better matrix due to the absence of silicate solution on the mortar after 3 days of curing at room temperature.

Mehdipour and Khayat (2017) observed in their studies, that a combination of higher particle packing with a reduced water demand resulted in significant increase in compressive strength after a long period of curing. At 3 days of curing, all the other mortar had silicate solution retained on them except M4. After 7 days of curing, it was also only M4 that produces a matrix with no silicate solution. Other recipes had silicate solution floating on top of it. This is to show that lowering the liquid solid ratio has a significant influence on the mortar synthesis.

After 28 days, mortar (M5) with a distribution modulus of 0.37 showed no silicate solution but the surface was moist and not as hard as mortar (M4) with a distribution modulus of 0.27. The reactivity rate is higher with q value of 0.27 due to presence of more fine materials that provide increased surface area. The higher the particle size, the lower the surface area.

It took 28 days for a mortar (M5) with a q value of 0.37 before the whole silicate solution could be involved in the reaction. This might be because with q value of 0.37 the reactivity rate was slow due to the presence of more coarse material in the mixture thereby limiting the dissolution of the slag particles.

Criado et al., (2007) noted that rate of activation of a geopolymer precursor is a function of size distribution of particle, source material chemistry and composition as well as the type, nature and concentration of the activator.

4.3 Compressive Strength

The Figure 16 below shows the compressive strength measurement of mortar produced from GD#1 at varying liquid solid ratios. The compressive strength was found to increase with the curing days. The highest compressive strength comes from mortar that has a liquid solid ratio of 0.15 with a q value of 0.27. It can be said that the highest
compressive strength were connected to lower solid liquid ratio and lower q value which results in higher rates of reaction.

The mortar (M4) shows the highest strength value of 16.5 MPa after 28 days of curing at room temperature. The mortar (M3) has the lowest compressive strength of 6.59 MPa after 28 days. This shows that the best activator is the one with 50:50 ratio of NaOH and K₂SiO₃ and this might have contributed to the high strength of M4 as shown in Figure 16. Mortar (M6) and (M7) could not achieve any strength gain due to unequal mass ratio.

From the Figure 16, it can also be discovered that the mortar (M5) with the same liquid solid ratio of 0.15 as M4 but with a different q value of 0.37 shows a much lower compressive strength of 11.13 MPa after 28 days. In this work, the reduction in the liquid solid ratio might have increased the dissolution rate of iron silicate species thereby improving the polycondensation of iron and silica species.

Machiels et al., (2014) noted that only a small fraction of silicon is added when the activating solution is raised and is rather insignificant in relation to what is present in the glass of the material. The compressive strength of mortar prepared using a single activator of either NaOH or K₂SiO₃ could not be measured as the mortar did not harden after 28 days and are therefore discarded.

It was observed that M6 (100:0) and M7 (0:100) geopolymer samples were not hardened after 40 days of curing. For M6, using a single activator of sodium hydroxide means that only dissolution might be taking place without binding activity due to the absence or little silicate present in the reaction. Onisei et al., (2015) noted that aluminum oxide precipitation will occur if the silicate is not present.

For mortar (M7), there is absence of sodium hydroxide which is an important activator to trigger the first process of dissolution of source materials. Onisei et al., (2015) noted that even though fayalite slag are not inert when undergoing alkaline activation, the release of silicon and aluminum are small relative to metakaolin. This means the dissolution rate is not enough in M7 since it is only silicate solution that is present.
Morsy et al., (2014) noted that there tends to be an alteration in the synthesis formation when there is too much silicate solution in the activator resulting in lower compressive strength. Activating with only silicate solution impedes the reactivity rate and alters the structural development of the mortar since dissolution is an important phase in geopolymer synthesis.

Figure 16: Compressive strength result for GD#1
Figure 17: Compressive strength result for GD#1a

The Figure 17 above shows the compressive strength of mortar samples made from batch GD#1a at varying solid liquid ratio. There was an increase in compressive strength from 3 days to 28 days for all mortars. For GD#1a, fayalite slag geopolymer mortar with a solid liquid ratio of 0.12 has the highest compressive strength while slag geopolymer mortar with solid liquid ratio of 0.15 shows the lowest compressive strength. The mortar (M9) achieved the highest strength gain with a compressive strength of 13.34 MPa after 28 days.

It is important to state that mortar sample (M8) has a compressive strength of 10.71 MPa after 28 days even though the liquid solid ratio is 0.1. The reason can be attributed to mix proportion as seen in Table 2. The mix proportion for M9 has higher percentage of fine particles and hence the need for high liquid solid ratio to achieve a mortar with high fluidity.
In reference to the 3 days strength gain, it was shown that two mortar samples (M10 and M12) with high amount of alkali hydroxide did not harden and therefore cannot be determined for the 3 days compressive strength. Even though they have different mixture compositions with similar q value as shown in Table 2, they could not harden after 3 days. This might be due to high amount of NaOH which increases the OH\(^-\) in the synthesis.

Maragkos et al (2009) discovered that the presence of high quantity of sodium hydroxide in the aqueous phase yields geopolymer of low compressive strength as a result of reduction in mass ratio of SiO\(_2\)/Na\(_2\)O which alters the polycondensation process and the binding activity. It was also observed from the Figure 16 and 17 that the compressive strength is highest when the mass ratio of NaOH/K\(_2\)SiO\(_3\) is 50:50.

Any reduction or increase in mass ratio of any of the activator above this ratio yields a geopolymer with lower compressive strength. This is to say that at equal mass ratio, the dissolution rate and the binding phase of iron and silica is increased thereby resulting in an increased compressive strength. The strength development for M11 and M13 are very slow for the first 3 days compared to M8 and M9 as depicted in Figure 17.

The slow development of compressive strength in mortar (M11 and M13) may be as a result of slower rate of dissolution of the iron and silica when it first had a contact with higher silicate content due to very low sodium hydroxide which is an important activator in dissolution process. At 28 days, there was a sharp rise in the compressive strength as M13 has a compressive strength 12.14 MPa. This shows that with higher silicate content compared to alkali hydroxide, a geopolymer of high compressive strength is achievable but it might take longer curing days to achieve sufficient dissolution of the source material. The presence of high amount of silicate is expected to quicken formation of the binder thereby increasing the late compressive strength of geopolymer product.
4.4 Setting time

The standard method for measuring the setting time of a geopolymer is the use of a Vicat needle apparatus. By noting the time at which the activator was added to the mixture up to the time of first needle penetration, the initial setting was determined when the needle penetrates 37mm of the mortar mix. The final setting time was obtained when the needle can penetrate only 3mm of the mortar mix.

![Graph showing setting time of geopolymer mortar](image)

Figure 18: Setting time of geopolymer mortar

The two matrices with high compressive strength was chosen for the setting time measurement as shown in Figure 18. The second mortar (M9) had the lower setting time with the initial setting time being 89 minutes while the final setting time was 326 minutes. The first mortar (M8) has a longer setting time with the initial setting time being 140 minutes while the final setting time was 378 minutes.

Both mortar were in compliance with the European standard (SPRS EN 196-3) which stipulates that initial setting time must not occur before 60 minutes and the final setting time must not exceed 10 hours. Even though the M8 has a lower liquid solid ratio, the setting time was still longer than M9. The reactivity might be lower in the M8 compared to the M9, because it has less fine particles.
Coarser cements are known to take a long time before they set while fine cement particles can undergo full hydration within a day. This can be the reason why coarse cement have reduced strength development compared to fine cements (Cetin et al., 2016).

4.5 Microstructural Characterization

4.5.1 Optical Microscopy

The optical microscopy images (Figures 19) show the microstructural characterization of the reaction in the fayalite geopolymer product. The Figure 19 below shows the microstructure of the fayalite slag mortar after seven days of curing.

Figure 19: Optical microscopy of selected geopolymer samples after 7 days

Fig 19 (b) shows a geopolymer mortar sample (M9) that had the highest compressive strength at a liquid solid ratio of 0.12. Figure 19 (a) shows a geopolymer mortar sample (M8) with lower compressive strength at a liquid solid ratio of 0.1. It was observed in Figure 19 (b) that there was a high particle packing efficiency. Machiels et al (2014) noted that the rate of glass dissolution increases with an increase in activating solution thereby increasing the formation of more matrix.
This is to confirm that particle packing is increased when there are more fine materials that can fill the void between bigger particles. The fine materials reacts with the activator due to increased surface area and forms a gel around the bigger particles. Machiels et al (2014) opined that only a small fraction of glass particles in fayalite slag undergoes full dissolution with the dissolution only occurring in the outer wall of bigger particles. The pores present in Fig 19 (b) are spherical pores formed as a result of air entrapped during mixing.

Figure 19 (a) has a structure that is less compact and the presence of bigger particles are visible. The sample can be regarded as heterogeneous as there is presence of large inter-particle pores and some cracks which is as a result of inability of geopolymer matrix to fill the empty spaces thereby slowing reaction rate. An increase in the hydration helps in filling the holes and pores in the matrix.

The microstructure of the selected geopolymer samples with high compressive strength after 28 days were examined. After 28 days, more geopolymer matrix has been formed as a result of continuous reaction between the activator and slag material and fill up the pores present in M 8.

**4.5.2 Scanning Electron Microscopy**

The scanning electron microscopy of the geopolymer samples are done to confirm the images of optical microscopy. Figure 20(b) shows that most of the fine materials are involved in the reaction thereby forming a binder around the bigger particles. The larger particles are seen in the image though in form of aggregate. The formation of gel around the bigger particles shows the continuous production of reaction products which is a true reflection of the geopolymerization process. This results in an increasing cementing ability between particles and hence an increased compressive strength. In Figure 20(a), there are aggregation of bigger particles with dry gel around it. The gel around the bigger particles.
The use of vibrator can be used to minimize the air voids that are entrained in the sample. Since ‘hitting the sample on the table ten times after casting’ was the method used in this research, this was not effective in removing the air voids which later form some holes in the samples after it hardens. The use of mould releasing agent can also be used to ensure the ease of removing the geopolymer mixture.

4.6 Water Absorption

The results shows that the average absorption is 5.28 percent. It was also discovered that permeability of the specimen is low as the saturated weight over 24 hours is low when compared to the initial weight of the specimen. Water absorption plays a crucial role in the durability of geopolymer samples. Rendell et al (2002) noted that a concrete is termed an average concrete when its water absorption rate does not exceed 5%. The compressive strength of the samples was also carried out after water absorption and compared with the unconfined compressive strength. This is depicted in the Figure 21 below.

From the Figure 21 below, the value of unconfined compressive strength after 28 days is 13.34 MPa while that of the compressive strength after water absorption is 23.84 (MPa). The compressive strength value after water absorption is almost double the
unconfined compressive strength value. The high compressive strength achieved after water absorption value might be influenced by their exposure to elevated temperature. A temperature of 80°C for a period of 24 hours prior to water absorption proved to have increased the strength of the samples since the specimen used for the determination of unconfined compressive strength was cured at room temperature.

Figure 21: Compressive strength of the M9 sample before and after the water absorption test. The compressive strength increased after the water absorption test, which was probably due to the drying procedure in elevated temperature. There was no sign of disintegration of the sample during the water absorption test.

The apparent density is relatively high compared to OPC concrete. This is due to the high density of fayalite slag which is 3000kg/m³ as shown in the Figure 22 below.
Figure 22: Apparent density of mortar (M9).
5 SUMMARY

This research was done to assess the usability of fayalite slag as a precursor for geopolymer when it is subjected to alkali activation as well as study their properties. To achieve this, a reduction in size was done and the particle size distribution of the material was determined. During the course of this study, mechanical and structural properties of geopolymer mortars were analyzed.

In this work, it was confirmed that the optimization of properties of the geopolymer is a function of liquid solid ratio, alkaline activator mass ratio and the particle size distribution modulus. During the optimization, the Emma software serves as a veritable tool in providing an appropriate mixture design by combining various size fractions.

Based on these, the main results are the following:

- Ball mill is effective milling method for fayalite slag. Three hour milling time produced material with median size of 10.08µm, which is sufficient fineness for most binder precursors.
- During optimization, a q value of 0.27 in the EMMA software was found suitable in selecting the best mixture design and this displays a good workability, good fit and high mechanical properties.
- The optimal particle size mix was obtained by mixing approximately one third of as-received fayalite slag, one third of 30 minutes milled fayalite slag and one third of three hour milled fayalite slag.
- Suitable liquid solid ratio is around 0.12-0.15 in order to achieve good workability for the mortar.
- A decrease in the liquid solid ratio resulted in an increase in the compressive strength. Up to 16.5MPa compressive strength was measured after 28 days hardening at room temperature.
- Geopolymer samples with highest compressive strength was attained with alkali activator that had NaOH/K$_2$SiO$_3$ mass ratio of 50:50. The development of the compressive strength is highly dependent of the alkali activator composition.
- Water absorption was only 5.3% showing that the prepared geopolymer has dense structure.
- Setting time of the mortar is in compliance with the European standard (SPRS EN 196-3).
- Fayalite slag geopolymer has relatively high apparent density (>3000 kg/m3) which is due to the high density of the fayalite slag.

This research was focused on valorization of fayalite slag through alkali activation, the material showed promising results and can be further improved by pulverizing the slag to smaller particle sizes i.e. milling for longer hours. Increasing the milling time will further increase the surface area thereby improving the rate of reactivity and consequently the compressive strength of the geopolymer matrix. Also the combination of different curing conditions can be employed i.e. curing in an elevated temperature for the first 24 hours and later transferring to room temperature. This is expected to increase the mechanical strength. Furthermore, future works should also study the durability of the designed fayalite slag geopolymer mortar.
6 BIBLIOGRAPHY


EN 933-1 (Part 1): Test for geometrical properties of aggregates


IS 4031 (Part 5): 1988- Methods of physical test for hydraulic cement


Li, C., Sun, H., & Li, L. (2010). A review: The comparison between alkali-activated slag (Si+ Ca) and metakaolin (Si+ Al) cements. *Cement and Concrete Research, 40*(9), 1341-1349.


